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*Quidquid agunt homines votum, timor, ira, voluptas,
gaudia, discursus, nostri farrago libelli est.*
(Juvenalis, Satires 1,85/86)

2004



Limburgs Universitair Centrum

Faculteit Wetenschappen

Research on Aromatic Poly(isothianaphthene) and Analogues by Structural Analysis of Oligomers and Model Compounds

Proefschrift voorgelegd tot het behalen van de graad van
Doctor in de Wetenschappen
aan het Limburgs Universitair Centrum te verdedigen door

960080

RAFAËL KIEBOOMS



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Diepenbeek 1995

15 JAN. 1996

Immensitas

Voorbij die bergen, baanloos, spreidt
het veld van onze onwetendheid

(G.Gezelle)

Dankwoord

Alhoewel een doctoraat bij aanvang lijkt op een één-persoons project, blijkt spoedig dat zonder hulp vele problemen onmogelijk opgelost kunnen worden. De talrijke interessante wetenschappelijke en niet-wetenschappelijke discussies hebben zonder twijfel hun bijdrage geleverd aan het tot stand komen van dit werk. Er rest mij bijgevolg nog het aangenaamste deel onder woorden te brengen, met name de dankbare herinnering aan alle personen, die elk op hun manier hun steentje bijgedragen hebben.

Op de eerste plaats zou ik mijn ouders willen danken, niet alleen voor hun voortdurende steun maar ook voor hun daadwerkelijke bijdrage onder de vorm van het aanhoren van enkele wetenschappelijk redevoeringen en het nalezen van dit proefschrift. Ook mijn broer Stefaan zou ik willen danken voor de hulp bij het temmen van de koppige maar zo noodzakelijke computers.

Mijn grote bewondering gaat ook uit naar Prof.Dr.J.Gelan voor zijn onbegrensde wetenschappelijke creativiteit en zijn vooruitstrevend enthousiasme op gebied van de informatisering van het labo.

Prof.Dr.D.Vanderzande ben ik dankbaar voor zijn begeleiding bij mijn eerste echte stappen in de Wondere Wereld der Scheikunde. Van hem leerde ik dat scheikunde niet alleen een wetenschap is maar ook een Kunst. Vooral voor de vele kansen en de vrijheid die hij me geboden heeft om mijzelf te ontplooien, ben ik hem ten zeerste dankbaar.

Dr.R.Carleer van het Fonds voor Technologisch Onderzoek (FTO) zou ik willen danken voor de vele wetenschappelijke discussies ondanks zijn enorm druk beladen tijdschema. In dit kader zou ik naast Guy, Linda en Ivo in het bijzonder ook Gerd Aelbers en Greet Cuyvers willen danken voor de AAS metingen, Jan Czech en Marleen Ruysen voor de massaspectroscopische metingen en vooral Martine Van Hamel voor haar hulp en geduld bij de FT-Raman en FT-IR metingen.

Prof.Dr.L.Van Poucke ben ik dankbaar voor het verlenen van zijn bereidwillige medewerking aan de uitvoering van de FT-Raman en FT-IR metingen.

Ook Dr.P.Adriaensens heeft in belangrijke mate bijgedragen tot het welslagen van dit werk. Geen enkele NMR opname kon perfect genoeg zijn en elke NMR analyse werd uiterst nauwkeurig nagekeken. Tenslotte hadden wij samen het genoegen op het einde van mijn doctoraat de *Drie Basis Regels van Computer Programma's* te leren kennen, namelijk (i) elk programma dat feilloos werkt, is verouderd; (ii) elk nuttig programma wordt onherroepelijk veranderd; (iii) elke fout wordt ogenblikkelijk als nieuwe functie opgenomen. Hieruit konden wij de conclusie trekken dat als een programma feilloos draait, men zich geen zorgen moet maken. Dit gaat vanzelf over.

Thanks to the work of my predecessor Ivan Hoogmartens I was given the possibility to cooperate with some outstanding laboratories.

First of all, the cooperation with the group of Prof. J.L. Brédas of the Université de Mons-Hainaut was a great privilege as much on the scientific level as on the level of the indoor soccer competitions. The many interesting discussions with Roberto Lazzaroni and C. 'Lillo' Quattrocchi provided some understanding but also resulted in more other interesting questions and problems to be investigated.

Next I would like to thank Prof. G. Zerbi of the Politecnico di Milano for the interesting discussions on the analysis of the 'mysterious' poly(isothianaphthene) vibrational spectra.

I would like to thank Marcus Swann from the group of Prof. D. Bloor (Physics Department) and Chris Drury from the group of Prof. G. Brooke (Chemistry Department) from the University of Durham for their most interesting discussions and for providing the fluorinated isothianaphthene oligomers and polymer.

I would also like to thank Prof. S. Lefrante from the Laboratoire de Physique Crystalline and Prof. M. Lapkowski (Silesian Technical University, Gliwice, Poland) for the possibility to perform the *in situ* FT-Raman measurements at the Institut des Matériaux de Nantes. This was a unique experience.

Dr. L. Van Meervelt van de K.U.Leuven zou ik willen danken voor de één-kristal structuur bepaling van het gesilyleerde isothianafteen monomeer en dimeer.

A. Veermans, R.Verlaek, S.Bremmes en S.Van Heel van de afdeling IR, Polymers & Resins, DSM Research (Geleen) zou ik willen danken voor hun hulp bij de UV-vis opnamen.

Zonder de hulp van meestertovenaar Jos Kaelen, onze glasblazer, zouden ettelijke schitterende ideeën nooit in de realiteit omgezet zijn. Zijn enorme zin voor kwaliteit en perfectie heb ik altijd ten zeerste bewonderd!

Naast het secretariaat SBG zou ik ook alle mensen (Christel, Koen, Sali, Jeanke, Tony, Johnny, Johan, ...) die op technisch vlak hun bijdrage geleverd hebben willen danken voor hun hulpvaardigheid.

Duncan Cadd zou ik heel speciaal willen danken voor het grondig nalezen en verbeteren van dit werk op het vlak van de Engelse woordenschat en spraakkunst.

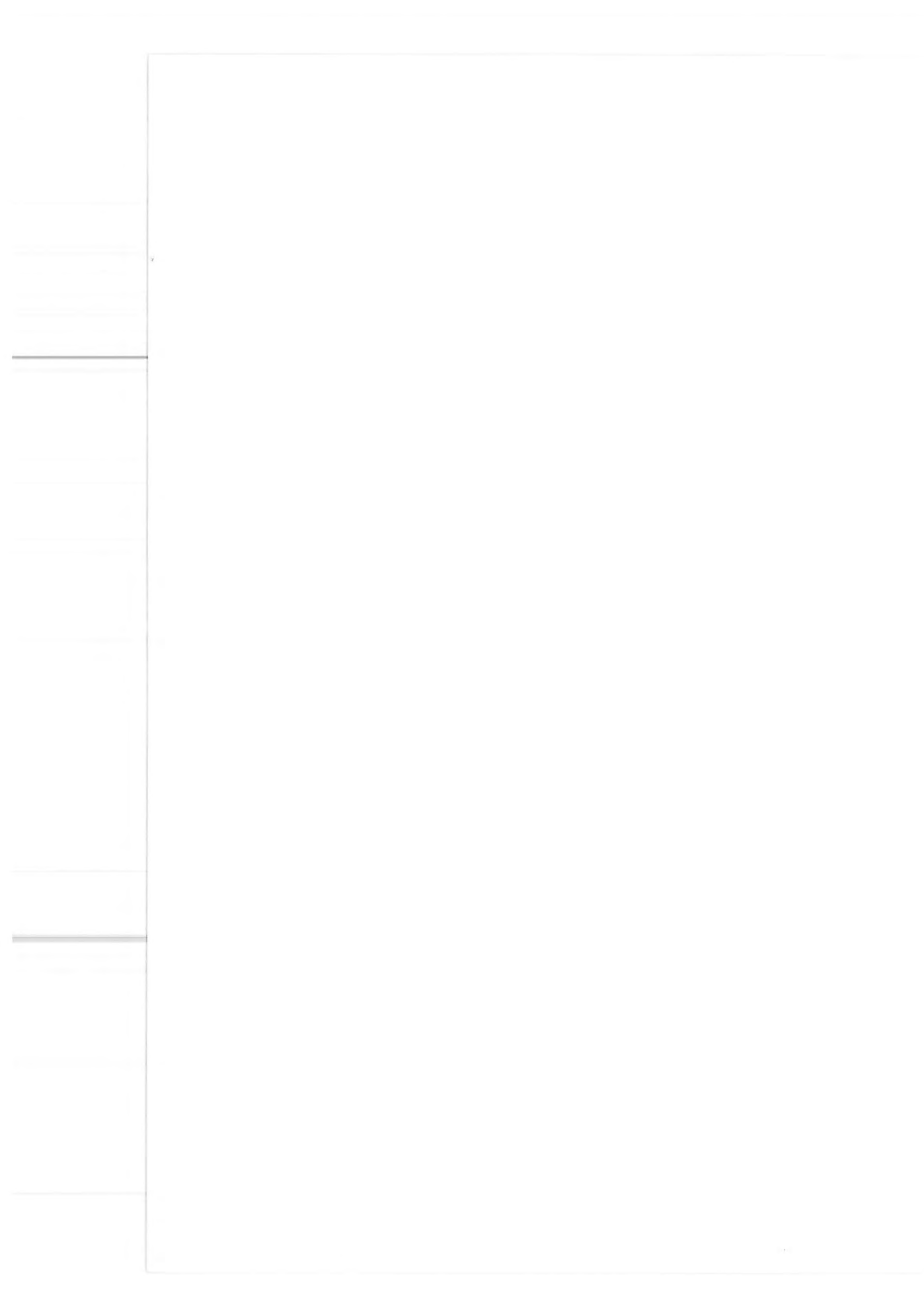
Mijn medelotgenoten Ivan, Frank, Anniek, Ingrid, Wanda, Sonja, Martine, Harald, Dino, Monique, Ben, Rint, Rob, Mik, An(n)(e), Wim, Margreet, Albert, Dirk, Dirk, ... willen danken voor de zangstonen in het labo, de gezellige avondjes en vooral voor de fantastische discussies over de meest waanzinnige onderwerpen. Aan de vraag of Alexander de Grote nu met de Kelten of de Noormannen de Maya's in Midden-Amerika is gaan veroveren, houd ik nog steeds slapeloze nachten over.

Tenslotte zou ik enerzijds het LUC en DSM, en anderzijds het IWONL en IWT willen danken voor hun financiële steun.

Na al deze jaren van studie en onderzoek waarin we een grote hoeveelheid ingewikkelde 'geleerdheid' de wereld ingestuurd hebben, zou ik willen eindigen met een laatste bedenking van de grote Franse denker Pascal:

Si on est trop jeune on ne juge pas bien, trop vieil de même.
Si on n'y songe pas assez... Si on y songe trop, on s'entête
et on s'en coiffe.
Si on considère son ouvrage incontinent après l'avoir fait, on
en est encore tout prévenu: si trop long après, on n'y entre
plus.
Ainsi les tableaux vus de trop loin et de trop près. Et il n'y a
qu'un point indivisible qui soit le véritable lieu, les autres
sont trop près, trop loin, trop haut ou trop bas. La
perspective l'assigne dans l'art de la peinture. Mais dans la
vérité qui l'assignera?

(B.Pascal, Pensées 19)



Abstract

A detailed analysis of the literature indicated that substituents can only be used at the level of improving properties during processing, that end groups are only important for those polymers where the energy difference between the aromatic and quinoid structure is very small, and that stability of π delocalisation is the most important tool for the design of low bandgap polymers.

From our research it appeared that, based on a detailed NMR and FT-Raman analysis of oligomers and model compounds, the low band gap of PITN could be associated with the quinoid structure. However, a theoretical analysis of the UV-vis data of a series of aromatic isothianaphthene oligomers indicates that a substantial lowering of the band gap can be obtained in planar aromatic isothianaphthene systems.

A parallel investigation of PTFITN, a soluble isothianaphthene analogue, gave some indications that this polymer should possess an aromatic structure. The aromatic structure makes it possible that the fluorines probably induce non planarity such that inter ring π -conjugation is lowered to a considerable extent. This could explain the increased band gap of 2.1eV observed by Swann et al.^[1]

Analysis of a series of aza-analogues of PITN revealed that in these materials it should be possible to combine a planar aromatic geometry with enhanced processability. The 4,5-diaza and 4,7-diaza isothianaphthene polymers can therefore be considered as very promising low band gap materials.

Finally, we showed that it is possible to combine the aromatic isothianaphthene ring system with another heterocycle such as thiophene in a *formal* copolymer. Through the development of a highly specific and efficient synthesis route to 1,3-dithienylisothianaphthene (DTI, **4**), we established the basis for the further synthesis and study of *formal* copolymers with tailor-made electronic properties.

(1) M.J. Swann, G. Brooke, D. Bloor. *Synth.Met.*, **55-57**, 281-286, (1993).

Abstract

Een gedetailleerde literatuur analyse toonde aan dat substituenten voornamelijk kunnen gebruikt worden bij het verbeteren van de materiaaleigenschappen tijdens de verwerking, dat eindgroepen alleen van belang zijn bij deze polymeren waar er een relatief klein energieverval bestaat tussen de aromatische en chinoidale structuur, en dat de stabiliteit van de π delokalisatie het belangrijkste hulpmiddel is bij het ontwikkelen van polymeren met een kleine bandafstand.

Uit dit onderzoekswerk is gebleken dat met behulp van een grondige NMR en FT-Raman analyse van oligomeren en model verbindingen, de kleine bandafstand van PITN geassocieerd kan worden met een chinoidale structuur. Een theoretische analyse van de UV-vis data van een reeks aromatische isothianafteen oligomeren geeft echter aan dat een substantiële verkleining van de bandafstand bekomen kan worden in planaire aromatische isothianafteen systemen.

Bij het onderzoek van PTFITN, een oplosbaar gefluoreerd PITN derivaat, werden aanwijzingen bekomen dat dit polymeer een aromatische structuur zou bezitten. De aanwezigheid van de fluoratomen in combinatie met een aromatische structuur kunnen bijgevolg de ketenoverspannende π conjugatie in zulke mate verhinderen dat een grotere bandafstand van 2.1 eV^[1] bekomen wordt.

Analyse van een serie aza analogen van PITN bracht aan het licht dat het mogelijk zou moeten zijn in deze materialen een planaire geometrie te combineren met een verbeterde verwerkbaarheid. De 4,5-diaza en 4,7-diaza isothianafteen polymeren kunnen bijgevolg beschouwd worden als veel belovende materialen met een kleine bandafstand.

Tenslotte toonden we aan dat het mogelijk is aromatisch isothianafteen ringsystemen te combineren met andere heterocyclische structuren, zoals thiofeen, ter vorming van een *formeel* copolymeer. Via het op punt stellen van een zeer specifieke en efficiënte synthese van 1,3-dithienylisothianafteen (4) werd de basis gelegd voor verdere ontwikkeling en onderzoek naar *formele* copolymeren met op maat gemaakte elektronische eigenschappen.

(1) M.J. Swann, G. Brooke, D. Bloor. *Synth.Met.*, **55-57**, 281-286, (1993).

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Arcadium petis, immensam petis!
(Oracle of Delphi)

Introduction

Besides poly(acetylene), an important class of conducting polymers are poly(aromatics) such as poly(paraphenylene), poly(paraphenylenevinylene), poly(pyrrole), poly(thiophene), poly(isothianaphthene) ... Due to the presence of an extended π -system these conjugated polymers are characterised by several particular properties. Enhanced conductivity, non linear optics, electronic and optical anisotropy, colour and transparency change are among the most fascinating features. However the enhanced conductivity obtained by doping is in most cases rather unstable. One of the possibilities to enhance further the conductivity and to improve its stability is through development of intrinsic conducting polymers.

Several factors determine the conductivity of conjugated polymers. Not only does the molecular structure play an important role but also the intermolecular interactions between polymer chains at a mesoscopic level. These interactions are in turn influenced by the macroscopic arrangement obtained during final processing. Except for the requirement that conducting polymers should possess an extended π -system, a clear correlation between some of the special properties of these materials and their molecular structure has not yet been well established. Although progress has been made in the development of soluble materials, the main difficulties experienced by fundamental research are the result of the low solubility and amorphous character of conjugated materials. An extensive characterisation therefore requires special spectroscopic methods as for example solid state NMR,^[1] and a combination of different techniques such as electrochemistry, UV-vis and FT-Raman. However, oligomers allow a detailed investigation of their structure and properties. The spectroscopic properties of these oligomeric compounds can be mapped precisely. In a second stage these data can be correlated with the special properties of these compounds and finally with the properties of the corresponding polymer through extrapolation.

For purposeful development of polymeric materials with intrinsic conductivity one first needs to acquire a fundamental understanding of the relationships between structure and properties. The data obtained from a thorough characterisation can be evaluated subsequently on a theoretical level to obtain a model which should allow the prediction of properties of conjugated materials. The need for an intimate interaction between theoretical and experimental research is more and more a *conditio sine qua non* in which the study of oligomers is not without significance.

Intrinsic conductive materials necessarily possess a low band gap. To study structure property relationships the use of the band gap should be considered as a probe for intrinsic conductivity. One important development in the search for intrinsic organic conductors was that upon fusing an additional benzene ring on the β - β' position of the thiophene ring, thereby obtaining poly(isothianaphthene) (PITN), the bandgap is decreased from about 2 eV to 1 eV. The halving of the bandgap was also predicted by the theoretical calculations of Brédas et al.^[2] In spite of the peculiar properties of PITN such as a low bandgap and transparency upon doping, a thorough characterisation^[1] of this material was begun only recently. This spectroscopic analysis provided the first experimental evidence for the quinoid structure of PITN. However, further theoretical calculations^[3] on the properties of PITN predict a further halving of the bandgap to 0.6 eV for PITN with a non planar aromatic ground state structure. It is thus most interesting to study the properties of PITN with an aromatic ground state structure. One of the ways to begin this investigation is by performing an in-depth characterisation of PITN oligomers^[4] with an aromatic structure (Figure 1.1) by means of NMR, XRD, UV-vis, FT-Raman spectroscopy.

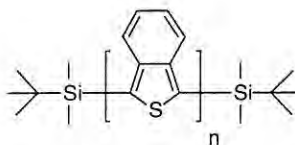


Figure 1.1 PITN oligomers with an aromatic ground state structure.

Spectroscopic analysis of conducting polymers is hindered by the fact that the solubility of a lot of conducting polymers is quite low. Solubility can however be enhanced by replacing the hydrogen nuclei by halogen nuclei.^[5] Brooke et al.^[6] managed to synthesise tetrafluorinated PITN which is soluble in organic solvents. The question arose whether this behaviour is associated with an aromatic or a quinoid structure.

Therefore, we started the analysis by comparing the spectroscopic properties of aromatic oligomers of this fluorinated polymer with those of the fluorinated polymer (Figure 1.2).

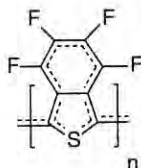


Figure 1.2 Poly(tetrafluoroisothianaphthene).

Poly(thieno[3,4-*c*]pyrazine) (Figure 1.3) is a polymer in which both low bandgap and enhanced solubility could be combined. Indeed, theoretical calculations by Nayak et al.^[7] indicate that this polymer should possess a bandgap of 0.12 eV in the planar aromatic ground state structure, which is again a halving of the bandgap as compared to planar aromatic PITN (0.21 eV).^[3] The solubility of this polymer can be influenced by the presence of nitrogens in the fused benzene ring. The presence of the lone pair on nitrogen could make it possible to dissolve the polymer in acids. Therefore, the assessment of the electronic properties of different nitrogen containing ring systems was started with a theoretical investigation performed by the group of Brédas. We subsequently wanted to carry out the synthesis of aromatic oligomers and model compounds to obtain spectroscopic data for the analysis of the structure of these polymers.

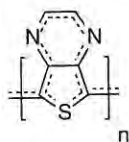


Figure 1.3 Poly(thieno[3,4-*c*]pyrazine).

Copolymers of different aromatic systems are predicted to possess properties in between those of the homopolymers.^[8-10] One of the best known examples is poly(paraphenylenevinylene), which can be considered as a copolymer from poly(paraphenylene) and poly(acetylene). Since the aromatic structure of PITN is

predicted to possess a relatively low bandgap it would be interesting to combine the aromatic isothianaphthene unit with other aromatic units such as thiophene. In this context it has been shown by McCullough that regioregular polymers possess superior properties.^[11, 12] One approach to obtain regioregular copolymers is to synthesise first the monomer containing both ring systems, followed by classical polymerisation procedures to obtain the polymer. Since no copolymerisation mechanism is involved, these copolymers should be rather considered as *formal* copolymers. Already several attempts^[13-18] have been made to use this approach in the synthesis of a polymer starting from a monomeric unit consisting of two thiophene units and one isothianaphthene unit. (Figure 1.4) We would like to find an easily-accessible synthesis to obtain such monomeric units and to use it in the preparation of other monomeric units containing isothianaphthene derivatives. An additional feature of these monomeric units is that they can be used as model compounds and as building block for oligomers with tailored properties.

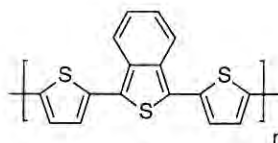


Figure 1.4 Formal copolymer of thiophene and isothianaphthene, poly(1,3-dithienyl isothianaphthene)

Composition of this work

In chapter 2 a brief survey is given about theories concerning intrinsic conducting polymers. For development of intrinsic conductive polymers it is important to understand clearly why some polymers possess higher conductivities than others and which principles are used to describe the origin of the band gap in conducting polymers. In chapter 3 a literature investigation was performed in order to find some theoretical and experimental data for evaluation of the relative importance of the different strategies to alter the band gap of conducting polymers. This is important for an efficient development of intrinsic conducting polymers, the so called 'low band gap' conjugated polymers.

The results of the NMR analysis of aromatic and some improved quinoid model compounds, the latter synthesised by Hoogmartens, is given in chapter 4. In chapter 5

the vibrational analysis of PITN, oligomers and model compounds are described. The results of theoretical calculations, single crystal structure determination and optical absorption spectroscopic measurements are reported in chapter 6.

The NMR and vibrational analysis of fluorinated isothianaphthene oligomers and the model compound, 1,3-dithienyl-4,5,6,7-tetrafluoroisothianaphthene, can be found in chapter 7.

Chapter 8 describes the conclusions of theoretical calculations performed by Quattrocchi on isothianaphthene derivatives containing nitrogen in the aromatic ring system. Also the results of the work to synthesise thieno[3,4-c]pyrazine oligomers are given.

The synthesis of the monomeric unit, 1,3-dithienylisothianaphthene, to be used in the preparation of *formal* copolymers is described in chapter 9. The developed synthetic method is also applied to other isothianaphthene derivatives.

Finally in chapter 10 we give some perspectives for further research in the field of isothianaphthene based low bandgap polymers.

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Low Bandgap Conjugated Polymers

2.1 Introduction

One of the important parameters in determining intrinsic conductivity is the value of the energy difference between valence and conduction band. This difference is called the bandgap E_g . In order to obtain a high intrinsic conductivity a substantial lowering of the bandgap value is one of the prerequisites. For the design of polymeric intrinsic conductors the lowering of the bandgap is achieved through variation of the polymer structure. First of all one needs to understand why conjugated polymers can present conductive behaviour and which theories describe how the value of the bandgap can be controlled.

2.2 Intrinsic Conducting Polymers

2.2.1 Poly(sulphur nitride)

One of the most important discoveries^[1] preceding the development of conducting organic polymers is the fact that the inorganic polymer poly(sulphur nitride) $(\text{SN})_x$ possesses a conductivity of 10^4 Scm^{-1} at room temperature which is almost comparable with the conductivity of copper ($\approx 6 \cdot 10^5 \text{ Scm}^{-1}$). Of fundamental importance to attaining the metallic state is the presence of unpaired electrons in the primary molecular units. In the case of poly(sulphur nitride), a single polymer chain can be considered schematically as a collection of covalently bonded monomeric NS free radicals each of which is the sulphur analogue of NO. The NS molecule, like NO, contains an unpaired electron in the lowest occupied π^* -antibonding molecular level. In principle in a polymer this type of π^*

level may form the basis of the metallic conduction band. This 'metallic' character of poly(sulphur nitride) appears to be an intrinsic property and is related with the presence of one unpaired electron at every SN unit. As a consequence the band in the polymer corresponding with the π^* -antibonding molecular level will be half filled. The absence of a forbidden gap makes complete delocalisation possible. Therefore conductivity in $(\text{SN})_x$ can be considered as similar to the conductivity of metallic conductors.^[2, 3]

In organic conjugated polymers the presence of unpaired electrons is rather an exception. This implies that the band structure will be characterised by completely filled valence bands. Most of the time there is a large bandgap between the filled valence band and the empty conduction band and therefore intrinsic conductivity will be very low.^[4]

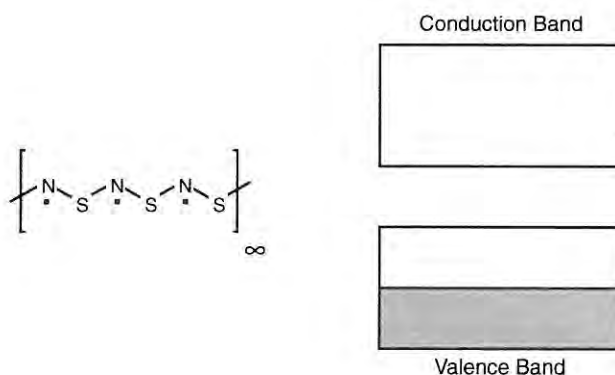


Figure 2.1 Poly(sulphur nitride), the first polymer exhibiting metallic conductivity.

2.2.2 The Peierls Instability

2.2.2.1 Introduction

The major breakthrough in the area of conducting plastics occurred when it was discovered that poly(acetylene), which has an intrinsic conductivity much lower than 10^{-5} Scm^{-1} , could be made highly conducting, 10^3 Scm^{-1} , by exposing it to oxidising (p-type doping, I_2 , Br_2 , FeCl_3 , ASF_5) or reducing agents (n-type doping, alkali metals).^[4] The most elementary presentation of the structure of poly(acetylene) is given in Figure 2.2.

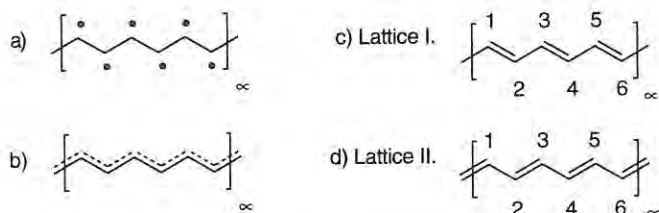


Figure 2.2 Trans poly(acetylene)

Ideally poly(acetylene) can be represented as a long chain of CH-groups each possessing an unpaired electron (Figure 2.2a). According to solid state physics this structure can be considered as a quasi one dimensional metal in which the metal atoms are replaced by CH radicals. Since there is only one unpaired electron per CH group a half filled band is obtained as in the case of poly(sulphur nitride). In this situation metallic conductivity could be possible. In reality poly(acetylene) is characterised by an alternating succession of short (double) bonds and long (single) bonds. This behaviour is described by the so-called Peierls instability.

The Peierls instability indicates why a half filled energy band is split up resulting in a completely filled valence band and an empty conduction band separated by a forbidden zone, the so-called bandgap. To understand this mechanism is of fundamental importance because it allows insight into why potential intrinsic conductors appear to be intrinsically insulating in the undoped state.

2.2.2.2 The Linear Chain Model

The transition from a regular linear chain structure to an alternating structure takes place according to a well defined mechanism. The regular linear chain cannot in any real situation be isolated from its environment but it must always be in contact with some form of a heat bath. This means that the atoms of the chain are vibrating around their equilibrium positions. When the vibrations of a solid are studied one finds that, as with the electronic energy levels themselves, the vibrational levels are discrete and that a given system will admit of a finite number of so-called *normal vibrations* such that they and their harmonics form all possible vibrational states of the system. In each of these normal vibrations the atoms move in very well determined relationships to one another. An example of such a normal mode is shown at the top of Figure 2.3. It is clear that when

the regular structure starts to vibrate in this particular mode it will go into an alternating form, as shown at the bottom of Figure 2.3. This will not be the case for other vibrational modes. The chain distortion cannot take place unless there is a normal mode which can drive the structure into the required configuration. Since the alternating form is lower in energy, the system becomes now trapped in this configuration.

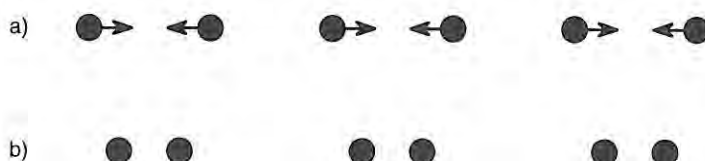


Figure 2.3 The anti symmetric vibration of the linear chain (normal vibration) which drives the Peierls distortion.

The principle of the Peierls distortion can be summarised as follows: if a system with a given symmetry has a top occupied electronic orbital which is degenerate, then this function will interact with a vibrational mode which has symmetry lower than that of the original system, causing it to distort from the original configuration and thus splitting the degeneracy, which results in the appearance of a state of lower energy. This principle is also well known under the name of the Jahn-Teller effect.^[5-10]

2.2.2.3 Poly(acetylene)

Although the Peierls model of the linear chain is important, since it has permitted understanding the structural instability of linear systems, genuine linear chains are of no serious practical interest, since they rarely occur in nature. If we consider a poly(acetylene) polymer, a material of considerable technological interest, we can see that it forms a zig-zag chain (Figure 2.2). Figure 2.2a shows the regular poly(acetylene) structure with a π orbital at each atom containing one unpaired electron. It is this electron which can be expected to form a mobile conducting band. However for poly(acetylene) there exists also a structure with alternating double (short) and single (long) bonds (Figure 2.2c and 2.2d) as the result of a Peierls distortion causing the degeneracy at the edge of the Brillouin zone to disappear and thereby lowering the Fermi level. However

since there is an energy gap at the Fermi level the material ceases to be a conductor and becomes an insulator.

As a consequence of this Peierls distortion two minima appear on the potential energy surface characterising poly(acetylene). These two minima correspond with two alternative crystal lattices (Figure 2.2c (Lattice I.) and 2.2d (Lattice II.)), which differ from each other by the way the short and long bonds alternate in the crystal lattice. In Lattice I. the distance between the lattice points 1-2, 3-4 and 5-6 are shorter as compared to the distance between 2-3 and 4-5. In Lattice II. the inverse situation occurs.

Particular for poly(acetylene) is that these two alternative lattices are iso-energetic or degenerate. The lattice with identical distances between the lattice points can be found in the potential energy diagram as a local maximum (Figure 2.4).

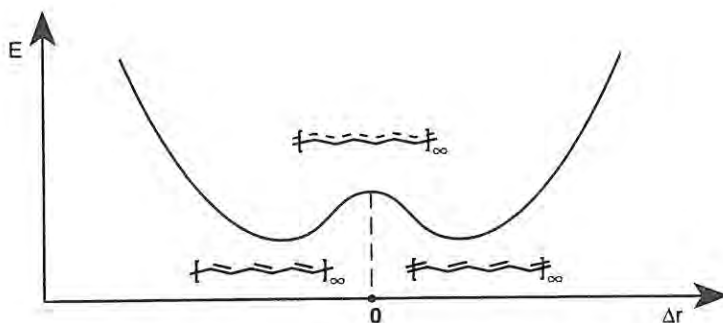


Figure 2.4 Potential energy diagram of trans-poly(acetylene).

The above picture is a simplified description that can be used as a qualitative model to understand the evolution of valence and conduction bands. For a complete description of the bandgap evolution it is necessary to include correlation effects and interactions between polymer chains themselves.

From the analysis of the structure of poly(acetylene) potential one dimensional conductors appear to lose their conducting properties because their lattice structure is driven towards an energetically more favourable configuration. However, some vibrational energy has to be spent for the change to take place. Most of the time the consumption of vibrational energy is compensated by the gain in electronic energy, although it can be seen that in general this is second order with respect to the electronic energy. It is therefore possible that the interactions between the electronic and vibrational states are such that they impede the energy compensation between vibrational energy loss and

electronic energy gain. In that specific situation the Peierls effect will not take place and an intrinsic conductor is obtained.^[6]

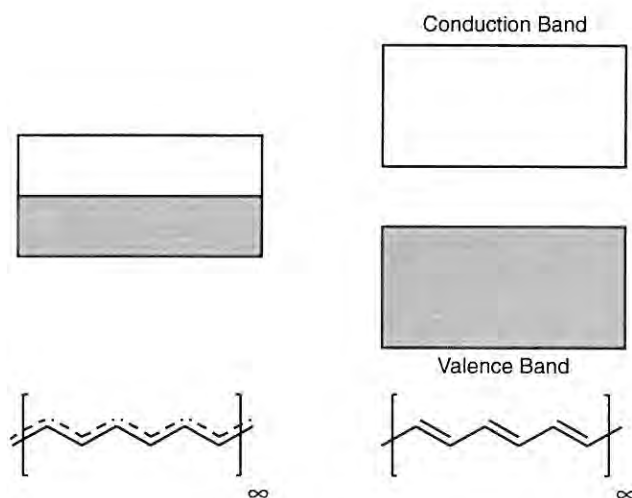


Figure 2.5 Simplified description of the band structure of poly(acetylene).

Aising^[11] formulated the conditions which a polymer has to fulfill in order to be a material showing metal-like conductivity. If an *isolated* polymer chain is considered, it will be conducting if the following rules can be applied. First, the polymer chain should possess an almost rigid backbone with a glide plane symmetry and/or a twofold screw axis symmetry because it will then show a double degeneracy at the zone boundary. On the other hand, it should have $4N+2$ electrons per unit cell. Under this condition the HOMO will be filled exactly up to the zone boundary. If this polymer is then crystallised into a solid and if it can be packed in such a way that the above-mentioned rules still apply, then the resulting system will still be conducting. In that case tridimensional packing effects will give rise to such a complex set of vibrational modes that one mode never will be found which cause the system to distort from the original configuration and the Peierls effect will be avoided.

To evaluate the effect of structural changes on the electronic properties the concept of bond length alternation was introduced. The value of the bandgap can be correlated with the bond length alternation Δr , defined as the length difference between a double and

a single bond. In 'metallic' poly(acetylene) (Figure 2.2a) all bonds are equal so that Δr is equal to 0 and therefore we have to deal with a conductor. The larger Δr , the more the Peierls effect is active and the larger the bandgap will be.^[12]

For the sake of completeness and as an example of a system with a lattice of different energy *cis*-poly(acetylene) will briefly be discussed. Again the Peierls distortion will cause the lattice with equal bond lengths (Figure 2.6a) to distort to a lattice with pronounced bond length alternation. For *cis* poly(acetylene) however the possibility exists to form two different alternating lattices (Figure 2.6b and 2.6c). These two lattices differ from each other through the presence of the short or double bonds at different lattice points. In contrary to *trans*-poly(acetylene) these two lattices are not iso-energetic. The lattice in Figure 2.6b has a more efficient conjugation and therefore a lower energy.^[13] (Figure 2.7)

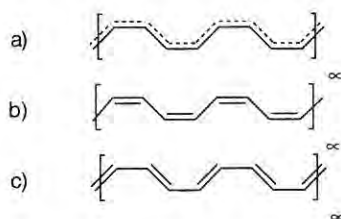


Figure 2.6 The lattice structure of *cis*-poly(acetylene).

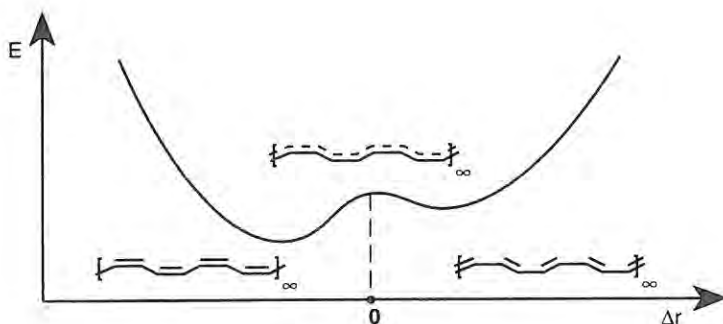


Figure 2.7 Potential energy diagram of *cis*-poly(acetylene).

2.3 Poly(aromatics)

2.3.1 The Valence Bond Theory

To clarify the further discussion concerning conducting poly(aromatics) it is worth while to elaborate on some principles described by the valence-bond theory (VB). The ideas of the valence-bond (resonance) theory are found to be of aid to organic chemists for rationalising in a simple manner the facts of organic structure and reactions. However, quantitative application is much harder for the VB method than for the Molecular Orbital (MO) method. Indeed for quantitative calculations the MO method has overshadowed the VB method. The main advantage of the VB method is of being based on the familiar chemical ideas of bonding and structure.^[14]

The VB theory is more closely related to the chemist's idea of molecules as consisting of atoms held together by localised bonds and views molecules as composed of atomic cores (nuclei plus inner-shell electrons) and bonding valence electrons. One begins with the atoms that form the molecule and pairs up the unpaired electrons to form chemical bonds. There are generally several ways of pairing up the electrons; each pairing scheme gives a valence-bond "structure" or resonance form.

Consider benzene as an example. When the π -electron approximation, i.e. treating the π electrons separately from the σ electrons, is used, the σ bonds are formed by sp^2 carbon hybrid AO's and $1s$ hydrogen orbitals; this leaves a p orbital on each carbon to form π bonds. Figure 2.8 shows the resulting covalent structures for pairing the π orbitals. Structures I. and II. are the so-called Kékulé structures, commonly represented as in Figure 2.9.

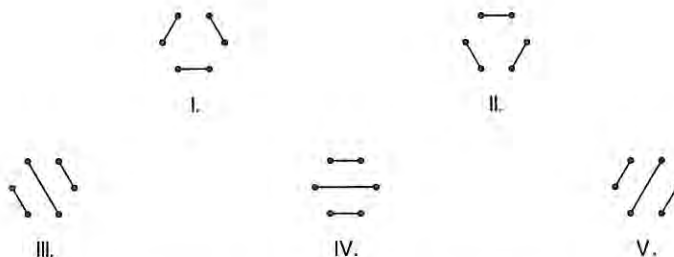


Figure 2.8 The pairing schemes for benzene.



Figure 2.9 The Kékulé resonance structures of benzene.

Each VB resonance "structure" is based on the same internuclear distance but a different electron pairing scheme. The resonance forms depicted in Figure 2.8 are a linearly independent set of bond eigenfunctions. The molecular wave function is then taken as a linear combination of these bond eigenfunctions for each resonance form and the variation principle is applied. The VB wave function is said to be a resonance hybrid of the various VB structures. Within this resonance hybrid the contribution of each resonance form is characterised by a certain weight corresponding with the square of its coefficient in the molecular wave function. For benzene it appears that the Kékulé structures make the greatest contribution. ($C_I, C_{II} \gg C_{III}, C_{IV}, C_V$)^[14]

$$\Psi_{\text{benzene}} = C_I \Psi_I + C_{II} \Psi_{II} + C_{III} \Psi_{III} + C_{IV} \Psi_{IV} + C_V \Psi_V$$

In the discussion of conducting polymers the main principles of the VB approach can be applied. First of all consider *trans*-poly(acetylene). For the Lattices I. and II. (Figure 2.2) the localised resonance pictures can be written as shown in Figure 2.10.

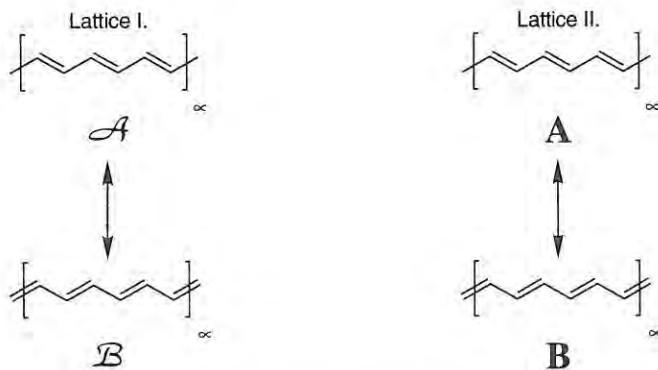


Figure 2.10 The resonance forms for the different Lattices of *trans*-poly(acetylene).

The wave functions, $\Psi_{\text{Lattice I.}}$ and $\Psi_{\text{Lattice II.}}$, of Lattice I. and Lattice II. respectively can then be written as follows

$$\Psi_{\text{Lattice I.}} = C_1 \mathcal{A} + C_2 \mathcal{B} \quad \text{with } C_1 > C_2$$

$$\Psi_{\text{Lattice II.}} = C'_1 \mathbf{A} + C'_2 \mathbf{B} \quad \text{with } C'_1 < C'_2$$

where A and B are the linear independent bond eigenfunctions obtained by a different pairing scheme of the unpaired electrons and C_1 and C_2 correspond with the weight of the contribution of each resonance form to the Lattice wave function. Since both lattices are iso-energetic it follows that $C_1 = C'_2$. The different contribution of both resonance forms to the final wave function allows us to understand in a qualitative way the notion of bond length alternation and the existence of a bandgap between valence and conduction band.



Figure 2.11 The Kékulé resonance forms of poly(paraphenylene).

Next we consider the case of poly(paraphenylene) (PPP). As shown in Figure 2.11 two Kékulé resonance forms can be written for PPP. Contrary to the case of benzene a third resonance form should be considered:

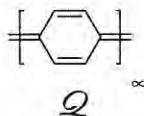


Figure 2.12: The quinoid resonance form of PPP.

This quinoid resonance form will have a considerable contribution to the total ground state π electron VB wavefunction. The ground state wavefunction of a polymer

containing exclusively aromatic units can therefore be considered as a linear combination of aromatic ($\mathcal{A}$) and quinoid ($\mathcal{Q}$) resonance forms.

In the ideal situation where all bond lengths are equal a conducting material is obtained. However, the Peierls distortion causes a breakdown of symmetry resulting in an alternation of single and double bonds. Again in the potential energy diagram two minima are found. (Figure 2.13) Since the aromatic resonance forms will make the greatest contribution, the contributions $C_{\mathcal{A}}$ of the aromatic resonance forms will be more important than the contribution $C_{\mathcal{Q}}$ of the quinoid resonance form.

$$\Psi_A = C_{\mathcal{A}}\mathcal{A} + C_{\mathcal{Q}}\mathcal{B} \quad \text{with } C_{\mathcal{A}} > C_{\mathcal{Q}}$$

Although when the contribution $C_{\mathcal{Q}}$ of the quinoid resonance form is more important than the contribution $C_{\mathcal{A}}$ of the aromatic resonance forms, a wave function Ψ_Q describing the quinoid structure is obtained.

$$\Psi_Q = C'_{\mathcal{A}}\mathcal{A} + C'_{\mathcal{Q}}\mathcal{B} \quad \text{with } C'_{\mathcal{A}} < C'_{\mathcal{Q}}$$

It is important to stress that in this way a difference is made between an aromatic structure (Ψ_A) and a quinoid structure (Ψ_Q) on the one hand and between an aromatic resonance form ($\mathcal{A}$) and a quinoid resonance form ($\mathcal{B}$) on the other hand.

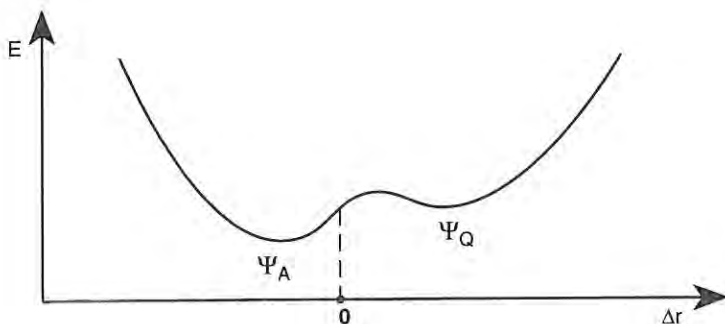


Figure 2.13 The potential energy diagram for polymers consisting of aromatic units.

2.3.2 Bond Length Alternation and Aromaticity

Brédas et al.^[15] studied the evolution of the bandgap of poly(thiophene) (PT) in function of the bond length alternation Δr . His polymer calculations are based on the use of the nonempirical valence enhanced Hamiltonian (VEH) pseudopotential technique. In the context of conducting polymers, this method has been shown to provide accurate estimates of important electronic parameters such as ionisation potentials or π - π^* transitions and bandgaps in a large series of hydrocarbon- or sulphur-containing conjugated systems.^[16] This technique is used in combination with MNDO geometry optimisations to obtain structural data. Brédas et al.^[12] stated that in the case of poly(aromatics) the notion of bond length alternation cannot be used as with poly(acetylene). The degree of bond length alternation, Δr , is therefore defined as the maximum difference between the length of a C-C bond inclined relative to the chain axis and a C-C bond parallel to the chain axis. For the normal aromatic ground state geometry, the Δr value is strongly negative and tends to be more and more positive as quinoid contributions to the geometry increase. As an example the aromatic and quinoid geometric structures of PT are shown in Figure 2.14.



Figure 2.14 The aromatic and quinoid structure of PT.

Figure 2.15 illustrates the evolution of the bandgap as quinoid contributions to the aromatic ground state of PT increase. Within the scope of the valence-bond discussion it can be said that the value of the bandgap is evaluated as a function of a decreasing contribution of the aromatic resonance form, i.e. decreasing value of C_A , or an increasing contribution of the quinoid resonance form, i.e. increasing value of C_Q . As the quinoid contributions to the geometry increase, we observe first that the bandgap decreases linearly. As Δr approaches $+0.06\text{\AA}$, the bandgap becomes very small. For $\Delta r > +0.06\text{\AA}$, the bandgap increases again. We can thus divide the V-shaped curve into two parts. The left part for $\Delta r < 0.06\text{\AA}$ corresponds to an aromatic type electronic structure ($C_A > C_Q$). The right part for $\Delta r > 0.06\text{\AA}$ corresponds with a quinoid structure ($C_A < C_Q$). Note, however, that this relationship established by Brédas et al.^[17] predicts that the corresponding polymeric chains will generally not have a metallic behaviour (except

as a result of accidental degeneracy) but would constitute semiconductors with possibly very small bandgaps. The potential energy diagram as shown in Figure 2.16 is similar to that of PPP (Figure 2.13).

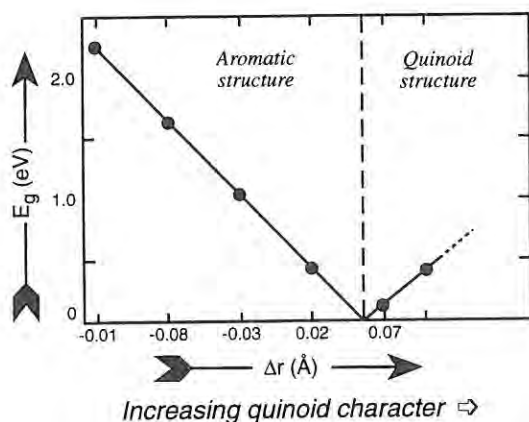


Figure 2.15 Evolution of the bandgap E_g (eV) in function of Δr .

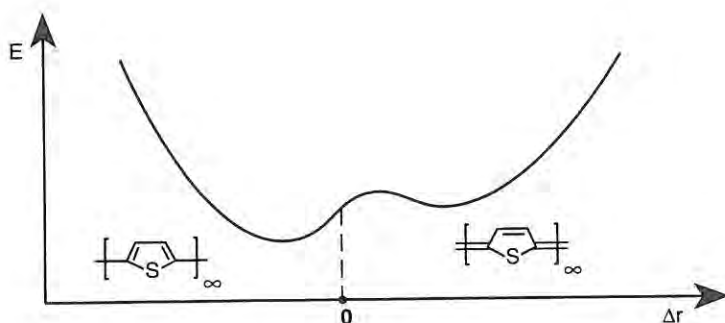


Figure 2.16 Potential energy diagram of PT.

This relationship can be applied in the search for new polymeric materials with a small bandgap. Indeed, to obtain a small bandgap in the aromatic ground state of a polymer as for example PT, quinoid contributions should be increased. These concepts had led to the synthesis by Wudl et al.^[18, 19] of poly(isothianaphthene) (PITN). PITN is a PT derivative where all thiophene rings are fused to a benzene ring along the β - β' thiophene bond. The presence of a benzene ring stabilises some quinoid contributions to

the ground state geometry of PITN. As a result the bandgap is found to decrease from 2.2 eV in PT to 1.0 eV in PITN.

This result appeared from Resonant Raman Scattering measurements by Poplawski et al.^[20] to be consistent within the framework established by Brédas. Indeed, systematic Resonant Raman Scattering measurements of poly(acetylene) and PT have shown a direct correlation between the π electron gap and the vibrational force constant. This experimental correlation can be explained within the simple Peierls model for degenerate ground state systems. In this model, larger dimerization amplitudes correspond, on the one hand to larger bandgaps and, on the other hand, to larger vibrational force constants. The results of their Resonant Raman Scattering measurements on PITN confirmed the arguments of Brédas that increased quinoid character of the backbone geometry reduces dimerization and thus the π electron gap becomes smaller.

2.3.3 Aromatic or Quinoid

The framework established by Brédas et al.^[15, 17] and the results obtained by Wudl et al.^[18] incited different theoretical research groups to investigate analogous systems and evaluate the relationship between bandgap and the aromatic and quinoid structures. The investigated systems each contain an additional fused benzene ring(s) in order to investigate the effect of further stabilising quinoid contributions to the ground state geometry. The investigated polymers are poly(thiophene) (PT), poly(isothianaphthene) (PITN), poly(isonaphthothiophene) (PINT) and poly(isoanthrothiophene) (PIAT) (Figure 2.17). The results of the calculations of the involved groups are summarised in Table 2.1. The following will give an comparative overview of these results concluding with short summary of the scarce experimental data on the structure of PITN.

Since the experimental results on PITN were quite encouraging, Brédas et al.^[15, 17] calculated the bandgap of PT and PITN to be 1.71 eV and 0.54 eV respectively. The difference of 1.17 eV between these values corresponds surprisingly well with the experimentally observed decrease of the bandgap going from PT to PITN by fusing an additional benzene ring onto the thiophene system. Analogous calculations were next performed on the bandgap of PINT and a vanishing small value of 0.01 eV was obtained. This suggested that PINT could be an example of a conducting polymer with a vanishing small bandgap.

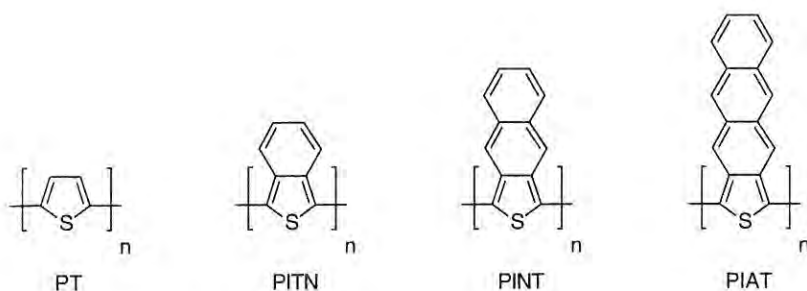


Figure 2.17 Chemical structures of poly(thiophene) (PT), poly(isothianaphthene) (PITN), poly(isonaphthothiophene) (PINT) and poly(isoanthrothiophene) (PIAT).

$E_g(\text{eV})$	PT	PITN	PINT	PIAT
Experimental	2.2	1.0	1.4	-
Brédas et al. ^[15, 17]	1.71	0.54	0.01	-
Brédas et al. ^[21]	A(p): 1.59 A(n): 1.68 Q: 0.26	A(p): 0.21 A(n): 0.61 Q: 1.19	-	-
Kertesz et al. ^[22]	A: 1.83 Q: 0.47	0.73 1.16	0.28 1.50	0.08 1.66
Nayak et al. ^[23]	A (p): 1.76	A (p): 0.68 A (n): 1.64 Q: 0.80	A (p): 0.37 A (n): 1.03 Q: 1.10	-

Table 2.1 Experimental and calculated values for the bandgap $E_g(\text{eV})$ of poly(thiophene) (PT), poly(isothianaphthene) (PITN), poly(isonaphthothiophene) (PINT) and poly(isoanthrothiophene) (PIAT). (Abbreviations: A, aromatic; Q, quinoid; p, planar; n, non planar)

In a more recent joint experimental and theoretical publication^[21] the results of NMR measurements performed on PITN and a series of selected molecular model compounds were combined with quantum-chemical calculations carried out on oligomers within the Austin Model 1 (AM1) and Valence Effective Hamiltonian (VEH) methodologies in order to study the differences between planar aromatic, non planar aromatic and quinoid PT and PITN.

As expected in the case of PT the situation is quite clear. The aromatic structure of PT is unequivocally more stable than the quinoid one. The energy difference of 8.7 kcal/mole between the two forms is very close to other literature data.^[23, 24] These calculations indicate however the planar aromatic form of PITN to be on the average 2.7 kcal/mole less stable than the quinoid form. This value is very close to the extrapolation of PRDDO result to infinite chain length: $\Delta E = 2.4$ kcal/mole in favour of the quinoid form.^[23] Rotation of the aromatic isothianaphthene units around the inter-ring single bonds to an average optimal dihedral angle of 27° , induces a small stabilisation of the aromatic ITN oligomers of the order of 0.5 kcal/mole per repeat unit, reducing the energy difference between the two valence bond isomeric structures to 2.2 kcal/mole.

In the planar aromatic form, PITN shows a very small bandgap (0.21 eV) while the value found for the quinoid polymer is much larger (1.19 eV). In the non planar aromatic form the bandgap increases to 0.6 eV due to partial loss of π conjugation. That value corresponds to that of a single chain "in the gas phase". Most probably, the solid-state packing would somewhat reduce the tilt angle between adjacent isothianaphthene units, thereby leading to a slightly smaller value of the bandgap. On the basis of these results they predicted aromatic and quinoid PITN to present markedly different optical signatures. As the calculated bandgap value of quinoid PITN appeared to be in better agreement with experimental data derived from optical spectroscopy (spectrum onset located at 1.0 eV and $\lambda_{\max}$ at 1.5-1.6 eV),^[18] it was suggested that PITN should possess a quinoid structure. Moreover these calculated values correspond quite well with earlier reported data.^[22, 23]

Kertesz et al.^[22, 25, 26] evaluated PT based polymers with an increasing number of fused benzene rings. For the geometry optimisations and to obtain the total energy of these polymers they used an MNDO method based on band theory instead of an MNDO method based on cluster calculations. For obtaining the energy bands, an energy band

version of the traditional Hückel theory was used. Apparently their type of full MNDO geometry optimisation for the infinite polymer PITN, regardless of the starting geometry, always converges to a quinoid structure. The opposite was found for the case of PPP, where only the aromatic structure is observed.



Figure 2.18 The aromatic and quinoid structure of PITN.

As noticed in the discussion of the valence-bond theory, the wavefunction of PPP, PT, poly(pyrrole) (PP) and poly(furan) (PF) is principally determined by the aromatic resonance form ($C_A > C_Q$). However in the case of PITN the quinoid resonance form should, according to Kertesz et al., possess a stability such that it has a more important contribution to the ground state wavefunction as compared to the aromatic resonance form ($C_A < C_Q$). Thus a switchover occurs in energetics from the aromatic structure of the quinoid form at the level of PITN in the series of Figure 2.17.

Table 2.1 displays the calculated values for the bandgap for each of the polymers as well in the aromatic ground state as in the quinoid ground state. As far as the aromatic ground state is concerned their results indicate a lowering of the bandgap in the series of Figure 2.17. This is in accordance with the results of Brédas et al.^[17]

However for a quinoid ground state the value of the bandgap will increase. This phenomenon is interpreted in Figure 2.19 and Figure 2.20 by treating the butadiene groups as successive perturbations to the frontier orbitals (HOMO and LUMO) of PT.

For the aromatic structure of PT the successive butadiene groups stabilise the LUMO and destabilise the HOMO, which results in a decrease of the bandgap. For the quinoid structure of PT the addition of successive butadiene groups stabilises the HOMO and destabilises the LUMO. As a result the bandgap increases steadily with increase in the number of rings in the system, until a level crossing occurs that tempers the further increase of the gap.

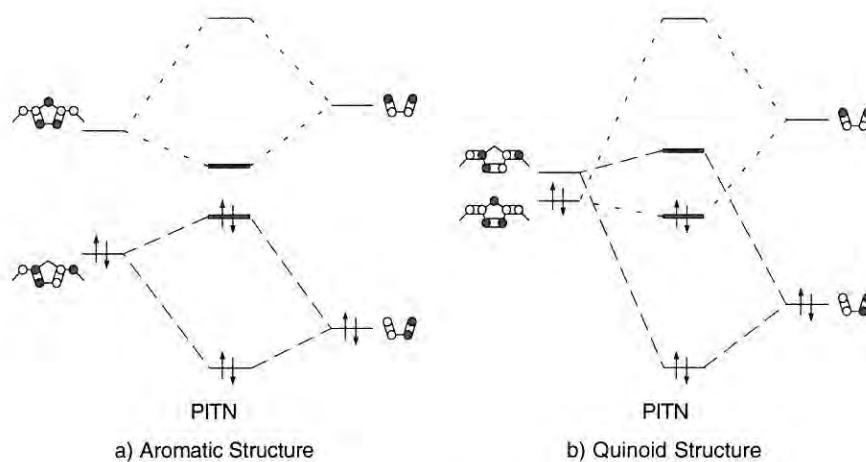


Figure 2.19 Perturbation of the frontier orbitals of aromatic and quinoid PT by one butadiene group resulting in the formation of PITN

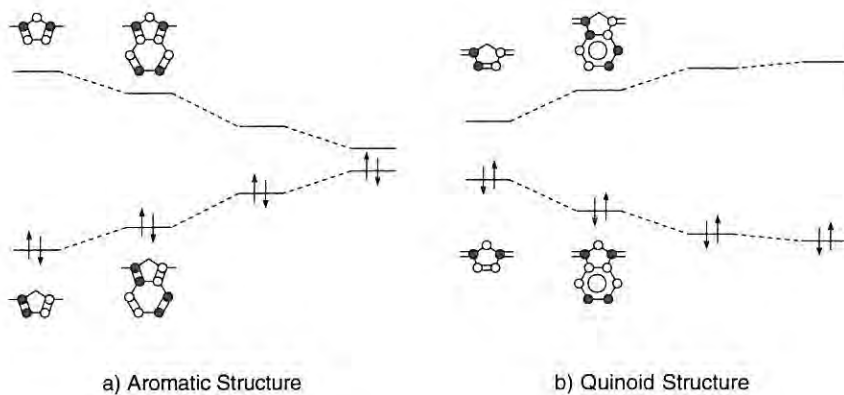


Figure 2.20 Perturbation of the frontier orbitals of aromatic and quinoid PT by successive butadiene groups resulting in the formation of PITN, PINT and PIAT.

Based on their band structure calculations within the MNDO approximations, Kertesz et al.^[22] predicted moreover the planar quinoid form of PITN to be the ground state geometry. They estimated an energy difference of 10.55 kcal/mole per ring between

the aromatic and quinoid forms of PITN. They postulated that the delocalisation energy of π -electrons over the neighbouring rings and the six-membered side rings offsets the repulsion energy arising from the steric interactions between hydrogen and sulphur atoms on adjacent units. Furthermore, they predicted an energy difference of 3.4 kcal/mole per ring between the coplanar and the non planar ($\phi = 95^\circ$) forms of the aromatic polymer favouring the latter conformation. This indicates that the energy loss due to the relaxation from the quinoid to the planar aromatic form is much larger than the energy gained from the relaxation from a planar aromatic to a twisted aromatic structure.

Since the semiempirical MNDO method was considered to yield relatively poor estimates for non bonded repulsions and rotation angles about single bonds in conjugated molecules, Nayak et al.^[23] could not consider the results of Kertesz et al.^[22] as definitive. Nayak et al. made use of the method of partial retention of diatomic differential overlap (PRDDO) to optimise the geometries of their systems and developed a method for extrapolating the ab initio and/or PRDDO oligomer energetics to the infinite system. This approach allowed them to perform assessment of the relative energies of the aromatic and quinoid forms at a highly theoretical level. Application of this method to PITN suggests that the ground state is quinoid, but the relative energies ($\Delta E = 2.4$ kcal/mole per repeat unit for the infinite chain) of the quinoid and aromatic forms are so close that both structures may exist as local minima in the real polymeric system. Steric effects may strongly favour nonplanar geometries, but electronic effects associated with increased conjugation along the backbone are also very significant and in some cases may be sufficient to force the polymer into a planar quinoid structure. The calculation of the bandgap of PT, PITN and PINT, based on the extended Hückel theory, agree well with the results of Kertesz et al.^[22] and those^[17] derived from VEH calculations.

Besides the quantum-chemical calculations, the experimental evidence available up to a few years ago is inconclusive. Because of the amorphous nature of most conjugated polymers, direct structural information obtained from X-ray or neutron diffraction remains limited. The X-ray photoelectron spectroscopy (XPS) valence spectrum of PITN has been found in good agreement with the theoretical curve calculated on the basis of an aromatic backbone.^[27] However, the overall density of valence states, which is probed by XPS, is expected to be very similar for both quinoid and aromatic structures, so that such experimental data cannot provide the clear signature of one of the two structures. From Raman scattering data on neutral and doped PITN, it has been proposed that the ground state geometric structure of the neutral system is quinoid and becomes aromatic

upon doping.^[28, 29] This hypothesis is based on the comparison between the measured frequencies and values calculated for the quinoid and aromatic structures from the force constants of thiophene and benzene. However, the experimental Raman frequencies are in agreement with the calculated values for the aromatic structure of PT only after a refinement procedure has been applied. When this procedure is used for PITN, the frequencies obtained for the aromatic and the quinoid structures are so similar to each other that it seems a very delicate matter to determine which set of results is closest to the experimental data. It thus appears that the question of the ground state geometry of PITN is not resolved unequivocally by those results. Only very recently comparison of ¹³C NMR CP/MAS and FT-Raman data of model compounds and PITN has indicated that the structure of PITN possesses a high quinoid character.^[21, 30-33]

2.4 Conclusions

Polymers that meet the requirements of a real intrinsic organic conductor seem to be very scarce. Until now, only poly(sulphur nitride) has shown metallic conductivity. Although poly(acetylene) is an ideal material to possess intrinsic conductivity, the effect of Peierls distortion cannot be avoided thereby increasing the bandgap. Undoped poly(acetylene) is therefore only characterised by semiconducting properties. In the case of poly(aromatics) one has to deal with an additional feature in terms of the stability of aromatic and quinoid structures. It has been predicted theoretically that the bandgap of semiconducting poly(aromatics) can be substantially lowered by stabilising quinoid contributions to the aromatic ground state geometry. This has been illustrated experimentally by synthesising PITN as a PT derivative with a benzene ring fused on the β - β' bond.

These results encouraged different groups to investigate theoretically the effect of further stabilising quinoid contributions to the ground state geometry. However, within the framework of the design of low bandgap conjugated polymers the theoretical results on PITN and other derivatives with additional fused benzene rings have important consequences. If the reasoning of Brédas et al. is pursued consequently, one should stabilise aromatic contributions to the quinoid ground state geometry of PITN. The final goal should be to influence the electronic ground state of a polymer such as to obtain that ground state configuration possessing the lowest bandgap.

As a consequence, structural modifications of polymers are of primary importance for the design of intrinsic conductive polymers. Through the use of hetero-atoms or

specific anti- or non-aromatic structures the ground state energy of poly(aromatics) could be manipulated in one or another direction.

2.5 References

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Lowering the Bandgap

3.1 Introduction

The theoretical results depicted in the previous chapter indicate that to lower the bandgap starting from PITN one has to stabilise aromatic contributions to the theoretically predicted quinoid ground state geometry rather than further continue stabilising quinoid contributions.

As a consequence, structural modifications of polymers are of primary importance for the design of PITN-based intrinsic conductive polymers. In this chapter we shall investigate which structural tools can be used for lowering the bandgap substantially. Therefore, the effect of substituents, end groups and the stability of π electron delocalisation will be discussed. The introduction of hetero-atoms or specific anti- or non-aromatic structures into a certain ground state geometry of a poly(aromatic) will be evaluated in combination with the effect of resonance.

3.2 Substituents

It should be stressed that substituents not only influence the bandgap but also other electronic parameters as the ionisation potential ($\approx$ top of the valence band energy) and the electron affinity ($\approx$ bottom of the conduction band energy). These parameters are of fundamental interest for applications such as the construction of electronic devices e.g. diodes and transistors.^[1] Although substituents have a non-negligible influence on electronic parameters, in general they are in the order of, as far as the bandgap is

concerned, only a few 0.1 eV. The changes appear to be insufficient to obtain a real low bandgap material.

For well known conducting polymers as poly(paraphenylene) (PPP), poly(thiophene) PT and poly(paraphenylenevinylene) (PPV) the influence of substituents has already been investigated on the experimental and theoretical level. However, in the case of PITN there is a lack of experimental data describing the influence of electron donating and electron withdrawing substituents. Therefore only some earlier theoretical investigations will be discussed.

Only Brédas et al.^[2, 3] reported the results of calculations on the 5,6-dimethyl, 5,6-dimethoxy and 5,6-dicyano substituted aromatic PITN derivatives. From these data it can be concluded that the overall effect of electron donating and electron withdrawing substituents is rather small and the reported bandgap values only show a difference of maximum 0.05 eV. The results of *ab initio* Hartree-Fock crystal orbital calculations^[4] for dihydroxy- and dicyano-substituted poly(isonaphthothiophene) point in the same direction.

In conclusion, experimental results indicate that the main interest in substituents is not at the level of the search for *intrinsic* low bandgap conducting polymers. The main interest should rather be situated at the level of fine-tuning of the electronic characteristics for well defined applications and at the level of processability. Indeed, McCullough et al.^[5, 6] and Riecke et al.^[7, 8] developed quasi-simultaneously, synthetic routes for pure and highly regioregular alkyl substituted thiophenes. The so-obtained poly(thiophene)s appeared to exhibit surprisingly high conductivities and a bandgap of 1.7 eV which is about 0.4 eV smaller than those reported for regiorandom poly(alkylthiophene)s.

3.3 End Groups

From the previous discussion on low bandgap conjugated polymers (chapter 2) it could be concluded that within the class of poly(aromatics) two ground state geometries are possible, the aromatic geometry and the quinoid geometry. If one wishes to compare the relative energies of these geometries for a hypothetical poly(aromatic), three situations are possible. In the first situation the ground state energy of the aromatic structure is significantly lower (Figure 3.1a) than the ground state energy of the quinoid structure (for example PT). In Figure 3.1c the potential energy diagram for the inverse situation is

showed (for example polynaphthothiophene). And finally the relative ground state energies of both the aromatic and quinoid structure might be almost equal (Figure 3.1b).

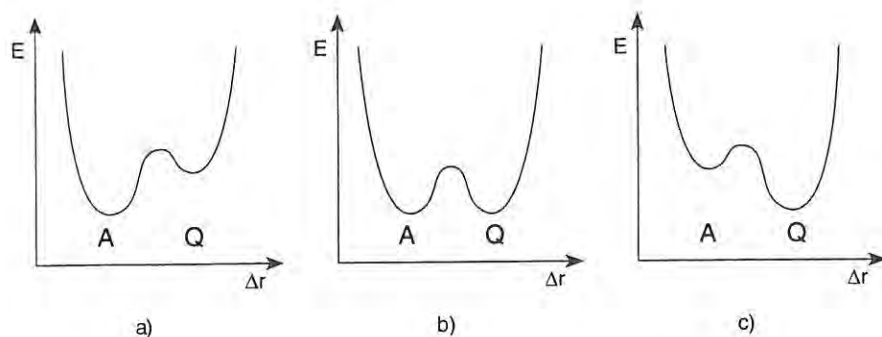


Figure 3.1 Potential energy diagrams for three possible ground state energy situations of a poly(aromatic).

The question arising at this point is to what extent the geometry of the polymer chain is determined by the energy difference between the aromatic and the quinoid structures. Quantum calculations^[9] have shown that the nature of the end groups and the structure of the chain are directly related. Defect-free systems correspond to the aromatic geometric structure while the presence of sp^3 defects or sp^2 end groups is related to the quinoid form. (Figure 3.2) In the case of PT, as the energy difference between the two forms is large (8.7 kcal/mole per repeat unit),^[9] quinoid oligomers of increasing length rapidly become less and less stable relative to their aromatic counterparts. For a certain chain length, one thus expects that an alternative structure possessing an aromatic character and two unpaired electrons will be favoured over the quinoid form. This has been observed from quantum chemical calculations on thiophene oligomers.^[9] Therefore, long quinoid oligothiophenes are not expected to exist, a situation that can be considered as typical of systems where the energy difference between the two forms is large.

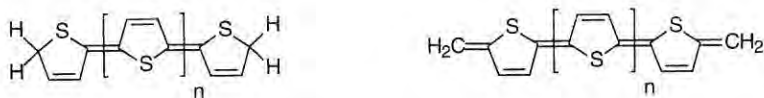


Figure 3.2 Different chain ends corresponding with a quinoid structure.

In contrast, the quinoid and aromatic forms of PITN appear to be almost isoenergetic (2.2 kcal/mole).^[9] Since this feature is observed with different theoretical methods, this small difference is to be considered an intrinsic characteristic of the PITN system. Consequently, both structures are predicted to be much more stable than the hypothetical diradical intermediate. Therefore, depending on the chemical strategy chosen for the polymerisation, one can select the structure which will be obtained, with small probability of crossing over to the other form through the high-energy diradical species. In this situation, the polymerisation mechanism and the nature of the monomer and of the end groups can orient the synthesis. Thus compounds containing from the beginning sp^3 CH_2 sites or carbonyl end groups will most probably result in PITN possessing a quinoid structure. On the other hand, altering on the same basis the synthetic conditions can lead to PITN with an aromatic geometric structure, as demonstrated by Okuda et al.^[10] who prepared the aromatic isothianaphthene tetramer using a 1,3-di(*tert*-butyldimethylsilyl) isothianaphthene monomer. (Figure 3.3)

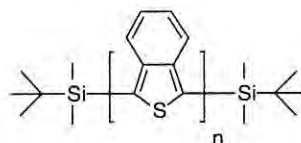


Figure 3.3 Aromatic isothianaphthene oligomers ($n = 1-4$) with geometry orienting silicon end groups.

3.4 Resonance

3.4.1 π Delocalisation across the Polymer Backbone

Chain extended π electron delocalisation or resonance across the different ring systems in poly(aromatics) is to an important extent dependant on the torsion angle θ between the monomer units (Figure 3.4).

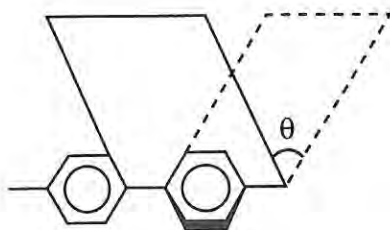


Figure 3.4 The torsion angle θ between two aromatic ring systems.

On the theoretical level, Brédas et al.^[11] studied the evolution of the bandgap in function of increasing torsion angle. As could be expected, the bandgap increased going from a coplanar situation (0°) to a perpendicular situation (90°). However, up to a torsion angle of about 40° , the bandgap showed no important changes. This effect was attributed to the $\cos\theta$ dependence of the π orbital overlap of neighbouring ring systems. Therefore substituents inducing only a small difference in torsion angle will not have a too important influence on the electronic properties. Analogous results were obtained by Lagerstedt et al.^[12] using HMO calculations. Conformational calculations on PT by Cui et al.^[13] indicated also an increase of the bandgap when the torsion angle increases. The value of the bandgap will rise to a maximum value at 90° , corresponding to no π electron interactions between neighbouring ring systems. Further increase of the torsion angle will result in a decrease of the bandgap as π electron interactions will increase again. The bandgap of 1.7 eV at a torsion angle of 180° (*trans* coplanar) agree relatively well with the experimental value of 2.1 eV of PT. At a torsion angle of 90° the bandgap will reach the maximum value of 4.5 eV. (Figure 3.5) This is an increase of about 2.4 eV. Changes in the torsion angle between 180° and 140° only results in an increase of 0.6 eV. Slight deviations from the coplanar situation will therefore result in moderate changes in the bandgap value.

All these different theoretical calculations are in accordance with one another. Therefore we can conclude that the difference between a full planar and a perpendicular configuration will be of a few eV. However due to a $\cos\theta$ dependence of the π electron overlap, a torsion angle up to about 40° will not induce a significant change of the bandgap value. More generally, all factors leading to a decreasing π delocalisation across the polymer backbone will result in a increasing of the bandgap and *vice versa*.

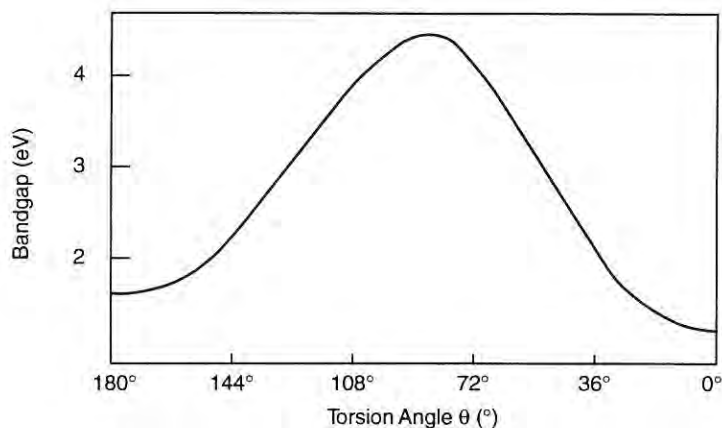


Figure 3.5 Evolution of the bandgap in function of the torsion angle.^[13]

However, the bandgap value will mostly change only to a small degree in one direction or another as shown by experimental results. Yasser et al.^[15] reported an unusual conjugated chain distortion of a sexithienyl oligomer induced by the presence of bulky triisopropylsilyl endgroups. The torsion angles of the different thiophene rings appeared to vary between 21° and 58°. However the difference between the $\lambda_{\max}$ of this compound and the non-substituted thiophene hexamer appeared not to be very important. On the other hand, increasing the π electron interaction by planar rigidification of a thiophene trimer using CH_2 bridges (Figure 3.6) leads to a lowering of the $\lambda_{\max}$ by about 20 nm ($\Delta E \approx 0.2$ eV).^[14]

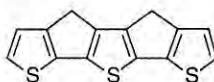


Figure 3.6 Rigidification by means of CH_2 bridges lowers the bandgap.^[14]

3.4.2 Resonance energy, Aromaticity and Bandgap

Since most of the conducting polymers contain aromatic ring systems, it is worthwhile to look closer into a possible correlation between resonance (or π delocalisation in terms of the valence-bond theory), aromaticity and the bandgap. The following discussion will be pursued within the framework of the Hückel Molecular Orbital (HMO) theory.^[16-26]

More generally speaking, the delocalisation stabilisation or resonance energy, RE, is defined as the difference between the total π electron energy, $E_{\pi, \text{HMO}}$, of a certain conjugated molecule obtained from the HMO approach and a corresponding hypothetical reference structure.

$$\text{RE} = E_{\pi, \text{HMO}}(\text{conjugated molecule}) - E_{\pi}(\text{reference structure})$$

The choice of a reference structure is more or less arbitrary. Classically the RE is defined as

$$\text{CRE} = E_{\pi, \text{HMO}} - n_{\text{=}}(2\alpha + 2\beta)$$

with CRE, the classical resonance energy, and $n_{\text{=}}$, the number of isolated carbon-carbon double bonds with the HMO calculated π electron energy of ethylene, i.e. $(2\alpha + 2\beta)$. This more traditional method to calculate the Hückel resonance energy of conjugated hydrocarbons by comparing the π electron energy, $E_{\pi, \text{HMO}}$, with $n_{\text{=}}(2\alpha + 2\beta)$ has some serious shortcomings. Indeed, this method predicts a substantial resonance energy for linear polyenes, whereas the experiment shows the resonance energy in these molecules to be rather small. Moreover, this method predicts substantial resonance energy for certain cyclic polyenes that experiment reveals to be unstable, with no aromatic character. A cyclic conjugated polyene is said to be *aromatic* when it shows substantially more stability than a hypothetical structure in which the double bonds do not interact with one another and when it undergoes substitution, rather than addition, when treated with electrophilic reagents thereby maintaining the cyclic conjugated π system.

To produce more reliable predictions of aromaticity, Hess and Schaad proposed a new definition for the resonance energy.^[17-25] Following a suggestion of Dewar,^[26]

Hess and Schaad calculated resonance energies of cyclic hydrocarbons by comparing the compounds' Hückel-theory $E_{\pi, \text{HMO}}$ with a value, $E_{\pi, \text{loc}}$, calculated for a hypothetical acyclic conjugated polyene with the same number and kinds of bonds as in the localised structure of the cyclic hydrocarbon. Thus

$$RE = E_{\pi, \text{HMO}} - E_{\pi, \text{loc}}$$

where $E_{\pi, \text{loc}} \approx \sum n_b E_{\pi, b}$ and n_b , the number of bonds of a given type, and $E_{\pi, b}$, an empirical energy parameter associated with a bond of type b . Hess and Schaad distinguish eight types of bonds over which the summation should go. Indeed, a conjugated hydrocarbon has three types of carbon-carbon single bonds and five types of double bonds, the types differing in the number of H atoms bonded to the carbons. In the calculations of the resonance energy, the terms involving α always cancel. In Table 3.1, showing the Hess and Schaad values, $E_{\pi, b}$, for the various bond types, the terms involving α will be omitted.

Bond Type	Calculated π bonding energy (β)
$\text{H}_2\text{C}=\text{CH}$	2.000
$\text{HC}=\text{CH}$	2.0699
$\text{H}_2\text{C}=\text{C}$	2.000
$\text{HC}=\text{C}$	2.1083
$\text{C}=\text{C}$	2.1716
$\text{HC}-\text{CH}$	0.4660
$\text{HC}-\text{C}$	0.4362
$\text{C}-\text{C}$	0.4358

Table 3.1 Hess and Schaad π bonding energy values (β) for the eight possible bond types.

Any acyclic or cyclic polyene can be constructed by various combinations of these eight types of bonds. Using the values of Table 3.1 one is able to calculate the π electron

energy, $E_{\pi,loc}$, for a localised cyclic polyene in an additive fashion. The resonance energy is then found as the difference between the cyclic polyene's Hückel π electron energy, $E_{\pi,HMO}$, and the quantity $E_{\pi,loc}$. This method gives the resonance stabilisation of cyclic polyenes relative to non cyclic polyenes. For comparison of a set of various types of compounds it is more significant to use the resonance energy per electron (REPE). A compound with a substantially positive REPE value is then predicted to be *aromatic*. A compound with a near-zero REPE is *non aromatic*. A compound with a substantially negative REPE is predicted to be *anti aromatic*, being less stable than if its double bonds were isolated from one another.

	RE (β)	REPE (β)	E_g (eV)
Benzene	0.390	0.065	3.4
Pyridine	0.348	0.058	-
Pyrazine	0.293	0.049	-
Pyrrole	0.233	0.039	3.1
Thiophene	0.193	0.032	2.1
Furan	0.044	0.007	2.3
Isobenzofuran	0.018	0.003	-
Isoindole	0.292	0.029	-
Isothianaphthene	0.247	0.025	1.1

Table 3.2 Resonance energy (RE) and resonance energy per electron (REPE) values for various heterocyclic polyenes following the method of Hess and Schaad together with the bandgap values (E_g) of the corresponding polymers.

An analogous approach for bond types containing oxygen,^[19] nitrogen^[19, 22] and sulphur^[21] heteroatoms made it possible to evaluate resonance energies in heterocyclic polyenes. Comparison with experiment shows that the Hess and Schaad method is highly successful in predicting aromaticity. Table 3.2 gives the RE and the REPE for heterocyclic polyenes (Figure 3.7) which can be used in synthesis of conducting polymers.

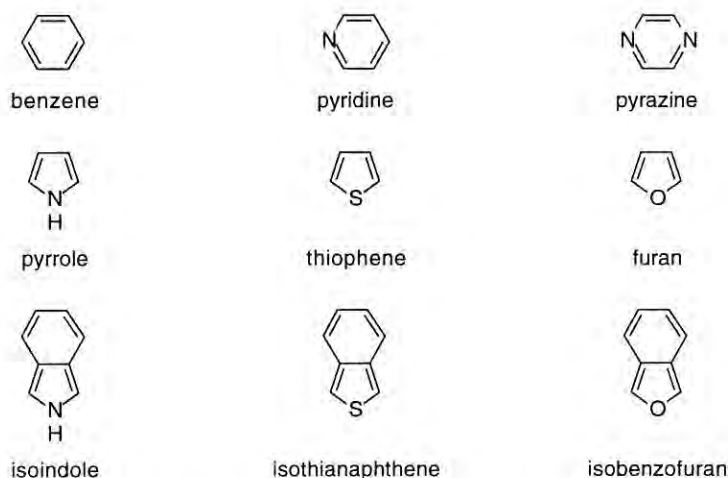


Figure 3.7 Various heterocyclic polyenes which can be used for the synthesis of conducting polymers.

In order to compare the REPE and the value of the bandgap (E_g) of the corresponding polymer the experimentally available values for the E_g of PPP, poly(pyrrole) (PP), PT, poly(furan) (PF) and PITN are also given in Table 3.2. From these data it appears that the bandgap decreases with decreasing REPE value. This means that the less aromatic, the lower the bandgap will be. The effect appears to be large enough to result in a decrease of the bandgap from PPP to PITN of about 2.5 eV.

However this evolution seems to be limited by the chemical stability of the involved ring systems. Indeed, the reported bandgap of PF appears to be larger than the bandgap reported for PT.^[27] Compared to pyrrole and thiophene, furan is the most chemically unstable as predicted by its REPE value of 0.007 (non aromatic). The presence of absorptions characteristic of aliphatic and carbonyl moieties in the vibration spectra of PF^[28] are attributed to its chemical instability, particularly in the oxidised doped state, and particularly with respect to ring opening by nucleophilic reagents. Therefore, electrical conductivities and free carrier mobilities were found to be considerably lower as compared to the other five-membered aromatic heterocycles. In some cases the ring opening process during polymerisation was so extensive that no conjugated material was obtained.

With the exception of PITN, it is calculated that the quinoid structure of the above mentioned polymers should possess a lower bandgap as compared to their aromatic

ground state structure. One method to lower the bandgap is to enhance quinoid contribution to the ground state. Another approach could be to introduce some anti aromaticity in the polymer backbone. There are experimental indications that this results in a lowering of the bandgap. Indeed, Lambert et al.^[29, 30] made some conducting polymers in which some anti aromatic character was introduced by adding a carbonyl group or a dicyano group to the thiophene monomer (cyclopenta[2,1-b;3,4-b']dithiophene-4-one and 4-dicyanomethylene-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene). (Figure 3.8) This results in a monomer with a π system with 12 electrons possessing a lower RE. Incorporation of an empty p orbital is believed to lower the bandgap to an important extent. The bandgap of both polymers is reported to be lower than 1.2 eV.

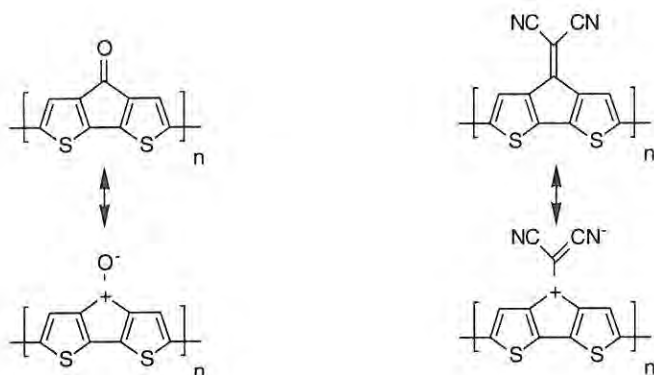


Figure 3.8 Two examples of polymers in which some anti-aromaticity has been introduced, poly(cyclopenta[2,1-b;3,4-b']dithiophene-4-one) and poly(4-dicyanomethylene-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene).

3.4.3 Resonance Stability of the Aromatic Monomer Unit

The method of Hess and Schaad indicates that the resonance stability of the classical aromatic five- and six-membered ring systems is determined to a large extent by the presence of heteroatoms. However, the influence of the heteroatom was initially assumed to be an essentially indeterminable effect on the σ bond of the carbon chain. Later, Mintmire et al.^[31] showed that many of the observed properties of heterocyclic ring chain polymers could be understood by incorporating the heteroatom p orbital into the π band structure and assuming no heteroatom effects on the σ bond structure, because the latter are theoretically difficult to predict and to understand fully. They suggested that the interaction of the lone pair of the sulphur heteroatom with the HOMO and LUMO of poly(acetylene) results in a larger bandgap for the aromatic structure of PT and on the other hand in a smaller bandgap for the quinoid structure. (Figure 3.9)

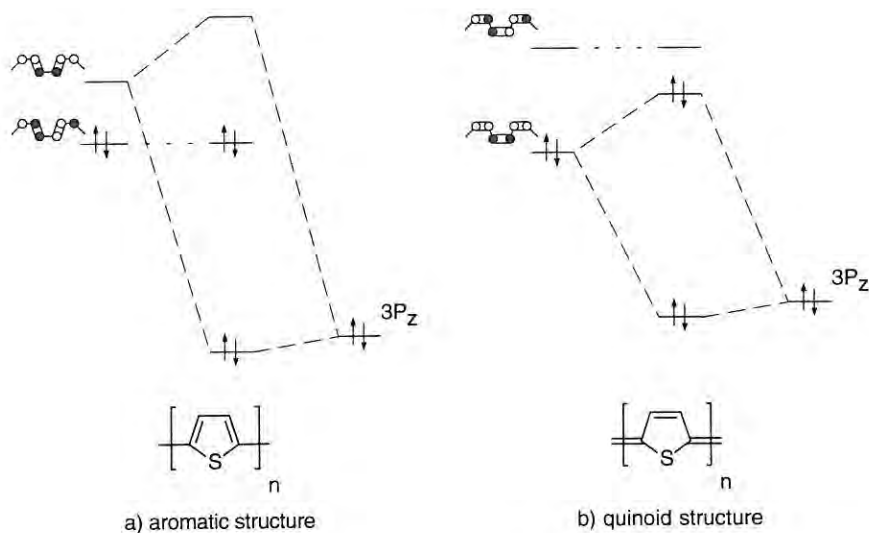


Figure 3.9 The interaction of the lone pair of the sulphur heteroatom with the HOMO and LUMO of poly(acetylene) results in a larger bandgap for the aromatic structure of PT and on the other hand in a smaller bandgap for the quinoid structure.

As already appeared from the qualitative aromaticity evaluation by Hess and Schaad, the presence of heteroatoms in aromatic ring systems can thus considerably influence the electronic properties. With the design of low bandgap conducting polymers in mind, the introduction of heteroatoms into the aromatic ring could be used to stabilise or destabilise aromatic or quinoid contributions to the ground state geometry of a certain polymer. The effect of such a substitution on the relative stability of aromatic ring systems can be assessed by means of the REPE as defined by Hess and Schaad.

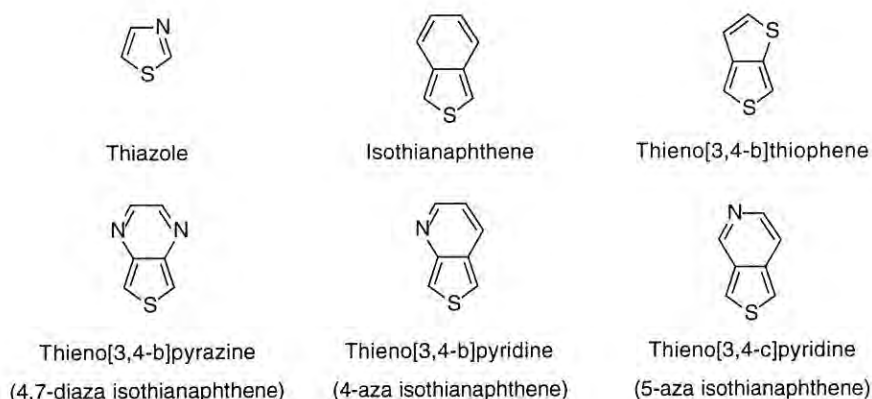


Figure 3.10 Introduction of nitrogen and sulphur in the thiophene and isothianaphthene ring systems.

Since the polymer obtained from isothianaphthene possesses a rather small bandgap of 1 eV, we chose to evaluate the relative resonance stabilities of some isothianaphthene derivatives in which additional heteroatoms were introduced. Indeed, it can be expected that the introduction of nitrogen or sulphur atoms into the additional benzene ring will influence the resonance stabilisation to a considerable extent. (Figure 3.10) If the heteroatom introduction occurs in the fused benzene ring this will have an important consequence on the resonance stabilisation of the aromatic and quinoid structure of the polymer. The resonance stabilisation of the quinoid structure will be more importantly influenced than the aromatic structure, since in the aromatic structure the resonance stabilisation is mainly governed by the thiophene aromaticity.

Although Hess and Schaad compared the aromaticity of a large number of heterocyclic compounds, only the data of cyclic systems containing one type of

heteroatom were reported. In order to be able to compare the ring systems listed in Figure 3.8 we needed to calculate the compound's Hückel π electron energy, $E_{\pi, \text{HMO}}$, and the π electron energy, $E_{\pi, \text{loc}}$, for the corresponding localised heterocyclic polyene using the different empirical π bond energies of carbon-carbon and carbon-heteroatom bonds.^[17-25]

Compound	$E_{\pi, \text{HMO}}$	$E_{\pi, \text{loc}}$	RE (β)	REPE (β)
benzene	8	7.6080	0.3920	0.0653
pyridine	7.2493	6.9010	0.3483	0.0581
pyrazine	6.4881	6.1951	0.2930	0.0488
pyrrole	5.4351	5.2018	0.2333	0.0389
thiazole	4.4921	4.286	0.2061	0.0344
thiophene	5.1855	4.9926	0.1929	0.0322
isoindole	11.0194	10.7266	0.2928	0.0293
isothianaphthene	10.7636	10.5174	0.2462	0.0246
4-aza isothianaphthene	10.0846	9.8395	0.2451	0.0245
5-aza isothianaphthene	10.0488	9.8111	0.2377	0.0238
4,7-diaza isothianaphthene	9.3628	9.1616	0.2012	0.0201
thieno[3,4-b]thiophene	8.1011	7.9552	0.1459	0.0146
furan	4.5982	4.5540	0.0442	0.0074
isobenzofuran	10.0960	10.0788	0.0172	0.0017

Table 3.3 Values for a series of aromatic heterocyclic systems of the Hückel π energy, $E_{\pi, \text{HMO}}$, the $E_{\pi, \text{loc}}$ of the localised reference structure as determined by Hess and Schaad,^[17] the RE and the REPE.

The calculation of $E_{\pi, \text{HMO}}$ was performed using a PC program by Vanderzande and the so obtained results were checked with the Macintosh program HMO-plus 1.5.1 by Wissner.^[32] Both programs are based on the classical literature of HMO theory.^[33-35] In order to use the results of Hess and Schaad for comparison with other heterocycles, the parameter set as published by Hess and Schaad was used to obtain $E_{\pi, \text{HMO}}$. However, the so obtained value of $E_{\pi, \text{HMO}}$ has to be corrected for the presence of the heteroatom electrons. Indeed, each isolated carbon atom has a π energy α , but that of a heteroatom contributing two electrons to the π system is $2(\alpha + h_x\beta)$ where h_x is a

coulomb integral heteroatomic correcting parameter. This parameter is determined by Hess and Schaad based on semiempirical methods. Therefore the obtained $E_{\pi, \text{HMO}}$ had to be corrected by subtracting for each heteroatom electron participating in the π system the corresponding coulomb integral parameter.^[19] Table 3.3 gives a list of the final corrected $E_{\pi, \text{HMO}}$, the $E_{\pi, \text{loc}}$ of the localised reference structure, the RE and the REPE of different aromatic compounds. The calculated values were compared with the available data of Hess and Schaad and appeared to be in excellent agreement with one another. Figure 3.11 gives a graphic representation of the lowering of the REPE in the different heterocyclic systems.

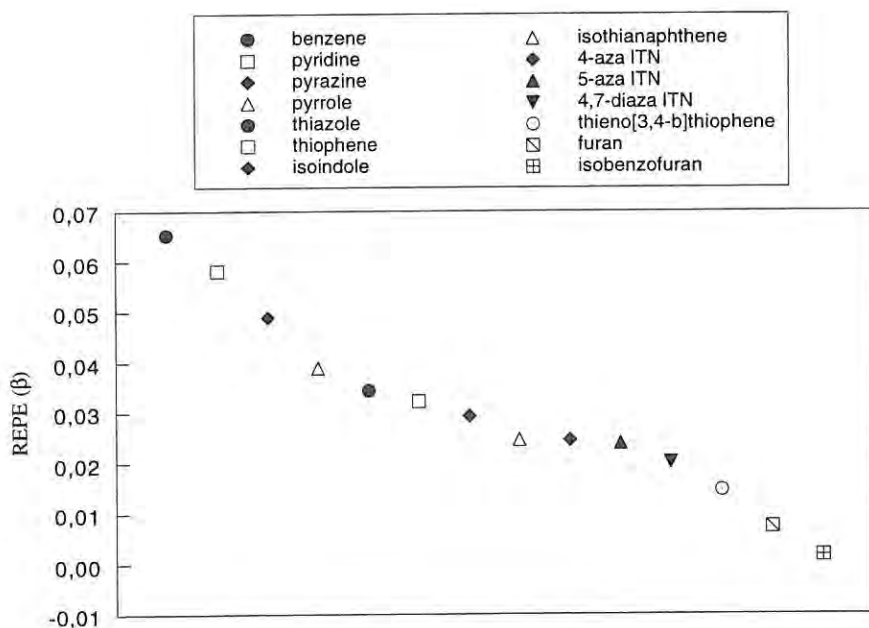


Figure 3.11 Comparison of the resonance energy per electron (REPE) for different aromatic heterocyclic ring systems.

From the comparison of the REPE isobenzofuran appears to be non aromatic which corresponds with its reactive nature. Furan has also a very small REPE and behaves much like a polyene as it undergoes Diels-Alder reactions readily while pyrrole and thiophene do not. Isothianaphthene has a REPE which is considerably lower than thiophene. As compared to thiophene the stability of isothianaphthene is not high due to

readily accessible pathways leading to benzene derivatives through for example Diels-Alder reactions as demonstrated by Cava et al.^[36] The introduction of one nitrogen atom does not lower the REPE substantially, but when a second nitrogen is introduced to obtain the 4,7-diaza derivative of isothianaphthene the REPE drops down further. Finally, thieno[3,4-b]thiophene, which can be considered as a thiophene derivative with instead of a β - β' fused benzene ring a β - β' fused thiophene ring, has a REPE which is even lower than that of the 4,7-diaza derivative of isothianaphthene. If there is a link between the REPE and the bandgap, than the above data indicate that poly(thieno[3,4-c]pyrazine) and poly(thieno[3,4-b]thiophene) could be interesting low bandgap polymers (Figure 3.12).

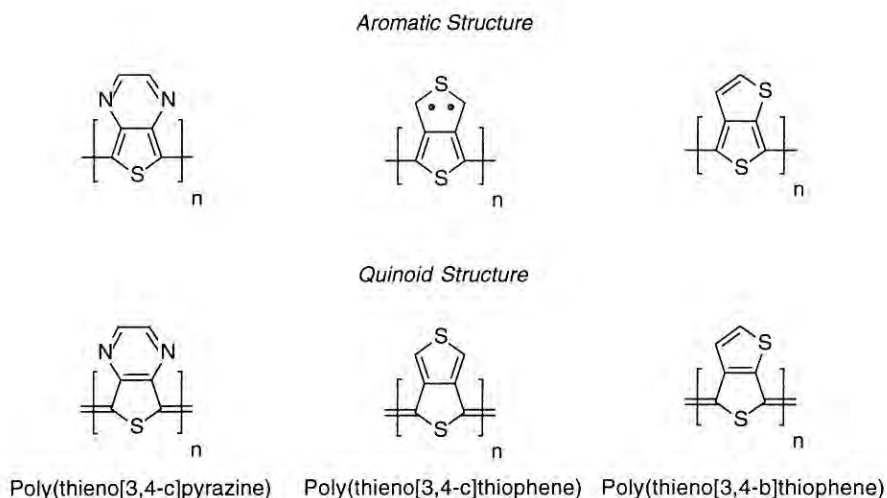


Figure 3.12 The aromatic and quinoid structure of conducting polymers obtained by the introduction of heteroatoms (nitrogen, sulphur) in the isothianaphthene ring system.

Indeed, theoretical calculations based on the extended Hückel and PRDDO methods^[37] on poly(thieno[3,4-c]pyrazine) indicate that this polymer should possess a bandgap which is about 0.12 eV for the aromatic planar structure and 0.7 eV for the quinoid structure. The same calculations predict the quinoid structure to be the most stable form. However the difference between the aromatic and the quinoid structure is about 4.2 kcal/mole per repeat unit. This energy difference is not very large and is comparable with that of PITN (2.4 kcal/mole) within the PRDDO approach. This implies

that also for poly(thieno[3,4-c]pyrazine) the synthesis method can play an important role in determining the final structure of the polymer. Other theoretical results^[4] based on *ab initio* Hartree-Fock crystal orbital calculations also indicate a lowering of the bandgap as compared to PITN. An additional characteristic of poly(thieno[3,4-c]pyrazine) is that due to the substitution of nitrogen in the 4 and 7 position, the steric interaction between hydrogen and sulphur has been lost. Therefore it should be possible in some way to obtain an aromatic planar conformation in this polymer. This configuration should correspond with a good conductivity due to enhanced extended π delocalisation.

A very recent publication, where the results of Raman spectroscopy were combined with theoretical calculations, indicate, however, that the ground state structure should be quinoid as in the case of PITN.^[38]

The first calculations evaluating the introduction of additional sulphur atoms into isothianaphthene like ring systems concerned poly(thieno[3,4-c]thiophene). In this polymer the fused benzene ring of PITN is replaced by a fused thiophene ring. However the VEH based calculations^[39] predict a larger bandgap for the aromatic structure of this polymer. Analysis of the HOMO and LUMO band structure showed the polymer to possess a pronounced quinoid structure. Since the aromatic structure will be characterised by the presence of a diradical, the quinoid structure will be substantially more stable as compared to the aromatic diradical. Calculations by Kertesz et al.^[40, 41] and Hong et al.^[42] also indicate that this polymer should possess a quinoid structure and a larger bandgap as compared to PITN.

Hong et al.^[42] also studied the electronic properties of poly(thieno[3,4-b]thiophene). In this polymer however they found a very slight energy difference of 0.3 kcal/mole per repeat unit between the aromatic and the quinoid structure whereas in poly(thieno[3,4-c]thiophene) this energy difference is about 30.5 kcal/mole per repeat unit. The bandgap of the aromatic structure was predicted to be somewhat higher as compared to PITN, but the bandgap of the quinoid structure should be lower as compared to the bandgap of quinoid PITN. The small energy difference between the aromatic and quinoid structure of poly(thieno[3,4-b]thiophene) makes it difficult to determine its most stable ground state structure. However, this implies also that its structure can be controlled by means of appropriate chemical synthetic methods.

3.4.4 Combination of Ring Systems with a Different Aromaticity

When two types of conducting polymers are combined to form a new polymer, the bandgap of the new polymer will be in between those of the corresponding homopolymers. A well known example is PPV which can be considered as a copolymer of PPP and poly(acetylene) and which has a bandgap in between those of the corresponding homopolymers.

Thus the combination of two different ring systems to form a copolymer allows an important control of electronic properties. Indeed, if for example isothianaphthene units are introduced in a thiophene backbone (Figure 3.13), one can expect the bandgap to lower significantly as compared to PT itself. A number of calculations^[43-45] support this idea and already several attempts^[46-51] have been made to obtain systems consisting of a combination of thiophene units and isothianaphthene type ring systems. Although these results mention bandgaps in between those of the homopolymer systems, the presence of important amounts of oligomeric material urges further investigation of the obtained products.

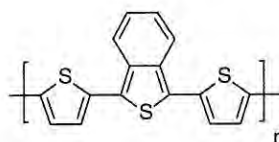


Figure 3.13 Example of a copolymer based on thiophene and isothianaphthene.

3.5 Conclusions

The aim of this overview was to look for structural tools which can be used for the design of low bandgap polymers. We therefore investigated through a detailed analysis of literature to what extent substituents, end groups and the stability of π delocalisation influences the electronic properties such as the bandgap.

In the case of PITN type polymers, theoretical calculations predict substituents not to alter the bandgap significantly. The main interest should rather be situated at the level of fine-tuning of the electronic characteristics for well defined applications and improving the properties during processing.

The nature of the end groups seems only to be important for those polymers where the energy difference between the aromatic and quinoid structure is very small. For these polymers, the structure and therefore the electronic properties could be controlled by appropriate synthesis methods.

Variation of the π delocalisation appears to be the most important tool to shape the electronic properties in a significant way. A fully planar extended π system favours electron delocalisation across the polymer backbone and thereby lowers the bandgap and improves conductive properties.

From classical Hückel Molecular Orbital theory and experimental data, there are some indications that a qualitative correlation may exist between the bandgap and the resonance stabilisation. Apparently a lower resonance stabilisation of an heterocyclic ring system coincides with a lower bandgap of the corresponding polymer. This qualitative correlation can be used as a rough guideline for further synthesis of low bandgap polymers but can by no means replace more sophisticated calculations.

Additionally, the introduction of additional heteroatoms has an influence as well on the resonance stability as on the geometric structure (lowering of steric interactions). And finally by combining different aromatic ring systems resulting in copolymers, the electronic properties can be substantially altered and are in general situated in between those of the corresponding homopolymers.

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Low Bandgap Conjugated Polymers. Improved Model Compounds for the Structural Analysis of Poly(isothianaphthene)

4.1 Introduction

In order to design new low bandgap conjugated polymers in a straightforward way, it is essential to understand the relationship between the structure and the corresponding electronic properties of these materials. Therefore, theoretical techniques to estimate electronic properties based on the structure should be combined with experimental structural data of already known compounds. Since the intrinsic conductivity (without doping) depends on the bandgap, the relationship^[1] between the degree of bond length alternation and the bandgap of non degenerate ground-state conjugated polymers is very useful. The bond length alternation of poly(thiophene) (PT) was reduced by fusing a benzene ring into each unit. The so-obtained poly(isothianaphthene) (PITN, **1**) possesses a 1 eV bandgap, as determined by optical absorption, compared to 2 eV for the parent thiophene polymer. This conjugated polymer may be dominated by either a quinoid or an aromatic electronic structure. Investigation of the electronic structure of PITN is not only interesting from a fundamental point of view but also important for the design of PITN derivatives with superior properties. Hoogmartens et al. therefore investigated the structure of PITN^[2, 3] with a joint experimental and theoretical approach.

The relative stability of the aromatic and quinoid forms of PITN was estimated on the basis of the energy per repeat unit (E_{pru}) using a series of oligomers. The energies of both geometric structures (AM1-optimized) are very close. The planar aromatic form is on the average 2.7 kcal/mole less stable than the quinoid form. Allowing the ITN units to rotate around the inter-ring bonds (to an average optimal dihedral angle of 27°) induces a small stabilisation of the aromatic ITN oligomers of the order of 0.5 kcal/mole per repeat unit. The bandgap was calculated with a valence effective Hamiltonian (VEH) on the

basis of the AM1-optimized geometry of the hexamers. These results showed that the VEH calculated bandgap for quinoid PITN ($E_g = 1.19$ eV) is in good agreement with the bandgap derived from optical spectroscopy (onset of the spectrum of the polymer located at 1.0 eV).^[4]

For the experimental structural analysis of PITN, Hoogmartens et al.^[5] focused on high resolution solid-state ^{13}C NMR. The ^{13}C chemical shift of the four inequivalent carbons of PITN (C3, C3a, C4 and C5) could be estimated with the aid of a multipurpose ^{13}C CP/MAS NMR pulse sequence. These values were compared to the data obtained on model molecules, unambiguously possessing either an aromatic or a quinoid structure. Isothianaphthene (**2**) and 1,3-bis(methylene)benzo[*c*]thiophene (**5**), referred to as the "first-order" model compounds, did not represent the structure of PITN well enough because the benzo[*c*]thiophene skeletons are not part of an extended conjugated π -system.

The simulation of the structure of PITN was improved in the so called 'second-order' model compounds 1,3-diphenylisothianaphthene (**3**) and 1,3-dibenzylidene isothianaphthene (**6**). Herein, the central ITN unit is inserted in a conjugated backbone due to the introduction of terminal phenyl rings. For the aromatic model compound (**3**), there is no correspondence whatsoever with PITN. In contrast, the chemical shifts of C3a and C5 in (**6**) are in nice agreement with the values of PITN. The observed significant difference for C3 and C4 was explained by the fact that the shift of these carbons in PITN is also influenced by the S-atom of the neighbouring unit. This situation is not accounted for by the second-order model compounds since there are no S-atoms in the aromatic side groups.

In this part,^[6] we present the synthesis and the NMR characterisation of aromatic (**4**, **7** – **10**) and quinoid (**11**, **12**) model compounds with S atoms in the aromatic side groups. Herein, the chemical environment of C3 and C4 is comparable to the situation in the polymer. These "third-order" model compounds allow us to study the influence of the S-atom in the neighbouring ring and to criticise the usefulness of the previously reported "second-order" model compounds. Finally it should be mentioned that the synthesis and analysis of all the quinoid model compounds were part of the Ph.D. research work by Hoogmartens.

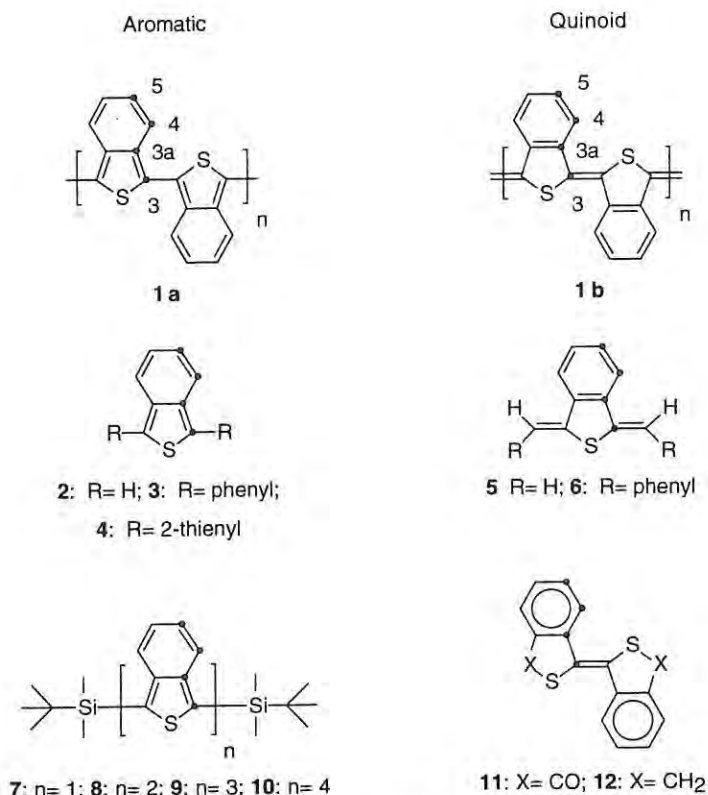


Figure 4.1 Chemical structures of PITN (**1**), first-order (**2** and **5**), second-order (**3** and **6**) and third-order (**4**, **7-10** and **11-12**) model compounds.

4.2 Full ¹H and ¹³C Chemical Shift Assignment

4.2.1 General Approach

The model compounds we are interested in for the ¹³C NMR characterisation of PITN often contain exclusively aromatic carbons. The resonances, representing these carbons in the ¹³C spectra are thus located in a small chemical shift region. For the structural analysis of our model compounds we need to perform a full proton and carbon chemical shift assignment. Therefore we developed a routine which permits discrimination between carbon or proton atoms even if their NMR signals are very close

together in the spectra. In addition this routine can be applied to most organic compounds.

In this procedure, we have to start with the analysis of the molecular structure in order to assign unambiguously at least one carbon or hydrogen atom. For this purpose one can make use of *chemical shift* (e.g. the shift difference between a carbonyl carbon atom and an aromatic carbon atom is large enough to be distinguished), *first order splitting or coupling pattern*,^[7] *coupling values*^[8] and *peak areas*. If necessary, *specific 1D-NMR techniques* (NOE and APT e.g.) can be applied to obtain an additional objective criterion for an unambiguous assignment. In some cases even the *heteronuclear coupling behaviour* of a particular carbon atom in 2D-NMR experiments may be used (see also the assignment of 1,3-dithienylisothianaphthene). The shifts of these atoms are then used as starting points to elaborate a pathway for further assignment using 2D-NMR techniques. In most cases a full proton and carbon shift assignment can be achieved using direct ^1H - ^{13}C heteronuclear correlations (optimised for $J_{\text{CH}} = 140$ Hz) and long range ^1H - ^{13}C heteronuclear correlations (optimised for $J_{\text{CH}} = 8$ Hz). In situations where the molecular structure does not allow a full chemical shift assignment based on two dimensional ^1H - ^{13}C heteronuclear correlation (HETCOR) alone, additional 2D-NMR experiments (COSY, ...) can be performed in order to obtain an unambiguous assignment.

4.2.2 Aromatic Model Compounds

The silylated isothianaphthene oligomers were synthesised according to the method of Okuda et al.^[9] For the synthesis of thiophthalic anhydride we used the method reported by Reissert et al.^[10] (Scheme 4.1). The numbering of carbons and protons used in the full proton and carbon shift assignment is given in Figure 4.2

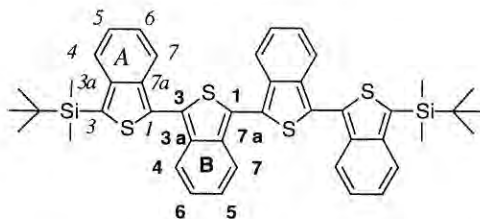
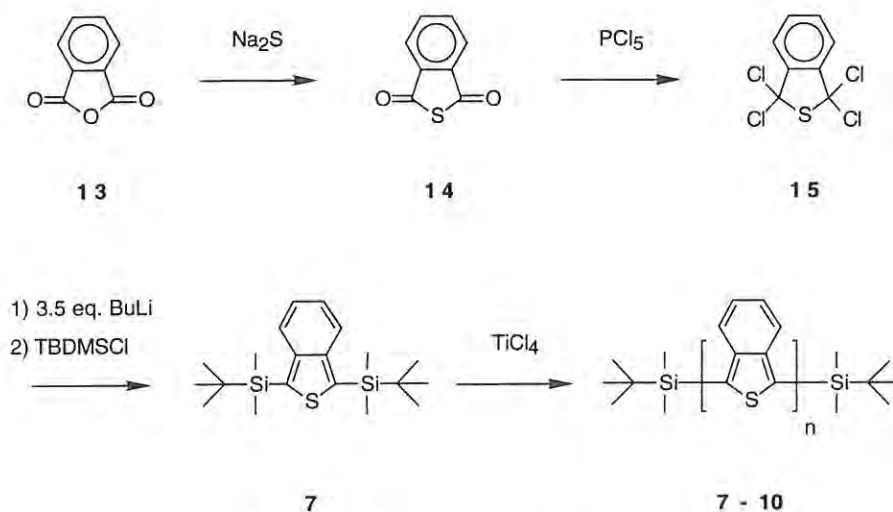


Figure 4.2 Numbering of the disilylated oligomers (7 - 10).



Scheme 4.1 Synthesis of the silylated isothianaphthene oligomeric model compounds (**7 - 10**).

(1) Disilylated Isothianaphthene Monomer (7) The integration allows us to attribute the singlets at 0.54 and 0.98 ppm in the aliphatic part of the ^1H NMR spectrum to the methyl groups attached to silicon and to the methyl groups of the *tert*-butyl group respectively. The three carbons of the silicon end group were assigned in the ^{13}C NMR spectrum on the basis of an attached proton test (APT) and the integration. In the APT, the signals of CH and CH_3 carbons remain positive while those of C and CH_2 carbons become negative when proper parameters are used. Thereby the signals at -3.9, 18.2 and 26.8 ppm correspond with the methyl carbon attached to the silicon atom, the quaternary carbon atom and the methyl carbon of the *tert*-butyl group, respectively. The methyl carbon attached to the silicon atom can be used as a starting point for further analysis of the HETCOR spectra.

For reasons of symmetry the protons H4[A] and H7[A] have identical chemical shifts as have H5[A] and H6[A] . The same remark can be made for the ^{13}C chemical shifts. A distinction between the protons H4[A] and H5[A] was made on the basis of a NOE-effect (due to the spatial proximity) between H4[A] and the methyl groups attached to silicon. In this double resonance experiment, the singlet at 0.54 ppm was selectively

irradiated. This permits us to assign the signals at 7.83 and 7.11 ppm to H4[A] and H5[A], respectively. As for all the oligomers two groups of signals are observed in the ^1H -NMR spectra. The group at 7.11 ppm can be assigned to H5/H6 and the group at 7.7-8.0 ppm to H4/H7 of both isothianaphthene ring systems.

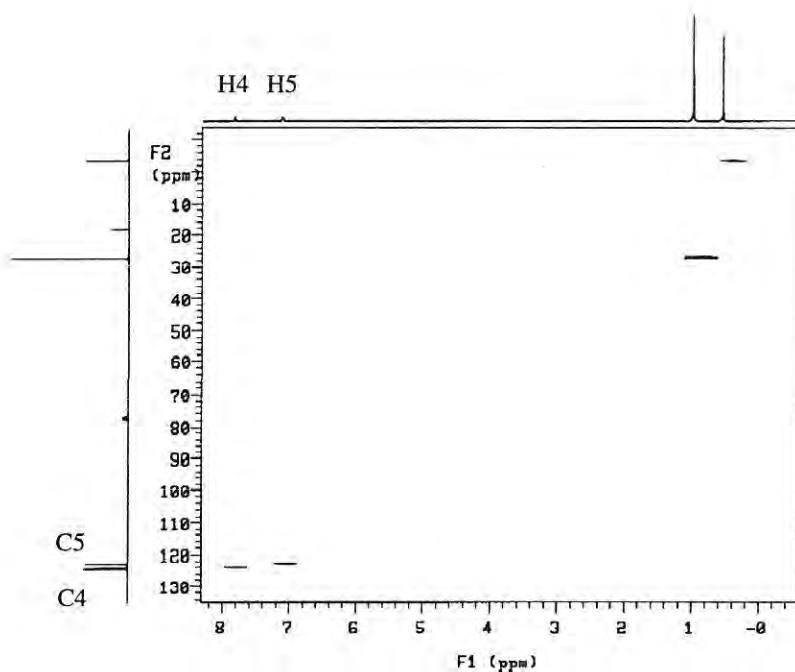


Figure 4.3 2D heteronuclear ^1H - ^{13}C correlation spectrum of **7** optimised for $J_{\text{CH}} = 140$ Hz (CDCl_3 , 30°C)

The assignment of H4[A] and H5[A] allows the assignment of the two protonated carbon atoms C4[A] and C5[A] to the signals at 124.0 and 122.6 ppm respectively, with the aid of the direct HETCOR-spectrum optimised for $J_{\text{CH}} = 140$ Hz. (Figure 4.3)

For the assignment of the quaternary carbons the HETCOR spectrum optimised for $J_{\text{CH}} = 8$ Hz is used. (Figure 4.4) Herein, correlations appear due to geminal and vicinal couplings. The starting point is the methyl groups attached to silicon (0.54 ppm). The signal at 135.0 ppm shows a correlation with the protons of these methyl groups. Since these aliphatic protons are too far removed from C3a[A] (four bonds), the correlation arises from the coupling with C3[A]. The remaining quaternary signal at 146.5 ppm is

therefore assigned to C3a[A] which is confirmed by the correlation with H7[A] and H5[A].

Assignments of the aliphatic nuclei of the silicon end groups in the other oligomers (di-, tri- and tetramer) are performed by following the same strategy as for the monomer mentioned above.

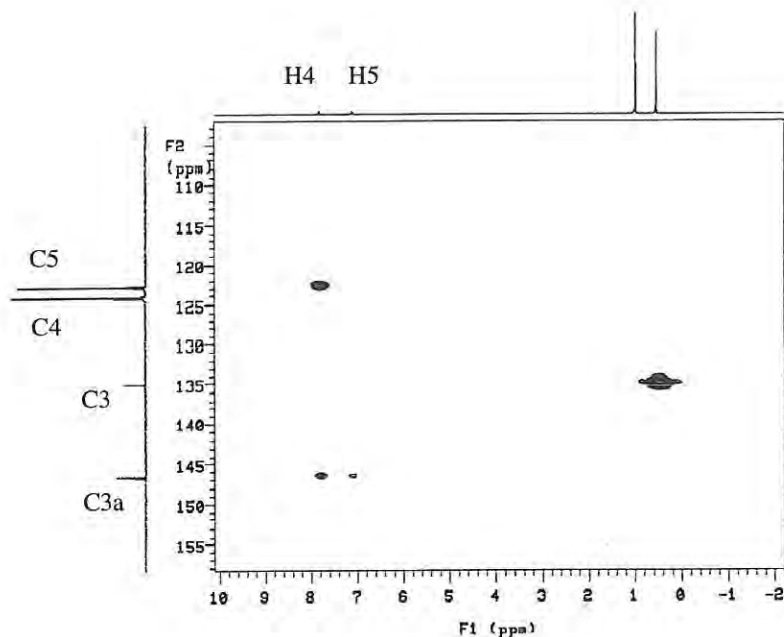


Figure 4.4 2D heteronuclear ^1H - ^{13}C correlation spectrum of **7** optimised for $J_{\text{CH}} = 8 \text{ Hz}$ (CDCl_3 , 30°C)

(2) **Disilylated Isothianaphthene Dimer (8)** In comparison to the monomer, two new signals in the ^1H NMR (H6[A] and H7[A]) appear. The hydrogens H5[A] and H6[A] collapse in the region 7.10 - 7.18 ppm because of the small difference in chemical environment. The hydrogens H4[A] and H7[A] are represented in the spectrum by two double doublets at 7.76 and 7.86 ppm, respectively. Differentiation between both hydrogen atoms could be made using NOE as in the monomer. This allows

us to assign H4[A] to the signal at 7.76 ppm. The remaining proton signal at 7.86 ppm can therefore be assigned to H7[A].

In the aromatic part of the ^{13}C NMR spectrum we see four new signals compared to the monomer. The protonated carbons C4[A] and C7[A] are assigned with a 2D-HETCOR spectrum optimised for $J_{\text{CH}} = 140$ Hz (Figure 4.5) to the signals at 123.9 and 122.0 ppm, respectively. Using 2D COSY distinction could be made between C5[A] and C6[A] which can therefore be assigned to the signals at 123.7 and 123.6 ppm, respectively.

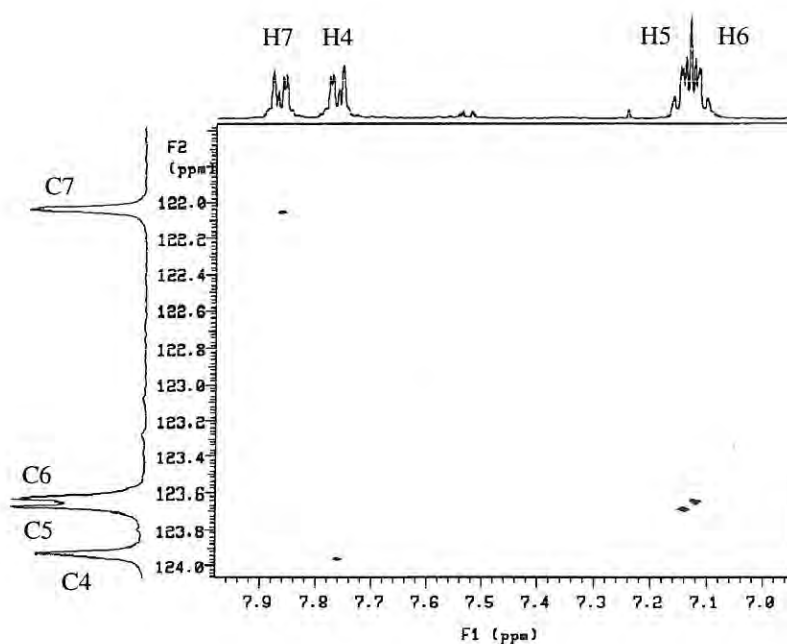


Figure 4.5 2D heteronuclear ^1H - ^{13}C correlation spectrum of **8** optimised for $J_{\text{CH}} = 140$ Hz (CDCl_3 , 30°C)

For the assignment of the quaternary carbon atoms again the starting point common to all oligomers can be used. In the 2D-HETCOR spectrum optimised for $J_{\text{CH}} = 8$ Hz, C3[A] correlates with the proton of the methyl group attached to the silicon atom and is thus assigned to the signal at 129.2 ppm. This assignment is further confirmed by the vicinal coupling with H4[A], assigned previously by means of NOE. Thoroughly

exploring the 2D-HETCOR spectrum optimised for $J_{\text{CH}} = 8$ Hz we find two groups of ^{13}C signals. The signals at 137.5 and 145.6 ppm show a correlation with the H5[A]/H6[A] multiplet as well as with H4[A] or H7[A] (Figure 4.6). On the other hand the signals at 129.2 and 132.2 ppm just show a correlation with H4[A] or H7[A]. As only C3a[A] can show long range couplings with H7[A] and H5[A] and only C7a[A] can show long range couplings with H4[A] and H6[A], we can assign the signals at 137.5 and 145.6 ppm to C7a[A] and C3a[A], respectively. In the remaining group the signal at 129.2 ppm has been assigned to C3[A] previously by its correlation with the proton of the methyl group attached to the silicon atom. The remaining quaternary signal at 132.2 ppm can therefore be assigned to C1[A], which is confirmed by its long range coupling with H7[A].

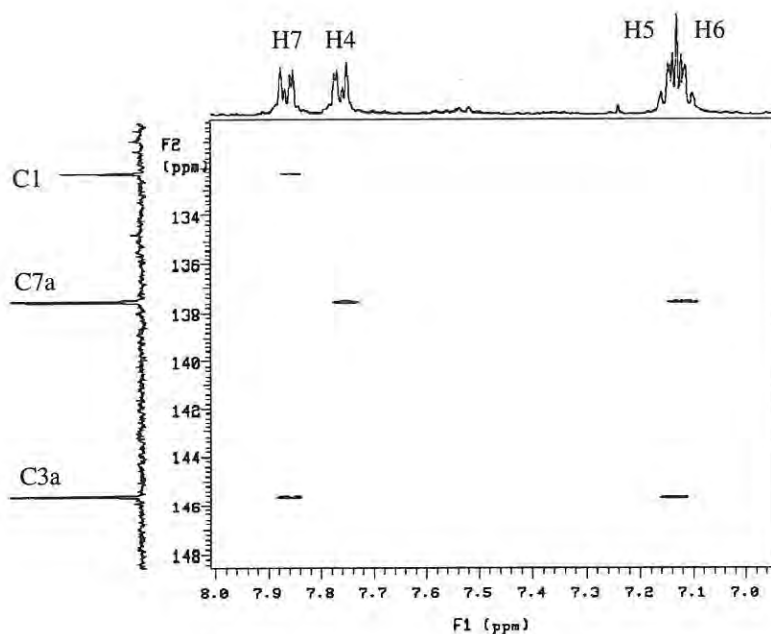


Figure 4.6 2D heteronuclear ^1H - ^{13}C correlation spectrum of **8** optimised for $J_{\text{CH}} = 8$ Hz (CDCl_3 , 30°C)

From this assignment it appears that in qualitative ^{13}C NMR spectra the signals of C1[A] and C3[A] show a lower intensity compared to C3a[A] and C7a[A]. Also within the monomer this intensity difference between C3[A] and C3a[A] can be observed. The

lower intensity of C1[A] and C3[A] originates from an inadequate relaxation through dipole-dipole interactions with neighbouring protons. C3a[A] and C7a[A] on the other hand are subject to a more efficient relaxation due to the relative closer proximity of the aromatic protons, resulting in a higher intensity of the ^{13}C NMR signals. Therefore the C1[A] and C3[A] groups show longer spin-lattice relaxation times and smaller NOE-effects which is reflected by smaller intensities in qualitative ^{13}C NMR spectra. This feature can be used in the further analysis of the trimer and tetramer.

(3) Disilylated Isothianaphthene Trimer (9) For reasons of symmetry the protons H4[B] and H7[B] have identical chemical shifts as have H5[B] and H6[B]. The same remark can be made for the ^{13}C chemical shifts. Due to very similar chemical environments, in the ^1H NMR spectrum of the trimer the new proton H5 of the B isothianaphthene ring collapses with H5 and H6 of the A ring, (7.10 - 7.18 ppm). We can assign the multiplet at 7.10 - 7.18 ppm to H5[A], H6[A] and H5[B].

To find the signal of H4[A], we have to use the NOE effect (due to the spatial proximity) between H4[A] and the methyl groups attached to silicon. This allows us to assign the signal at 7.75 ppm to H4[A]. H4[B] is represented in the spectrum by a double doublet (7.86 ppm), which is less distorted than the patterns of H4[A] and H7[A] because of molecular symmetry. The remaining multiplet at 7.94 ppm can then be assigned to H7[A].

As the ^1H NMR spectrum has been assigned completely, the protonated carbons C4[A], C7[A] and C4[B] are assigned with a 2D-HETCOR spectrum optimised for $J_{\text{CH}} = 140$ Hz. C4[A] is assigned to the signal at 124.0 ppm. C7[A] and C4[B] have to be assigned to the same signal at 121.9 ppm. However, at the 140 Hz optimisation level no distinction could be made between C5[A], C6[A] and C5[B] because of the overlap in the ^1H dimension.

Considering the quaternary carbons, in analogy to the monomer and dimer they can be divided into two groups. The carbons C3[A], C1[A] and C3[B] are removed from the aromatic protons further than the carbons C3a[A], C7a[A] and C3a[B], resulting in smaller intensities.

In the first group C3[A] can be assigned through the very specific long range coupling with the silicon end group to 129.8 ppm. Through comparison of this result with the shift of C3[A] in the dimer there is only a difference in chemical shift of about 0.6 ppm. It seems reasonable to expect the shift of C1[A] not to undergo substantial changes; therefore in comparison with the dimer we can assign the shift at 131.6 ppm to C1[A]. The shift difference is in this case even lower: 0.4 ppm. The remaining signal at

126.7 ppm within this subgroup of quaternary carbon atoms should then be considered as new and can be assigned to C3[B].

The second group of quaternary carbon atoms can be assigned using 2D-HETCOR optimised for $J_{\text{CH}} = 8$ Hz due to the long range coupling of C3a[A], C7a[A] and C3a[B] with H7[A], H4[A] and H7[B], respectively to 145.6, 137.6 and 136.5 ppm. The fact that the signal of C3a[A] is isolated (145.6 ppm) from the others can be explained by the influence of the bulky end groups. This is further confirmed by the chemical shift of C7a[B] in the tetramer (136.6 or 136.7 ppm, Figure 4.7).

As the shifts of C5[A], C6[A] and C5[B] could not be assigned using 2D-HETCOR optimised for $J_{\text{CH}} = 140$ Hz we have to revert to the 2D-HETCOR spectrum optimised for $J_{\text{CH}} = 8$ Hz. C5[A], C6[A] and C5[B] show a vicinal long range coupling with H7[A], H4[A] and H7[B] and can therefore be assigned to 123.8, 123.9 and 124.7 ppm. This is also confirmed by comparison of the shifts of C5[A] and C6[A] in the dimer. The difference in chemical shift is only 0.2 ppm and the signal at 124.7 ppm appears to be the new signal compared to the dimer.

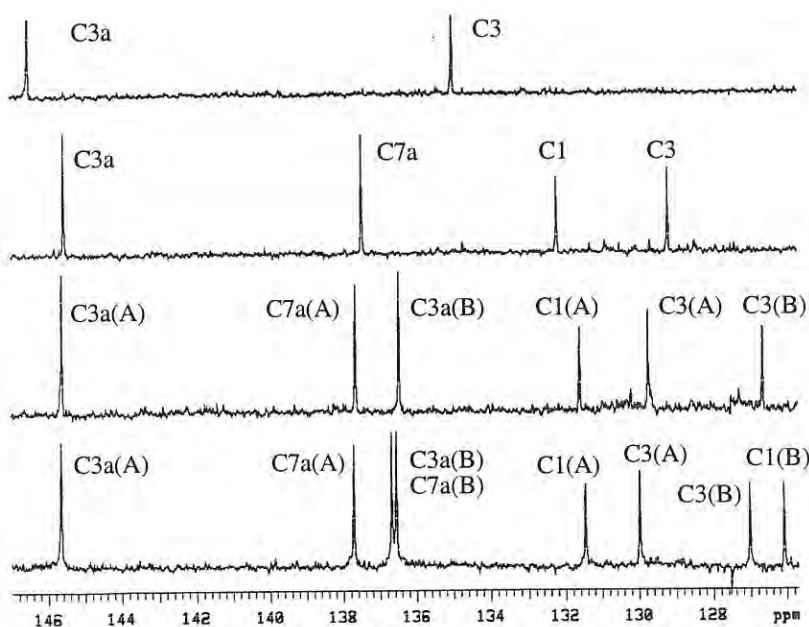


Figure 4.7 Proton decoupled ^{13}C NMR spectra of (7 - 10) showing the signals from the quaternary carbon atoms.

(4) Disilylated Isothianaphthene Tetramer (10) Due to very similar chemical environments, in the ^1H NMR spectrum of the tetramer the new proton H6 of the B isothianaphthene ring merges with H5 and H6 of the A ring and H5 of the B ring. We can therefore assign the multiplet at 7.10 - 7.18 ppm to H5[A], H6[A] and H5[B], H6[B].

The assignment of H4[A] is again based on the NOE effect between H4[A] and the methyl groups attached to silicon. This allows us to assign the signal at 7.76 ppm to H4[A]. If we take into account that the H7 protons of both rings have almost identical chemical environments we may assume that the shifts of H7[A] and H7[B] will merge, as is the case with the H5 and H6 protons. On the basis of integration and comparison with the trimer we thus assign the multiplet at 7.99 ppm to these protons. The remaining multiplet at 7.89 ppm can then be assigned to H4[B].

On the basis of direct heteronuclear coupling we can now try to assign the protonated carbon atoms. H4[A] shows a coupling with the carbon shift at 124.0 ppm, which can thus be assigned to C4[A]. In the case of the H4[B] multiplet we note a coupling with the signal at 122.0 ppm assigning thereby C4[B]. The multiplet belonging to the H7 protons shows a correlation with the signal at 121.9 ppm. Therefore this signal can be assigned to C7[A] and C7[B]. At the 140 Hz optimisation level the coalescence of the proton shifts of H5 and H6 again prevent the assignment of the corresponding carbon atoms. However further assignment can be performed through the 2D-HETCOR optimised for $J_{\text{CH}} = 8\text{ Hz}$. H4[A] can show a long range coupling with C5[A] (geminal) and C6[A] (vicinal). On the other hand H4[B] can show a long range coupling with C5[B] (geminal) and C6[B] (vicinal). This makes it possible to break down this group of protonated carbon atoms into two groups. The signals at 123.8 and 123.9 ppm should belong to ring A and the signals at 124.9 and 125.0 ppm to ring B. This is confirmed by comparison with the other oligomers since chemical shifts are not subject to drastic changes when the carbon atoms are situated in an identical chemical environment, going from one oligomer to another. As we note only one long range coupling signal and since the 2D-HETCOR is optimised for $J_{\text{CH}} = 8\text{ Hz}$, we may assume the signals to originate from a vicinal coupling. On the basis of this vicinal coupling of H4[A] and H4[B] we therefore can assign C6[A] and C6[B] to 123.9 and 125.0 ppm. As a consequence the remaining signals C5[A] and C5[B], coupling with the H7 multiplet, are assigned to 123.8 and 124.9 ppm.

Due to the differences in intensities we can again divide the quaternary carbon signals into two groups, the C1/C3 carbon atoms with a lower signal intensity and the C3a/C7a carbon atoms with a higher signal intensity. In the first group we can assign

C3[A] based on its long range coupling with the protons of the methyl groups attached to silicon. In this way the signal at 130.0 ppm corresponds with C3[A]. From comparison (Figure 4.7) with dimer and trimer there is a remarkable similarity in the shifts of this carbon atom. Further assignment of the quaternary carbon atoms is however not possible through the 2D-HETCOR optimised for $J_{\text{CH}} = 8\text{Hz}$. Therefore we have to base our assignment on the comparison of tetramer with dimer and trimer (Figure 4.7). Former assignments prove this to be a reliable alternative. This way we are able to assign C1[A] and C3[B] to 131.5 and 127.0 ppm, respectively. The signal at 126.1 ppm appears to be the new signal and can therefore be assigned to C1[B]. In the second group of quaternary carbon atoms again no assignment can be performed with regard to the 2D HETCOR optimised for $J_{\text{CH}} = 8\text{Hz}$. Therefore the assignment of C3a[A], C7a[A], C3a[B] and C7a[B] to 145.6, 137.7, 136.6* and 136.7* ppm respectively is also based on comparison with the smaller oligomers (*: may be interchanged) (Figure 4.7).

(5) 1,3-Dithienylisothianaphthene **(4)** 1,3-Dithienylisothianaphthene was synthesised by a cyclisation^[11] of *o*-dithienoylbenzene with diphosphorus pentasulphide. The reaction of 2-thienyl magnesium bromide with phthaloyl dichloride results in a rather low yield of the *ortho* aryl diketone due to several competitive reactions. One of the problems in this context is that an intramolecular reaction of the oxygen atom of one of the carbonyl groups with the other carbonyl group may give rise to disubstituted phthalides. Therefore, phthaloyl dichloride was first converted into 1,2-(*S*-(2-pyridinyl))benzenedithioate before performing the Grignard reaction.^[12] The synthesis of these compounds will be discussed in detail in chapter 9.

For the assignment of the starting points we first need to analyse the ^1H NMR spectrum. On the basis of the coupling constants and the coupling patterns we can distinguish between the protons of the thiophene ring ($\delta = 7.14, 7.34$ and 7.36 ppm) and the protons of the isothianaphthene ring ($\delta = 7.13$ and 7.94 ppm). Furthermore, the specific coupling pattern of H4', one of our starting points, allows us to assign H4' to the multiplet at 7.14 ppm. This multiplet overlaps with one of the signals belonging to an isothianaphthene proton.

The long range 2D-HETCOR, showing mainly vicinal couplings, also shows geminal and direct correlations. Since C3/C1 is the only quaternary carbon atom to show a long range coupling with a proton from the isothianaphthene ring and a proton from the thiophene ring and since quaternary carbon atoms can easily be distinguished from protonated carbon atoms using the Attached Proton Test (APT) 1D-NMR experiment or

the direct 2D HETCOR experiment, the starting point C3/C1 can be assigned to 126.5 ppm. As C3/C1 can only couple with H4/H7 and H3' since the other protons are too far removed from C3 (more than three bonds), we can assign them to 7.94 and 7.34 ppm respectively. By this we can completely assign the ^1H -NMR spectrum since the two remaining signals belong each to another ring system. H5/H6 of the isothianaphthene ring corresponds with the double doublet at 7.13 ppm, and H5' with the double doublet at 7.36 ppm. The carbons C3a/C7a can be assigned to 135.4 ppm since it is the only signal to show a long range coupling with H7/H4 as well as H5/H6 and C3a/C7a is the only quaternary carbon that fulfils these requirements.

In the direct 2D-HETCOR optimised for $J_{\text{CH}} = 140$ Hz the five expected direct correlation signals are found. As the assignment of the ^1H -NMR spectrum is completed, all the protonated carbon atoms can be assigned: C4/C7 to 121.5 ppm, C5' to 125.5 ppm, C3' to 125.6 ppm, C4' to 127.9 ppm and C5/C6 to 124.8 ppm. Finally, from H4' we can assign C2' through a vicinal long range coupling to 135.7, which is confirmed by the fact that C2' is the only remaining quaternary carbon atom not assigned previously.

4.2.3 Quinoid Model Compounds

Although the NMR analysis has already been described in the Ph.D. work of Hoogmartens, nevertheless we would like to report the final revised analysis of (11) and (12) for the sake of completeness.

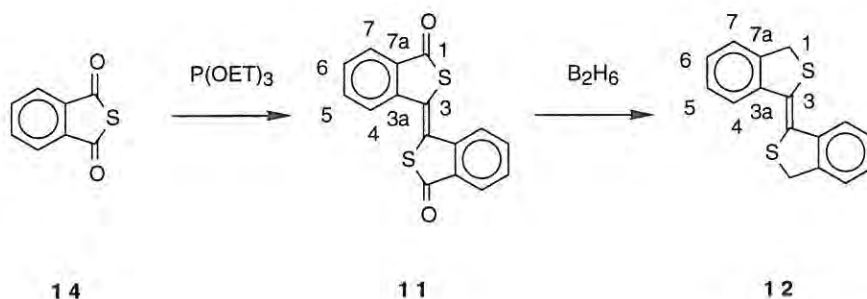
(1) *trans*-3,3'-Bibenzo[*c*]thienylidene-1,1'-dione (11) *Trans*-3,3'-bibenzo[*c*]thienylidene-1,1'-dione has already been synthesised by the reaction of 2-thiophthalic anhydride with 2 equiv. of triethyl phosphite in xylene^[13] and with an excess of triethyl phosphite.^[14] For this compound, a melting point of ± 350 °C was reported. However thermogravimetric analysis (TGA) of this product shows weight loss at 350 °C. The physical transition observed at 350 °C using differential scanning calorimetry (DSC) disappeared when cooling down. These observations indicate that we are dealing with a sublimation point instead of a melting point. Infrared,^[13] mass spectrometry^[15] and X-ray diffraction^[16] analyses are already described elsewhere, but no NMR data are available from these reports.

We first focus on the ^1H NMR spectrum of (11). At this stage we can only subdivide the four multiplets on the basis of their coupling pattern. H5 and H6 will show a triplet (7.83 or 7.61 ppm). H4 and H7 on the other hand will show a doublet (8.34 or 8.00 ppm). For further assignment we have to make an appeal to the HETCOR

optimised for $J_{\text{CH}} = 8\text{ Hz}$. Carbonyl carbon atoms have shifts situated in the region between 160 and 200 ppm. This allows us to assign C1 unambiguously to 190.1 ppm. As C1 can only have a vicinal coupling with H7, the shift at 8.00 ppm arises from H7. Therefore H4 can be assigned to 8.34 ppm. C3 is the only carbon atom to show a vicinal coupling with H4 and not at all with H5 or H6 (triplet) as a result of which we can assign C3 to the shift at 128.3 ppm. The remaining carbon atoms C3a and C7a can be assigned through their vicinal coupling with H7 and H4 to 142.3 and 134.3 ppm, respectively. Since C3a and C7a can only show long range coupling with H5 and H6, respectively, the shifts of these protons can be assigned to 7.83 and 7.61 ppm, respectively. The assignment of H5 and H6 was further confirmed by a 2D-COSY experiment. With all the ^1H NMR chemical shifts known, the protonated carbons can be unambiguously assigned with a 2D heteronuclear correlation experiment optimised for $J = 140\text{ Hz}$.

At this stage, it should be noticed that the ^{13}C chemical shift for C3a and C5 of this compound Q3 previously reported by Hoogmartens et al.^[17] is not correct since H5 and H6 were interchanged at that time.

(2) *trans*-3,3'-Bibenzo[*c*]thienylidene (12) *trans*-3,3'-Bibenzo[*c*]thienylidene (**12**) was synthesised by the reduction of the corresponding dione (**11**). We chose diborane (B_2H_6) as the reducing agent since it was previously used for the reduction of 1,8-naphthalide to 2,1,3-*peri*-naphthopyran.^[18] Sodium borohydride (NaBH_4) and boron trifluoride etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) were employed for the *in situ* generation of B_2H_6 .



Scheme 4.2 Synthesis of the quinoid model compounds (**11**) and (**12**).

The signal at 4.51 ppm in the ^1H NMR spectrum corresponds with the aliphatic protons H1. The two triplets in the aromatic part of the ^1H NMR spectrum of (**12**) arise from the protons H5 and H6, whereas the doublets arise from H4 and H7. The aliphatic carbon atom C1 resonates at 38.0 ppm, which is confirmed by its direct coupling with H1 in the 2D HETCOR experiment optimised for $J_{\text{CH}} = 140$ Hz. For further assignment we first have to analyse the 2D HETCOR experiment optimised for $J_{\text{CH}} = 8$ Hz. H7 can be assigned to 7.35 ppm on the basis of its long range vicinal coupling with C1, since other protons are more than three bonds removed from C1. Therefore H4 can be assigned to the remaining doublet at 8.24 ppm. In the same way C3 can be assigned to 127.4 ppm through its long range vicinal coupling with H4. This is confirmed by the very low intensity of the C3 signal originating from an inadequate relaxation through dipole-dipole interactions with neighbouring protons. The assignment of the ^{13}C NMR spectrum can be completed using the 2D HETCOR experiment optimised for $J_{\text{CH}} = 140$ Hz. C4 and C7 can thus be assigned to 125.2 and 125.0 ppm. The carbon signals of C5 and C6 collapse at 126.9 ppm in the carbon spectrum. For this reason we did not perform a selective irradiation experiment for the unambiguous assignment of H5 and H6. Finally, a distinction between the two remaining quaternary carbons was made on the basis of a shorter spin lattice relaxation time (T_1) for C7a relative to C3a which results in a smaller intensity for C3a compared to C7a. This makes it possible to assign 141.0 and 140.4 ppm to C7a and C3a respectively. This is further confirmed in the 2D HETCOR experiment optimised for $J_{\text{CH}} = 8$ Hz where C3a and C7a show a vicinal long range coupling with H7 and H4 respectively.

4.3 Discussion

The ^{13}C chemical shifts of the carbons C3, C3a, C4 and C5 of the central part of the third-order aromatic and quinoid model compounds will now be compared with the corresponding second-order model compounds and to the values of PITN. The comparison with the second-order model compounds allows us to determine the influence of the S atom in the aromatic side groups and to criticise the usefulness of the previously reported second-order model compounds. The third-order aromatic and quinoid model compounds have to be mutually compared in order to check whether the ^{13}C shift of these carbons is a selective criterion of the geometric structure of PITN. Finally, these shifts are compared with the polymer data. The latter were determined with the aid of a multipurpose solid state ^{13}C CP/MAS NMR pulse sequence. For the quaternary carbons, C3 and C3a, chemical shifts of 126 and 139 ppm (± 0.5 ppm), respectively were

obtained while the protonated carbons are located at 125 and 128.5 ppm (± 1 ppm). We assumed that $\delta C5 > \delta C4$, a feature which was observed in the aromatic as well as the quinoid model compounds (second- and third-order).

4.3.1 Aromatic Model Compounds

(1) **1,3-Dithienylisothianaphthene (4)** In comparison to 1,3-diphenylisothianaphthene (3), it appears that the chemical shifts of C3a, C4 and C5 of (4) remain largely unaffected (Table 4.3). This means that the S atom of the neighbouring thiophene ring has no significant influence on the chemical shift of C4 nor a very weak electronic interaction through space with H4, which can only be explained by a rotation around the inter-ring (C3-C2') bond. In contrast, the introduction of a S atom in the neighbouring ring(s) has induced a change in the chemical shift of C3 of about 8 ppm (electronic interaction through the bonds). The shift of this carbon in the second-order model compound was therefore useless in the comparison with PITN.

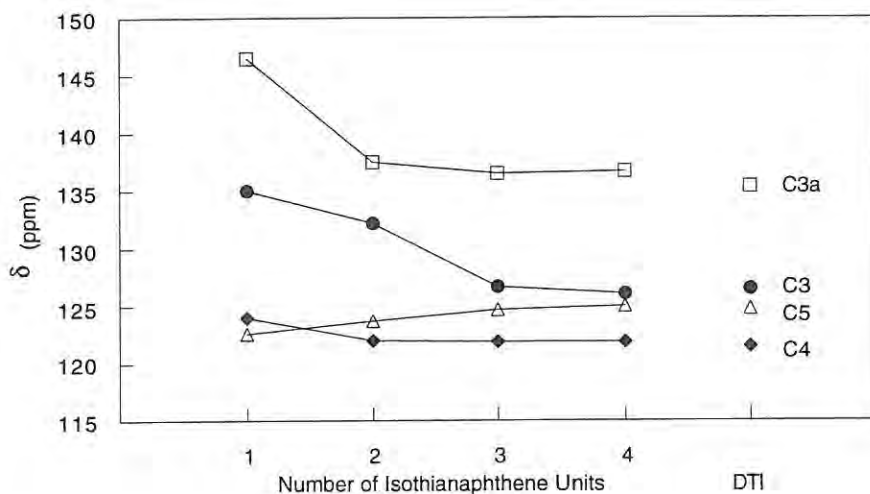


Figure 4.8 Evolution of the ^{13}C chemical shifts of the "central" carbon atoms C3, C3a, C4 and C5 of the isothianaphthene oligomers of (7 - 10) as a function of chain length.

(2) Disilylated isothianaphthene oligomers (7-10) The ^{13}C chemical shift data of the oligomers are summarised in Table 4.1. In general, comparable carbons seem to have comparable chemical shifts in the different oligomers except for C3[A] in the monomer and the dimer (135.0 cf. 129.2 ppm). For these oligomers to be useful as model compounds for the corresponding polymer, they should contain one or more isothianaphthene rings which are no longer influenced by the end groups. This is indicated by a convergence of the chemical shift as a function of chain length. Therefore, we plotted the ^{13}C chemical shifts of the "central" carbons as a function of chain length (Figure 4.8). It should be noticed that the central aromatic carbons are uniformly referred to as C3, C3a, C4 and C5 although they correspond to C1, C7a, C7 and C6 in ring A of the dimer and in ring B of the tetramer, respectively.

	7	8	9		10	
			Ring A	Ring B	Ring A	Ring B
C3	135.0	129.2	129.8	126.7	130.0	127.0
C3a	146.5	145.6	145.6	136.5	145.6	136.6 ^a
C4	124.0	123.9	124.0	121.9	124.0	122.0
C5	122.6	123.7	123.8	124.7	123.8	124.9
C6		123.6	123.9		123.9	125.0
C7		122.0	121.9		121.9	121.9
C7a		137.5	137.6		137.7	136.7 ^a
C1		132.2	131.6		131.5	126.1

Table 4.1 ^{13}C chemical shifts (CDCl_3) of the disilylated monomer (7), dimer (8), trimer (9) and tetramer (10) of isothianaphthene. (a: may be interchanged.)

From Figure 4.8, it can be seen that C4 and C5 are almost independent of the end groups. Therefore the chain length is not important as far as the shifts of these carbons are concerned. For C3a, only the shift in the monomer is not suitable. The shift of the central C3 in the dimer (C1[A]) is still affected by the end groups and a convergence is only reached starting from the trimer. For these oligomers, at least three isothianaphthene units are necessary in order to use the central part as a model for the structure of the corresponding polymer (for ^{13}C NMR purposes). The data in Figure 4.8 also illustrate

that the usefulness of a certain molecule as a model compound can only be determined with the aid of a better model compound (e.g. if the data of the tetramer were not available, the convergence of C3 could not be observed). Therefore, the trimer and the tetramer can now be used to criticise the previous model compounds. The chemical shifts of the carbons of the central unit of the tetramer are very close to those observed for (4) (Table 4.3). The introduction of some critical structural requirements (an aromatic isothianaphthene ring with aromatic side groups possessing a S atom) in a molecule seems to be enough to function as a useful model compound.

	7	8	9		10	
			Ring A	Ring B	Ring A	Ring B
H4	7.83	7.76	7.75	7.86	7.76	7.89
H5	7.11	7.10-7.18	7.14-7.18	7.14-7.18	7.12-7.20	7.12-7.20
H6		7.10-7.18	7.14-7.18		7.12-7.20	7.12-7.20
H7		7.86	7.94		7.99	7.99

Table 4.2 ^1H chemical shifts (CDCl_3) of the disilylated monomer (7), dimer (8), trimer (9) and tetramer (10) of isothianaphthene.

4.3.2 Quinoid Model Compounds

(1) ***trans*-3,3'-Bibenzo[*c*]thienylidene-1,1'-dione** (11) *trans*-3,3'-Bibenzo[*c*]thienylidene-1,1'-dione was the first molecule which gave us an idea about the influence of a S-atom in the neighbouring (quinoid) ring. As can be seen from Table 4.3, the shifts of C3, C4 and C5 have changed drastically in contrast to the second-order model compound (6). The changes for C3 and C4 may be mainly caused by the neighbouring S atom although it is hard to differentiate it from the contribution of the carbonyl end groups.

(2) ***trans*-3,3'-Bibenzo[*c*]thienylidene** (12) The influence of the carbonyl end groups, as mentioned above, has been removed in (12). From the comparison with (6), it appears that the neighbouring S atom has a very strong effect on the shift of C3. This feature has previously been observed in the aromatic model compounds. But in

contrast to the aromatic case, the shift of C4 has also significantly changed. As a consequence, the interaction between H4 and the neighbouring S atom, mainly weakened in aromatic isothianaphthene systems by inter-ring rotation, is more intense in planar quinoid systems. If one takes into account the shift differences as a result of the electron withdrawing effect of a carbonyl end group, it is clear that the data from (**11**) follow the same trend and are consistent with the data from (**12**).

Compound	C3	C3a	C4	C5
3	134.2	135.3	121.2	124.2
4	126.5	135.4	121.5	124.8
10	126.1	136.7	121.9	125.0
PITN	126.0	139.0	125.0	128.5
12	127.4	140.4	125.2	126.9
11	128.3	142.3	126.9	133.8
6	136.8	139.1	120.8	128.5

*Table 4.3 Comparison of the ^{13}C chemical shift data ($\delta(\text{ppm})$) of PITN, the aromatic (**3**, **4** and **10**) and the quinoid (**6**, **11** and **12**) model compounds.*

4.3.3 Comparison to PITN

The ^{13}C chemical shift data of the disilylated tetramer (**10**) and *trans*-3,3'-bibenzo[*c*]thienylidene (**12**) will now be used for comparison with the polymer data. We should however first check whether the shifts of C3, C3a, C4 and C5 are significantly different in an aromatic and in a quinoid environment. As we can see from Table 4.3, the shift of C3 is comparable in both structures and cannot be considered to be a selective criterion for the geometric structure. The other carbons C3a, C4 and C5, however, show differences of about 2-4 ppm between the aromatic and the quinoid model compound. The shifts of these carbons in PITN and the quinoid model compound (**12**) correspond well, while there is no correspondence whatsoever between PITN and the aromatic tetramer (**10**). These data confirm previous results that the geometric structure of PITN shows a strong quinoid character.^[3]

4.4 Synopsis

In order to analyse the geometric structure of insoluble PITN, Hoogmartens et al.^[5] estimated the ^{13}C chemical shift of the four inequivalent carbons (C3, C3a, C4 and C5) on the basis of a multipurpose solid state ^{13}C CP/MAS NMR pulse sequence. These data were used to compare to those of model molecules unambiguously possessing either an aromatic or a quinoid structure. The "first-order" model compounds (2) and (5) appeared to be useless for the comparison with the polymer data since the benzo[c]thiophene skeletons were no part of a conjugated π -system. The simulation of the structure of PITN was improved in the "second-order" model compounds (3) and (6). For the aromatic model compound, there is no correspondence whatsoever with PITN while the chemical shifts of C3a and C5 in the quinoid model compound are in nice agreement with the values of PITN. The observed significant difference for C3 and C4 was explained by the fact that the shift of these carbons in PITN is also influenced by the S atom of the neighbouring unit. This situation is not accounted for in the second-order model compounds since they possess no S atoms in the aromatic side groups. This phenomenon obliged us to synthesise new "third-order" model compounds in which the chemical environment of C3 and C4 is also comparable with that in the polymer.

For the aromatic third-order model compound (4), it appeared that the ^{13}C chemical shifts of C3a, C4 and C5 remain largely unaffected in comparison with the second-order model compound (3). This means that the S atom in the neighbouring thiophene ring has no significant influence on the chemical shift of C4. In contrast, the S atom in the neighbouring ring(s) has induced a change in the shift of C3 of about 8 ppm. This third-order model compound seemed to be a very good model for aromatic PITN since the ^{13}C data are very close to those of the central isothianaphthene ring in a disilylated aromatic tetramer (10).

For the third-order quinoid model compound (12), the neighbouring S atom has a strong influence on the shift of C3 in comparison with the second-order model compound 6. But in contrast to the aromatic case, the shift of C4 has also significantly changed. As a consequence, the interaction between H4 and the neighbouring S atom, mainly weakened in aromatic isothianaphthene systems by inter-ring rotation, is more intense in planar quinoid systems.

For the comparison with PITN, only the carbons C3a, C4 and C5 of (10) and (12) are valuable since C3 shows almost the same shift in the aromatic and the quinoid model compound. The shift of the three former carbons in PITN and in the quinoid model compound (12) correspond well while there is still no correspondence whatsoever between PITN and the aromatic tetramer (10). These results are in favour of previous

conclusions by Hoogmartens et al.^[3] indicating that the structure of PITN possesses a strong quinoid character. However, it should be noticed that, because of the small energy difference (≈ 2 kcal/mole per repeat unit) between the quinoid and the aromatic form derived from theoretical calculations, the structure of PITN may be determined much more by the chemistry of polymerisation rather than the energy difference between the alternative structures. In fact the synthesis of the aromatic oligomers (**7-10**) can be viewed as an illustration of this principle.

4.5 References

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The Structure of Poly(isothianaphthene) A Vibrational Spectroscopic Study

5.1 Introduction

FT-Raman spectroscopy uses the inelastic scattering of light to study molecular vibrations. This inelastic scattering of light is the result of a perturbation of the molecular electronic configuration by an incident photon resulting in the emission of a scattered photon with lower or higher energy. The efficiency of this interaction is related to the ease with which the electron distribution of the molecule may be perturbed or distorted, i.e. the polarizability. If the polarizability of the molecule is changed during a particular molecular vibration, then that vibration can be effective in generating a Raman-shifted photon upon interaction with an incident photon. Due to their delocalised character, the distribution of π electrons is more easily polarised than those of σ electrons. Since it is an inherent feature of conducting polymers to possess an extended π system, FT-Raman spectroscopy can be an interesting tool for the study of the electronic structure of conducting polymers.

The difference between the aromatic and quinoid structure of PITN is based on a difference in the structure of the π electron distribution. In the aromatic structure the π electrons are more or less concentrated in the isothianaphthene ring system, which can be considered as a thiophene ring perturbed by butadiene.^[1-3] In the quinoid structure, on the one hand π electrons are pinned in the fused benzene ring and on the other hand, the presence of inter-ring double bonds favours to a certain extent delocalisation across the polymer backbone. This difference in the structure of the π electron system should find expression in a difference of the FT-Raman spectra of aromatic and quinoid model compounds. Also in the field of FT-Raman spectroscopy, the comparison of the

spectroscopic characteristics of well-defined model compounds with the corresponding polymer have been of valuable aid for the interpretation of vibrational spectra.^[4]

Therefore, our goal in this chapter is to use the FT-Raman spectra of aromatic and quinoid model compounds as fingerprints characteristic of the aromatic and quinoid π electronic structure and compare them with the spectra of pristine (undoped) and doped PITN. Comparison of model compound spectra with polymer spectra is only possible if the π system of the model compound is large enough; the intensity of the Raman lines corresponding with features of the π system will then outshine those originating from aliphatic or other structures. This should appear from a comparison of the FT-Raman spectra of the series of silylated oligomers. Also the spectra of some more simple aromatic model compounds will be looked at. It should be mentioned that the quinoid model compounds are part of the Ph.D. work of Hoogmartens; the results will only be used to complete the overview of the still on-going discussion on the structure of PITN assessed by FT-Raman spectroscopy so far.

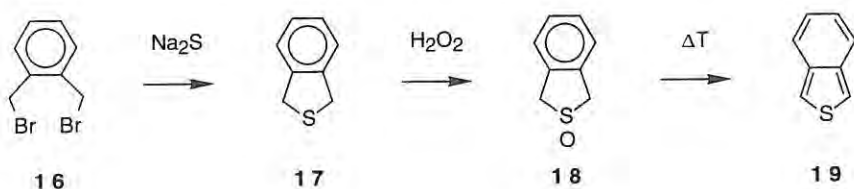
A first analysis of some of these results has been made by the group of Zerbi et al.^[5] and these findings have also been incorporated in this section. However, it should be stressed that the aim here is not to give a complete and detailed vibrational spectroscopic explanation of relationships between the FT-Raman features and the structure of PITN. A detailed vibrational analysis of conducting polymers is not always as straightforward as it seems to be. This has been demonstrated by the analysis of polyacetylene.^[4] Vibrational spectroscopic data of PITN and some of the model compounds are far from complete and therefore it is expected that, when new experimental data become available in near future, the discussion will lead to a more detailed understanding of the origin of the vibrational characteristics of PITN. Finally, the kind collaboration of Prof. M. Lapkowski and Prof. S. Lefrant of the Laboratoire de Physique Cristalline de l'Institut des Matériaux de Nantes allows the presentation of some of the preliminary results of *in situ* FT-Raman measurements on electrochemically polymerised PITN.

5.2 *In situ* FT-Raman analysis of electrochemical polymerised PITN

FT-Raman spectroscopy using an excitation wavelength of 1064 nm allows the recording of spectra of products contained in a small glass vessel. This makes the FT-Raman technique very suitable for *in situ* measurements on polymer films deposited electrochemically on an electrode. Moreover, electrochemical doping can be followed

spectroscopically as a function of the applied potential. For this purpose a specially designed electrochemical cell was used.

The isothianaphthene monomer (**2**) used in the electrochemical polymerisation was obtained via the classical synthetic route.^[6-10] (Scheme 5.1) The monomer (**2**) could be obtained from pyrolysis of 1,3-dihydrobenzo[*c*]thiophene-*S*-oxide (**18**) according to Cava et al.^[11] The synthesis of 1,3-dihydrobenzo[*c*]thiophene-*S*-oxide (**18**) was performed according to the method of Drabowicz et al.^[12] The synthesis of 1,3-dihydrobenzo[*c*]thiophene (**17**) and 1,3-dihydrobenzo[*c*]thiophene-*S*-oxide (**18**) has already been reported by Hoogmartens.^[13]



Scheme 5.1 The synthesis of isothianaphthene.

The PITN film was deposited from a monomer (**2**) solution in dry deoxygenated acetonitrile on a gold electrode by repeated potential cycling under inert atmosphere. An example of a cyclic voltammogram is given in Figure 5.1. In a glove box the gold electrode was washed to remove remaining monomer (**2**) and electrolyte solution and it was then transferred to a monomer free 0.1M tetrabutyl ammonium tetrafluoroborate/acetonitrile solution in a specially designed electrochemical cell. This cell was hermetically sealed and placed in the FT-Raman apparatus. The polymer film was first conditioned by repeating the redox cycles several times.^[14]

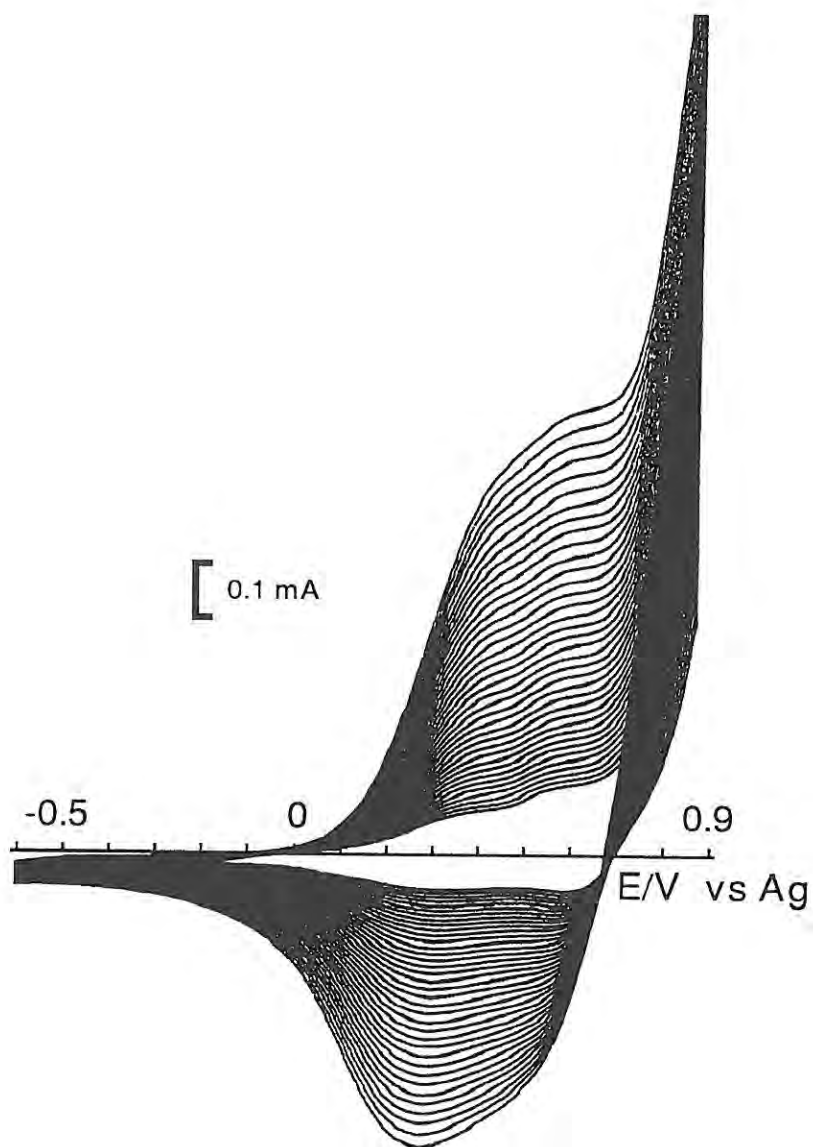


Figure 5.1 Cyclic voltammogram of PITN grown on an Au working electrode (anode) by repetitive cycling in a monomer (2) solution of dry and deoxygenated acetonitrile. Scan rate, 50mV/s; reference electrode, Ag/AgCl; cathode, platinum; electrolyte solution, 0.1M tetraphenylphosphonium chloride in acetonitrile.

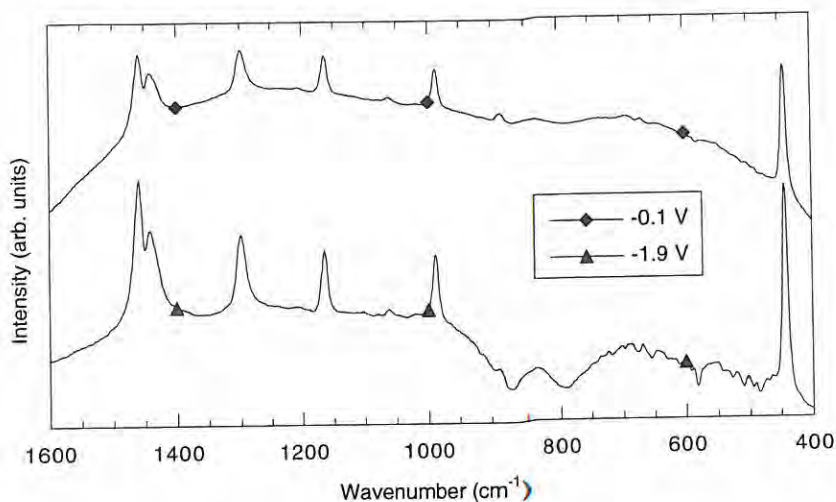


Figure 5.2 In situ FT-Raman spectra (λ_{exc} , 1064 nm) of electrochemical n-doped PITN (-0.1 and -1.9 V, respectively).

Figure 5.2 shows the spectra of slightly n-doped PITN (-0.1 V). This spectrum is characterised by a broad continuum, probably as the result of fluorescence. On this continuum there are six strong Raman bands at the following wave numbers: 1459, 1441, 1300, 1164, 989 and 443 cm^{-1} . This spectrum corresponds very well with the FT-Raman spectrum of chemically synthesised and dedoped PITN reported by Hoogmartens et al.^[15] Next additional spectra were recorded at increasing negative potentials (-0.3, -0.6, -0.8, -1.0, -1.2, -1.4, -1.7 and -1.9 V). Before recording the spectrum at a more negative potential, the film was dedoped by repeated redox cycles in order to remove any remaining effect of the previous doping process. Surprisingly, progressive decreasing potentials vs Ag/AgCl-electrode up to -1.9 V did not result in a significant change of the FT-Raman spectrum and all the spectra showed a broad continuum.

On the other hand an electrochemically deposited PITN film was progressively p-doped up to 1.2 V. (Figure 5.3). Spectra were taken at 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.1 and 1.2 V. The spectrum at 0.1 V is considered to be only slightly p-doped. Six strong Raman signals are present at 1459, 1442, 1300, 1164, 989 and 442 cm^{-1} . This spectrum corresponds well with the reported spectrum of the pristine polymer^[15] and the spectrum of slightly n-doped PITN. The broad continuum present in the n-doped spectra however clearly disappears as p-doping is increased. At 0.4 V important changes in the FT-Raman spectrum occur. Indeed, an additional signal appears at 1402 cm^{-1} as a shoulder. The

signal at 1302 cm^{-1} broadens and small signals appear at 1192 cm^{-1} and 1059 cm^{-1} . Finally, a signal at 464 cm^{-1} begins to appear.

At 0.6 V the relative intensity of the signals at 1445 cm^{-1} and 1415 cm^{-1} increases compared to the signal at 1459 cm^{-1} , which is only present as a very weak shoulder. A shoulder (1286 cm^{-1}) on the signal at 1304 cm^{-1} indicates that a second signal is present. The relative intensities of the smaller signals at 1192 cm^{-1} and 1059 cm^{-1} increase and the signal at 465 cm^{-1} also becomes more important. The signal previously at 443 cm^{-1} shifts to 448 cm^{-1} .

At 0.8 V the signal at 1415 cm^{-1} shifts to 1419 cm^{-1} . Together with the signal at 1443 cm^{-1} a broad band is formed. The maximum of the broad band at 1304 cm^{-1} is shifted to 1308 cm^{-1} , while a shoulder is present at about 1281 cm^{-1} . The smaller signals at 1192 cm^{-1} and 1059 cm^{-1} further rise in intensities. The signal at 466 cm^{-1} becomes more and more important compared with the other signal which is now at 452 cm^{-1} .

At 1.0 V the spectrum has changed significantly compared with the spectrum at 0.1 V . Between 1400 cm^{-1} and 1500 cm^{-1} a broad band is formed. This band appears to be formed by four signals at 1384 , 1418 , 1440 and 1456 cm^{-1} . The signal previously at 1308 cm^{-1} is now at 1314 cm^{-1} and a second peak can be distinguished more clearly at 1297 cm^{-1} . The peak at 1202 cm^{-1} now broadens and becomes more intense than the peak at 1169 cm^{-1} . The peak at 989 cm^{-1} which previously remained unchanged also broadens a little. The two signals at 455 cm^{-1} and 466 cm^{-1} are now almost equal in intensity. At 1.1 eV the spectrum further changes. The broad band between 1400 cm^{-1} and 1500 cm^{-1} is characterised by four signals; the signals at 1438 cm^{-1} and 1383 cm^{-1} are the most intense, the two others are situated at 1455 cm^{-1} and 1418 cm^{-1} but less intense. The signals at 1319 cm^{-1} and 1299 cm^{-1} are now almost equal in intensity. The peak at 1202 cm^{-1} has now the largest intensity. On this signal a shoulder is present at 1189 cm^{-1} and a smaller peak can be found at 1171 cm^{-1} . The signal at 997 cm^{-1} now also shows a shoulder at 987 cm^{-1} indicating the presence of a second signal. At 461 cm^{-1} only one signal remains. At 1.2 V the spectrum shows that decomposition of the PITN film has started. However the main signals of the spectrum taken at 1.1 V can still be distinguished.

This data indicates that the signals at 1459 , 1441 , 1300 , 1164 , 989 and 443 cm^{-1} are characteristic for the pristine polymer. p-Doping results in an important change of the Raman spectrum. The signals at 1415 , 1192 , 1059 and 464 are clearly the result of the doping process.

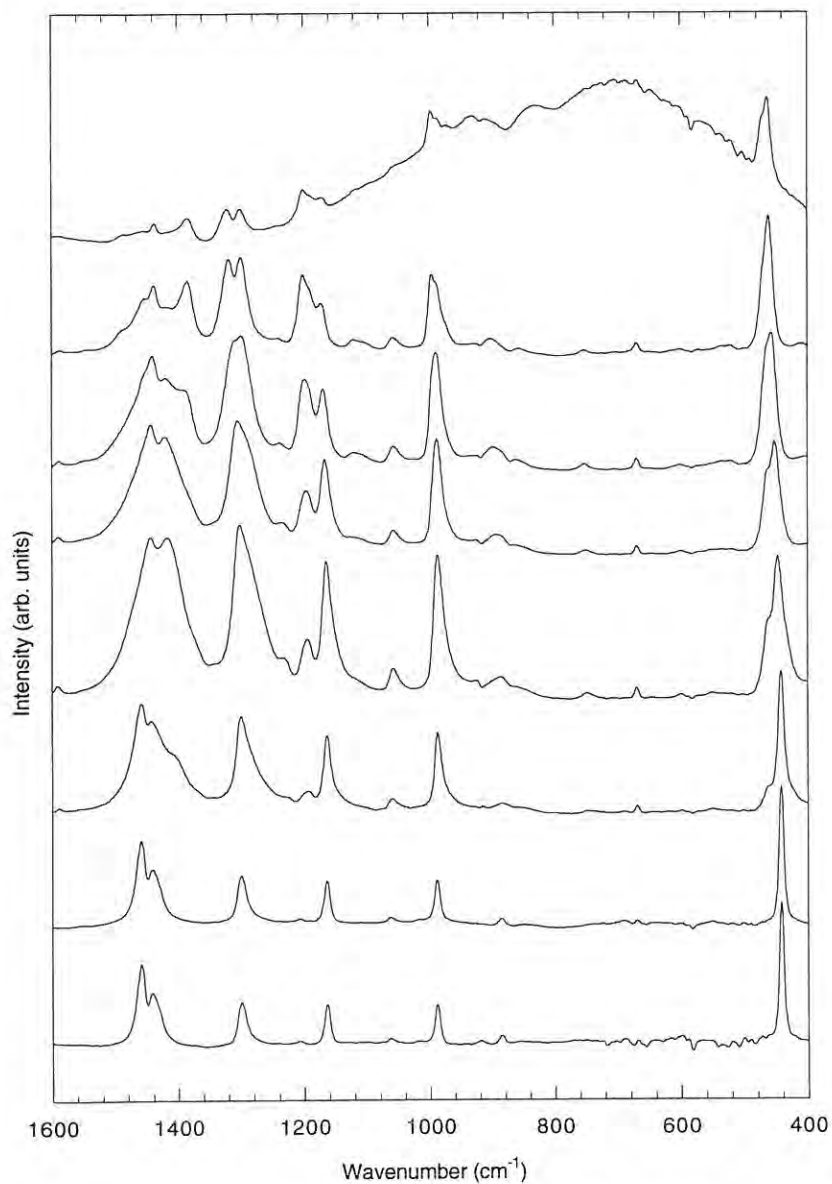


Figure 5.3 In situ FT-Raman spectra (λ_{exc} , 1064 nm) of PITN progressively p-doped at different potentials; 1.2, 1.1, 1.0, 0.8, 0.6, 0.4, 0.2 and 0.1 V, respectively.

5.3 FT-Raman spectra of aromatic PITN model compounds

There are two types of aromatic model compound which appeared useful for comparison with the polymer, namely the series of disilylated oligomers and 1,3-dithienylisothianaphthene (**4**). On the level of ^{13}C NMR spectroscopy the trimer (**9**), tetramer (**10**) and 1,3-dithienylisothianaphthene (**4**) appeared to be quite good model compounds.

Since these compounds could be obtained as crystalline or powdery products, it is not a great problem to record the FT-Raman spectrum. For this purpose the purified product is placed in an aluminium holder and fixed in the sample compartment. However it should be mentioned that the Raman spectrum is very sensitive towards impurities. When the product is not well purified, the recording of the Raman spectrum yields a broad continuum with low resolution.

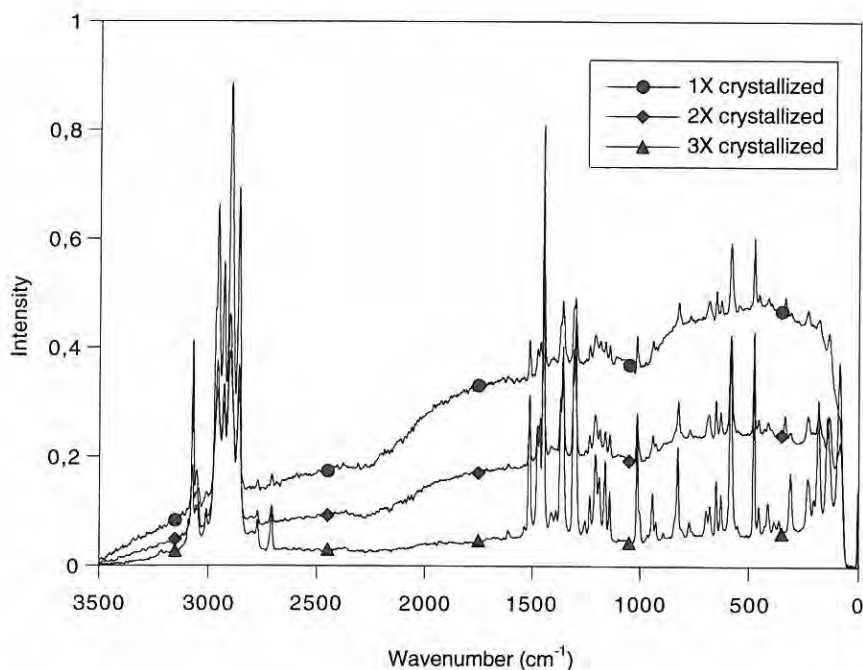


Figure 5.4 Repeated crystallisations of the silylated isothianaphthene monomer (**7**) improves the quality of the FT-Raman spectrum significantly (crystallised once, twice and three times, respectively).

As demonstrated in Figure 5.4, repeated crystallisations improve significantly the quality of the Raman spectrum. Also better spectra are obtained from freshly crystallised product. Prolonged conservation in for example the refrigerator apparently does not affect the purity but the quality of the Raman spectrum deteriorates to a large extent.

In Figure 5.5 the FT-Raman spectra of the silylated oligomers are compared with one another. As the monomer (**7**) is a small highly symmetric molecule a lot of Raman signals are present. The signals at about 3000 cm^{-1} correspond with the aliphatic end groups. The relative intensities of the aliphatic part and the aromatic part of the FT-Raman spectrum are in this compound comparable. Going from monomer (**7**) to dimer (**8**) the first major difference is the important decrease in relative intensity of the signals corresponding with the aliphatic end groups. This trend continues in the trimer (**9**). Finally in the tetramer (**10**), the intensity of the signals corresponding to the aromatic π system are so intense that the intensity of the aliphatic signals is almost negligible. Also the intensity of the signals of the π system is ten times larger in the tetramer (**10**) as compared with the monomer (**7**). Furthermore, whereas the spectrum of the monomer (**7**) is rather complex, the spectra of dimer (**8**), trimer (**9**) and tetramer (**10**) progressively simplify. Finally, the general aspect of the spectrum of the trimer (**9**) and the tetramer (**10**) is quite similar. The spectrum of the tetramer (**10**) can be considered as a prototype of an ITN oligomeric chain in which a dominant contribution by the "quinoid" structure necessarily cannot exist. The length of the chain is such that end-group effects are reduced, thus allowing to consider the system as the best approximation to PITN in the "aromatic" structure.

For the sake of completeness the FT-IR spectra of the oligomers are shown Figure 5.6 together with the FT-IR spectrum of the dedoped polymer. Within the series of oligomers (**7** - **10**) a great similarity is apparent.

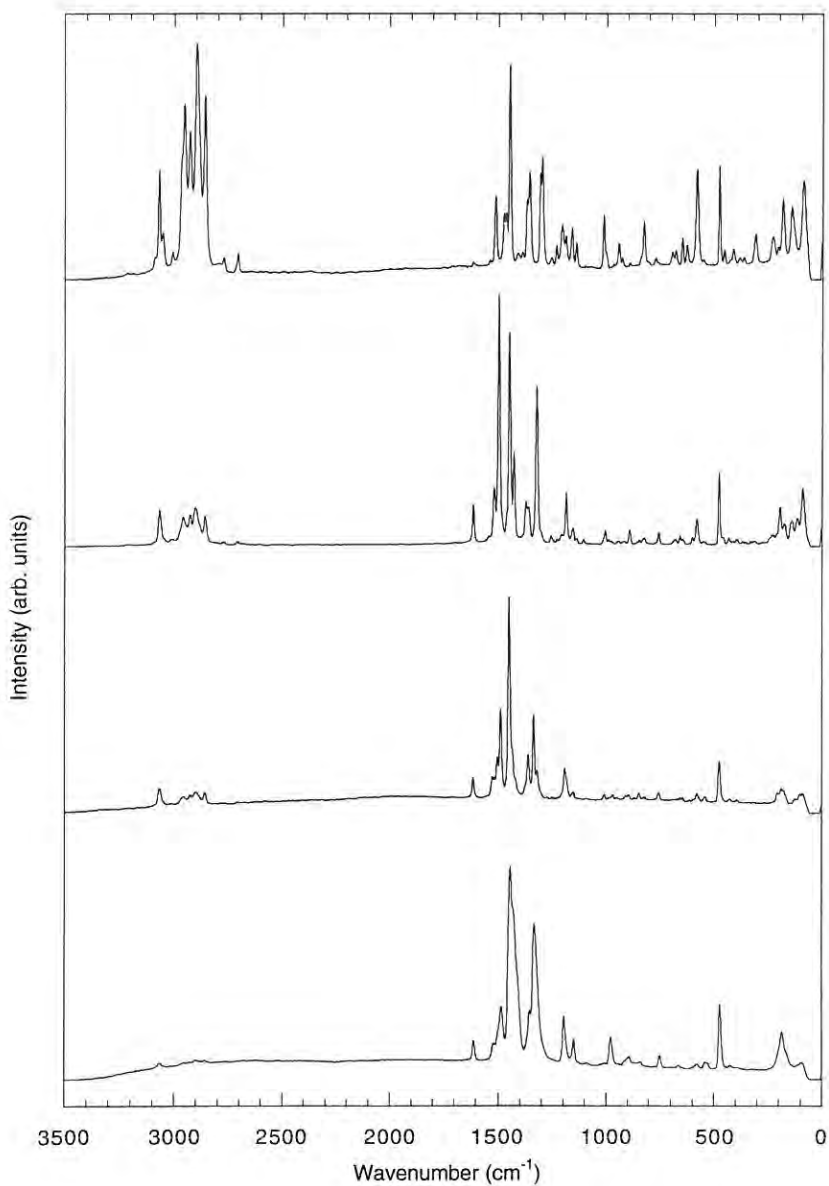


Figure 5.5 The FT-Raman spectra of the silylated isothianaphene oligomers: monomer (7), dimer (8), trimer (9), and tetramer (10), respectively.

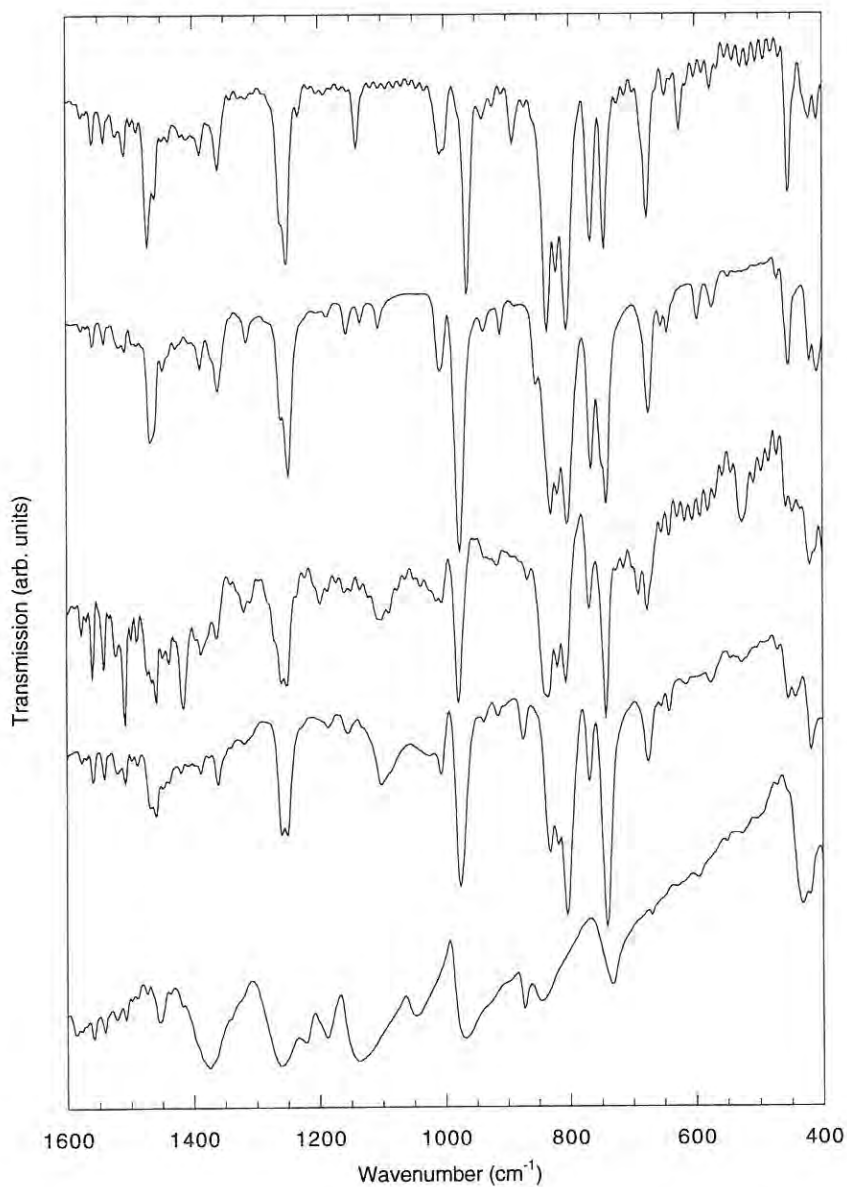


Figure 5.6 The FT-IR spectra of the silylated isothianaphthene oligomers (monomer (7), dimer (8), trimer (9), and tetramer (10), respectively), and dedoped PITN (synthesised by W.Bijnens).

5.4 Comparison between model compounds and PITN

From Raman scattering data on neutral and doped PITN, it has been proposed that the ground state geometric structure of the neutral PITN system should be quinoid and becomes aromatic upon doping.^[16, 17] This hypothesis is based on the comparison between the measured frequencies and values calculated for the quinoid and aromatic structures from the force constants of thiophene and benzene. However, the experimental Raman frequencies are in agreement with the calculated values for the aromatic structure of poly(thiophene) only after a refinement procedure has been applied. When this procedure is used for PITN, the frequencies obtained for the aromatic and the quinoid structures are so similar to each other that it seems a very delicate matter to determine which set of results is closest to the experimental data. In spite of these efforts, this work was not able to make a contribution towards the solution of the dilemma "quinoid/aromatic".

Figure 5.7 depicts the FT-Raman spectra of 1,3-dithienylisothianaphthene (**4**) and the silylated isothianaphthene tetramer (**10**) together with the spectrum of pristine PITN. For the sake of comparison, the spectra of 1,3-diphenylisothianaphthene (**3**) and *trans*-3,3'-bibenzo[*c*]thienylidene (**12**), the best quinoid model compound so far, are also shown in Figure 5.6. The latter two compounds were both synthesised by Hoogmartens.^[13, 18]

The FT-Raman spectra are interpreted in the framework of the "effective conjugation coordinate"-theory (ECC). The ECC theory has proven to be successful in the structural characterisation of many classes of polyconjugated materials. In the case of poly(aromatics) the effective conjugation coordinate (or $\mathcal{A}$ coordinate) is basically defined as the collective geometrical evolution of the network by stretching of single and double carbon-carbon bonds in transforming from the aromatic structure to the quinoid structure. This theoretical approach allows to understand why the few selective strong Raman intensities in the spectra of poly(aromatics) are associated with the large molecular polarizability changes due to the existence of a very mobile and highly polarizable charge density wave of π electrons, which is selectively excited by the motions along the $\mathcal{A}$ coordinate. The ECC-theory thus allows to probe delocalisation of π electrons along the chain backbone using the vibrational data from FT-Raman measurements. A more detailed description of the ECC-theory and its applications can be found in the following references [4, 19-22]

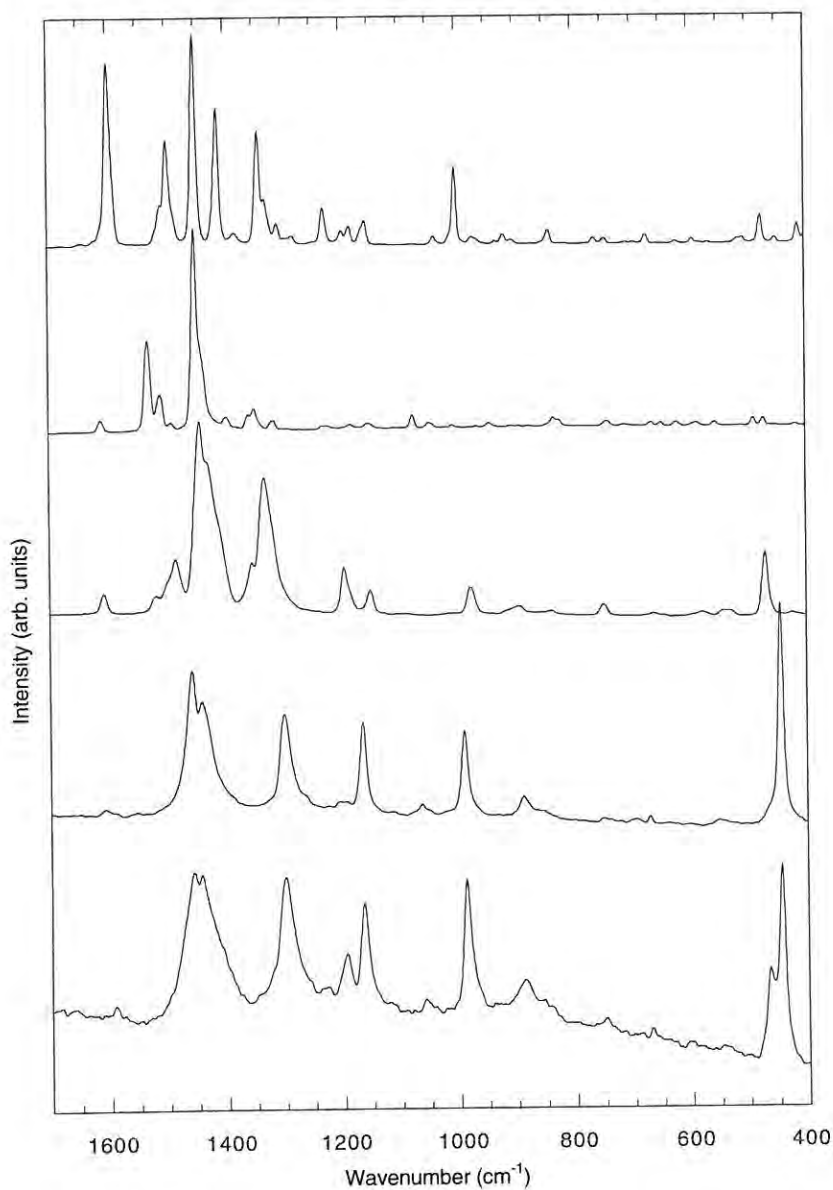


Figure 5.7 The FT-Raman spectra of 1,3-diphenylisothianaphthene (**3**), 1,3-dithienylisothianaphthene (**4**), the silylated isothianaphthene tetramer (**10**), pristine PITN and trans-3,3'-bibenzo[c]thienylidene (**12**), respectively.

Since in this part we do not aim to present a complete theoretical analysis, a more simplified analysis of the spectra is given in view of the fact that a more detailed study of the problem through more elaborate measurements is to be performed in the near future.

The analysis proceeds by determining whether in the Raman spectra of the molecules studied, selective enhancement of a few totally symmetric modes takes place.^[4, 5, 20] From the extent of enhancement one can derive information on the extent of electron-phonon coupling along the $\mathcal{A}$ coordinate. Through a comparative and correlative analysis of the Raman spectra of the model compounds and PITN we shall try to find evidence for the ground state structure of PITN.

The Raman spectrum of 1,3-diphenylisothianaphthene (**3**) is not particularly selective since it shows a large population of strong, medium and weak bands. This means that delocalisation between the central ITN unit and the two external benzene rings is not large. This observation is easily accounted for by the fact that steric factors prevent the two benzene rings from being co-planar with the ITN unit, thus decreasing the value of the hopping integral between the p_z orbitals of the adjacent benzene rings. If no sizeable intramolecular delocalisation occurs, no sizeable electron-phonon coupling takes place along a preferential vibrational trajectory ($\mathcal{A}$ coordinate); it follows that no selective strong intensity enhancement of a few modes can be observed. In accordance with other spectroscopic data, the ITN unit of this compound must have the "aromatic" structure. Some useful vibrational assignments can be made for use in further analysis. The strong and sharp line at 1594 cm^{-1} can be assigned to the vibrations of the aromatic rings at either side of the ITN unit. Of the lower frequency lines at 1494 cm^{-1} (sharp), and at 1449 cm^{-1} (very strong), the latter can be assigned to the vibrations of the benzene ring condensed with the thiophene ring in the β - β' position inside the ITN unit.

In 1,3-dithienylisothianaphthene (**4**) the π system is better simulated through the replacement of the benzene units by thiophene ring systems. In this compound the through space effect of the aromatic sulphur atom on the ITN unit is taken into account. Moreover, steric factors should allow us to obtain a more planar extended π system. The possibility of obtaining a planar system should give rise also to a more pronounced electron/phonon coupling along the $\mathcal{A}$ coordinate, which should be reflected in the selective enhancement of a few vibrational modes. The Raman spectrum of this compound is more simple as compared with 1,3-diphenylisothianaphthene (**3**). Only a few lines are present between 1300 and 1600 cm^{-1} . The signals at lower frequencies are very weak. The signal at 1611 cm^{-1} , associated with the vibrations of the thiophene side groups, appears to be very low in relative intensity in contrast to the corresponding signal in the spectrum of 1,3-diphenylisothianaphthene (**3**). The relative intensity of the signal at

1452 cm^{-1} has become very strong in comparison with the signal at 1611 cm^{-1} . Lowering the steric factors thus results in the selective enhancement of a few signals in the FT-Raman spectrum, i.e., the signals at 1532 and 1452 cm^{-1} . These signals correspond with the signals at 1494 cm^{-1} and 1449 cm^{-1} of 1,3-diphenylisothianaphthene (**3**) and which can be associated with ITN units having an "aromatic" structure.

As already shown in sec.5.3, the FT-Raman spectrum of the silylated tetramer (**10**) can be considered as a prototype of an ITN oligomeric chain in which a dominant contribution by the "quinoid" structure necessarily cannot exist. The length of the chain is such that the end-group effects are reduced, thus allowing us to consider the system as the best approximation to PITN in the "aromatic" structure. The lines at 1486 and 1444 cm^{-1} can directly be associated with the lines at 1494 and 1449 cm^{-1} of 1,3-diphenylisothianaphthene (**3**) and the signals at 1532 and 1452 cm^{-1} of 1,3-dithienylisothianaphthene (**4**). These lines correspond, as discussed above, with ITN units possessing an "aromatic" structure. In the spectrum of the ITN tetramer (**10**) we can identify an additional line at 1333 cm^{-1} as characteristic of the ITN unit not strongly perturbed by a "quinoid"-type delocalisation.

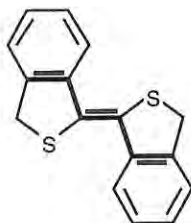


Figure 5.8 The presence of an "all-trans" configuration in *trans*-3,3'-bibenzo[c]thienylidene (**12**) in which electron/phonon coupling can occur more effectively.

The FT-Raman spectra of pristine PITN and *trans*-3,3'-bibenzo[c]thienylidene (**12**) will be analysed in a parallel fashion. The first striking observation is that, in spite of their structural differences, the Raman spectra of these two molecules are practically identical. On the other hand their chemical identity has been carefully verified.^[15, 18, 23, 24] This apparent discrepancy finds its solution with the help of the ECC-theory. The Raman spectrum of *trans*-3,3'-bibenzo[c]thienylidene (**12**) is certainly extremely simple, thus indicating the existence of a large selective enhancement of a few modes associated with large electron/phonon coupling due to delocalisation. *trans*-3,3'-Bibenzo[c]thienylidene (**12**) is in fact simply a dimer in which inter-unit delocalisation is

purposely forced by the chemical structure. In *trans*-3,3'-bibenzo[*c*]thienylidene (**12**) we notice the existence of the sequence —C=C—C=C—C=C— , necessarily planar and in "all-*trans*" configuration, in which delocalisation certainly takes place. (Figure 5.8) It is a common experience that electron/phonon coupling occurs more effectively when double bonds are in the *trans* configuration. It has been shown that large delocalisation occurs in *trans* poly(acetylene) or in shorter all-*trans* monomers; on the contrary strong confinement of π electrons takes place in *cis* polyacetylene.^[25] It has been proven that the result of the "trans effect" will dominate the possible contributions by eventual *cis* structures.^[15] The information derived from the spectrum of this quinoid model compound forms the basis for the interpretation of the Raman spectra of pristine PITN. The spectrum of PITN is practically superimposable upon that of *trans*-3,3'-bibenzo[*c*]thienylidene (**12**). This is evidence that PITN contains the relevant sequence of three conjugated *trans* double bonds as in *trans*-3,3'-bibenzo[*c*]thienylidene (**12**).

Since there is no correspondence with the "aromatic" features derived from the spectra of aromatic model compounds, it follows that the Raman spectrum of pristine PITN proves that PITN possesses a "quinoid" ground state structure.

The information obtained from the analysis of model compounds and pristine PITN allows a tentative evaluation of the FT-Raman spectra of doped PITN. As in the case of polyacetylene the spectra of slightly doped PITN are very similar to that of the pristine material. Only at large doping levels is the Raman spectrum expected to show important differences. However the FT-Raman spectrum of n-doped PITN (Figure 5.2) does not undergo spectroscopic changes, even when high potentials up to -1.9 V are applied. Since such large potentials are applied, it is reasonable to suppose that the material is doped. It seems as if the FT-Raman signals originating from the *trans*-configuration overwhelm those originating from the doped structure. On the other hand the FT-Raman spectrum of p-doped PITN (Figure 5.3) increasingly changes until degradation of the material prevents further measurements. At a doping potential of 0.4 V the first changes are noticed. Four new signals appear at 1402 cm^{-1} , 1192 cm^{-1} , 1059 cm^{-1} and 464 cm^{-1} . The intensity of these signals increases as the doping level increases up to 0.8V. At 1.0 V a new signal appears at 1384 cm^{-1} . This signal increases in intensity until degradation of the material at 1.2 V occurs. These signals, originating from the process of doping, can now be compared with the Raman lines of the model compounds in order to obtain information on the structure of the doped material. On the one hand, the signals appearing in the spectrum of the doped material does not correspond whatsoever with the signals associated with the aromatic ITN unit in the silylated ITN tetramer (**10**) (1486, 1444 cm^{-1} and 1333 cm^{-1}). On the other hand, these new signals do not correspond exactly with

Raman lines in the spectrum of the quinoid model compound. Therefore, the origin of the new signals cannot be associated with the presence of a geometry corresponding with a pure aromatic nor a pure quinoid ground state-like structure.

5.5 Conclusions

From comparison of the FT-Raman spectra of a series of silylated aromatic oligomers it could be concluded that the tetramer (**10**) can be considered as a prototype for "aromatic" PITN. Indeed, the length of the chain appeared to be large enough to minimise the effects of the end groups. From the comparison of 1,3-diphenylisothianaphthene (**3**), 1,3-dithienylisothianaphthene (**4**) and the silylated isothianaphthene tetramer (**10**), three lines in the FT-Raman spectrum could be identified as being characteristic for ITN units possessing an "aromatic" structure, i.e. 1486 cm^{-1} , 1444 cm^{-1} and 1333 cm^{-1} . However the FT-Raman data of pristine PITN appeared to match almost exactly the data of a quinoid model compound. From this comprehensive analysis of the Raman spectra of model compounds, purposely synthesised to mimic the "quinoid" or "aromatic" structure, it is possible to reach the conclusion that the molecular structure of PITN in the electronic ground state is quinoid. This is the first time that some experimental evidence has been found from vibrational spectroscopy that a low band gap conjugated material in the pristine state is quinoid. This result also complements the results obtained from NMR spectroscopy.^[15, 18, 23, 26]

Also the doping process of electrochemical synthesised PITN has been followed by means of in situ FT-Raman spectroscopy ($\lambda_{\text{exc}} = 1064\text{ nm}$). During the process of n-doping no changes in the aspect of the FT-Raman spectrum could be observed. The process of p-doping, however, gives rise to additional Raman lines, i.e. 1402 cm^{-1} , 1384 cm^{-1} , 1192 cm^{-1} , 1059 cm^{-1} and 464 cm^{-1} , which become more important in function of increasing p-doping. Using the FT-Raman features of the "aromatic" and "quinoid" model compounds the structure of the doped material could not be associated with a pure aromatic nor a pure quinoid geometry. The identification of the origin of these new lines necessitates additional vibrational spectroscopic research.

5.6 References

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Nullum magnum ingenium sine mixtura dementiae fuit
(Seneca, De Tranquillitate Animae 17,10)

Optical Absorption Spectra of Aromatic Isothianaphthene Oligomers: Theory and Experiment

6.1 Introduction

Conjugated polymers are at present intensively studied because of their increasing technological applications. Much attention has been devoted to the synthesis of low-band-gap polymers, i.e. macromolecular materials which could be intrinsically good electrical conductors without the need of doping. Poly(isothianaphthene) (PITN) is prototypical for this class of polymers; it presents an experimental band gap of 1 eV.^[1, 2] Over the past few years, theoretical and experimental efforts have been devoted to the determination of the ground state geometry of the polymer,^[3-7] which has been the object of controversy in the literature. Recently, Hoogmartens et al. have been in the position to confirm by means of a joint experimental and theoretical study that the quinoid form is favoured above its aromatic counterpart.^[7, 8] These experimental results have been further confirmed by the analysis of improved model compounds.^[9] However, since the two forms are almost isoenergetic, according to theoretical calculations both ground state structures could actually exist, depending, for instance, on the polymerisation route.

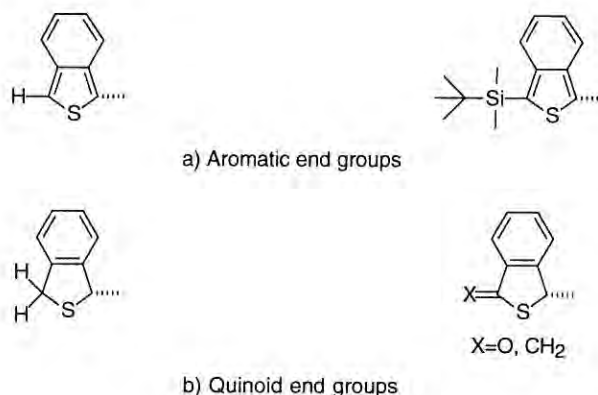


Figure 6.1 Illustration of the different chain ends possible in either aromatic (a) or quinoid (b) isothianaphthene oligomers.

According to quantum-chemical modelling,^[3, 5, 7] the nature of the end groups and the geometric structure of the chains are directly related; it has been shown that systems where terminal α carbons are linked by a single bond to the external group (Figure 6.1a) present an aromatic character. This result is confirmed by the work of Okuda et al.^[10] who have prepared *tert*-butyldimethylsilyl-substituted oligomers which possess an aromatic structure. The quinoid structure is obtained by either adding a second hydrogen atom or attaching a double bond to each of the terminal α carbon sites. (Figure 6.1b)

The band structure of PITN has been calculated by means of the valence effective Hamiltonian (VEH) method;^[7, 11] the results indicate that the aromatic polymer should possess a bandgap even smaller than that of quinoid PITN (0.2 - 0.6 vs 1.2 eV). On the basis of this interesting feature, we have undertaken a theoretical and experimental study of the electronic properties of isothianaphthene oligomers (from the monomer (7) up to the tetramer (10)) capped by disilyl groups. The investigation of aromatic oligomers of increasing size should lead to improved understanding of the electronic properties, in particular the optical absorption spectrum of aromatic PITN chains.

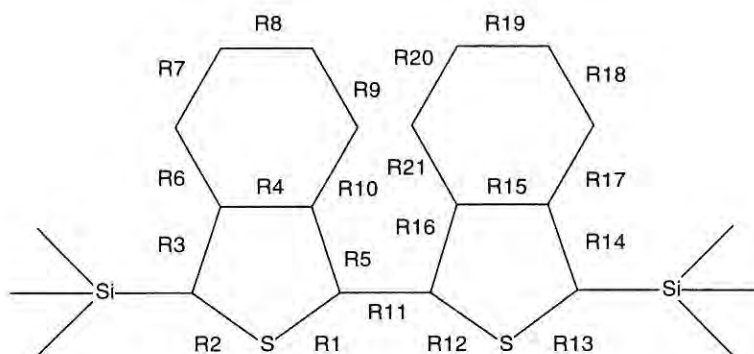
As a first step, geometry optimisations were carried out on a series of isothianaphthene oligomers at the Austin Model 1 (AM1) level. This method is parameterized to give good estimates of geometries and heats of formation of organic compounds. The theoretical data were compared with the results of X-ray diffraction experiments performed on a disilyl substituted isothianaphthene dimer (8). Attempts to grow large single crystals of longer oligomers have not been successful. Based on the AM1-optimized geometries, the intermediate neglect of differential overlap (INDO) method, coupled to single configuration interaction (SCI), was then used to calculate the

electronic transition energies and related oscillator strengths. In parallel, we have synthesised bis(*tert*-butyldimethylsilyl)-isothianaphthene oligomers from the monomer (7) up to the tetramer (10), according to the method described by Okuda et al.^[10] The experimental optical absorption spectra, taken in n-hexane, were compared to the theoretical curves. The origin and the evolution of the experimental absorption peaks were analysed on the basis of the calculated data.

The theoretical calculations of this section were part of the Ph.D. work performed by Quattrocchi at the University of Mons-Hainaut within the group of Brédas. For further details on the theoretical methodology the interested reader is referred to the Ph.D. thesis of Quattrocchi. The single crystal structure determination of the dimer (8) has been performed by Van Meervelt at the K.U.Leuven.^[12]

6.2 Comparison of Calculated and Experimental Geometries

The AM1-optimized geometries of the oligomers are, as expected, typical of an aromatic conjugated backbone; the α - β carbon-carbon bonds of the thiophene subunit are rather short (1.40 - 1.41 Å) while the β - β carbon-carbon bonds have a single bond character (ca. 1.45 Å), the interring bond length is calculated to be short (1.42 Å) compared with X-ray diffraction measurements performed on thiophene oligomers.^[13-16] This feature has already been reported in previous calculations^[7] and is typical of the AM1 parameterization. The dihedral angle (θ) formed by the planes of two adjacent rings is calculated to be 151.6°, the two sulphur atoms thus pointing in opposite directions (*anti* conformer). These optimised geometries are similar to those calculated with the AM1 method on unsubstituted aromatic isothianaphthene oligomers.^[7]



	AM1	XRD		AM1	XRD
R1	1.649	1.721	R12	1.649	1.714
R2	1.643	1.719	R13	1.643	1.717
R3	1.401	1.412	R14	1.401	1.415
R4	1.451	1.446	R15	1.451	1.444
R5	1.402	1.393	R16	1.402	1.393
R6	1.424	1.424	R17	1.424	1.431
R7	1.367	1.364	R18	1.367	1.363
R8	1.424	1.425	R19	1.424	1.425
R9	1.368	1.350	R20	1.368	1.356
R10	1.420	1.430	R21	1.420	1.422
R11	1.471	1.471			

Table 6.1 Bond lengths $R_i(\text{\AA})$ of the disilyl terminated dimer (**8**) of isothianaphthene obtained at the AM1 level and by single crystal structure determination (XRD). The AM1 geometry optimisation is performed with the interring bond length and the dihedral angle between bonds R1-R11-R12 forced at 1.471 Å and 50°, respectively. The average standard deviation for the experimental bond lengths (XRD) is 0.004 Å.

The experimental geometry of the 3,3'-bis(*tert*-butyldimethylsilyl)-1,1'-bisisothianaphthene (**8**) was obtained by single-crystal X-ray diffraction; the experimental bond lengths for this compound are reported in Table 6.1 together with the AM1 results. Globally, the AM1-optimized geometry of the dimer is in good agreement with the experimental values. There are, however, some significant differences:

(1) The dihedral angle (θ) in the crystal is about 50°, the two sulphur atoms pointing in the same direction. This is in contrast with what is found experimentally in

thiophene oligomers, which all adopt an anti planar conformation in the crystal^[13-16] (note that an *anti* conformation leads to a reduction of the total dipole moment of the molecule, which is in principle favoured). The *syn* conformation that the molecule adopts in the crystal likely comes as a consequence of packing effects dominated by the bulky side groups, a feature which cannot be taken into account in the calculations.

(2) The calculated bond lengths between carbon and sulphur atoms are shorter by about 0.07 - 0.08 Å than the experimental data; this feature is related to the AM1 parameterization.

(3) The bond length connecting the two isothianaphthene units is measured to be 1.471(4) Å long, which is close to the value determined by X-ray diffraction experiments in thiophene oligomers, ≈ 1.45 Å.^[13-16] As expected from the AM1 parameterization, the corresponding calculated value is shorter by about 0.05 Å.

Therefore a geometry optimisation have been carried out for a dimer where the single interring bond and the dihedral angle (θ) are set at the experimental values, i.e., 1.471 Å and 50°, respectively. The AM1 optimisation (Table 6.1) shows that the geometry remains clearly aromatic and similar to that calculated for the fully optimised dimer; the main change is the shortening of the R5 distance, but only 0.008 Å, due to the fact that this bond is influenced by the interring bond length. Quattrocchi also considered a system where the two rings are let free to rotate but where the interring bond is fixed to 1.471 Å; in that case, the optimal dihedral angle (θ) is 151.3°, i.e., very close to the value calculated for the dimer without any constraint.

Finally, geometry optimisations have been performed on oligomers (from dimer up to the tetramer), freezing the interring bond length and the dihedral angle (θ) at 1.471 Å and 130° respectively. In such a conformation, the systems are out of planarity by 50°, as in the crystal of the dimer (8), but adjacent sulphur atoms point in opposite directions. This allows a linear oligomer chain, instead of the helicoidal conformation induced by a *syn* conformation between the units. The optimised geometries are calculated to be very close to those of the corresponding *syn* conformers, the largest bond length difference being in the order of 0.005 Å.

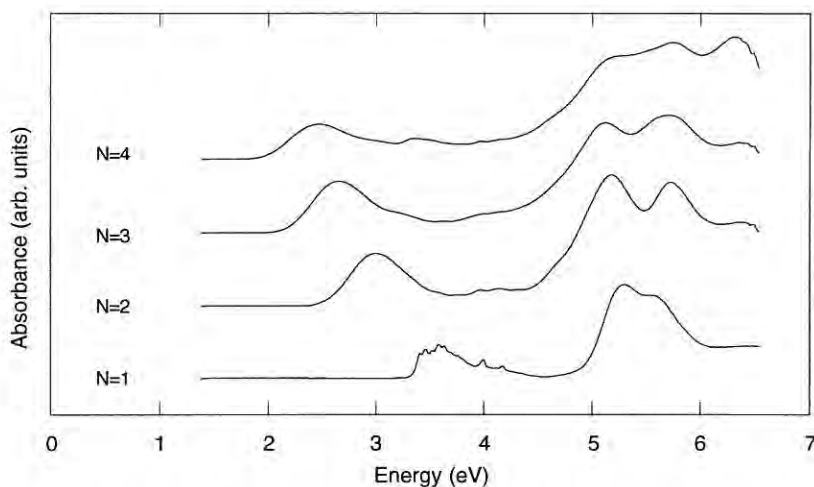


Figure 6.2 Experimental absorption spectra of the isothianaphthene oligomers (7 - 10) recorded in *n*-hexane (*N* being the number of units).

6.3 Comparison of Calculated and Experimental Absorption Spectra

For comparison with the theoretical data we chose to record the spectra in *n*-hexane. Due to the apolarity of *n*-hexane possible solvent effects are minimised. Furthermore, *n*-hexane is transparent for UV-vis wavelengths up to 200 nm whereas dichloromethane only permits spectra to be recorded up to 250 nm. The experimental absorption spectra of the oligomers (going from monomer (7) up to the tetramer (10)) are presented in Figure 6.2. At least three main peaks or shoulders can be found in the range of 2 - 6 eV. As is expected for conjugated compounds, the first absorption is shifted to lower energies upon increasing the length of the oligomers. The peak positions evolve by 1.12 eV, from 3.58 eV in the monomer (7) down to 2.46 eV (505 nm) in the tetramer (10). The second transition, which is more intense than the first one, lies at about 5.2 - 5.3 eV in all spectra, and there occurs a third transition at about 5.8 eV. It is striking that from the isothianaphthene monomer (7) up to the isothianaphthene tetramer (10) the λ_{max} of the first absorption peak (2.46 eV, 505 nm) is shifted more efficiently to lower energies, whereas a silylated thiophene octamer only shows an absorption maximum at 2.71 eV (458 nm).^[17] As far as the absorption maximum is concerned the silylated isothianaphthene tetramer (10) can thus be compared to poly(thiophene). In order to assess eventual solvent effects exactly the same measurements were performed in

dichloromethane, a more polar solvent. However no significant difference in the position of the absorption maxima could be observed.

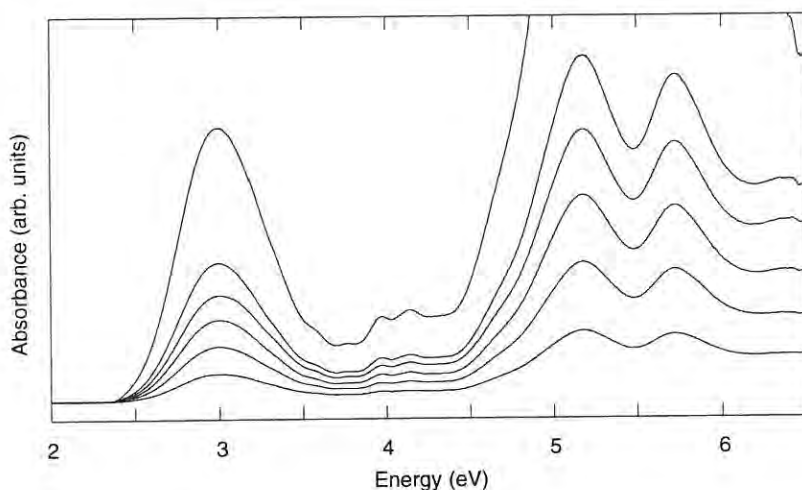


Figure 6.3 Dilution series of the optical absorption spectra of the isothianaphthene dimer (8) in the range of 10^{-4} to 10^{-5} M.

Furthermore, for each compound a dilution series of six solutions is made in the range of 10^{-4} to 10^{-5} M. (Figure 6.3) At these concentrations, the Lambert-Beer equation ($A = \epsilon c l$; with c , the concentration in mole/L and l , the path length (1 cm)) holds and the molar extinction coefficient, ϵ , can be calculated. For this purpose the absorption intensity, A , was determined at the maxima present in the spectra, and plotted as a function of the concentration, c . On each set of six values a linear regression was performed. The value of ϵ can be obtained from the slope of the result of the linear regression. The correlation coefficient for each set was larger than 0.999. The λ_{max} and corresponding ϵ for the spectra recorded in *n*-hexane are summarised in Table 6.2. Table 6.3 shows the data of the spectra recorded in dichloromethane. Since dichloromethane is not transparent below 250 nm, only the data corresponding with the first absorption maxima are given.

Solvent: n-hexane	λ_{max} (nm)	E (eV)	ϵ
Monomer (7)	347	3.58	10 542
	235	5.29	29 349
	224	5.55	(shoulder)
Dimer (8)	415	2.99	15 595
	240	5.18	38 812
	217	5.72	36 749
Trimer (9)	468	2.65	20 781
	243	5.11	44 496
	217	5.71	47 297
Tetramer (10)	505	2.46	13 835
	243	5.10	(shoulder)
	216	5.76	45 935

Table 6.2 UV-vis data of the silylated isothianaphthene monomer (7), dimer (8), trimer (9) and tetramer (10) recorded in n-hexane.

Solvent: CH ₂ Cl ₂	λ_{max} (nm)	E (eV)	ϵ
Monomer (7)	348	3.56	10 038
Dimer (8)	405	3.04	13 552
Trimer (9)	480	2.58	19067
Tetramer (10)	513	2.42	8 842

Table 6.3 UV-vis data of the silylated isothianaphthene monomer (7), dimer (8), trimer (9) and tetramer (10) recorded in dichloromethane.

In order to rationalise these absorption data, the optical absorption spectra of the four oligomers have been simulated at the theoretical level. At this stage, it must be pointed out that the calculated spectrum of the *syn* dimer, $\theta = 50.0^\circ$, differs only very slightly from that of the corresponding *anti* conformer, $\theta = 130.0^\circ$ (small variations appear in the relative intensities of the two peaks, but the transitions occur at the same energies). In solution, it is well-established that conjugated chains are more flexible than in the solid state;^[14, 18] individual units can thus rotate more easily around the interring bond, solvation energy compensating for the loss of π conjugation. Therefore, the

conformation with $\theta = 130^\circ$ has been considered since it has the advantage of better modelling a linear polymer chain.

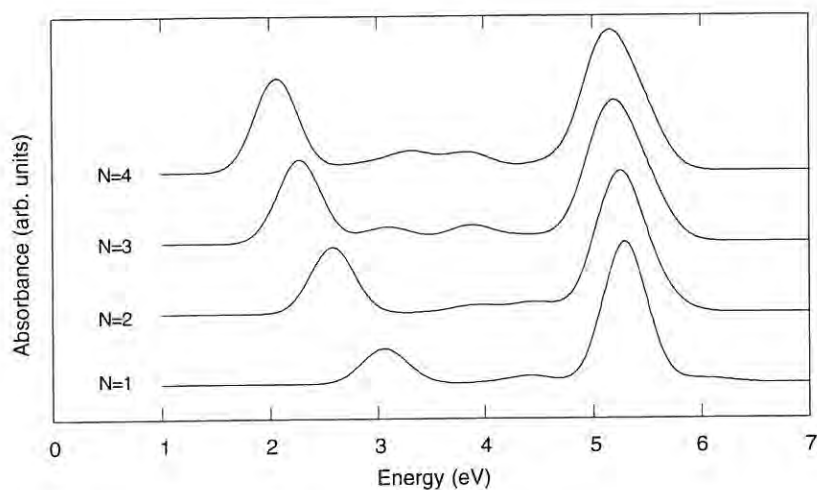


Figure 6.4 Theoretical absorption spectra for the 130° -twisted isothianaphthene oligomers (N being the number of units).

N	experimental (n-hexane)	Theoretical	
		$\theta = 130^\circ$	$\theta = 180^\circ$
1	3.58	3.03	3.03
2	2.99	2.58	2.40
3	2.65	2.28	1.88
4	2.46	2.07	1.56
6		1.88	1.18

Table 6.4 Experimental and theoretical positions of the low-energy peak (eV) as a function of the number of isothianaphthene units (N).

The theoretical spectra shown in Figure 6.4 display two major absorption peaks in the range of energies going from 0 to 6 eV. The first transition is red-shifted as the size of the oligomers (and thus the conjugation length) increases, as observed in the experimental spectra. (Table 6.4) This absorption is assigned to a $\pi \rightarrow \pi^*$ transition, primarily involving the promotion of one electron from the HOMO to the LUMO; both levels are delocalised (d), i.e., the wave functions extend over the whole molecule. For the monomer, the absorption lies at 3.03 eV and goes down to 2.07 eV in the tetramer, i.e., a 0.96 eV shift compared to a 1.12 eV shift in the experimental spectra (Table 6.4). The roughly 0.5 eV difference in peak positions between theory and experiment is not obvious to interpret in detail since many factors can play a role such as the presence of a distribution of conformations in solution, influence of the dielectric medium, geometry differences, or possible shortcomings of the INDO parameterization. The major feature is, however, that the experimental and theoretical results present the same trend, a marked decrease in transition energy as the conjugation length increases. In linear fully aromatic PITN (i.e., in the infinite chain limit), we thus can expect that the first transition occurs at even lower energy, due to extended conjugation; furthermore, in the solid state, packing effects are likely to induce the polymer to adopt a conformation closer to a planar structure, in particular if the end groups are less bulky than those used here for synthetic purposes. This would reduce the band gap energy even more compared to the transition energies reported in this work for twisted oligomers. Indeed, we calculate that planarity leads to a further decrease of the transition energy (Table 6.4). For instance, in the case of the tetramer, the decrease is on the order of 0.5 eV.

Figure 6.5 represents the evolution of the lowest transition vs the inverse number of units for both the theoretical and experimental spectra. From these data, we extrapolate to the band-gap energy of an infinite chain. As is usually the case when doing such extrapolations, the value for the monomer (7) does not fit linearly with the other data, probably due to the lack of interunit conjugation and it is therefore neglected. At the theoretical level, the linear regression made on four points ($N=2, 3, 4, 6$) leads to a small energy gap value of 0.63 eV for planar aromatic PITN, which is consistent with our previous VEH results.^[7] Since the torsion of the rings around the interring bond decreases conjugation, the energy difference between the valence band and the conduction band leads to an extrapolated value of 1.55 eV for the 130° twisted polymer. The band gap energy of the polymer, as extrapolated from three experimental points ($N=2, 3, 4$), is estimated to lie at 1.94 eV. Note the similarity in slopes for the theoretical curve of the 130° twisted chains and the experimental curve. The slope of the theoretical curve is larger, which is again an indication of stronger conjugation. We can thus point

out that (i) the molecules adopt a strongly non planar conformation in solution because the chains are highly flexible, i.e., the isothianaphthene units can easily undergo rotations around the interring bond which will drastically reduce the π conjugation in the polymer, and (ii) aromatic planar PITN should possess an energy gap value much lower than estimated from the spectra recorded in this work.

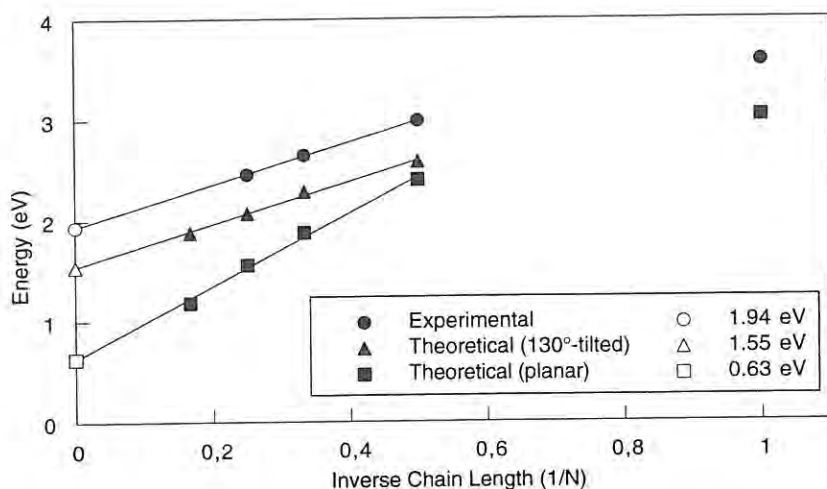


Figure 6.5 Energy of the HOMO-LUMO transition energy (eV) vs the inverse of the chain length for the theoretical spectra of the planar and 130°-twisted oligomers and the experimental spectra of the synthesised compounds (N being the number of units).

It is also important to mention that calculations performed on analogous oligomers in the quinoid form indicate that the first absorption peak lies at higher energies than in the corresponding planar aromatic molecules (e.g., 3.11 vs 1.56 eV in the tetramer). Again, this result is consistent with the VEH calculations^[7] and confirms that the planar aromatic form of PITN possesses a lower band gap energy than the quinoid polymer.

The second absorption peak is calculated to appear around 5.2 eV, in agreement with the experimental spectra. In contrast to the first transition, this peak is only slightly affected by chain length. It varies from 5.29 eV for $N=1$ to 5.16 eV for $N=4$. This perfectly matches the evolution observed in the experimental curves; the corresponding peak or shoulder slightly shifts to lower energies, going from 5.30 eV ($N=1$) to 5.16 eV

($N=4$). In order to determine the origin of the second peak, the spectrum of the monomer has been analysed in detail. In that energy range, the expansion coefficients are significant for three configurations: (i) the first one corresponds to a transition from the HOMO—1 level to the LUMO level; (ii) the second one comes from a HOMO—2 to LUMO transition; and (iii) the last configuration involves the HOMO and LUMO+3 levels. The corresponding orbital wave functions are depicted in Figure 6.6.

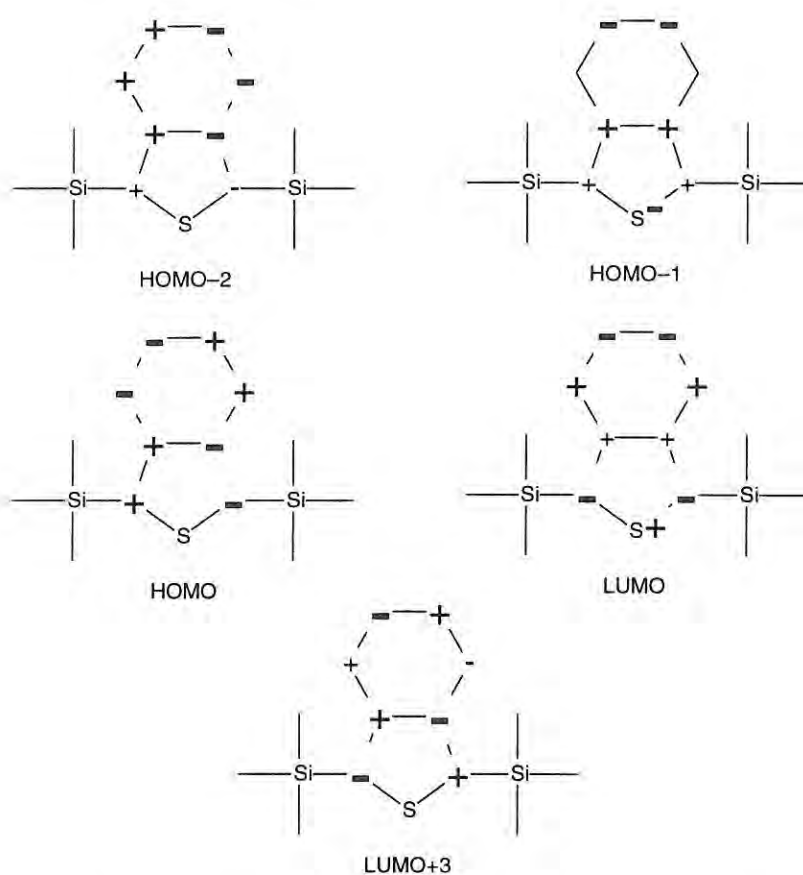


Figure 6.6 Bonding - antibonding pattern of the molecular orbitals involved in the second absorption peak of the monomer.

The analysis of the LCAO coefficients shows that the orbital wave functions of the occupied levels for the first two configurations (i.e., HOMO—2 and HOMO—1) are mainly localised (l) within the fused phenyl ring. The bonding - antibonding patterns

correspond to those of the degenerate HOMO levels in benzene, where the first transition occurs around 6 eV. Globally, the second absorption peak originates from transitions involving localised (HOMO—2 and HOMO—1) and delocalised (HOMO, LUMO, and LUMO+3) π levels. The first two configurations are $l \rightarrow d^*$ type transitions, whereas the third one is a $d \rightarrow d^*$ type transition. Because of contributions to the second absorption peak coming also from localised levels, we expect that the effect of chain length on the transition energy is weaker than for the first absorption peak which only involves delocalised levels. A similar behaviour has been obtained in poly(paraphenylenevinylene) and poly((2,5)dimethoxy-1,4-paraphenylenevinylene) oligomers,^[19] where the peaks originating from transitions which involve localised levels do not present any significant shift to lower energies as the oligomers become longer.

It is interesting to note that both theoretical and experimental absorption spectra present low-intensity absorption features between the two main peaks. In the case of the monomer it primarily corresponds to a HOMO to LUMO+4 transition with a weak transition dipole moment.

Finally we point out that no transition is predicted around 5.8 eV, even though there occurs an absorption that can be observed in all experimental spectra. We believe this discrepancy has to be related to shortcomings in the INDO parameterization with regard to silicon.

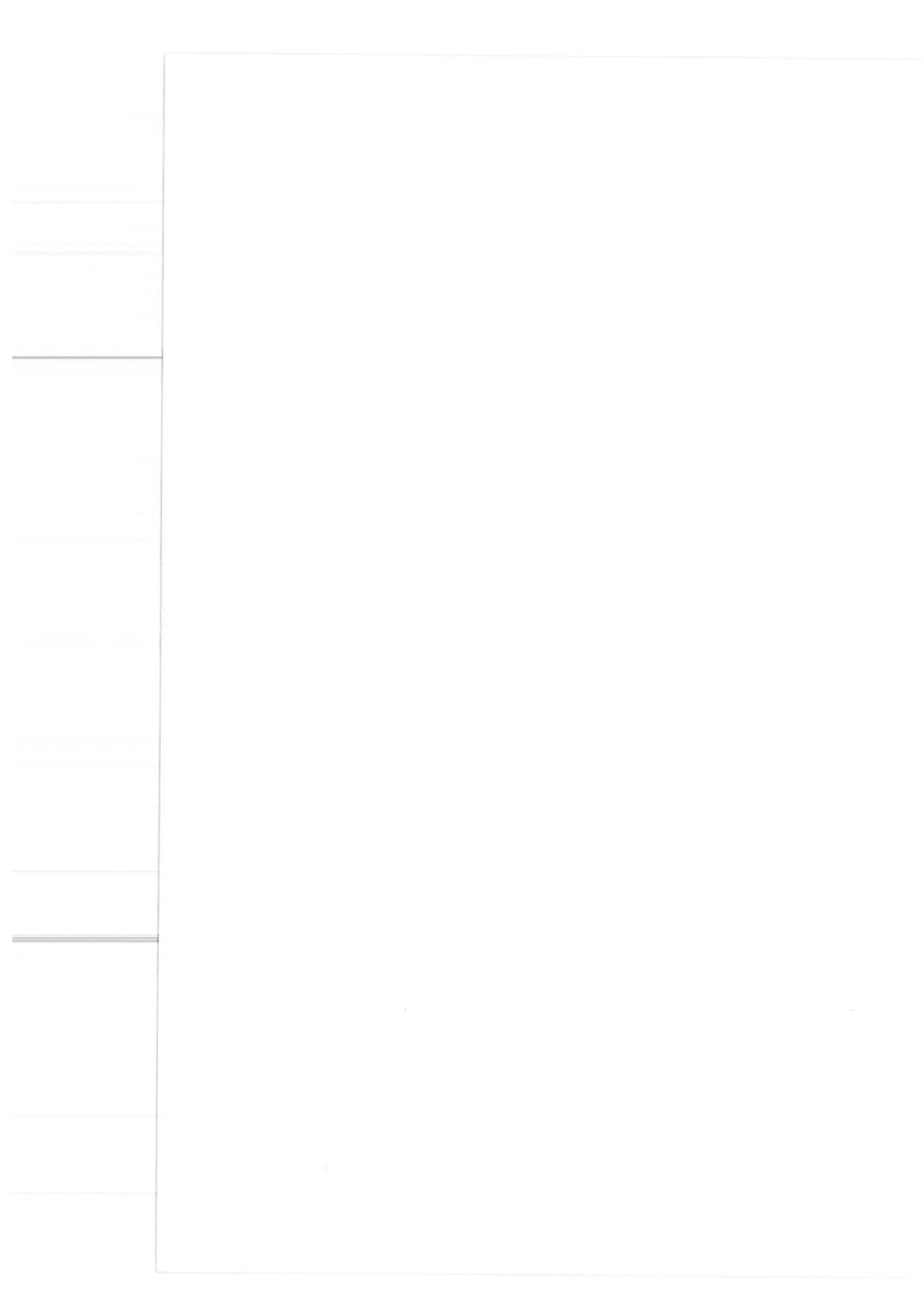
6.4 Conclusions

Using the INDO/SCI formalism, we have analysed the optical spectra of aromatic isothianaphthene oligomers from monomer up to tetramer. Two main absorption peaks are observed in the visible-near UV region. The low-energy absorption, corresponding to a $d \rightarrow d^*$ type transition from the HOMO level to the LUMO level, is shifted to lower energies when the chain length is increased. The extrapolations made from the HOMO—LUMO transitions of the oligomers to the band gap energy of aromatic PITN lead to a very small energy gap value of 0.63 eV for the planar system and a value of 1.55 eV for the 130° twisted infinite chain. The value calculated for the tilted system is in good agreement with the extrapolation of the first energy transition of the oligomers recorded in *n*-hexane, 1.94 eV. These results point out that in solution, the aromatic oligomers adopt a strongly non planar conformation, increasing significantly the HOMO—LUMO transition relative to that of a planar aromatic system.

The second strong optical absorption peak is described by electronic excitations involving mostly $l \rightarrow d^*$ type transitions. The localised molecular orbitals being less affected by the extent of conjugation than the delocalised levels, the position of the second peak evolves smoothly as the chain length increases, which is in good agreement with the features of the experimental spectra.

6.5 References

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Spectroscopic Analysis of Poly(tetrafluoroisothianaphthene) and Aromatic Model Compounds

7.1 Introduction

Low-bandgap conjugated polymers form an important class of advanced materials offering a combination of intriguing properties. In addition to an enhanced intrinsic conductivity the anticipated enhanced nonlinear optical properties suggest that these compounds may play an important role in the future development of polymer based electronics and photonics.

In order to design new low-bandgap conjugated polymers an in-depth understanding of the relationship between the structure and the corresponding electronic properties of these materials is essential. Since poly(isothianaphthene) (PITN) possesses a 1 eV bandgap^[1] as determined by optical absorption, this polymer has been under investigation for some time in order to establish a deeper understanding of the relationship between its structure and its observed low-bandgap. The first quantum chemical calculations by Brédas^[2] were performed on the "aromatic" form (**1a**) using the geometry of the monomer as a basis. These results correctly confirmed the 1eV reduction of the bandgap going from poly(thiophene) to PITN. However Lee et al.^[3] using a MNDO geometry optimisation, suggested that PITN should possess a "quinoid" structure (**1b**) in its ground state. Subsequently, with the partial retention of diatomic differential overlap, Nayak et al.^[4] found that the quinoid form of PITN is very slightly favoured over the aromatic one. Since there was a lack of experimental evidence the question whether the structure of PITN is aromatic or quinoid, remained open. It is only recently that experimental results based on comparison of model compounds with NMR^[5, 6] and FT-Raman^[7-12] spectroscopic data of the polymer indicate that PITN should possess a

geometric structure with a strong quinoid character. Therefore, in order to succeed in the targeted development of new low-bandgap polymers, theoretical techniques to estimate electronic properties should be combined with experimental structural data.

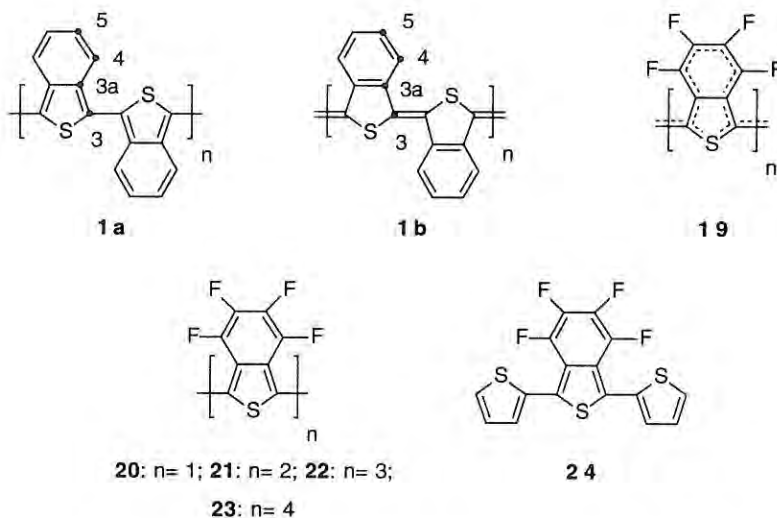
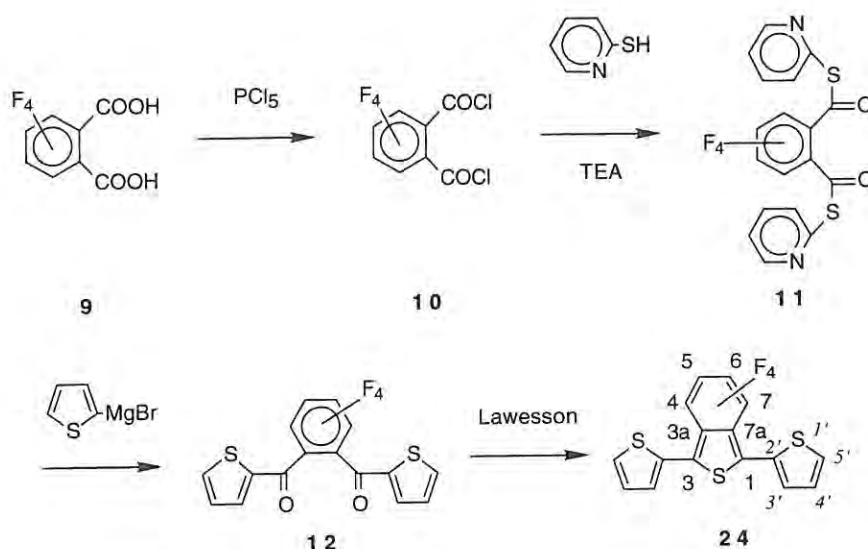


Figure 7.1 Aromatic (**1a**) and quinoid (**1b**) structures of PITN; PTFITN (**19**); the fluorinated aromatic oligomers (**20** - **23**) and an aromatic model compound, 1,3-dithienyl-4,5,6,7-tetrafluoroisothianaphthene (TFDIT) (**24**).

The surprisingly low bandgap of PITN and its transparency upon doping^[1, 13, 14] lead to the investigation of PITN derivatives with enhanced processability and stability.^[15-18] Since it was suggested^[19] that the replacement of hydrogen by fluorine should provide, due to the absence of hydrogen, more stable materials less susceptible to atmospheric oxidation and an improved solubility, Brooke et al.^[20] attempted the synthesis of poly(4,5,6,7-tetrafluoroisothianaphthene) (PTFITN) (**19**). PTFITN is a PITN derivative which is surprisingly soluble in chlorinated as well as in other organic solvents. However the UV-visible spectrum shows a bandgap of 2.1 eV. This result is in sharp contrast with the value of 1eV obtained for PITN. Increased non-bonding and dipole-dipole interactions induced by the substitution of fluorines in the 4 and 7 position, causing non planar conformations, were proposed as an explanation for the enlargement of the bandgap. However, to understand more clearly the structural cause of this enlargement of the bandgap, a detailed analysis of the structure of the polymer is required.

Since the presence of the fluorine atoms has a drastic effect on the geometric structure of PTFITN we wondered if we could find spectroscopic evidence for a shift towards an aromatic from a quinoid structure for PTFITN. For this purpose we need a set of oligomeric model compounds which should allow us to determine by extrapolation the spectroscopic characteristics of the corresponding polymer.



Scheme 7.1: Synthesis of the aromatic model compound TFDTI (24).

Recently^[21] the synthesis of aromatic fluorinated isothianaphthene oligomers has been accomplished. In this chapter we first focus on a detailed NMR analysis of this set of aromatic fluorinated isothianaphthene oligomers (**20** - **23**) containing up to four monomer units. As showed previously^[6] the ^{13}C chemical shifts of the central carbon atoms in this kind of oligomers tends to reach a convergence limit from the trimer. We also synthesised 1,3-dithienyl-4,5,6,7-tetrafluoroisothianaphthene (TFDTI) (**24**). (Scheme 7.1) This molecule can be considered as a model compound for the aromatic structure of the corresponding fluorinated isothianaphthene polymer. Comparison of its spectroscopic data with the data obtained from analysis of the series of oligomers should test the possibility of use of (**24**) as a model for the aromatic structure.

Finally we report on the vibrational spectroscopic data of PTFITN and related aromatic model compounds to find out to what extent FT-IR and FT-Raman can provide in additional information on the electronic structure of PTFITN.

It should be mentioned that without the synthetic skills of C. Drury and the most interesting discussions of M. Swann of the University of Durham, these analyses would not have been possible.

7.2 Full ^1H , ^{13}C and ^{19}F Chemical Shift Assignment of the Aromatic Model Compounds

7.2.1 General Approach

The fluorinated aromatic oligomeric compounds (**20** - **23**) and (**24**) contain exclusively sp^2 carbon nuclei causing signals in the ^{13}C NMR spectra which are located in a narrow chemical shift region. For the structural analysis of the oligomers and the model compound we need to perform an unambiguous chemical shift assignment of the carbon, proton and fluorine signals.

An analysis strategy^[6] which permits discrimination between carbon or proton atoms, even if their NMR signals are very close together in the spectra, has already been developed in chapter 4. In this section we show how this approach can be extended to a full unambiguous assignment of the chemical shifts in compounds containing fluorine nuclei, bearing in mind that the main principles also apply to other NMR nuclei.

In this procedure, we start with the unambiguous assignment of at least one carbon, hydrogen or fluorine atom based on the molecular structure in order to be able to establish a further assignment pathway. For this purpose one makes use of *chemical shift*, *first order splitting or coupling pattern*,^[22] *coupling values*,^[23] and *peak areas*. If necessary *specific 1D-NMR techniques* (nuclear Overhauser effect (NOE), attached proton test (APT), attached fluorine test (AFT), proton and fluorine (de)coupling, selective irradiation e.g.) and the *heteronuclear coupling behaviour* of a particular atom in 2D-NMR experiments will be applied to obtain an additional objective starting point. The chemical shifts of these assigned atoms are then used as starting points to elaborate a pathway for further assignment of the signals originating from the other nuclei.

In general a full proton and carbon shift assignment can be achieved using direct ^1H - ^{13}C heteronuclear correlations (optimised for $J_{\text{CH}} = 140$ Hz) and long range ^1H - ^{13}C heteronuclear correlations (optimised for $J_{\text{CH}} = 8$ Hz). However in these fluorinated compounds the direct and long range ^1H - ^{13}C heteronuclear correlations will be further used as starting point for the two dimensional fluorine homonuclear (^{19}F - ^{19}F COSY) and heteronuclear (^{19}F - ^{13}C HETCOR) correlation pathway.

7.2.2 Parameterization of 1D and 2D ^{19}F NMR Experiments

Before starting the ^{19}F NMR experiments the fluorine spectra were referenced externally against fluorobenzene (35% in CFCl_3 with 12.5% CDCl_3 for lock) at -113.43 ppm which was referenced against CFCl_3 at 0 ppm.^[24, 25]

For optimisation of the parameters used in ^{19}F decoupling and ^{19}F - ^{13}C HETCOR experiments 2,2-difluorotetrachloroethane, $\text{CClF}_2\text{CCl}_3$, was used. The fluorines have a chemical shift of -61.448 ppm and the carbon shifts are 126.193 ppm and 96.375 ppm. Since two fluorines are present on the same carbon nucleus the ^{19}F coupled ^{13}C NMR spectrum shows a triplet for the fluorinated carbon atom, which is used for calibration of the Waltz decoupling. For the ^{19}F - ^{13}C HETCOR experiments the ^{19}F pulse width needed to be calibrated very accurately by means of a DEPT sequence.

Direct ^{19}F - ^{13}C HETCOR experiments were performed with optimisation at different values for J . The best results for direct ^{19}F - ^{13}C heteronuclear correlation were obtained at an optimisation value for $J = 255$ Hz. Geminal coupling between ^{19}F and ^{13}C occurs at values of J between 20 and 45 Hz. To exclude vicinal couplings ($^3J = 10 - 20$ Hz) the heteronuclear correlation experiment was optimised for $J = 45$ Hz. At this optimisation some direct couplings are still present. In order to be able to distinguish between different types of fluorinated carbon atoms an analogous pulse sequence as for the APT was used to discriminate between CF and CF_3 fluorinated carbon atoms and C and CF_2 carbon nuclei. In this type of 1D NMR experiment, the signals of CF- and CF_3 -carbons become negative while those of C- and CF_2 -carbons remain positive when the correct parameters are used. The evolution time in this case was set at $1/J_{\text{CF}} = 3.92 \cdot 10^{-3}$ seconds. Due to its analogy with APT this test will further be referred to as attached fluorine test (AFT). Notice that the fluorine coupling remains in the APT spectra while the proton coupling remains in the AFT spectra. The numbering of the hydrogen, carbon and fluorine nuclei used in the NMR analysis is shown in Figure 7.2. In the monomer (20) for reasons of symmetry the nuclei at position 4[A] and 7[A] have identical chemical

shifts, as have the nuclei at position 5[A] and 6[A]. The same remark can be made for ring B in the trimer (22).

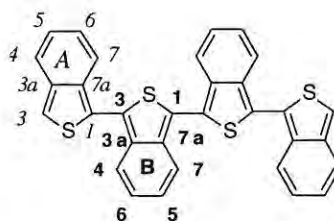


Figure 7.2 Numbering of the isothianaphthene ring systems in the tetrafluorinated oligomers (20 - 23).

7.2.3 Aromatic Model Compounds

(1) 4,5,6,7-tetrafluoroisothianaphthene (monomer) (20) Since there is only one hydrogen present in these compounds the signal in the ^1H NMR spectrum at 7.82 ppm can be assigned to H3. With the aid of the direct ^1H - ^{13}C HETCOR-spectrum optimised for $J_{\text{CH}} = 140$ Hz, C3 can be assigned to the signal at 115.55 ppm which is confirmed by APT. The long range ^1H - ^{13}C HETCOR-spectrum optimised for $J_{\text{CH}} = 8$ Hz (vicinal couplings) can then be used to assign C4 to 138.34 ppm because C4 is the only fluorinated carbon which can couple with H3 since C5 is too far removed from H3. From this assignment and the AFT it follows that the signal at 136.66 ppm belongs to C5, the remaining fluorinated carbon. The remaining quaternary carbon atom C3a can be assigned to the signal at 125.68 ppm. This is confirmed by the combination of APT and AFT. Based on the direct ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 255$ Hz we can assign F4 and F5 to -149.22 ppm and -162.99 ppm respectively. This assignment is in agreement with literature data^[26] of comparable compounds.

This unambiguous chemical shift assignment allows us to analyse further some aspects of the 2D ^{19}F - ^{13}C HETCOR spectra. From the direct ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 255$ Hz we can localise the direct ^{19}F - ^{13}C coupling signals. With this knowledge and with the full chemical shift assignment we can now investigate the ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 45$ Hz. Besides the expected geminal and some direct couplings for C3a, C4 and C5, an unanticipated long-range 4J coupling between C3 and F5 is also clearly observed.

(2) **Dimer (21)** H3 can be assigned to the signal at 8.00 ppm in the proton spectrum. The assignment strategy is similar to that employed for the monomer (**20**). Again H3 is used as the starting point for further assignments. The direct ^1H - ^{13}C HETCOR-spectrum optimised for $J_{\text{CH}} = 140$ Hz permits the assignment of C3 to the signal at 117.51 ppm which is confirmed by APT and AFT (Figure 7.3).

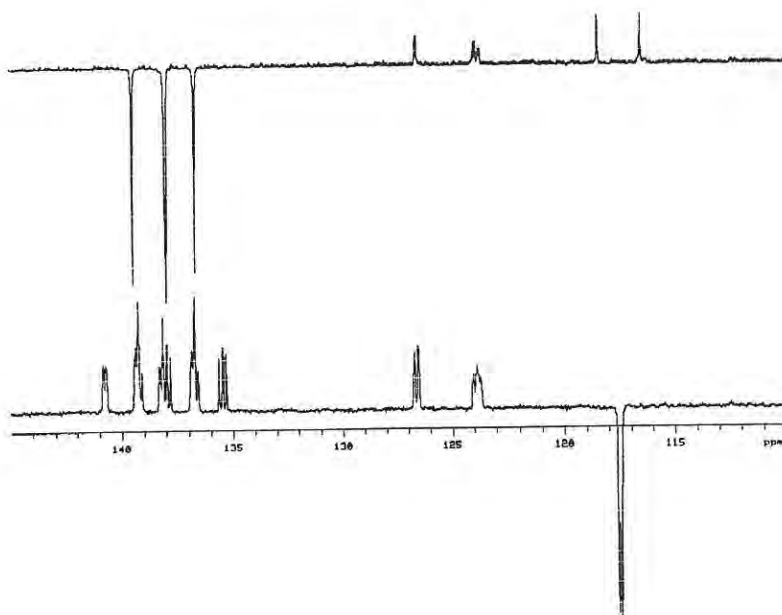


Figure 7.3 Attached fluorine test (AFT) and attached proton test (APT) of **21**, respectively (CDCl_3 , 30 °C).

For the assignment of C4 the long range ^1H - ^{13}C HETCOR-spectrum optimised for $J_{\text{CH}} = 8$ Hz is used. Thus C4 corresponds to the signal at 138.01 ppm. This assignment is further confirmed by the fact that a proton coupling of 3.8 Hz is present on the ^{19}F decoupled carbon signal. Based on the direct ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 255$ Hz (Figure 7.4) we can assign F4 to the signal at -149.31 ppm. For further assignment we need to identify F5 or F6. Due to the value of a F-F *ortho* (20 Hz) and F-F *para* (12-14 Hz) coupling^[24], the ^{19}F - ^{19}F COSY (Figure 7.5) will show correlation signals for F4 both with F7 and F5, while F6 (F-F *meta* coupling: 2-3 Hz) will not

correlate with F4 and therefore can be assigned to -160.36 ppm. Through the direct ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 255$ Hz we can now assign C6 to 137.96 ppm. With F4/C4 and F6/C6 known, we can now analyse the ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 45$ Hz (Figure 7.6) for assignment of C5 and C7. From analysis of the monomer (**20**) spectrum we find that only direct and geminal ^{19}F - ^{13}C couplings will be present as far as the fluorinated carbon nuclei are concerned. Since the direct ^{19}F - ^{13}C couplings of F4/C4 and F6/C6 can be identified through the ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 255$ Hz the other correlation signals originate from a geminal coupling. F4 can only show a geminal coupling with the C5. This allows us to assign C5 to 136.68 ppm. On the other hand F6 has a geminal coupling with C5 and C7. Since C5 has been assigned previously, the remaining signal at 139.46 belongs to C7. Based on the ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 255$ Hz we can now assign F5 and F7 to -162.06 and -150.10 ppm respectively. This assignment was expected from the monomer (**20**) ^{19}F spectrum (F4 and F7 around -150 ppm and F5 and F6 around -160 ppm).

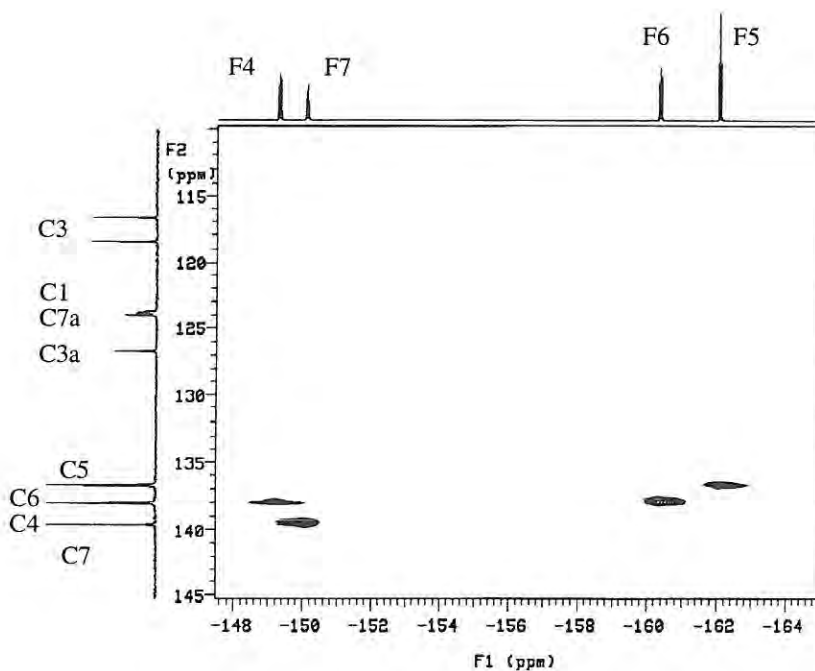


Figure 7.4 2D heteronuclear ^{19}F - ^{13}C correlation spectrum of **21** optimised for $J_{\text{CF}} = 255$ Hz (CDCl_3 , 30 °C).

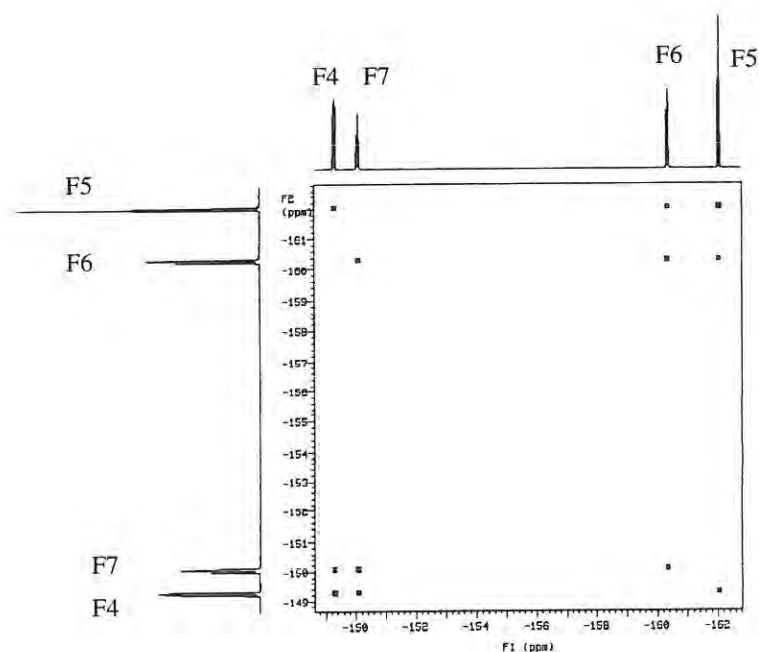


Figure 7.5 2D heteronuclear ^{19}F - ^{19}F correlation spectrum (COSY) of **21** (CDCl_3 , 30 $^\circ\text{C}$).

Finally, we only have to assign the quaternary carbon atoms. For this purpose we have to analyse again the ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 45$ Hz (Figure 7.6). For consistency with the ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 45$ Hz of the monomer (**20**), we identify all the correlation signals present as originating only from direct and geminal couplings. Although no other long range correlation signals than geminal correlations are present we again notice a correlation between the protonated carbon C3 and F5. This ^4J coupling was also present in the monomer (**20**) and probably finds its origin in the particular geometry of the isothianaphthene ring system. If such a coupling exists between C3 and F5 then an analogous coupling should exist between C1 and F6. Indeed, in the ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 45$ Hz there is a correlation signal between F6 and the quaternary carbon atom at 123.74 ppm, which therefore can be assigned to C1. The two remaining correlation signals from F4 and F7 with the other quaternary carbon atoms result from a geminal coupling. This allows us to

assign C3a and C7a to the signals at 126.60 ppm and 123.93 ppm respectively. In the fluorine decoupled spectrum the presence of a proton coupling of 2.5 Hz (2J) on the carbon signal at 126.60 ppm (C3a) and of 7.9 Hz (3J) on the carbon signal at 123.93 ppm (C7a) and 123.74 ppm (C1) confirms these assignments. Since for C1 the value of the coupling correspond with a vicinal long range coupling this means that in this specific case coupling takes place across an heteroatom.

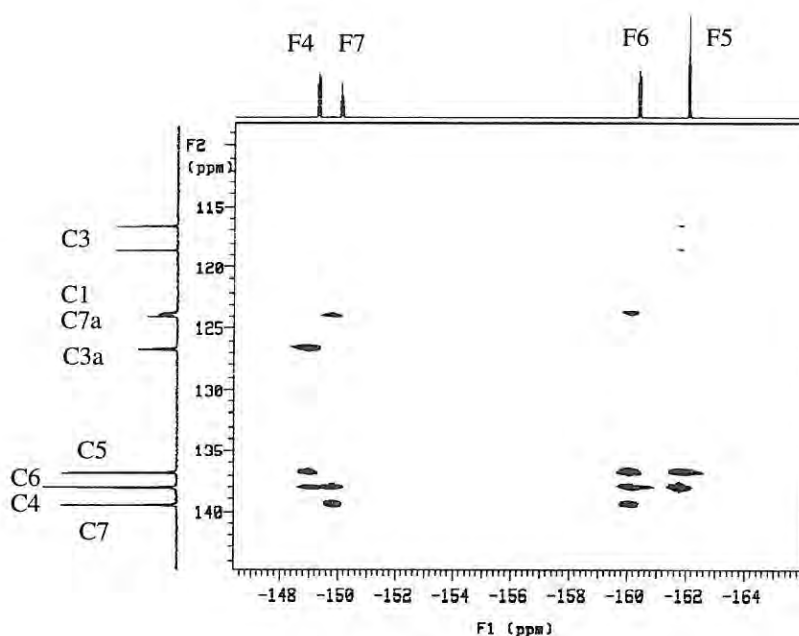


Figure 7.6 2D heteronuclear ^{19}F - ^{13}C correlation spectrum of **21** optimised for $J_{\text{CF}} = 45$ Hz (CDCl_3 , 30 °C).

(3) **trimer (22)** H3(A) can easily be assigned to the signal at 8.05 ppm. As previous the direct ^1H - ^{13}C HETCOR-spectrum optimised for $J_{\text{CH}} = 140$ Hz permits to assign C3(A) to the signal at 118.10 ppm which is confirmed by APT. Through the long range ^1H - ^{13}C HETCOR-spectrum optimised for $J_{\text{CH}} = 8$ Hz we can associate C4(A) with the signal at 138.08 ppm which is confirmed by the presence of some proton coupling in the fluorine decoupled spectrum. This allows us using the direct ^{19}F - ^{13}C

HETCOR-spectrum optimised for $J_{\text{CF}} = 255$ Hz to assign F4(A) to the signal at -148.97 ppm.

In the ^{19}F - ^{19}F COSY F4(A) shows a coupling signal with the fluorine signal at -161.66 ppm and -149.70 ppm. Since we know from the analysis of monomer (**20**) and dimer (**21**) that the signals of F4/F7 and F5/F6 are situated around -150 ppm and -160 ppm respectively we are able to assign the signals at -161.66 ppm and -149.70 ppm to F5(A) and F7(A) respectively. Therefore F6(A) should be assigned to the multiplet between -159.6 and -159.8 ppm. For the identification of F4(B) and F5(B) it is quite reasonable to make the assumption, which is based on the assignment of the fluorine atoms in the monomer (**20**) and dimer (**21**). Therefore we assign F4(B) to the remaining signal at -149.41 ppm. F5(B) on the other hand can also be associated with the multiplet between -159.6 ppm and -159.8 ppm. Through selective irradiation of F7(A) and F4(B) it is however possible to discriminate between F6(A) and F5(B). The triplet of F6(A) should be transformed into a doublet when F7(A) is irradiated whereas the doublet of F5(B) should become a singlet upon irradiation of F4(B). This allows us to assign F6(A) and F5(B) to the signals at -159.66 ppm and -159.67 ppm respectively.

Since all the fluorine chemical shifts are known the fluorinated carbon atoms can easily be assigned through the direct ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 255$ Hz. Therefore C5(A), C6(A), C7(A), C4(B) and C5(B) are associated with the signals at 136.79, 138.18, 139.45, 139.30 and 137.97 ppm respectively.

The assignment of the quaternary carbon atoms can only be based on the analysis of the ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 45$ Hz. The part of the 2D spectrum showing the correlation signals between the fluorinated carbon atoms and the fluorines conforms with the particular pattern that one may expect from a combination of direct and geminal couplings. Furthermore we notice the ^4J correlation between C3(A) and F5(A) as in the monomer (**20**) and dimer (**21**). In analogy with the assignment in the dimer (**21**) we can assign C1(A) to 122.81 ppm based on the presence of a ^4J correlation signal with F6(A) and the presence of a proton coupling originating from H3. As we may expect C3a(A) and C7a(A) to show only geminal correlations with F4(A) and F7(A) respectively we can assign them to the signals at 126.72 and 124.06 ppm respectively. This assignment is confirmed by the presence of a geminal and vicinal proton-carbon coupling of 2.7 and 7.8 Hz respectively. Since the presence of the ^4J correlation signal is consistent in the monomer (**20**), dimer (**21**) and ring A of the trimer (**22**) (Figure 7.7) we can now use this phenomenon to assign C3(B) to the signal at 125.37 ppm. As a consequence the remaining quaternary signal at 124.70 ppm should therefore be assigned to C3a(B), which is confirmed by its geminal coupling with F4(B).

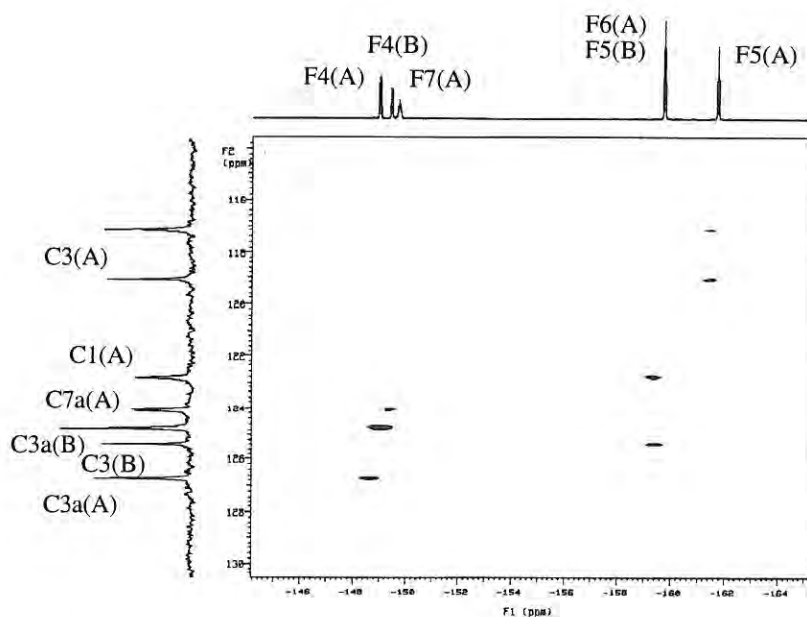


Figure 7.7 2D heteronuclear ^{19}F - ^{13}C correlation spectrum of **22** optimised for $J_{\text{CF}} = 45 \text{ Hz}$ (CDCl_3 , 30°C) showing the quaternary carbon nuclei.

(4) tetramer (23) The assignment of the only proton H3(A) to 8.068 ppm is rather straightforward. From the fluorine decoupled spectrum we can easily assign C3(A) to the signal at 118.31 ppm. As in the other oligomers one of the fluorinated carbon signals (138.08 ppm) shows a small proton coupling and can therefore be assigned to C4(A). This allows to identify F4(A) at -148.96 ppm using the direct ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 255 \text{ Hz}$. Through ^{19}F - ^{19}F COSY we found F5(A) to correspond with the signal at -161.65 ppm and as a consequence C5(A) is located at 136.80 ppm with the aid of the direct ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 255 \text{ Hz}$. Based on the same reasoning as for the trimer (**22**) we found from ^{19}F - ^{19}F COSY that F6(A) and F7(A) are to be assigned to the signals at -159.56 and -149.78 ppm respectively. Direct fluorine-carbon coupling allows us to assign C6(A) and C7(A) to the signals at 138.22 and 139.43 ppm respectively. To assign the other fluorinated carbons and fluorines of ring B we have to take recourse to comparison of the ^{19}F decoupled ^{13}C NMR spectrum of the trimer (**22**) and the tetramer (**23**) (Figure 7.8).

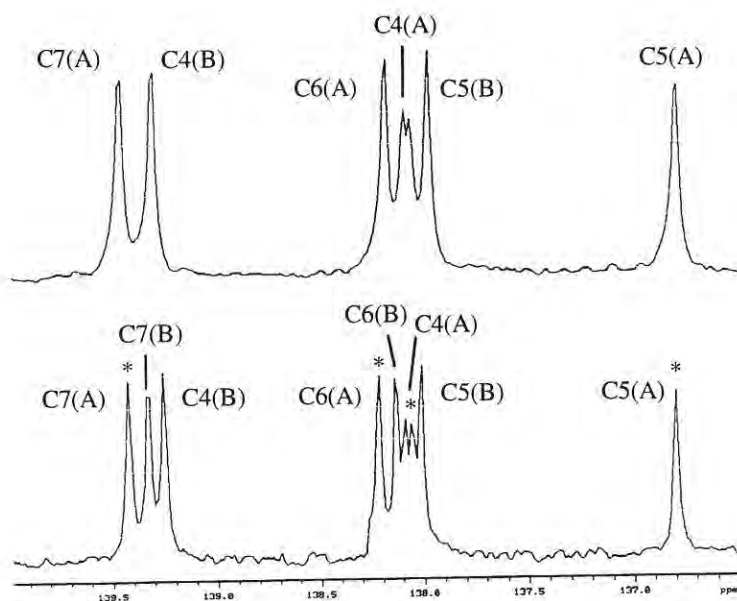


Figure 7.8 Comparison of the ^{19}F decoupled ^{13}C NMR spectra of the fluorinated carbon nuclei of **22** and **23**. (* : assigned on the basis of HETCOR, COSY, ...)

The chemical shifts marked with an asterisk in the spectrum of the tetramer (**23**) have been assigned using HETCOR and COSY. The assigned shifts from ring A differ very little from the corresponding shifts in the trimer (**22**) spectrum. We can thus presume the carbon signals of C4(B) and C5(B) do not undergo an important change in chemical shift. Therefore we assign C4(B) and C5(B) to 139.26 and 138.01 ppm respectively. From this comparison between trimer (**22**) and tetramer (**23**) it appears that the carbons C4/C7 and C5/C6 are grouped around 139 ppm and 138 ppm respectively, with the exception of C4(A) and C5(A). This observation can be used to assign the two remaining carbon signals at 139.34 and 138.14 ppm to C7(B) and C6(B) respectively. This assignment is in agreement with the direct ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 255$ Hz. Indeed, C4(B) and C7(B) show a coupling with the multiplet at -149.20, the 'F4/F7' side of the fluorine spectrum. On the other hand C5(B) and C6(B) show a correlation signal with -159.45 and -159.14 ppm, two multiplets at the 'F5/F6'

side of the fluorine spectrum. This allows us in addition to assign F4(B), F7(B), F5(B) and F6(B) to -149.20, -149.20, -159.45 and -159.14 ppm respectively. This assignment is further confirmed with the aid of selective irradiation at the different fluorine resonances.

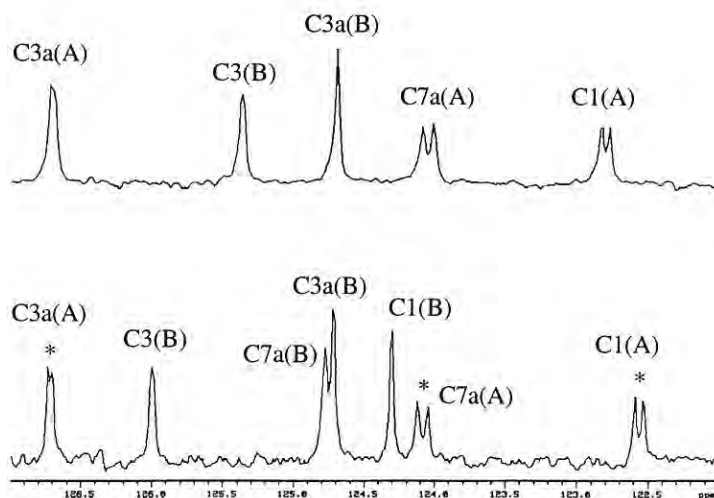


Figure 7.9 Comparison of the ^{19}F decoupled ^{13}C NMR spectra of the quaternary carbon nuclei of **22** and **23**. (* : assigned on the basis of the coupling pattern)

The assignment of the quaternary carbon atoms is complicated in the higher order oligomers by the fact that we have to rely entirely on long range correlations to complete our assignment. Moreover since we have to differentiate between several quaternary carbon nuclei a relatively high resolution long range ^{19}F - ^{13}C HETCOR-spectrum is needed. However the low solubility of the tetramer (**23**) makes this long range HETCOR experiment rather time-consuming. This led us at first to rely on additional information provided by the comparison of ^{19}F and ^1H decoupled ^{13}C NMR spectra. The signals at 122.56, 124.08 and 126.72 ppm are the only quaternary carbon atom signals to possess a proton coupling (Figure 7.9) and should therefore belong to nuclei of ring A. When we compare subsequently this part of the ^1H decoupled ^{13}C NMR spectrum of trimer (**22**) and tetramer (**23**) we are able to assign these signals to C1(A), C7a(A) and C3a(A)

respectively. This assignment is further confirmed by a long range ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 45$ Hz (spectrum not shown). This spectrum allows us to associate C3a(B) and C7a(B) with the signals at 124.72 and 124.78 ppm respectively. Comparison of the ^1H decoupled ^{13}C NMR spectrum of trimer (22) and tetramer (23) permits us to assign C3a(B) to 124.72 ppm, which implies that C7a(B) should be assigned to the signal at 124.778 ppm. For the assignment of the remaining quaternary carbon atoms C3(B) and C1(B) we have to take recourse to the specific ^4J coupling between C1-F6 and C3-F5 consistently present in the long range ^{19}F - ^{13}C HETCOR-spectrum optimised for $J_{\text{CF}} = 45$ Hz of the other oligomers. This allows us to assign C3(B) and C1(B) to 124.30 and 126.00 ppm respectively.

(5) 1,3-dithienyl-4,5,6,7-tetrafluoroisothianaphthene (24)

Investigation of the molecular structure of compound (24) suggests two starting points for spectral assignment. The first one is the ^1H NMR shift of H4' which is characterised by its specific coupling pattern. This coupling pattern is made up by two coupling constants originating from two different *ortho* couplings. Therefore H4' can be assigned to the multiplet at 7.11 ppm. Following to this, C4' can be assigned to the signal at 129.85 ppm using the direct ^1H - ^{13}C HETCOR spectrum optimised for $J_{\text{CH}} = 140$ Hz. From the long range ^1H - ^{13}C HETCOR spectrum optimised for $J_{\text{CH}} = 8$ Hz C2' can be assigned to the chemical shift at 132.70 ppm since it is the only quaternary carbon nucleus able to show a long range coupling with H4'. The presence of proton coupling to this signal in the fluorine decoupled spectrum confirms this assignment.

Based on quantitative ^{13}C , APT and AFT experiments the signal at 127.85 ppm in the proton decoupled ^{13}C NMR spectrum appears to be the result of the collapse of a quaternary and two protonated carbon signals. Since this makes it impossible to use the long range ^1H - ^{13}C HETCOR spectrum optimised for $J_{\text{CH}} = 8$ Hz for identification of the other thiophene proton and carbon signals we have to revert to comparison with analogous 1,3-dithienyl isothianaphthene compounds.^[6, 27] This allows us to assign H3' and H5' to 7.43 and 7.27 ppm, respectively. With the aid of the direct ^1H - ^{13}C HETCOR spectrum optimised for $J_{\text{CH}} = 140$ Hz we can as a consequence assign C3' and C5' to the signals at 129.16 ppm and 127.845 ppm.

Since one of the remaining quaternary carbon signals is coalesces with C5' it is impossible to use as a second starting point the fact that C3 is the only remaining quaternary carbon atom within the isothianaphthene ring to be able to show a long range coupling with H3' of the thiophene ring. Indeed the correlation signal corresponding with H3' in the long range ^1H - ^{13}C HETCOR spectrum optimised for $J_{\text{CH}} = 8$ Hz can also

originate from the coupling of C5' with H3' and as a consequence it is not clear whether the correlation signal of the signal at 127.845 ppm with H3' is the result of two couplings, namely C3 with H3' and C5' with H3', or results from the coupling of C5' with H3' alone. Since in this circumstance it is impossible to determine whether the quaternary carbon atom at 127.6 ppm shows a long range coupling with H3' or not, we need another starting point for further analysis.

Based on the NMR analysis of the isothianaphthene ring systems of the fluorinated oligomers the F4/F7-side of the spectrum was localised at about -149 ppm and the F5/F6-side at about -160 ppm. Since we note two fluorine signals at -145.68 ppm and -161.70 ppm, it is reasonable to associate F4 and F5 respectively with these signals. As the fluorine signals have been assigned we can now use the direct ^{19}F - ^{13}C HETCOR spectrum optimised for $J_{\text{CF}} = 255$ Hz to assign the fluorinated carbon atoms. Thus C4 and C5 correspond with the shifts at 139.13 and 137.15 ppm respectively. Using the long range ^{19}F - ^{13}C HETCOR spectrum optimised for $J_{\text{CF}} = 45$ Hz we can next assign C3a to the signal at 121.78 ppm due to the presence of a geminal correlation signal. This assignment is further confirmed by the presence of an pronounced fluorine coupling in the proton decoupled ^{13}C NMR spectrum. Next we remark a 4J long range coupling between F5 and a quaternary carbon atom present in the long range ^{19}F - ^{13}C HETCOR spectrum optimised for $J_{\text{CF}} = 45$ Hz. In the fluorinated oligomers this observation appeared to be very characteristic for fluorinated isothianaphthene ring systems. Since we were able to identify this correlation signal as the result of a coupling between F5 and C3, we can assign C3 to the quaternary carbon signal at 127.86 ppm.

7.2.4 Discussion

It has been shown previously^[5, 6] that the ^{13}C chemical shifts of the central part of suitable oligomers can be used to discriminate between different molecular structures, e.g. between aromatic and quinoid geometries. Therefore the chemical shifts of the carbons C3, C3a, C4 and C5 of the central part of the fluorinated aromatic model compounds will now be compared with each other in order to ascertain if within these series of model compounds convergence in the chemical shifts has been reached.

The ^{13}C chemical shift data of the oligomers (20 - 23) are summarised in Table 7.1. For these oligomers to be useful as model compounds of the corresponding polymer, they should contain one or more isothianaphthene rings which are no longer influenced by the end groups, in which in this case there is a hydrogen nucleus present, H3(A). That this is indeed the situation is indicated by a convergence of the chemical shift

as a function of chain length. Therefore, we plotted the ^{13}C chemical shifts of the "central" carbons as a function of chain length. (Figure 7.10) It should be noticed that the central aromatic carbons are uniformly referred to as C3, C3a, C4 and C5 although they correspond to C1, C7a, C7 and C6 in ring A of the dimer (**21**) and in ring B of the tetramer (**23**), respectively.

	20	21	22		23		24
			Ring A	Ring B	Ring A	Ring B	
C3	115.55	117.51	118.10	125.37	118.31	126.00	127.68
C3a	125.68	126.60	126.72	124.70	126.72	124.72	121.78
C4	138.34	138.01	138.08	139.30	138.08	139.26	139.13
C5	136.66	136.68	136.79	137.97	136.80	138.01	137.15
C6		137.96	138.18		138.22	138.14	
C7		139.46	139.45		139.43	139.34	
C7a		123.92	124.06		124.08	124.78	
C1		123.74	122.81		122.56	124.30	

*Table 7.1 ^{13}C chemical shifts (CDCl_3) of the fluorinated monomer (**20**), dimer (**21**), trimer (**22**) and tetramer (**23**) of 4,5,6,7-tetrafluoroisothianaphthene and the shifts of the isothianaphthene ring of 1,3-dithienyl 4,5,6,7-tetrafluoroisothianaphthene (**24**).*

From Figure 7.10 it can be seen that the shifts for C4 and C5 are almost independent of the end groups, therefore, the chain length is unimportant as far as the shifts of these carbons are concerned. This result is in agreement with analogous results^[6] obtained on a set of aromatic disilylated isothianaphthene compounds. C3a reaches a plateau from the dimer (**21**) onwards, only the shift in the monomer (**20**) is not suitable for comparison with the polymer. The most drastic changes takes place for the shift of the quaternary carbon atom C3 because it is protonated in the monomer (**20**). However convergence is already reached going from trimer (**22**) to tetramer (**23**). Since C3 can be considered to form the backbone of these oligomers, the chemical shift of this carbon will be subject to more pronounced changes due to a difference in endgroups. Going from monomer (**20**) to dimer (**21**) a hydrogen is replaced by a fluorinated

isothianaphthene group. Hence for these oligomers, at least three isothianaphthene units are necessary in order to use the central part as a model for the structure of the corresponding polymer (for ^{13}C NMR purposes).

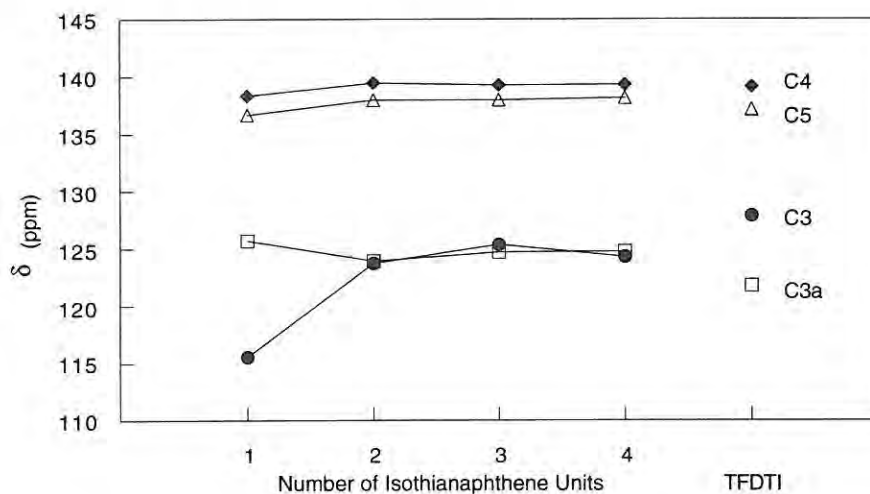


Figure 7.10 Evolution of the ^{13}C chemical shifts of the "central" carbon atoms C3, C3a, C4 and C5 of the fluorinated isothianaphthene oligomers (20 - 23) as a function of the chain length. Comparison of the ^{13}C chemical shifts of the "central" carbon atoms C3, C3a, C4 and C5 of the fluorinated tetramer (23) with the "central" carbon atoms of TFDTI (24).

	20	21	22		23		24
			Ring A	Ring B	Ring A	Ring B	
H3	7.82	8.00	8.05		8.07		
F4	-149.22	-149.31	-148.97	-149.41	-148.96	-149.20	-145.68
F5	-162.99	-162.06	-161.66	-159.67	-161.65	-159.45	-161.70
F6		-160.36	-159.66		-159.56	-159.14	
F7		-150.10	-149.70		-149.78	-149.20	

Table 7.2 ^1H and ^{19}F chemical shifts (CDCl_3) of the fluorinated isothianaphthene model compounds (20 - 23) and (24).

In order to evaluate to what extent we can extract some structural information from a more simple model compound, we also synthesised TFDTI (**24**). In this compound the fluorinated isothianaphthene core is surrounded by two thiophene ring systems in order to simulate an extended π -system and the spatial interaction between the sulphur and the fluorine of neighbouring ring systems. However it should be noticed that the use of a thiophene ring system to simulate a neighbouring fluorinated isothianaphthene ring is not ideal. From comparison of the chemical shifts of (**24**) with the 'central' carbon atoms of the fluorinated tetramer (**23**) we see that there is already a relatively good correspondence between the shifts of C4 and C5 of both compounds. However, a significant difference is present between the quaternary carbon nuclei. Results for the oligomers show that the quaternary carbon nuclei turned out to be more sensitive towards substitution. This difference in chemical shift can be explained when we take into account the fact that we use two electron rich thiophene ring systems to simulate the relatively electron-poor neighbouring isothianaphthene ring systems. Therefore the difference in shift of C3 and C3a of (**24**) with those of the tetramer (**23**) can be understood in terms of differences in electron density caused by the thiophene rings. The increase of electron density on C3 will cause an upfield shift, whereas a decrease of the electron density on C3a causes a downfield shift as compared to the tetramer (**23**). Despite such inherent imperfection, this model compound allows one to obtain a reliable idea about the chemical shift value of C4 and C5 in an aromatic fluorinated isothianaphthene ring system.

7.2.5 Conclusion

A detailed analysis based on 1D and 2D NMR techniques was used to evaluate the evolution of the chemical shifts of equivalent carbon nuclei in oligomeric fluorinated isothianaphthene model compounds unambiguously possessing an aromatic structure. For this purpose the principle of full chemical shift assignment was extended to include NMR experiments based on fluorine homonuclear (^{19}F - ^{19}F COSY) and heteronuclear (^{19}F - ^{13}C HETCOR) correlations. Also a new 1D experiment was developed to discriminate between CF/CF_3 and C/CF_2 carbon nuclei. Due to its analogy with the Attached Proton Test (APT) it was referred to as Attached Fluorine Test (AFT). From this NMR analysis the shifts of the "central" carbon atoms within these model compounds show a clear convergence from trimer (**22**) to tetramer (**23**). The chemical shift values of the 'central' carbon atoms can therefore be considered as being representative for fluorinated poly(isothianaphthene) possessing an aromatic structure. Furthermore the analysis of a more simple model compound indicates that from this

model compound it is also possible to obtain a reliable indication of the chemical shift value of C4 and C5, despite the important structural and chemical changes induced by the fluorine nuclei. Finally a detailed analysis of the ^{19}F chemical shifts in the tetramer (**23**) revealed the highly twisted character of the oligomeric backbone.

7.3 FT-Raman and FT-IR Analysis of the Aromatic Model Compounds

The information obtained from FT-Raman spectra of aromatic and quinoid isothianaphthene model compounds appeared to be of valuable aid for the interpretation of the FT-Raman spectrum, within the framework of the discussion on the ground state structure of PITN. Therefore, the FT-Raman spectra of the series of aromatic tetrafluorinated isothianaphthene oligomers (**20** - **23**) should allow us to gather sufficient information to enable us to say whether the polymer PTFITN is aromatic or not. First we shall compare the spectra of the series of PTFITN oligomers. Next the spectrum of the disilylated tetramer (**10**), the fluorinated tetramer (**23**) and the model compound TFDTI (**24**) will be evaluated. Figure 7.11 shows the FT-Raman spectra of the fluorinated monomer (**20**), dimer (**21**), trimer (**22**) and tetramer (**23**), respectively. As in the case of the silylated monomer (**7**), the fluorinated monomer (**20**) shows a rather complex FT-Raman spectrum. The spectrum of the dimer (**21**) is much simpler. However, it is only from the trimer (**22**) onwards that the intensity of a few signals appears to be selectively enhanced. The spectrum of the tetramer (**23**) appears to be almost identical to that of the trimer (**22**). As in the case of the disilylated oligomers, a convergence is reached going from trimer (**22**) to tetramer (**23**). This shows again that it is reasonable to consider the spectrum of the tetramer (**23**) as a prototype for the tetrafluorinated ITN unit with an aromatic structure. The spectrum of the fluorinated tetramer (**23**) is compared in Figure 7.12 with the spectrum of the disilylated tetramer (**10**), the simpler model compound TFDTI (**24**) and the spectrum of PTFITN with a chain length of about 500 units. The spectra of both the disilylated and the fluorinated tetramer show the characteristic features associated with "aromatic" ITN units. The strong signal at 1458 cm^{-1} corresponds with the signal at 1444 cm^{-1} in the silylated tetramer (**10**). So do the signals at 1493 cm^{-1} and 1354 cm^{-1} in the spectrum of the fluorinated tetramer (**23**) correspond with the signals at 1486 cm^{-1} and 1333 cm^{-1} , respectively, in the FT-Raman spectrum of the disilylated tetramer (**10**). However, the signals in the FT-Raman spectrum of the fluorinated tetramer (**23**) are sharper indicating a less efficient delocalisation between the different ITN units. The difference in wavelength most probably finds its origin in the fact that all the hydrogen atoms are replaced by fluorine atoms.^[28]

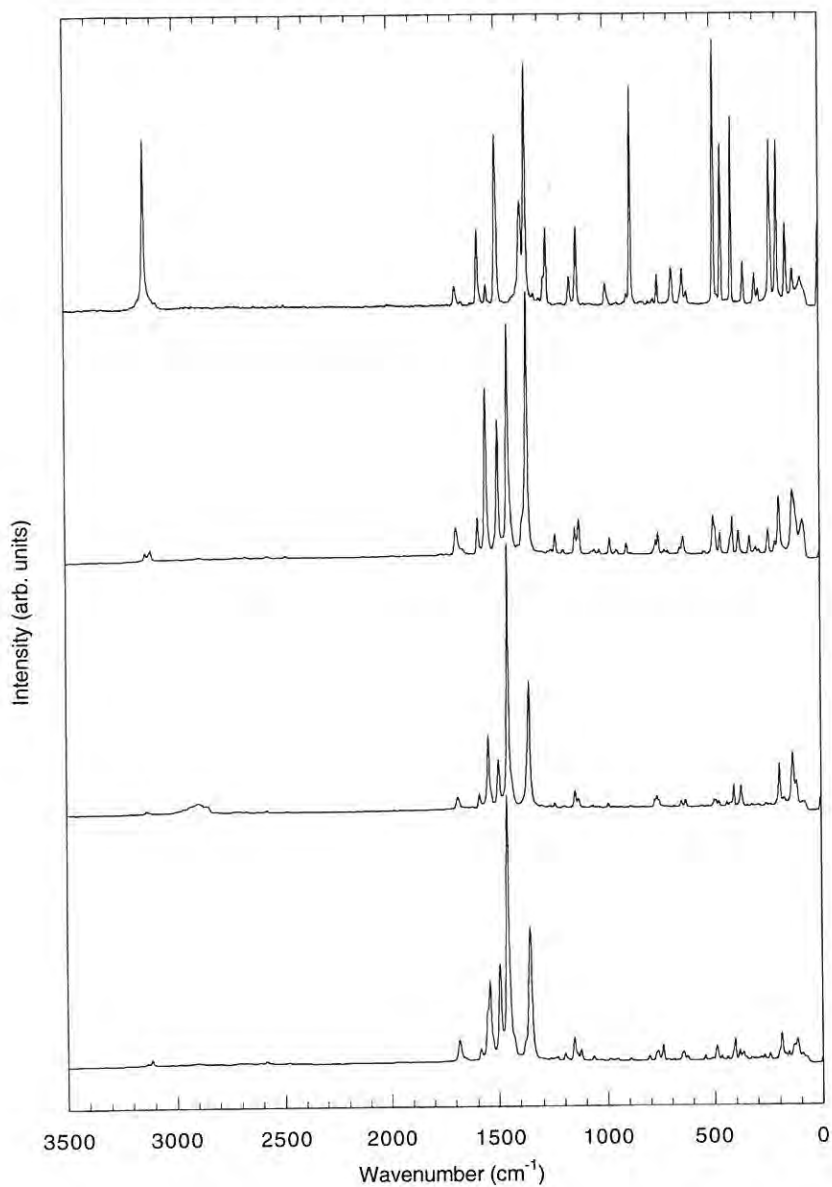


Figure 7.11 The FT-Raman spectrum of the fluorinated monomer (20), dimer (21), trimer (22) and tetramer (23).

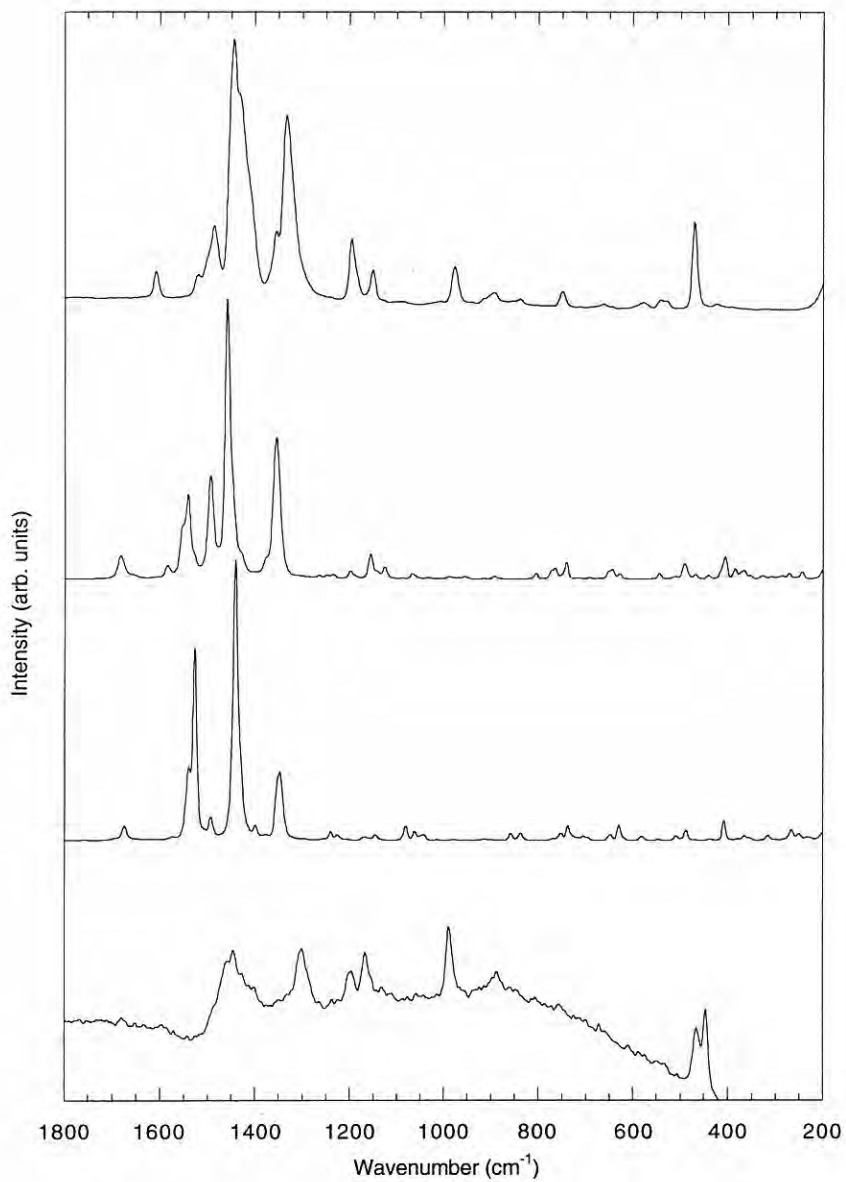


Figure 7.12 The FT Raman spectra of the disilylated tetramer (10), the fluorinated tetramer (23), TFDTI (24) and PTFITN (19), respectively.

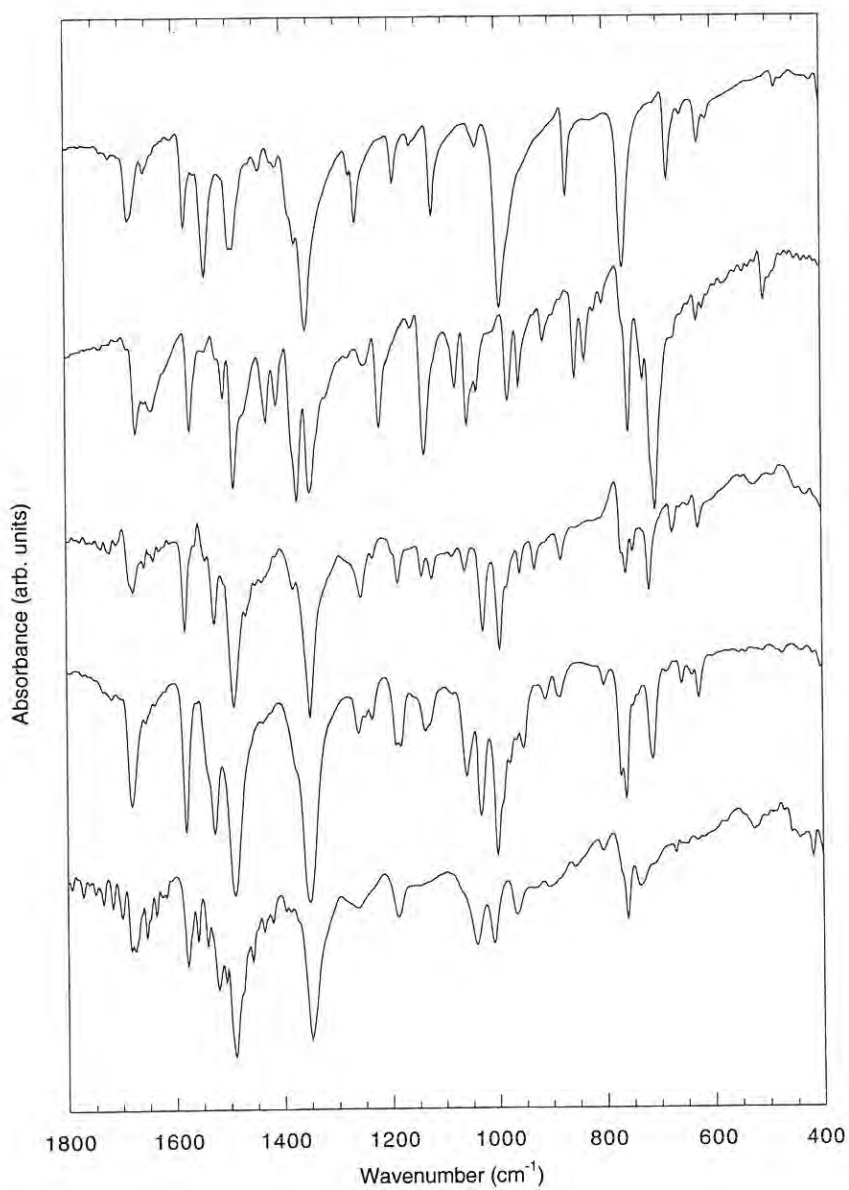


Figure 7.13 FT-IR spectra of the tetrafluorinated monomer (20), dimer (21), trimer (22), tetramer (23) and polymer (220 units) (19), respectively.

The spectrum of TFDTI (**24**) is nicely characterised by the typical aromatic ITN features derived from the disilylated tetramer (**10**) and the non-fluorinated 1,3-dithienyl isothianaphthene. The signals with the largest intensity, i.e., 1526 cm^{-1} , 1441 cm^{-1} and 1347 cm^{-1} , correspond with the tetramer (**23**) signals at 1540 cm^{-1} , 1493 cm^{-1} and 1354 cm^{-1} . This shows that in this case TFDTI (**24**) can also be used on the level of FT-Raman spectroscopy as a model compound to obtain information on the π system of aromatic ITN units.

The FT-IR spectra of the fluorinated oligomers are depicted in Figure 7.13. Only the fingerprint region is shown, because in the polymer spectrum no signals appear at higher wavenumbers. Many signals appear due to the presence of the fluorines. However, in these FT-IR spectra there is also some resemblance between the oligomer spectra. As in the case of the FT-Raman spectra we can consider the IR spectrum of the tetramer (**23**) as the best polymer simulation possible of all model compounds at our disposal.

7.4 Comparison between Polymer and Model Compounds

In the ^{13}C NMR spectrum of PTFITN synthesised at the University of Durham we find three signals. The fluorinated carbons C4 and C5 can be associated with the signals at 139.32 ppm and 138.32 ppm, respectively. The signal at 124.90 ppm corresponds most probably with C3 as well as C3a. From comparison of these chemical shifts with those of the aromatic fluorinated tetramer (**23**), there appears to be a strong correspondence.

Also the correspondence (Figure 7.13) between the FT-IR spectra of the aromatic oligomers and the PTFITN spectrum indicates that there should exist a structural similarity between these materials.

When comparing the FT-Raman spectra of the fluorinated tetramer (**23**) and PTFITN there appears to be a discrepancy with the conclusions from ^{13}C NMR and FT-IR spectroscopy and with the surprising high solubility in common organic solvents. The last spectrum from Figure 7.12 is taken from a polymer sample obtained from the University of Durham. As we could not succeed in obtaining a FT-Raman spectrum from pure polymer, the material was imbedded in a KBr pellet. The rather low quality of the spectrum in Figure 7.12 is attributed to the difficulties in recording the spectrum. However, a spectrum with signals of sufficient intensities could be recorded. The spectrum of pristine PTFITN shows a lot of differences as compared with the aromatic

model compounds. Moreover, there is a striking resemblance with the FT-Raman spectrum of PITN electrochemically doped at 0.8 V. (Figure 5.3) Indeed, the signals at 1445, 1300, 1196, 1166, 989, 465 and 445 cm^{-1} correspond almost exactly with the signals present in the mentioned doped PITN spectrum. Thus, on the one hand the spectrum does not match the spectral features of aromatic ITN units but on the other hand it does not correspond completely with the spectrum of pristine PITN possessing a quinoid structure.

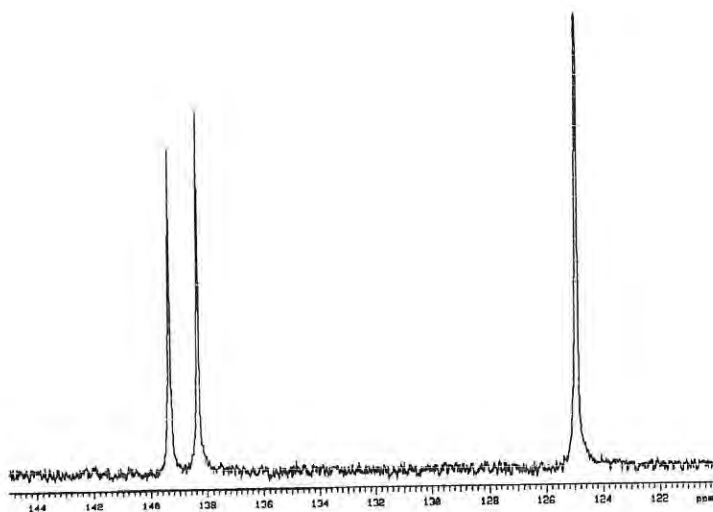


Figure 7.14 The ^{13}C NMR spectrum of PTFITN (220 units).

Since it is known that electron/phonon coupling occurs more effectively when double bonds are in the *trans* configuration, the presence of a few "quinoid"-like defects could enhance the characteristic "quinoid" modes to such an extent that the FT-Raman spectrum is dominated by the signals originating from quinoid defects rather than by signals originating from an overall aromatic structure. Since PTFITN has been synthesised^[21] by dehydrogenation of a precursor polymer or by oxidative electrochemical polymerisation of 4,5,6,7-tetrafluoroisothianaphthene, it may be possible that quinoid defects could be present. A straightforward interpretation of these data is, however, not evident as at this moment a detailed structure analysis of doped PITN has

not yet been performed nor do we have at our disposal the experimental data of quinoid tetrafluorinated model compounds.

7.5 Synopsis

In the search for PITN derivatives with enhanced processability and stability, Brooke et al.^[21] synthesised poly(4,5,6,7-tetrafluoroisothianaphthene). To understand the effect of fluorine on the structure and the properties of this material, a detailed spectroscopic characterisation was carried out. At first, a series of aromatic tetrafluorinated isothianaphthene oligomers were analysed by means of 1D and 2D NMR spectroscopic techniques to obtain an unambiguous full chemical shift assignment of the hydrogen, carbon and fluorine signals. The shifts of the "central" carbon atoms of these oligomers showed a clear convergence going from trimer (**22**) to tetramer (**23**). The chemical shift values of the 'central' carbon atoms can therefore be considered as being representative for fluorinated poly(isothianaphthene) possessing an aromatic structure. Furthermore the analysis of a more simple model compound, TFDTI (**24**), indicates that from this model compound it is also possible to obtain a reliable indication on the chemical shift value of C4 and C5, despite the important structural and chemical changes induced by the fluorine nuclei.

The characteristic convergence going from trimer (**22**) to tetramer (**23**) appeared also from FT-IR and FT-Raman spectroscopic data. Also on the level of FT-Raman spectroscopy the spectrum of TFDTI (**24**) showed the characteristic features of "aromatic" isothianaphthene units.

The spectroscopic data of the polymer are consistent with the NMR and FT-IR data of the aromatic oligomers. This consistency could indicate that the polymer can possess an aromatic structure. However, the FT-Raman spectrum of the polymer does not correspond with the typical features of the spectrum corresponding with "aromatic" ITN units, but rather with the spectrum of doped PITN. The explanation for this discrepancy is not obvious since there is a lack of data on the structure of quinoid PTFITN as on the structure determination of doped PITN.

7.6 References

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Quid si etiam jucunda memoria est praeteritorum memoria?
(Cicero, De Finibus, 2,32,105)

Nitrogen-Containing Poly(isothianaphthene) Derivatives

8.1 Introduction

In the field of conjugated polymers, the design of low-bandgap materials has been of particular interest during the past decade. Polymeric compounds with a small energy difference between the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) electronic bands are potentially good intrinsic electrical conductors or semiconductors without the need of any chemical or electrochemical doping. Moreover, they show a certain transparency in either the neutral or doped state. Finally they are of interest in the field of nonlinear optics.

One promising strategy to accomplish this goal is to derivatize conjugated polymers that possess a modest bandgap and are easy to substitute. This approach was first considered by Wudl et al.,^[11] who were successful in reducing the bandgap of poly(thiophene) (PT) by fusing a benzene ring on the β - β' positions of the thiophene unit, thereby forming poly(isothianaphthene) (PITN). The optical absorption spectrum of PITN has an onset at about 1 eV.

The ground state geometry of PITN, which directly influences its electronic properties, has been under investigation for a long time. Although the most stable valence-bond structure of PT is clearly aromatic, that of PITN has been matter of controversy.^[1-10] Recently a joint experimental and theoretical approach^[11, 12] and a vibrational spectroscopic study^[13] (See also Chapter 5) confirmed the conclusions of the earlier works of Kertesz et al.,^[5, 14] showing that the quinoid form of PITN is favoured over its aromatic counterpart. However, the energy difference between the two PITN structures is rather small (about 2.2 kcal/mole), suggesting that both structures may exist, depending, for instance on the synthetic route and the nature of the end groups. The band

gap energy of the quinoid form of the polymer, calculated with the Valence Effective Hamiltonian method, is 1.19 eV,^[11] which is in excellent agreement with the experimental data (onset at 1eV, λ_{max} at about 1.5eV).

The successful idea of Wudl et al.^[1] has led other research groups to work along the same line. PITN has then become the starting compound which is considered for substitution in order to reduce the band gap even further. Nayak et al.^[6] have performed a theoretical study on a derivative of PITN, namely poly(thieno[3,4-*b*]pyrazine) (which hereafter will be referred to as the 4,7-diaza PITN derivative). These authors have calculated, at the Extended Hückel level, that the band gap would be 0.12 eV and 0.7 eV in the aromatic and quinoid forms, respectively. Using the PRDDO method, they found that the quinoid geometric structure is more stable by 4 kcal/mole per repeat unit compared to the aromatic form. For comparison, note that Extended Hückel calculations on aromatic PITN result in energy gap values of 0.68 eV in the *anti* planar conformation and 1.64 eV when the dihedral angle between adjacent ITN units is 150° (non planar *anti* conformation), while the band gap of quinoid PITN is calculated to be 0.80 eV. The PRDDO stabilisation energy between the two PITN isomers is 2.4 kcal/mole per repeat unit in favour of the quinoid structure.^[6]

The 4,7-diaza PITN derivative thus appears to be an attractive candidate as a low band gap compound. Pomerantz et al.^[15] have undertaken the synthesis of the poly(2,3-dihexylthieno[3,4-*b*]pyrazine). Their results indicate that a soluble polymer with a band gap of about 0.95 eV was formed. This band gap value is only slightly lower than that of PITN.

On the basis of these interesting theoretical and experimental results, we have started a joint experimental and theoretical investigation with the group of Prof. Brédas to investigate the geometric and electronic structures of aza and diaza derivatives of PITN. In the first part we report briefly the results and interpretation of quantum-chemical calculations performed by Quattrocchi. The second part describes the attempts to synthesise model compounds of the 4,7-diaza derivatives. For the latter section the help of F. Baldewijns is gratefully acknowledged.

8.2 Nitrogen - containing Poly(isothianaphthene) Derivatives

The structure of aza and diaza derivatives of PITN can be considered as systems in which the phenyl groups fused onto the thiophene units are replaced by six-membered rings containing one or two nitrogen atoms, namely, pyridine, pyridazine, pyrimidine

and pyrazine. The substitution of one or two carbons of the benzene ring with nitrogen atoms is intended to affect the relative stabilities of the aromatic and quinoid forms and possibly further reduce the polymer bandgap. The PITN - derivatives are referred to as 4-aza; 5-aza; 4,6-diaza; 4,5-diaza; 5,6-diaza and 4,7-diaza according to Figure 8.1. Note that there are different ways of fusing the pyridine and pyrazine rings onto the backbone; the 4-aza and 5-aza compounds derive from the fusion of pyridine rings while the fusion of pyridazine rings leads to either the 4,5-diaza or 5,6-diaza systems. To obtain full geometry optimisations the semi empirical Hartree-Fock Austin Model 1 (AM1) technique was used. The polymer band structures are determined by means of the Valence Effective Hamiltonian (VEH) method, which is well known for its accurate determination of the major electronic properties of both conjugated and non conjugated polymers.^[11] For further details concerning the theoretical methodology, the interested reader is referred to the PhD thesis of Quattrocchi.

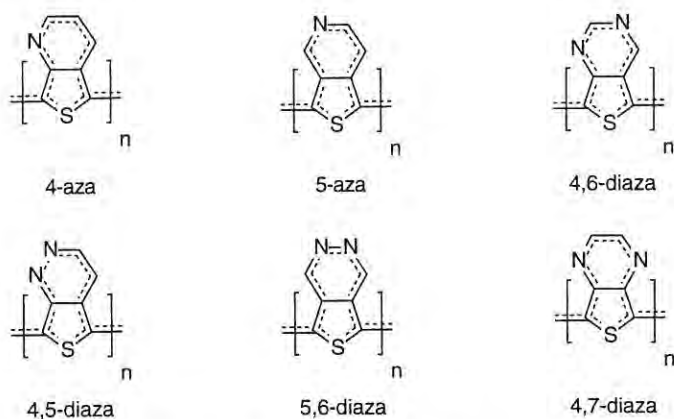


Figure 8.1 The nitrogen derivatives of PITN subjected to a quantum-chemical investigation of the relationship between their aromatic or quinoid structure and corresponding electronic properties.

8.3 Geometric Structure

The AM1-optimized geometries of aromatic and quinoid dimers are in accordance with similar structural features reported in literature.^[6] It is, however, important to point out that adjacent units of the 4-aza, 5-aza, 4,5-diaza and 4,6-diaza derivatives can be linked in three different ways: head-to-head, head-to-tail, and tail-to-tail. (Figure 8.2) In

the case of the 5,6-diaza and 4,7-diaza systems, the monomer unit possesses C_{2v} symmetry and there exists thus only one way to connect the oligomers. However, even if the mode of connection influences the oligomer conformation (planar - non planar), it does not have a significant influence on the bond lengths and bond angles.

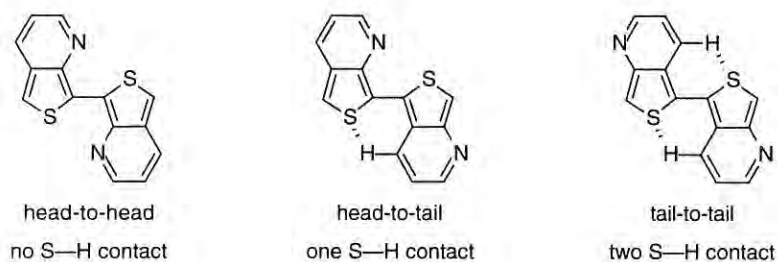


Figure 8.2 Representation of the three modes of connection in the dimers of the 4-aza derivative.

In the aromatic structure, the oligomers can adopt a planar or non planar conformation in order to prevent steric repulsions. The units connected in the tail-to-tail mode (Figure 8.2) show two non bonded contacts between sulphur and hydrogen atoms which induce a dihedral angle of about 15° - 25° between the planes of adjacent units, as in PITN itself.^[11] The optimal distance between the sulphur atom and the hydrogen atom is calculated to be about $2.5\text{\AA}$ and it decreases to $2.35\text{\AA}$ in a hypothetical planar conformer. On the contrary, in the head-to-tail (one S—H contact) and head-to-head (no S—H contact) connections, the chains remain fully planar. The conformation is thus controlled by the number of S—H interactions between the adjacent rings. Nayak et al.^[6] have also found a planar conformation for the aromatic dimer of the 4,7-diaza derivative where no S—H contact is present.

Accordingly, it is clear that all aromatic oligomers of the 5-aza and 5,6-diaza compounds are found to be non planar since two consecutive units of these systems always show two S—H contacts, independently from the mode of connection. However (even though we have to bear in mind that the AM1 method generally tends to underestimate the torsion potential barriers in such systems), the calculated torsion barrier is so small that the monomer units are likely to rotate easily around the interring single bond in the aromatic form. For instance, the energy differences are calculated to be less than 0.4 kcal/mole between the fully-optimised twisted and planar dimers.

In the quinoid structure, all dimers adopt a planar conformation, whatever the connection pattern. This is due to the fact that the inter-ring bond presents a double bond character which thus prevents the monomer units from rotating. Again, these results are in agreement with those of Nayak et al.^[6] for the 4,7-diaza compound. These authors calculate the energy to be the lowest for the planar conformation in the quinoid dimer.

8.4 Energetics Aspects

The relative stabilities of the aromatic and quinoid forms of the aza and diaza polymer derivatives are estimated on the basis of the energy per repeat unit (E_{pru}) for oligomers with increasing chain length. In all cases the $E_{\text{pru}}(\text{N})$ values appear to converge rapidly with the size of the oligomers, as reported in previous work.^[11]

A major aspect of the AM1 results is that the energies of the aromatic and quinoid geometric structures are very close to each other in all derivatives, the differences being smaller than 3 kcal/mole.ru. (Table 8.1) On one hand, the 5-aza and 5,6-diaza systems, which possess two S—H non bonded contacts per two adjacent units (as in PITN), present a quinoid structure slightly more stable than the aromatic counterpart by about 1.9 kcal/mole.ru and 0.6 kcal/mole.ru, respectively. These values can be compared to that obtained for PITN, 2.2kcal/mole.ru. In the 4-aza derivative, the two valence bond forms are found to be isoenergetic: the $E_{\text{pru}}(\text{N})$ values are calculated to be identical for the two structures. (Table 8.1) On the other hand, the aromatic form of the 4,5-diaza; 4,6-diaza; and 4,7-diaza derivatives is favoured over its quinoid counterpart by about 1.2 kcal/mole, 0.9 kcal/mole and 2.9 kcal/mole, respectively.^[16] Note that the situation is much more clear-cut for PT; in that case, the AM1 results indicate that the aromatic form is more stable by about 8.7 kcal/mole.ru with respect to the quinoid structure.^[11]

	N=2	N=3	N=4	N=6	$\Delta E_{\text{pru}}(\text{A-Q})$
4-aza (A)	60.1	59.9	59.8	59.4	0.0
4-aza (Q)	60.3	59.7	59.7	59.4	
5-aza (A)	61.1	61.3	61.2	61.2	1.9
5-aza (Q)	59.0	59.4	59.5	59.3	
4,5-diaza (A)	82.3	82.1	81.9	81.6	-1.2
4,5-diaza (Q)	83.7	83.0	83.1	82.8	
5,6-diaza (A)	84.1	84.9	84.9	85.0	0.6
5,6-diaza (Q)	82.9	84.1	84.3	84.4	
4,6-diaza (A)	71.3	71.2	71.0	70.6	-0.9
4,6-diaza (Q)	72.0	72.0	71.8	71.5	
4,7-diaza (A)	70.5	71.0	70.9	70.9	-2.9
4,7-diaza (Q)	74.1	73.8	73.8	73.8	

Table 8.1 Energy per repeat unit, $E_{\text{pru}}(N)$, for the aza and diaza derivatives of PITN in the aromatic (A) and quinoid (Q) forms. All values are in kcal/mole.repeat unit. The rightmost values correspond to the difference between the aromatic and quinoid E_{pru} values for the hexamers.

From these results it appears that the relative stabilities of the two forms depend not only on the number of nitrogen atoms but also on their positions in the fused rings. The latter point is illustrated by the fact that the 4-aza and 5-aza isomers do not present the same most stable geometric structure. A similar behaviour is found for the 4,5-diaza and 5,6-diaza derivatives.

A likely explanation for the difference between the energetics of the aromatic and quinoid forms for the PITN-derivatives compared to those of the parent polymer arises from the weaker aromaticity of the nitrogen-containing six-membered rings, compared to benzene. Since the benzene ring is more aromatic than the thiophene ring, as a result, the aromaticity of the benzene is dominant in fused systems like PITN. This results in a quinoid structure for PITN. The substitution of carbon atom(s) by nitrogen atom(s)

reduces the aromaticity of the fused rings. Therefore, the quinoid structure is less favoured in the aza-derivatives as compared to PITN.

In order to clarify this point, we first compare the relative stabilities between the two structures of the 5-aza compound and PITN (1.9 *versus* 2.2 kcal/mole.ru, both in favour of the quinoid form). The slight decrease when going from the PITN to the 5-aza derivative arises from the weaker resonance energy (RE) of the pyridine ring relative to benzene. It is then more difficult for the nitrogen-containing ring to impose its aromaticity to the thiophene unit and the energy difference is reduced. A second example further illustrates this phenomenon: in the 5,6-diaza compound, the quinoid form is favoured only by 0.6 kcal/mole.ru over its aromatic counterpart, due to the fact that the RE of the pyridazine ring, which contains two nitrogen atoms, is further reduced compared with that of pyridine and benzene. These aromaticity considerations are supported by the results of Dewar et al., who have calculated the resonance energies of some aromatic compounds with the AM1 method which have been used here. These authors have determined for benzene, pyridine, pyridazine, RE values of 28.3, 25.6 and 22.7 kcal/mole, respectively. This confirms that the stronger the RE, the larger the energy difference between the two forms gets in favour of the quinoid structure for the backbone.

However, the aromaticity of the fused rings is not the only factor which contributes to establishing the most stable ground state geometry for these polymers. On the basis of this parameter the energies of the aromatic and the quinoid structures in the 4-aza and the 4,5-diaza derivatives should be equal to those of their corresponding 5-aza and 5,6-diaza isomers, since they possess the same fused ring. The fact that these polymers indeed have different stabilities indicates that the positions of the nitrogens in the fused rings also influence the relative stabilities of the derivatives.

In fact, another notable feature appearing in the 4-aza and 4,5-diaza derivatives is the presence of non bonded contacts between sulphur atoms and nitrogen atoms located in the 4 positions on adjacent rings. The two heteroatoms are close enough (typically 2.90-2.98 Å in the aromatic forms and 2.85-2.91 Å in the quinoid forms) to interact, which can modify the relative stabilities of the compounds (note that the sum of the sulphur and the nitrogen atoms van der Waals radii is 3.35 Å). Indeed, as mentioned above, the systems possessing nitrogen atoms in positions 4 or 7, i.e., close to the sulphur atoms, present either an aromatic geometric structure (4,5-diaza; 4,6-diaza and 4,7-diaza) or their forms are isoenergetic (4-aza). The influence of such sulphur-nitrogen interactions is significantly supported by the fact that the 4,7-diaza compound which always possesses two S—N non bonded contacts per sulphur atom (Figure 8.3), is found to have the largest energy difference in favour of the aromatic geometric structure.

It thus appears that a large number of S—N contacts leads to a stabilisation of the aromatic geometric structure (or, in other words, a destabilisation of the quinoid form). Along the same line, the 4,5-diaza and 4,6-diaza systems, which both possess two nitrogen atoms per fused ring, including one in the 4 position, show almost the same energy difference between the aromatic and quinoid forms. (Table 8.1) The small stability difference between these two polymers probably arises from the aromaticity difference between pyridazine (the fused ring in 4,5-diaza) and pyrimidine (the fused ring in 4,6-diaza).

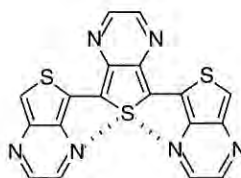


Figure 8.3 Illustration of the two S—N contacts occurring for each monomer unit of the 4,7-diaza compound.

From Table 8.1 we can quantify the effect of S—N interactions, by comparing on one hand, the $E_{\text{TPU}}(\text{N})$ values of the aromatic and quinoid structures in the 4-aza and 5-aza isomers and, on the other hand, those calculated in the 4,5-diaza and 5,6-diaza systems. In both cases, the RE of the fused rings are equal, which allows one to point out the influence of the nitrogen locations. The stabilisation energy of the aromatic form coming from one S—N non bonded contact per monomer unit is estimated to be 1.9 kcal/mole.ru [i.e., 1.9-0.0] and 1.8 kcal/mole.ru [i.e., 1.2-(-0.6)], respectively. The energetic effect induced by S—N interactions appears thus to be on the order of the energy difference between the aromatic and quinoid structures of PITN (2.2 kcal/mole.ru). Therefore, the weaker RE of the nitrogen six-membered rings compared with that of benzene and the fact that S—N interactions tend to stabilise the aromatic form, combine to lead to a transition from a quinoid structure to an aromatic structure for the backbone when going from PITN to aza derivatives which present S—N non bonded contact(s).

Another argument pointing to the destabilisation effect of the S—N interactions on the quinoid form arises from the fact that the relative stabilities of the three differently-connected dimers in the 4-aza, 4,5-diaza and 4,6-diaza systems are reversed when going from one geometric structure to the other: the head-to-head dimers (two S—N contacts), which are the most stable dimers in the aromatic form, become the most unstable in the quinoid structure. On the contrary, the tail-to-tail dimers (no S—N contacts) are the most

stable in the quinoid form and the most unstable in the aromatic structure. The energy differences between the head-to-head and tail-to-tail dimers in both structures are on the order of 3-5 kcal/mole. Furthermore, in the 5-aza derivatives, where there occurs no S—N contact, the three dimers have almost the same energy in the two forms.

The stabilising influence of S—N contacts on the aromatic form is further supported by the evolution of the torsion barrier for rotation around the interring bond. In the 4,7-diaza dimer, the planar conformation (two S—N contacts) is more stable than the 90°-tilted conformation (where S—N interactions are completely absent) by 5.6 kcal/mole. This energy difference decreases to 3.2 kcal/mole between the planar (one S—N contact) and perpendicular 4-aza head-to-tail dimers. Finally, in the 5-aza and 5,6-diaza systems, which do not present S—N interactions in any conformation, the rotation barrier is only 0.9-1.0 kcal/mole, a value identical to that obtained in a PITN dimer (1.0 kcal/mole).

In the light of these results, it is reasonable to consider that the relative stabilities of the two forms in the aza and diaza PITN-derivatives is influenced not only by the aromaticity of the rings fused onto the thiophene unit but also by S—N interactions which stabilise (destabilise) the aromatic (quinoid) geometric structure of the backbone.

It is to be noted that the PRDDO calculations of Nayak et al.^[6] indicate for the 4,7-diaza polymer, a quinoid structure more stable by 4.2 kcal/mole over its aromatic counterpart. More recently, *ab initio* 3-21G calculations of Kertesz et al. have indicated that the quinoid form of the 4,7-diaza derivative is more stable by about 13 kcal/mole relative to the aromatic form. This result is not only in contrast to our results but also to the accepted relative resonance energies of benzene and pyrazine. At present stage, there seems not to be a clear understanding of the origin of these discrepancies.

8.5 Electronic Structure

In Table 8.2, the polymer bandgaps of all aza and diaza PITN-derivatives in both forms are reported. The compounds are connected in a regioregular way (head-to-tail) and adopt a planar conformation. Except for the 5-aza and the 5,6-diaza systems which always present two S—H contacts between adjacent units and hence are expected to be non planar.

The bandgap values are of the same order as those calculated for PITN.^[11] As pointed out when discussing the energetic aspects, the electronic properties do not depend only on the nature of the fused rings but the position of the nitrogen atom(s) is also of prime importance.

In order to illustrate this point, we can compare the bandgap energy of the 4,5-diaza and 5,6-diaza isomers. In the 4,5-diaza polymer, the energy gap is calculated to be as small as 0.27 eV in the aromatic form, which is found to be the most stable; while it is estimated at 1.51 eV in the quinoid structure. In contrast, the polymer bandgap of the 5,6-diaza derivative in the aromatic form is calculated to be 0.84 eV in the planar (180°) conformation and increases to 0.94 eV when a dihedral angle of 165° is considered between the planes of adjacent units. In the most stable quinoid structure, the bandgap value is estimated to be smaller (0.52 eV). Note that the 5,6-diaza polymer is the only derivative which possesses a calculated bandgap smaller in the quinoid form than in the aromatic structure, as in the case of PT. An analysis of the LCAO coefficients shows that the electronic perturbation induced by the fused rings is rather weak, which is consistent with a situation similar to that found in PT.

Derivative	Aromatic (A)	Quinoid (Q)	Most stable form
4-aza	0.60	1.31	isoenergetic
5-aza	0.71-(0.92)	1.31	Q
4,5-diaza	0.27	1.51	A
5,6-diaza	0.84-(0.94)	0.52	Q
4,6-diaza	1.05	1.46	A
4,7-diaza	0.18	1.29	A
PITN	0.21-(0.61)	1.19	Q

Table 8.2 VEH calculated bandgap energy (E_g) for the aza and diaza polymers and PITN in the aromatic (A) and quinoid (Q) forms (head-to-tail connections). All values are in eV. The values given between parentheses for the 5-aza and 5,6-diaza polymers and PITN correspond to a non planar conformation.

Although the two valence bond forms of the 4-aza system are almost isoenergetic, the energy gap values differ significantly: 0.60 eV in the aromatic structure *versus* 1.31 eV in the quinoid form. The experimental absorption spectrum of the 4-aza polymer could thus provide some information on the actual geometric structure of the compound. The 5-aza isomer possesses a calculated band gap of 1.31 eV in its most stable quinoid form, a value slightly larger than that of quinoid PITN (1.19 eV). In the aromatic planar (180°) conformation, the energy gap is calculated to be 0.71 eV and increases to 0.92 eV when adjacent rings are tilted by 159° relative to each other.

Both forms of the 4,6-diaza polymer present calculated energy gap values larger than 1 eV. Thus, at the theoretical level, this system does not appear to possess the most interesting electronic parameters within this series of aza and diaza derivatives.

The compound with the most interesting electronic properties is the 4,7-diaza derivative. The bandgap energy is calculated to be as low as 0.18 eV in the aromatic structure which is favoured by 2.9 kcal/mole over its quinoid counterpart. The calculated gap value of the quinoid polymer is found to be much larger (1.29 eV). Our bandgap results are in agreement with the PRDDO/extended Hückel approach of Nayak et al.^[6] which gives a value of 0.12 eV in the aromatic form and a larger value 0.80 eV in the quinoid structure. However, as noted above, these authors have found an opposite result concerning the relative stabilities of the 4,7-diaza valence-bond structures.

We mentioned before that Pomerantz et al.^[15] have prepared poly(2,3-dihexylthieno[3,4-*c*]pyrazine). The experimental results indicate that the polymer should possess a band gap of 0.86-1.02 eV as a film and 1.14 eV in chloroform solution. Recently Kastner et al.^[17] have confirmed the optical absorption measurements of Pomerantz and co-workers. The absorption spectrum is dominated by the first inter-band transition with an onset at 0.9 eV and a peak at 1.3 eV. These experimental data agree well with the calculated bandgaps for the 4,7-diaza polymers in the quinoid form (0.80 for Nayak et al.^[6] and 1.29 eV in this work). Note that we have calculated that the polymer bandgap for the aromatic 4,7-diaza derivative increases to 0.83 eV when the *anti* conformation of the chain becomes non planar with adjacent rings tilted by 150° with respect to each other. This energy gap value is also very close to the experimental data.

At the present stage it is difficult to make a definitive statement as to the exact form of the backbone structure in the 4,7-diaza polymers reported by Pomerantz et al.^[15] and Kastner et al.^[17] In the latter case, the calculated Raman spectrum for the quinoid structure has been found to be in good agreement with the experimental Raman data. However, the degree of polymerisation or the nature of the endgroups have not been reported. The nature of the end groups most generally corresponds either with an aromatic or a quinoid structure and in the case of almost isoenergetic valence-bond structures they can induce an aromatic or a quinoid backbone.

8.6 Synopsis

Geometry optimisations and electronic-structure calculations have been performed on PITN derivatives where one or two carbon atom(s) in the fused rings are substituted by one or two nitrogen atom(s). At the AM1 level, the conformation of the chains in the

aromatic structure depends on the mode of connection between adjacent rings: on one hand, tail-to-tail units are twisted with respect to one another due to the presence of two S—H interactions between neighbouring rings. On the other hand, in the head-to-head (no S—H contact) and head-to-tail (one S—H contact) configurations, the chains remain fully planar. The quinoid oligomers also adopt a planar conformation.

It appeared that the relative stabilities of the aromatic and quinoid forms of the PITN derivatives are influenced by two factors:

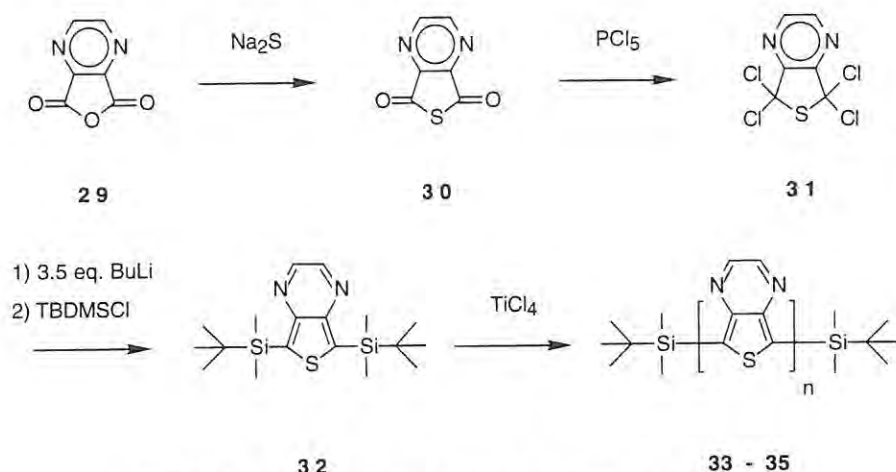
The first factor is the aromaticity of the nitrogen containing rings, which is weaker than that of benzene. It is therefore more difficult for fused rings to preserve their fully π delocalised character and the quinoid structure is less predominant in the N-derivatives compared to PITN.

The second factor is the appearance of non bonded S—N interactions which stabilise (destabilise) the aromatic (quinoid) structure. Hence, the derivatives which possess a nitrogen atom located in the 4 or 7 positions, either present a more stable aromatic structure (4,5-diaza, 4,6-diaza, and 4,7-diaza compounds) or the two forms are isoenergetic (4-aza system). On the contrary, the quinoid structure of 5-aza and 5,6-diaza compound is found to be more stable than its aromatic counterpart, but with a smaller energy difference as compared to PITN.

As the stability aspects, the electronic properties depend not only on the nature of the fused rings but also on the positions of the nitrogens since two isomers such as for instance the 4,5-diaza and 5,6-diaza systems present different calculated bandgaps although they are based on the same fused rings. The 4,5-diaza and 4,7-diaza polymers appear very promising: they present very small calculated energy gap values, 0.27 eV and 0.18 eV, respectively, in their most stable geometric structure.

8.7 Synthesis of 4,7-diaza Model Compounds

These interesting theoretical results encouraged us to attempt the synthesis of 4,7-diaza model compounds. The method of Okuda et al.^[18] appeared to be most appropriate for the synthesis of a series of aromatic disilylated isothianaphthene oligomers. These oligomers allowed us to elucidate more clearly the ground state structure of PITN. Our goal thus was to synthesise an analogous series of aromatic 4,7-diaza oligomers. Analysis of these model compounds should allow us to correlate the results of theoretical calculations with experimentally obtained spectroscopic data.



Scheme 8.1 Synthesis of the silylated 4,7-diaza oligomeric model compounds according to the method of Okuda et al.^[18]

2,3-Pyrazinedicarboxylic anhydride (**29**) was not commercially available and was prepared according to literature^[19-21] by refluxing 2,3-pyrazinedicarboxylic acid in acetic anhydride. When the reaction mixture was allowed to cool down, the 2,3-pyrazinedicarboxylic anhydride (**29**) precipitates as white crystals. Disappearance of the broad OH band at $3200\text{--}3000\text{ cm}^{-1}$ in IR indicated formation of the anhydride. For further purification the obtained crystals were crystallised from acetone or THF, dried on a vacuum pump and as such used in the next reaction. The following step in the oligomer synthesis was the preparation of the thioanhydride derivative (**30**). This was achieved by mixing intimately the purified 2,3-pyrazinedicarboxylic anhydride with $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ crystals. During the process of pulverising first a red solid was formed, which was transformed in a pale yellow liquid after thoroughly mixing. This liquid was diluted by adding water and was finally slowly added to a 5% HCl solution. The addition resulted in the formation of a red precipitate which was filtered and dried in a desiccator above phosphorus pentoxide. Further purification was hindered by low solubility in a whole series of solvents and decomposition upon heating with formation of sulphur and H_2S . Only acetone and acetonitrile appeared to be good solvents. In ethyl acetate and THF a slight amount of precipitate was formed. Data obtained from mass spectroscopy, however, indicated that the thioanhydride derivative (**30**) was formed. ^1H NMR spectroscopy, using d-DMSO, as solvent indicated the presence of a small amount of another product. However since we were not successful in purifying the obtained thioanhydride (**30**), we chose to use the material in the next step without further purification. To obtain the pyrazine derivative of 1,1,3,3-tetrachlorothiophthalan (**31**),

the thioanhydride was heated at 160°C in presence of PCl_5 . After addition and evaporation of a small amount of toluene, a black residue was obtained. This residue could be dissolved in chloroform. However, neutralisation of remaining PCl_5 and POCl_3 by washing with a 1M NaHCO_3 solution resulted in a colloidal mixture which was very difficult to handle. Extensive use of solvents and filtering procedures yielded finally a dark-coloured liquid which was dried over magnesium sulphate. However, analysis of the composition of this mixture by TLC in different solvent systems revealed the presence of a large amount of products almost inseparable by column chromatographic techniques.

From the difficulties experienced it was clear that the same chemistry as used by Okuda et al.^[18] for the classical ITN unit cannot be applied to the pyrazine derivative in a straightforward manner. Therefore this route was abandoned and the synthetic effort was focused on the synthesis of nitrogen derivatives of 1,3-dithienyl isothianaphthene, a more simple model compound which nevertheless is able to provide sufficient spectroscopic information on the involved isothianaphthene unit.

8.8 Conclusions

From theoretical calculations it appeared that the replacement of carbon atoms in the ITN ring system by nitrogen atoms influences the relative stabilities of the aromatic and quinoid forms on two levels. First of all, due to the weaker aromaticity of the nitrogen containing ring, it is more difficult to preserve their fully π delocalised character and the quinoid structure is less predominant in the N-derivatives compared to PITN. A second factor appeared to be the presence of non bonded S—N interactions which stabilise (destabilise) the aromatic (quinoid) structure. From analysis of the calculated electronic properties it appeared that there is a dependence not only on the nature of the fused rings but also on the positions of the nitrogens. Finally, the 4,5-diaza and 4,7-diaza polymers appear very promising: they present very small calculated energy gap values, 0.27 eV and 0.18 eV, respectively, in their most stable geometric structure.

An attempt was made to synthesise a series of aromatic 4,7-diaza oligomers based on the method of Okuda et al.^[18] However, it appeared that the chemistry used by Okuda et al. is not suitable to be used with pyrazine derivatives. Therefore, the synthetic effort was focused on the synthesis of the nitrogen derivatives of 1,3-dithienyl isothianaphthene, a more simple model compound.

8.9 References

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What of the hunting, hunter bold?
 Brother, the watch was long and cold.
What of the quarry ye went to kill?
 Brother, he crops in the jungle still.
Where is the power that made your pride?
 Brother, it ebbs from my flank an side.
Where is the haste that ye hurry by?
 Brother, I go to my lair to die.
 (R.Kipling, The jungle books)

Synthesis of 1,3-Dithienylisothianaphthene Derivatives

9.1 Introduction

Conducting polymers have been the subject of intensive research for some time. The best known conducting polymers are poly(aniline), poly(paraphenylenevinylene), poly(pyrrole) and poly(thiophene) (PT). In the case of these polymers techniques have been developed to obtain good processability. Poly(isothianaphthene) (PITN) is another conducting polymer with most intriguing properties such as a low band gap of 1 eV and the ability to become transparent upon doping. However PITN has not yet found wide application in the development of electronic devices due to the lack of a simple polymerisation route, leading to a processable material. The main problem should be attributed to the difficult accessibility of monomeric isothianaphthene compounds. Extensive work on isothianaphthene compounds has been accomplished by Cava et al.^[1-3] From their work it appears that isothianaphthene monomers are relatively unstable and their synthesis is laborious. Although progress has been made on the development of a straightforward polymerisation route to PITN,^[4] it seems interesting to develop on the other hand synthetic procedures which lead to different types of monomeric isothianaphthene derivatives. These compounds should combine the interesting electronic properties of isothianaphthene with the possibility of enhancing stability and processability of the resulting polymer. The combination of the ITN unit with other aromatic heterocycles is an approach which is able to meet the requirements of enhanced

stability and processability. Indeed, the control of the chemistry of for example PP and PT has made an important step forward during the last decade.^[5-13] The most promising results in this field were obtained by McCullough et al.,^[12, 13] which were able to synthesise soluble alkyl substituted and highly regioregular PT. Therefore, it is worthwhile to develop a new class of materials in which the already-demonstrated properties of PT are combined with the promising electronic properties of PITN. This class of polymers would consist of a well-defined combination of thiophene and isothianaphthene units. Moreover, since perfectly regioregular polymers^[12, 13] show superior electronic properties and while tailoring the bandgap is predicted to be easier in regular copolymers,^[14-16] it is preferable to produce regular copolymers rather than random copolymers. In the case where the regularity of the copolymer is a direct result of the molecular structure of the monomer, we prefer to classify these materials as *formal* copolymers of isothianaphthene and another aromatic heterocycle. The most obvious example of a *formal* copolymer is a polymer in which the monomeric compound combines ITN unit as well as thiophene units. In order to avoid random copolymerisation this monomeric compound should be totally symmetric. One interesting compound is 1,3-dithienylisothianaphthene (DTI (**4**)) in which two thiophene rings are combined with one isothianaphthene ring. (Figure 9.1)

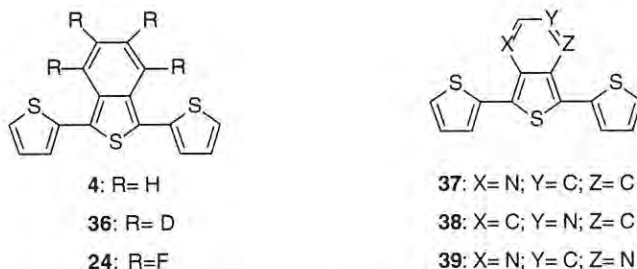


Figure 9.1 1,3-Dithienylisothianaphthene derivatives as monomeric units for the synthesis of formal copolymers.

The presence of thiophene rings on both sides of the ITN unit will favour the aromatic over the quinoid ground state geometry. As far as the bandgap is concerned, a value in between those of PT and aromatic PITN is thus to be expected.^[14, 16, 17] Moreover, the thiophene ring systems allows one to obtain easily processable polymers through, for instance, use of thiophenes with additional side chains. Certainly in the case of PT the incorporation of side chains is a technique which is now common use in

improving solubility and therefore processability properties. Furthermore, DTI (**4**) can be used in the development of oligomers with tailored electronic properties. Recently^[18-21] it was shown that one does not always need polymers to obtain electronic materials with outstanding properties. Even oligomeric compounds can meet the criteria for materials used in the preparation of advanced electronic devices. In the case of organic semiconducting materials based on oligomers the solid state properties are directly connected with these of the individual molecules and their spatial order. Recently it appeared to be possible to obtain devices with anisotropic properties^[19, 21] through control of the mesoscopic order of oligomers. The control of mesoscopic order is to a considerable extent influenced by the nature of substituents and end groups, a feature which can in its turn be controlled by a well-chosen synthetic route. Oligomeric compounds not only allow the obtaining of materials with high purity but also allow easy control of the electronic properties. Moreover the structure of these compounds can readily be determined by a whole series of spectroscopic methods, facilitating thereby the unravelling of the correlation between the structure and the resulting electronic properties. Finally, oligomers present an additional advantage of allowing calculations^[22] to be performed at a highly sophisticated level.

The most straightforward way to synthesise isothianaphthene derivatives is through ring closure of *ortho* diketones by means of P_4S_{10} ^[23] or Lawesson's reagent.^[24, 25] From literature^[24, 26] the preparation of these *ortho* diketones appeared to be the major bottleneck to elaborate an efficient isothianaphthene synthesis. Although the use of Diels-Alder type reactions^[23, 27-33] has been proposed, the use of this type of reaction for synthesis of a wide series of *ortho* diketone derivatives is rather limited. Since it is known that the Friedel Craft type reaction with phthaloyl dichloride (**40**)^[26, 34-36] on thiophene results in the formation of 3,3-dithienyl-3*H*-isobenzofuran-1-one (**44**), the use of Grignard-type reactions to make diketones is the only alternative.

In a Grignard reaction with 2-thienylmagnesiumbromide as the Grignard reagent one can use different substrates. In literature the use of phthaloyl dichloride (**40**)^[26, 37-41] phthalic anhydride (**13**)^[42-48] and thiophthalic anhydride (**14**)^[24, 49, 50] has been reported in the synthesis of *ortho* diketones. However, the results of different authors appeared not to be entirely consistent with one another. Due to the inconsistency in literature data, we decided to revise the synthesis of *ortho* diketones in order to develop a convenient route to *ortho* diketones. Therefore we tested the results of Grignard reactions on the above series of substrates as well as on two new but no less interesting substrates, 1,2-(*S*-phenyl)-benzenedithioate (**41**) and 1,2-(*S*-(2-pyridinyl))-benzenedithioate (**42**). (Figure 9.2) The latter compounds have a thioester functional group, which is reported to yield selectively ketones^[51-57] from Grignard reactions.

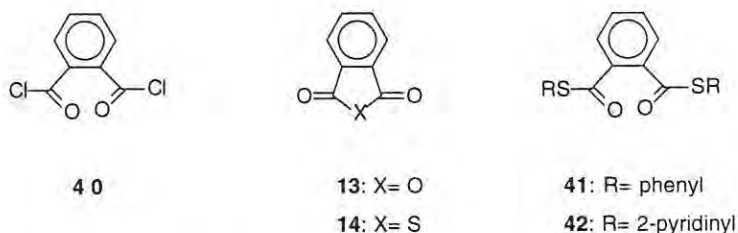


Figure 9.2 Substrates to be used in the development of a suitable Grignard synthesis of *ortho* diketones.

Once an appropriate route to *ortho* diketones and thus DTI (**4**) had been developed, we investigated the application of this route in the synthesis of DTI derivatives. (Figure 9.1) Besides the synthesis of 1,3-dithienyl-4,5,6,7-tetradeuteroisothianaphthene (**36**) for vibrational spectroscopic purposes and 1,3-dithienyl-4,5,6,7-tetrafluoroisothianaphthene (TFDTI) (**24**), the synthesis of different nitrogen substituted derivatives was attempted.

9.2 Synthesis of *ortho* diketones

As mentioned before, the bottleneck in the synthesis of DTI (**4**) was the preparation of the *ortho* diketone (1,2-thienoyl benzene, (**43**)). We therefore first focussed on the synthesis of this compound, as the synthesis of DTI (**4**) by ring closure with P_4S_{10} ^[23] or Lawesson^[24, 25] is rather straightforward. For the synthesis of the 1,2-dithienoyl benzene (**43**) we investigated successively the Grignard reaction of 2-thienylmagnesiumbromide on phthaloyl dichloride (**40**), phthalic anhydride (**13**), thiophthalic anhydride (**14**) and the two thioester compounds (**41**) and (**42**).

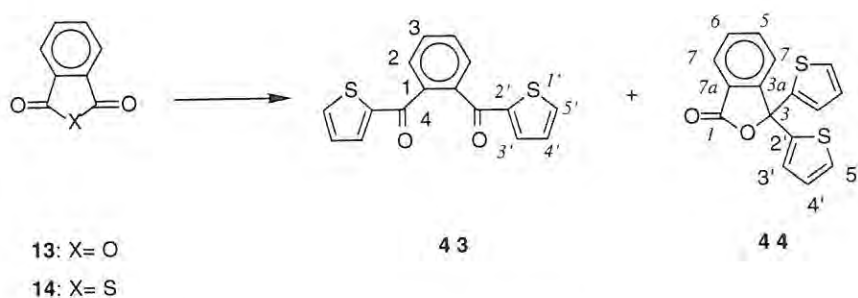
9.2.1 Phthaloyl dichloride

The investigation of the Grignard reaction on phthaloyl dichloride (**40**) was based on the method of Jensen.^[38] The reaction was performed by adding the thienylmagnesiumbromide to a solution of phthaloyl dichloride (**40**) in ether at a temperature of -78°C . However, only a yield of about 10% was obtained and the material contained a small amount of coloured matter which was very difficult to remove. Even

the slow addition of the Grignard reagent to a solution of phthaloyl dichloride (**40**) in THF at -78°C or the use of a 1:2 toluene mixture^[46] resulted in a very poor yield of the *ortho* diketone (**43**) besides the formation of alcohols and many other side products. These results were later confirmed by Bäuerle et al.^[26], who did not succeed at all in obtaining the 1,2-dithienoylbenzene. Apparently, two acid chlorides in the *ortho* position are too reactive towards this kind of nucleophilic substitution even at lower temperatures.

9.2.2 Phthalic Anhydride and Thiophthalic Anhydride

Another possible starting product in this reaction is phthalic anhydride (**13**). (Scheme 9.1) Since the reactivity towards a second nucleophilic substitution is seriously reduced after the opening of the anhydride ring system we performed the Grignard reaction at somewhat higher temperatures than usual. Therefore, we used refluxing solvent mixtures of toluene/ether in a ratio of 1:2, 1:3 and 4:1.^[46] According to qualitative TLC analysis of the reaction mixtures the best results were obtained in the solvent mixture with a ratio of 1:2 (boiling temperature of 58°C). After purification by means of column chromatography a yield of 15% of the *ortho* diketone (**43**) was obtained. However, a significant amount of 3,3-dithienyl-3*H*-isobenzofuran-1-one (**44**) (29%) was also obtained. Performing the reaction at lower temperatures did not improve the yield of the *ortho* diketone (**43**).



Scheme 9.1 Formation of two isomeric compounds, 1,2-thienoyl benzene (**43**) and 3,3-dithienyl-3*H*-isobenzofuran-1-one (**44**) upon addition of 2-thienylmagnesiumbromide to (thio)phthalic anhydride.

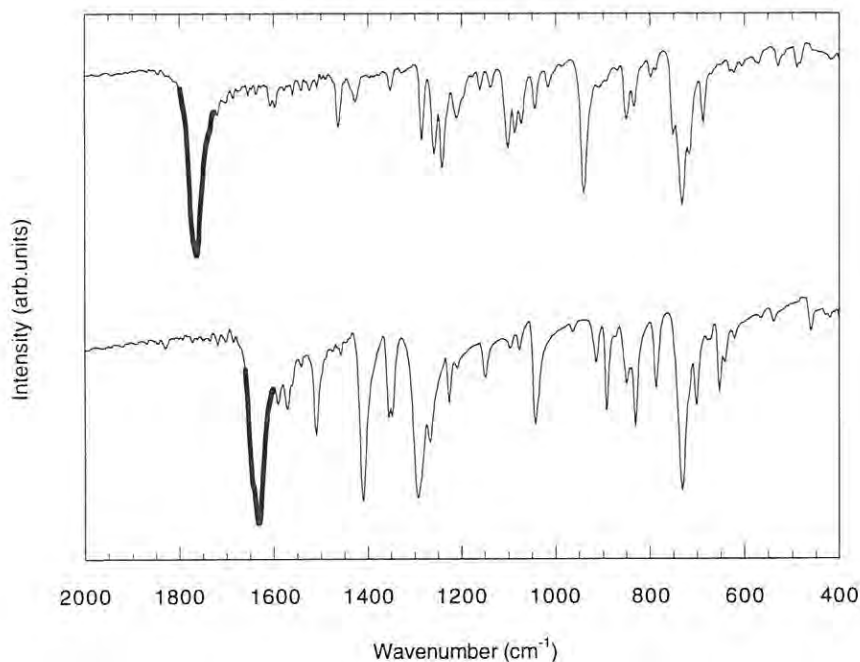


Figure 9.3 Comparison of the IR spectra of the 3,3-dithienyl-3H-isobenzofuran-1-one (**44**) and 1,2-dithienyl benzene, respectively. The IR spectrum of 3,3-dithienyl-3H-isobenzofuran-1-one (**44**) is characterised by a carbonyl group absorbing at about $\nu=1750\text{ cm}^{-1}$ whereas the carbonyl group of the diketone (**43**) absorbs at $\nu=1630\text{ cm}^{-1}$.

As sulphur has better leaving group characteristics, we performed analogous reactions on the thiophthalic anhydride (**14**). (Scheme 9.1) The synthesis of thiophthalic anhydride (**14**) was carried out following the method of Reissert et al.^[58] In analogy to the previous Grignard reaction on phthalic anhydride (**13**), the Grignard reaction was carried out in a refluxing 1:2 toluene/ether mixture. The work-up of the final reaction mixture was accompanied by considerable evolution of H_2S . However, the main reaction product appeared to be the 3,3-dithienyl-3H-isobenzofuran-1-one (**44**) compound. From a DIP-MS analysis of the reaction products, obtained from a reaction carried out in pure THF solution, it appeared that monosubstituted thiocarboxylate is formed as an important intermediate. When diethyl ether at 0°C is used as solvent a precipitate is formed during addition of the Grignard reagent. The yield of *ortho* diketone (**43**) is higher than in the other cases (40%). When the reaction is carried out in diethyl ether at room temperature, one obtains a yield of about 60%. Apparently, lower temperatures favour the formation

of monosubstituted intermediates. This indicates that the thiocarboxylate formed after the first attack by the Grignard reagent does not contain a suitable leaving group. A second inconvenience is the formation of a huge amount of H_2S during acid work-up and the formation of a precipitate during the addition.

The specific structure of the isomeric 3,3-dithienyl-3*H*-isobenzofuran-1-one (**44**) was proved by means of IR-spectroscopy, (Figure 9.3) the carbonyl group of γ -lactones absorbing at higher energy ($\nu=1750\text{ cm}^{-1}$) than the one of the diketone (**43**) ($\nu=1630\text{ cm}^{-1}$). Moreover, ^1H -NMR spectroscopy shows a coupling pattern of an asymmetric *ortho* substituted benzene ring (Figure 9.4) and the ^{13}C NMR spectra shows the chemical shift of an aliphatic quaternary carbon nucleus at 99.1 ppm. In addition the structure of the 3,3-dithienyl-3*H*-isobenzofuran-1-one (**44**) was confirmed by the characteristic loss of CO_2 in mass spectroscopic studies.

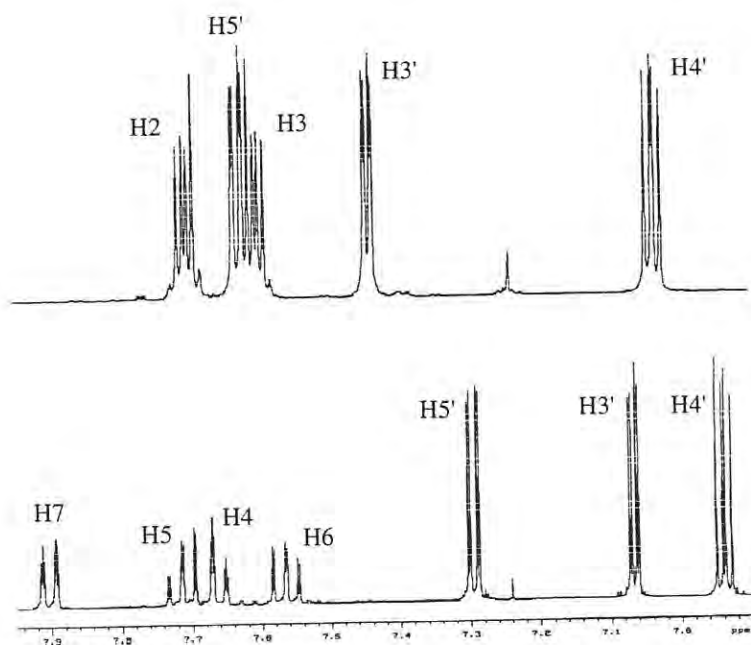


Figure 9.4 The ^1H NMR spectrum of the symmetric and the asymmetric *ortho* substituted benzene ring system of the diketone (**43**) and the 3,3-dithienyl-3*H*-isobenzofuran-1-one (**44**), respectively.

We also carefully analysed the structure of 1,2-dithienoyl benzene and 3,3-dithienyl-3*H*-isobenzofuran-1-one (**44**) by means of 2D NMR techniques. Since these isomeric compounds present quite different NMR characteristics it is worthwhile to describe their full chemical shift assignment because this will help to unravel the structure of analogous nitrogen-substituted derivatives.

1,2-dithienoyl benzene (43) In this compound for reasons of symmetry the nuclei in the benzene ring are numbered for NMR purposes as indicated in scheme 9.1. First of all we can differentiate between the proton shifts of the thiophene and benzene ring systems based on the coupling constants and their ^1H - ^1H COSY coupling pattern. Therefore we can associate the proton signals at 7.03, 7.44 and 7.63 ppm with the three thiophene protons. On the other hand the shifts at 7.60 and 7.70 can be associated with the two benzene protons.

The most interesting starting point for construction of the chemical shift assignment pathway is the carbonyl carbon nucleus C4 at 188.2 ppm. Since C4 cannot show a long range coupling with H4' and H5' of the thiophene, the correlation signal in the long range ^1H - ^{13}C HETCOR optimised for $J = 8\text{ Hz}$ with the thiophene ^1H -signal at 7.44 ppm should therefore be assigned to H3'. Based on the direct ^1H - ^{13}C HETCOR optimised for $J = 140\text{ Hz}$, C3' should resonate at 135.1 ppm. Due to the presence of a long range coupling between C3' and H5', H5' can be assigned to the chemical shift at 7.63 ppm. The remaining thiophene proton resonance at 7.03 ppm can as a consequence be assigned to H4'. This assignment is confirmed by the presence of two geminal proton couplings of 3.8 Hz and 5.0 Hz, a feature which appears also from the ^1H COSY spectrum. Indeed, H4' is the only hydrogen nucleus which can show a homonuclear correlation signal with H3' and H5'. The direct ^1H - ^{13}C HETCOR optimised for $J = 140\text{ Hz}$ allows us subsequently to assign C4' and C5' to 128.0 and 134.9 ppm respectively. Since C4 has already been assigned the only quaternary carbon nucleus that is able to show a long range coupling with H3' and H4' is C2' and can as a consequence be assigned to the signal at 144.0 ppm. The remaining quaternary carbon nucleus resonating at 139.4 ppm can therefore be assigned to C1.

The remaining protons to be assigned belong to the central benzene ring. As C4 can only show a long range coupling with H2, the signal at 7.70 ppm should be associated with this hydrogen nucleus. This implies that the remaining signal resonating at 7.60 ppm belongs to H3. Both the multiplets of H2 and H3 are characterised by the same values for the coupling constants. This coupling pattern is specific for a symmetric *ortho* substituted

benzene ring system. The assignment of the corresponding carbon signals of C2 and C3 is obtained based on the direct ^1H - ^{13}C HETCOR optimised for $J = 140\text{ Hz}$. Therefore C2 and C3 are assigned to 129.2 ppm and 130.6 ppm.

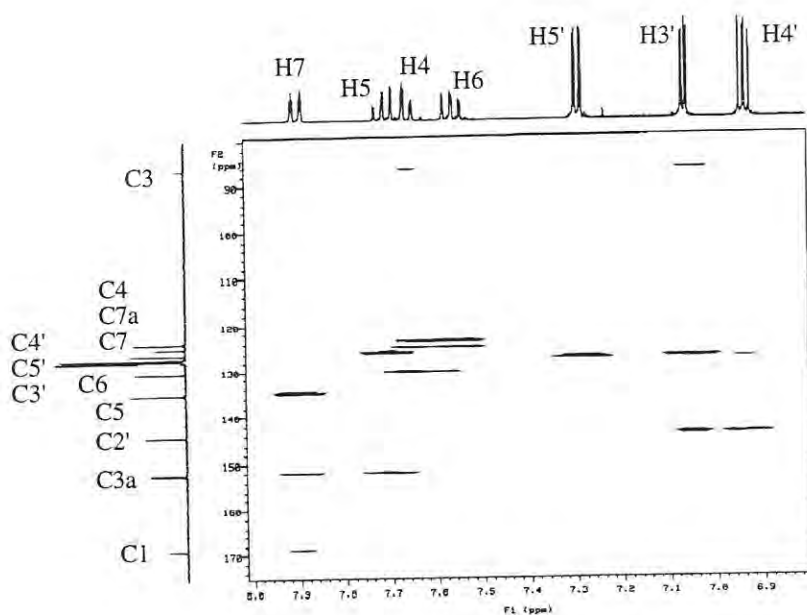


Figure 9.5 2D heteronuclear ^1H - ^{13}C correlation spectrum of 3,3-dithienyl-3H-isobenzofuran-1-one (**44**) optimised for $J_{\text{CH}} = 8\text{ Hz}$ (CDCl_3 , $30\text{ }^\circ\text{C}$).

3,3-dithienyl-3H-isobenzofuran-1-one (44) Since C1 is the only carbonyl carbon nucleus it can unambiguously be assigned to the signal at 168.74 ppm. C1 can only show a long range coupling with H7. (Figure 9.5) Thus the chemical shift at 7.90 ppm can be associated with H7. Since the *ortho* substituted benzene ring lost its symmetry due to the 3,3-dithienyl-3H-isobenzofuran-1-one (**44**) structure, four different proton chemical shifts will be present. Since H7 has been assigned, the other benzene protons can easily be assigned using the ^1H - ^1H COSY spectrum. (Figure 9.6) Therefore H4, H5 and H6 resonate at 7.66, 7.71 and 7.56 ppm respectively.

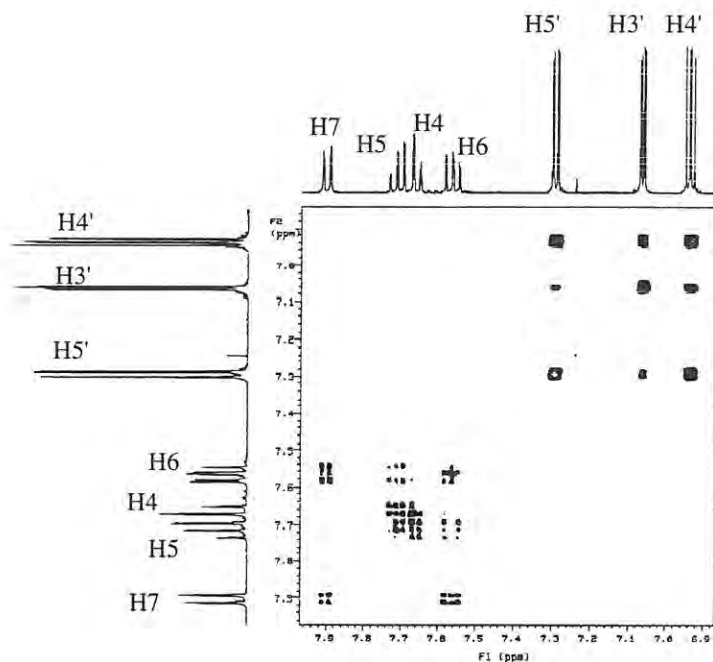


Figure 9.6 2D heteronuclear ^1H - ^1H correlation spectrum (COSY) of 3,3-dithienyl-3H-isobenzofuran-1-one (**44**) (CDCl_3 , 30 $^\circ\text{C}$).

The assignment of the corresponding carbon nuclei follows from the direct ^1H - ^{13}C HETCOR optimised for $J = 140\text{ Hz}$. (Figure 9.7) Thus C4, C5 and C6 are assigned to the signals at 123.48, 134.57 and 130.05 ppm respectively. Furthermore, on the one hand C3a shows a long range coupling with H7 and H5 and on the other hand C7a shows a long range coupling with H6 and H4. Based on this very specific combination of correlation signals C3a and C7a appear to resonate at 151.89 and 124.80 ppm respectively. As C3 is the only aliphatic quaternary carbon nucleus it can be assigned to the signal at 86.26 ppm. Moreover this assignment is confirmed by the fact that C3 is the only carbon nucleus to show a long range coupling with one of the benzene protons and one of the thiophene protons. The full chemical shift assignment of the thiophene ring system can now be made unambiguously. Indeed, C2' is the only remaining quaternary carbon atom and can therefore be associated with the signal at 143.87 ppm. The long range correlation signal of C3 with the thiophene chemical shift at 7.06 ppm can only

originate from a long range coupling with H3'. H4' is characterised by the presence of two correlation signals in the ^1H - ^1H COSY spectrum and can therefore be assigned to the signal at 6.94 ppm. The remaining proton chemical shift at 7.29 ppm should as a consequence belong to H5'. The direct ^1H - ^{13}C HETCOR optimised for $J = 140\text{ Hz}$ allows finally the assignment of the remaining protonated carbon signals at 127.30, 126.81 and 127.10 ppm to C3', C4' and C5'.

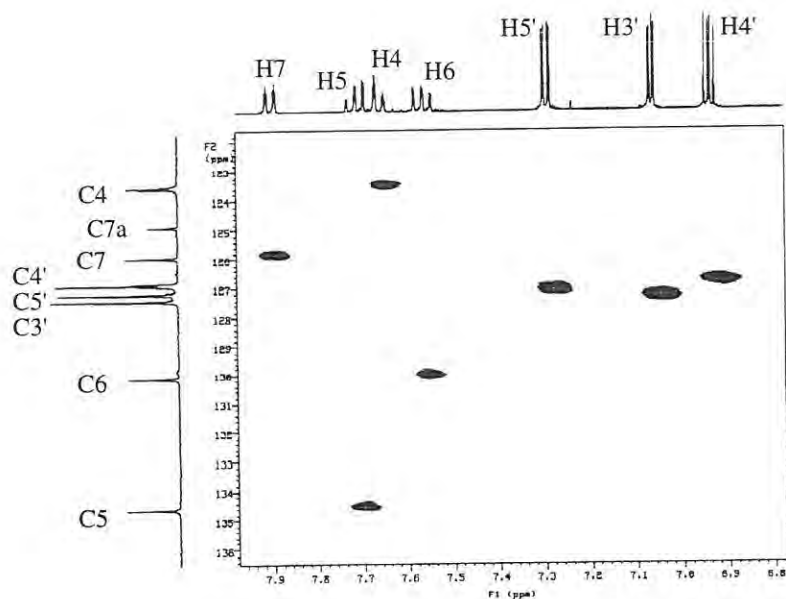


Figure 9.7 2D heteronuclear ^1H - ^{13}C correlation spectrum of 3,3-dithienyl-3H-isobenzofuran-1-one (**44**) optimised for $J_{\text{CH}} = 140\text{ Hz}$ (CDCl_3 , $30\text{ }^\circ\text{C}$).

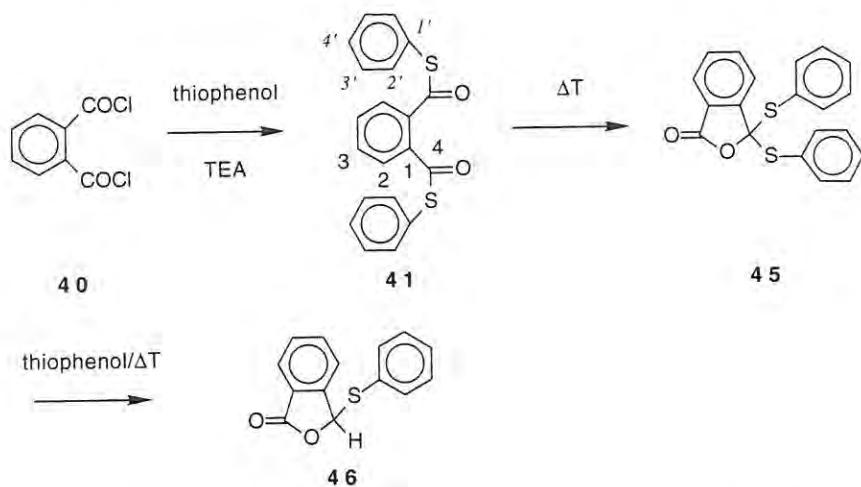
9.2.3 1,2-(*S*-phenyl)-benzenedithioate and 1,2-(*S*-(2-pyridinyl))-benzenedithioate

Since phthaloyl dichloride (**40**) is too reactive towards Grignard reactions and since phthalic anhydride (**13**) and thiophthalic anhydride (**14**) do not possess a very good leaving group, we investigated the use of a more convenient functional group, i.e. a thioester. A dithioester compound has two functional groups with a lower reactivity as

compared to phthaloyl dichloride (**40**). Cardellicchio et al.^[53] describe a highly efficient route to ketones through reaction of Grignard reagents with S-phenyl thioesters in the presence of iron catalysts. Another method for efficient synthesis of ketones is reported by Araki et al.^[56] and is based on the use of S-(2-pyridinyl) thioesters. Therefore we have to synthesise the corresponding S-phenyl dithioester (**41**) and S-(2-pyridinyl) dithioester (**42**).

Thus in a first approach for the synthesis of the S-phenyl dithioester (**41**), phthaloyl dichloride (**40**) was added slowly to a solution of thiophenol and triethylamine (TEA) in tetrahydrofuran (THF) according to the method of Araki et al.^[56] (Scheme 9.2). This resulted however in the formation of two reaction products. Since both products possess the same molecular mass, we were dealing with two isomeric compounds. The first product is characterised by an IR-absorption at 1670 cm^{-1} and the ^1H NMR spectrum shows a typical symmetric substitution of the benzene ring. The other product possesses an IR-absorption at 1770 cm^{-1} , a ^1H NMR spectrum showing a typical asymmetric substitution of the benzene ring, the presence of an aliphatic quaternary carbon nucleus at 99.1 ppm and the loss of CO_2 in DIP-MS. From this spectroscopic data we can conclude that the first product should be the desired dithioester (**41**). The second product, however, should possess a 3,3-di(S-phenyl)-3*H*-isobenzofuran-1-one structure (**45**). Carefully monitoring the reaction as a function of time revealed that there occurs a conversion from the thioester to 3,3-di(S-phenyl)-3*H*-isobenzofuran-1-one (**45**). At room temperature this process takes a few days but at elevated temperatures the conversion is completed within an hour. Moreover when the reaction is carried out in presence of an excess of thiophenol, the 3,3-di(S-phenyl)-3*H*-isobenzofuran-1-one (**45**) appeared to transform into two other products. The first one could be identified as being the phenyl disulphide based on mass spectroscopy and melting point (61°C). The second product possesses an IR-absorption at 1770 cm^{-1} , the ^{13}C NMR spectrum indicates the presence of an aliphatic quaternary carbon nucleus at 86.4 ppm, and the ^1H NMR spectrum still showed the asymmetric substitution on the benzene ring. But at 6 ppm a new signal appeared with an integration corresponding with one hydrogen nucleus. All this spectroscopic data indicates the formation of 3-(S-phenyl)-3*H*-isobenzofuran-1-one (**46**) in which one of the thiophenol groups is replaced by a hydrogen nucleus. The formation of disulphide in the presence of an excess of the corresponding thiol indicates that radical scavenging has taken place. Indeed it is known that thiols act as radical scavengers^[59] with formation of the corresponding disulphide. Since the radical scavenging is accompanied with a proton transfer, a stable radical is formed at the 3-position of the 3,3-di(S-phenyl)-3*H*-isobenzofuran-1-one (**45**) structure. This could

explain the replacement of the thiophenol group by a proton in presence of an excess of thiophenol. Starting from a solution of 3,3-di(S-phenyl)-3H-isobenzofuran-1-one (**45**) in THF and heating it up in the presence of a large excess of thiophenol yielded an almost quantitative conversion into 3-(S-phenyl)-3H-isobenzofuran-1-one (**46**) and the formation of an equimolar amount of disulphide.



Scheme 9.2 Synthesis of 1,2-(S-phenyl)-benzenedithioate and isomerisation into 3,3-di(S-phenyl)-3H-isobenzofuran-1-one (**45**). 3-(S-phenyl)-3H-isobenzofuran-1-one (**46**) is formed due to scavenge of a stabilised radical on 3,3-di(S-phenyl)-3H-isobenzofuran-1-one (**45**) in presence of a large excess of thiophenol.

In order to obtain mainly the dithioester (**41**) we need therefore to work at lower temperatures with a slight deficiency of thiophenol. Moreover, since the reaction proceeds quite quickly one needs to stop this reaction at an early stage. Therefore, phthaloyl dichloride (**40**) was added rapidly to a vigorously stirred solution of thiophenol and TEA in THF at 0°C. When addition was completed, the reaction was immediately quenched by addition of an HCl-solution (1%). Since the lactone (**45**) is soluble in diethyl ether but not the thioester (**41**), purification can be done by simple crystallisation from dichloromethane/diethyl ether giving a yield of 77%. An alternative for this route is the method of Sheenan et al.^[60] This method consists in adding phthaloyl dichloride (**40**) dropwise at a temperature of 0°C to thiophenol in a methanolate solution. The thioester (**41**) precipitates from solution therefore preventing any isomerisation to the lactone structure resulting in a yield of about 94%.

Since it appears that the process of lactone formation is thermodynamically favoured, one may also expect this kind of intramolecular cyclisation reaction to occur during Grignard reactions on compounds containing *ortho* carbonyl oxygen nuclei. Indeed, in the Grignard reaction on phthalic anhydride (**13**) and thiophthalic anhydride (**14**) important amounts of the corresponding lactone could be isolated.

Since we had control of the thioester synthesis, the next step consisted in performing the Grignard reaction in presence of iron catalysts. Therefore the Grignard reagent was slowly added at 0°C to the thioester (**41**) in a solution of THF in the presence of a catalytic amount of tris(acetylacetonate) iron (III). However this reaction did not result in the formation of the 1,2-dithienoyl benzene and a significant amount of 3,3-di(S-phenyl)-3*H*-isobenzofuran-1-one (**45**) was isolated.

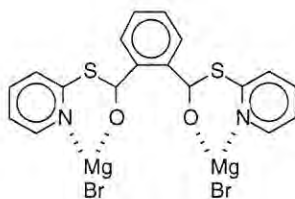
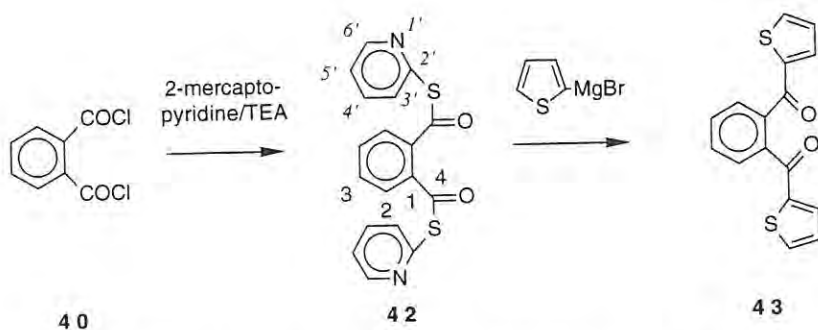


Figure 9.8 The formation of two six-membered complexes during the Grignard reaction on 1,2-(S-(2-pyridinyl))-benzenedithioate.

Since the use of the S-phenyl dithioester (**41**) did not yield the 1,2-dithienoyl benzene (**43**), we used instead of the S-phenyl dithioester (**41**) the S-(2-pyridinyl) dithioester (**42**).^[54] This thioester was prepared according to the adapted method of Araki et al.^[56] We did not succeed in preparing the S-(2-pyridinyl) dithioester (**42**) according to the method described by Sheehan et al.^[60]

The high reactivity of S-(2-pyridinyl) thioesters toward Grignard reagents with selective formation of ketones was attributed to the formation of a stable six-membered intermediate which would further react during the addition reaction. The stable complex should in our case also prevent any intramolecular isomerisation by 'freezing' the intermediate in an organometallic complex. (Figure 9.8) The final elimination occurs during acid work-up causing the organometallic complex to break up. Thus the Grignard reagent was added slowly to the S-(2-pyridinyl) dithioester (**42**) in a solution of THF at 0°C. (Scheme 9.3) No precipitate was formed during reaction, allowing homogeneous

mixing of the reaction products throughout the addition process. The reaction was finally quenched by addition of HCl (10%). After a classical work-up a yield of 95% of the *ortho* diketone (**43**) was obtained. Eventually the product can be used in the next reaction without further purification.



*Scheme 9.3 Synthesis of 1,2-(S-(2-pyridinyl))-benzenedithioate (**42**) and 1,2-thienoyl benzene (**43**).*

From these results it is clear that the use of thioesters in the synthesis of *ortho* diketones presents several important advantages. This S-(2-pyridinyl) dithioester method is the first reported highly efficient and selective synthesis of *ortho* diketones. Moreover the synthesis of the thioester is straightforward and does not require laborious and time-consuming purifications.

9.2.4 Synthesis of Deuterated and Fluorinated *ortho* Diketones.

As stated above, DTI (**4**) and its derivatives are of interest in theoretical calculations and spectroscopic analysis of the isothianaphthene ring system. Based on these spectroscopic and theoretical analyses a detailed set of information can be build up, characterising isothianaphthene ring systems in an extended π -system. To posses such a spectroscopic data base is of utmost importance for the structural analysis of isothianaphthene-containing polymers. In this context the usefulness of DTI (**4**) as a model compound for an NMR based structural analysis of PITN has already been demonstrated.^[61] To allow a more detailed analysis of IR and FT-Raman spectra of isothianaphthene polymers one needs to analyse the vibrational spectra of the

isothianaphthene core. For identification and calculation of isothianaphthene vibrations, relatively simple model compounds are again of great importance in acquiring reliable information on the vibrational characteristics of the isothianaphthene ring system. For the analysis of vibrational spectra of the isothianaphthene ring system, the replacement of hydrogen nuclei by other nuclei induce bands to shift due to a difference in mass. The synthesis of the deuterated (**36**) and fluorinated (**24**) DTI should be viewed in this context. The substitution of the hydrogen nuclei on the isothianaphthene ring by deuterium and fluorine will only affect vibrations originating from the isothianaphthene ring. The fluorinated DTI (**24**) can also be used for comparison with the corresponding fluorinated isothianaphthene polymer.^[62]

Since the deuterated and fluorinated phthaloyl dichloride derivatives are not commercially available, we have to start with the synthesis of the corresponding phthaloyl dichloride from the corresponding *ortho* dicarboxylic acid. Two methods were tested. The method using PCl₅ appeared to give better results as compared to the SOCl₂ method. The basic principle of the PCl₅ method is to heat a mixture of the phthalic acid with PCl₅ slowly to 180°C. At about 60°C a large amount of HCl gas is formed and should be neutralised by passing the gas through a concentrated KOH solution. This method gives a yield of around 90% for most of the *ortho* dicarboxylic compounds.

Next, the method as described in Scheme 9.3 was followed for the synthesis of the deuterated and fluorinated 1,2-dithienyl benzene. The deuterated compound does not show an important difference as far as the chemical reactivity is concerned. Therefore it could be synthesised in a straightforward way according to the synthesis developed above.

Due to the high electronegativity of the fluorine nucleus, the reactivity of the carbonyl group is enhanced. For synthesis of the corresponding phthaloyl dichloride (**26**) this is not a problem, but for the synthesis of the S-(2-pyridinyl) dithioester (**27**) the enhancement of the reactivity is a major problem. Preparation of the S-(2-pyridinyl) dithioester (**27**) based on the use of TEA as a base appeared not to be successful. The S-(2-pyridinyl) dithioester (**27**) could however be isolated through addition of the phthaloyl dichloride (**26**) to a sodium methanolate solution of 2-mercaptopyridine at -78°C. The best results were obtained in a dry, oxygen and moisture free atmosphere as the product is much more reactive than the protonated derivative. The tetrafluoro diketone (**28**) was obtained via the Grignard reaction by adding 2-thienylmagnesiumbromide to a solution of the S-(2-pyridinyl) dithioester (**27**) in THF at 0°C. The yield of 87% is comparable to the yield of protonated 1,2-thienyl benzene (**43**).

9.3 Synthesis of Nitrogen Derivatives

From theoretical calculations^[63, 64] it appeared that the replacement of carbon atoms in the ITN ring system by nitrogen atoms influences the relative stabilities of the aromatic and quinoid forms on two levels. First of all, due to the weaker aromaticity of the nitrogen containing ring, it is more difficult to preserve their fully π delocalised character and the quinoid structure is less predominant in the N-derivatives compared to PITN. A second factor appeared to be the presence of non bonded S—N interactions which stabilise (destabilise) the aromatic (quinoid) structure. These S—N interactions will also play a role in the conformation of the polymer chain. From analysis of the calculated electronic properties it appeared that there is a dependence not only on the nature of the fused rings but also on the positions of the nitrogens. Finally, quantum chemical calculations^[63, 64] indicate that polymers containing isothianaphthene derivatives in which carbon nuclei are replaced by nitrogen in the fused benzene ring of the ITN ring system should possess even lower band gaps. The 4,5-diaza and 4,7-diaza polymers appeared to be quite promising: they present very small calculated energy gap values, 0.27 eV and 0.18 eV, respectively, in their most stable geometric structure.^[64]

Therefore, aza and diaza derivatives of ITN are the most interesting systems to be used in a *formal* copolymer. Since we established a convenient route towards the synthesis of *ortho* diketones, we investigated to what extent this method can be applied for the synthesis of aza and diaza derivatives of PITN. Based on our method we tried out the synthesis of dithienyl thieno[2,3-*c*]pyridine (37), dithienyl thieno[3,4-*c*]pyridine (38), dithienyl thieno[2,3-*c*]pyrazine (39). (Figure 9.1) The starting materials were *ortho* dicarboxylic acids, for these compounds are readily available commercially.

An additional feature is that these compounds can be used to get a rough idea about the spectroscopic characteristics of the corresponding aza and diaza ITN homopolymers.

9.3.1 Dithienyl thieno[2,3-*c*]pyridine

For all the nitrogen compounds we have to start from the corresponding phthalic acid. We used both the methods based on PCl_5 and SOCl_2 to synthesise the corresponding phthaloyl dichloride. When the reaction was completed, purification by vacuum distillation yields 90% of the 2,3-pyridinoyl dichloride (both methods). The synthesis of the S-(2-pyridinyl) dithioester (48) was performed using the TEA method

with a yield of 68%. It should be noticed that this thioester is not soluble in THF or other solvents suitable for Grignard reactions. The only solvent appeared to be pyridine, but this is not a good Grignard solvent since the Grignard reagent readily decomposes.^[65]

At first the Grignard reaction was carried out in the usual way in a solution of THF at 0°C. However, the characteristic IR absorption at 1760 cm⁻¹, the presence of an aliphatic quaternary carbon signal at 86.8 ppm and the loss of CO₂ in the mass spectra indicate the formation of a compound with the 3,3-dithienyl-3*H*-furo[2,3-*c*]pyridin-1-one (**47**) structure in relatively high yield of 64%. Even carrying out the reaction at higher temperatures to enhance solubility did not solve the problem. Since we obtained almost a single pure compound, the question arises whether the product possesses structure (**47a**) or structure (**47b**). (Figure 9.9)

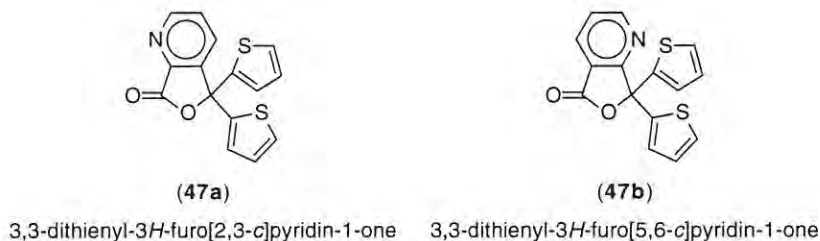


Figure 9.9 The structure of the two possible isomeric reaction products as a result from the Grignard reaction of 2-thienylmagnesiumbromide on (**48**).

A detailed structure analysis based on the use of a combination of 2D ¹H-¹³C heteronuclear correlation NMR experiments optimised for J=140 Hz and J= 8Hz helps to elucidate the structure of the obtained compound. The full chemical shift assignment has been carried out as on the previous compounds and the same numbering is used as with compound (**44**). But in the case of nitrogen-containing aromatic ring systems, the full chemical shift assignment is hindered to a considerable extent. Indeed the presence of the nitrogen disturbs strongly the normal long range coupling behaviour^[66] between proton and carbon nuclei. This means that in the long range ¹H-¹³C HETCOR optimised for J= 8 Hz of pyridine and pyrazine compounds also geminal and direct couplings will appear. As could be expected the direct ¹H-¹³C HETCOR optimised for J= 140Hz is not influenced by the presence of nitrogen nuclei.

Based on the integration a distinction can be made between the protons from the pyridine ring system and those of the thiophene ring system as the latter chemical shifts will integrate for two protons. Thus the signals at 6.96, 7.20 and 7.32 ppm originated

from thiophene protons whereas the signals at 7.53, 8.22 and 8.94 ppm belong to pyridine protons.

C3, being an aliphatic quaternary carbon nucleus, resonates at 86.79 ppm. The correlation signal between C3 and the thiophene proton chemical shift at 7.20 ppm in the long range ^1H - ^{13}C HETCOR optimised for $J = 8$ Hz (Figure 6) allows us to assign this signal to H3'. H4' and H5' can subsequently be assigned to 6.96 and 7.32 ppm based on the ^1H - ^1H COSY spectrum. C3', C4' and C5' can then be assigned using the direct ^1H - ^{13}C HETCOR optimised for $J = 140\text{Hz}$ to 127.46, 126.94 and 127.26 ppm respectively. Since C2' is the only quaternary carbon nucleus that is able to show long range couplings with thiophene protons it can be associated with the signal at 142.00 ppm.

From the full chemical shift assignment of the S-pyridinyl thioesters and the pyrazine derivatives, it has been shown that the hydrogen situated next to an imine nitrogen in general resonates at lower field around 9 ppm. This observation is in accordance with chemical shifts reported in literature.^[66] Thus we can assign the signal at 8.94 ppm to H5 based on its chemical shift position. Using the direct ^1H - ^{13}C HETCOR optimised for $J = 140\text{Hz}$, C5 can be assigned to the signal at 155.87 ppm. The presence in the long range ^1H - ^{13}C HETCOR optimised for $J = 8\text{Hz}$ of direct, geminal and vicinal long range correlation signals of H5 with the remaining protonated carbon nuclei reflects the considerable change in the values of the coupling constants. Important is the presence of a long range correlation signal of H5 with the signal of a quaternary carbon nucleus at 169.43 ppm. The carbon C1 of the carbonyl group as well as C7a, situated in the *para* position, are too far removed from H5 to give rise to a correlation signal. Therefore the signal at 169.43 ppm should correspond with C3a. H6 can unambiguously be assigned to the signal at 7.53 ppm since it is the only remaining proton to show two correlation signals in the ^1H - ^1H COSY spectrum. Subsequently H7 can be assigned to the chemical shift at 8.22 ppm. Based on the direct ^1H - ^{13}C HETCOR optimised for $J = 140\text{Hz}$ C6 and C7 can as a consequence be assigned to the signal at 124.80 ppm and 134.72 ppm. Since C3a is situated in the *para* position relative to H6 and too far from the carbonyl C1, the correlation signal of H6 with the quaternary carbon signal at 118.79 ppm can be attributed to C7a. The only remaining signal at 166.86 ppm can finally be assigned to C1. The assignments of the carbon signals of the pyridine ring system are also in accordance with literature data.^[66]

The question now arises whether the pyridine nitrogen is situated at the carbonyl side (**47a**) or at the aliphatic side (**47b**) of the 3,3-dithienyl-3*H*-furopyridin-1-one compound. If the nitrogen is situated at the carbonyl side there should be a long range correlation signal between C3 and H7. However, the presence of a long range correlation signal between C1 and H7 and the absence of a correlation signal between C3 and a

pyridine proton, indicates the nitrogen to be situated at the aliphatic side of the 3,3-dithienyl-3*H*-furo[5,6-*c*]pyridin-1-one compound. (Figure 9.10) This full chemical shift assignment therefore indicates the reaction product to possess structure (**47b**) (Figure 9.9) (3,3-dithienyl-3*H*-furo[5,6-*c*]pyridin-1-one).

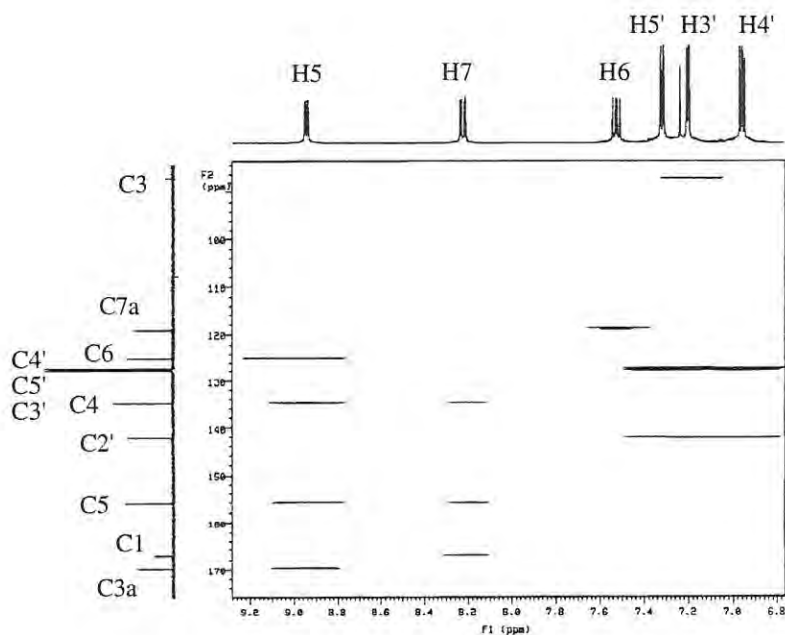
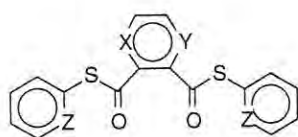


Figure 9.10 2D heteronuclear ^1H - ^{13}C correlation spectrum of 3,3-dithienyl-3*H*-furo[5,6-*c*]pyridin-1-one (**47b**) optimised for $J_{\text{CH}} = 8$ Hz (CDCl_3 , 30 $^\circ\text{C}$).

From previous experiments, 'freezing' the intermediate in an organometallic complex appeared to be an efficient method to prevent isomerisation. Obviously in this case the intermediate was not 'frozen' and could give rise to the formation of the lactone. Since the imine nitrogen enhances the reactivity of the thioester (**48**) in position 2, it is reasonable to suppose that this thioester (**48**) will be the first subject to a nucleophilic attack by the Grignard reagent. As soon as the enolate is formed it should be trapped by the organometallic complex. However, in this situation competition could be possible between the enolate and the nitrogen of the central pyridine ring system to form the complex. Due to this competition the enolate is not trapped in a straightforward way,

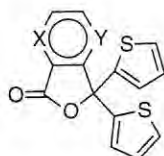
possibly resulting in an unstable organometallic complex. As a consequence such a situation can give rise to an intramolecular reaction. This leads to the lactone compound (**47b**) possessing a specific structure in which the thiophene rings are on the same side as the nitrogen of the pyridine ring as confirmed by the NMR spectroscopic analysis.



48: X = N; Y = C; Z = N

49: X = N; Y = N; Z = N

50: X = N; Y = N; Z = C



47b: X = C; Y = N

51: X = N; Y = N

Figure 9.11 The dithioester compounds to be used in the Grignard synthesis and the reaction products of the Grignard reaction on compound (**48**) and (**49**), respectively.

9.3.2 Dithienyl thieno[3,4-c]pyridine

Since the nitrogen in the 2,3-dithioester pyridine (**48**) interferes with the formation of a stable six ring intermediate, we tried to perform the synthesis of the 3,4-pyridine derivative. In this compound the nitrogen should be too far removed to be able to interfere with the organometallic complex. Although the 3,4-pyridinoyl dichloride could be obtained in a yield of 91%, we were not able to isolate the 3,4-pyridine thioester. The reaction based on TEA resulted mainly in the formation of the 2-pyridine disulphide.

9.3.3 Dithienyl thieno[3,4-c]pyrazine

In the synthesis of the pyrazinoyl dichloride a yield of only about 30% was obtained. This was mainly due to decomposition at higher temperatures. Also for the S-(2-pyridinyl) dithioester (**49**) syntheses, lower yields of about 40% were obtained as compared to other thioester syntheses.

The Grignard reaction was carried out in a solution of THF at 0°C. Again spectroscopic data indicated the formation of the lactone compound 3,3-dithienyl-3*H*-furo[2,3-*c*]pyrazin-1-one (**51**) (IR: 1765 cm⁻¹, ¹³C NMR: 85.1 ppm). Also in this compound we can suppose the competition between the pyrazine nitrogens and the enolates to be the basic reason for lactone formation.

A possible solution for this competition problem is to make use of the fact that the pyrazine possesses two nitrogens. The idea was if one carries out the Grignard reaction on the S-phenyl dithioester (**50**) we can use both nitrogens of the pyrazine ring system for the formation of the organometallic complex. The synthesis of the S-phenyl derivative (**50**) could be accomplished with a yield of 57%. Next the Grignard reaction was carried out but unfortunately no diketone was formed. Instead mainly two products (**52**) and (**53**) were isolated as shown in figure 9.12, besides some unreacted S-phenyl dithioester (**50**). The structure of compound (**52**) and (**53**) was confirmed by IR and mass spectroscopic data. Additional evidence for the structure of compound (**53**) was also obtained by a full chemical shift assignment based on 1D and 2D NMR homo- and heteronuclear correlation experiments.

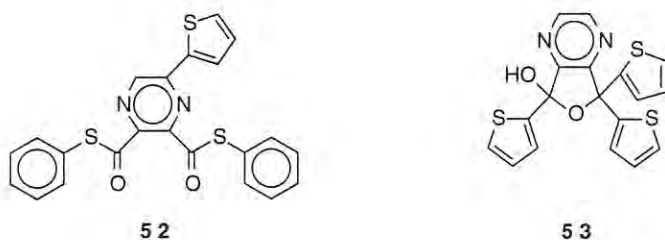
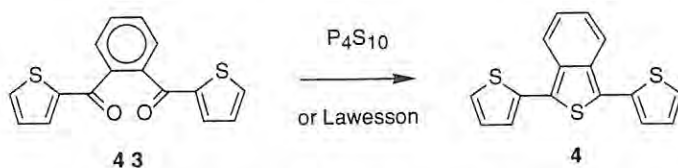


Figure 9.12 Reaction products of the Grignard reaction on compound (**50**)

9.4 Synthesis of DTI-derivatives by Ring closure of *ortho* Diketones

Finally the isothianaphthene core is formed through ring closure of the *ortho* diketone (**43**) by means of P₄S₁₀^[23] or Lawesson's reagent.^[24] Both procedures were performed but the procedure based on the use of Lawesson's reagent appeared to be more efficient and easier to work-up as compared to the use of P₄S₁₀. In the latter case one also has to counter the formation of important amounts of H₂S. The overall yield of DTI (**4**) based on this reaction scheme is 51%. This is the highest reported overall yield for

the synthesis of DTI (**4**) reported so far. The yield of deuterated DTI (**36**) is comparable to that of the protonated DTI. In case of the TFDTI (**24**), the yield is somewhat higher, namely 95%.



Scheme 9.4 Ring closure of the *ortho* diketone (**43**) by means of P₄S₁₀^[23] or Lawesson's reagent.^[24]

The NMR data of deuterated DTI (**36**) confirms our assignment of C4 and C5 of the isothianaphthene ring. Indeed, the signals of deuterated carbon nuclei show a triplet because ²H is a I=1 nucleus. The difference of 0.5 ppm as compared to the protonated DTI (**4**) should be attributed to the presence of some isotope effect.

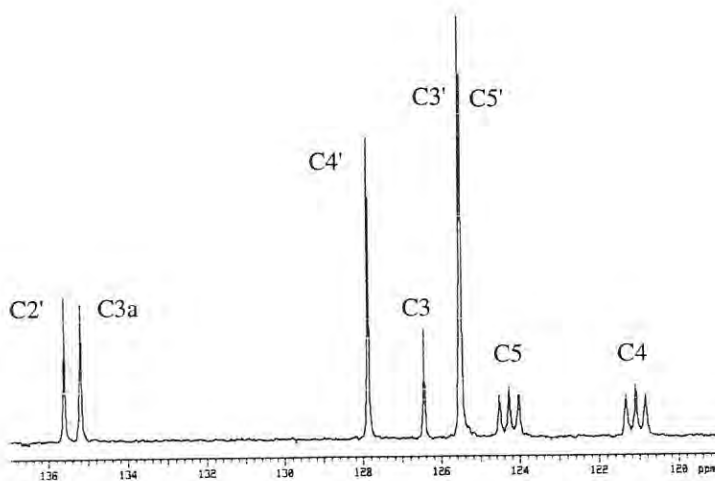


Figure 9.13 ¹³C NMR spectrum of deuterated DTI (**36**).

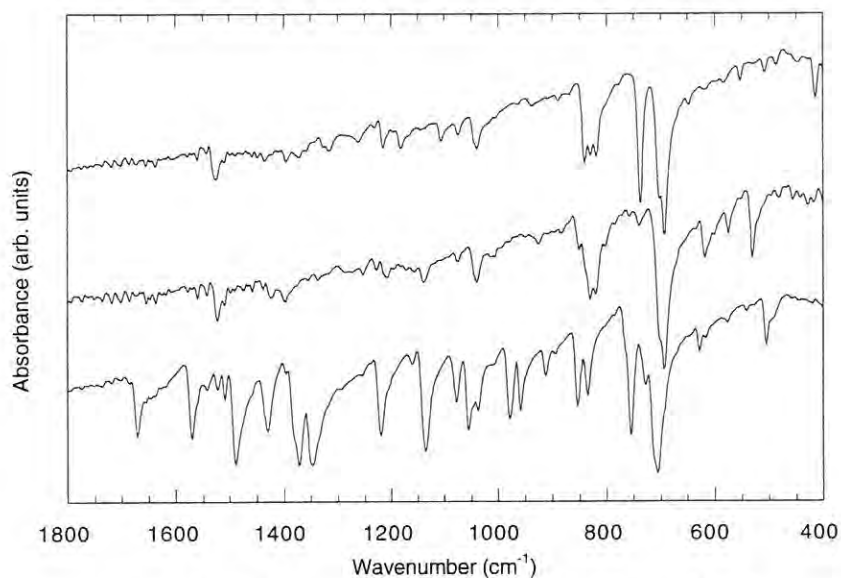


Figure 9.14 FT-IR spectra of DTI (**4**), 1,3-dithienyl-4,5,6,7-tetradeuteroisothianaphthene (**36**) and TFDTI (**24**), respectively.

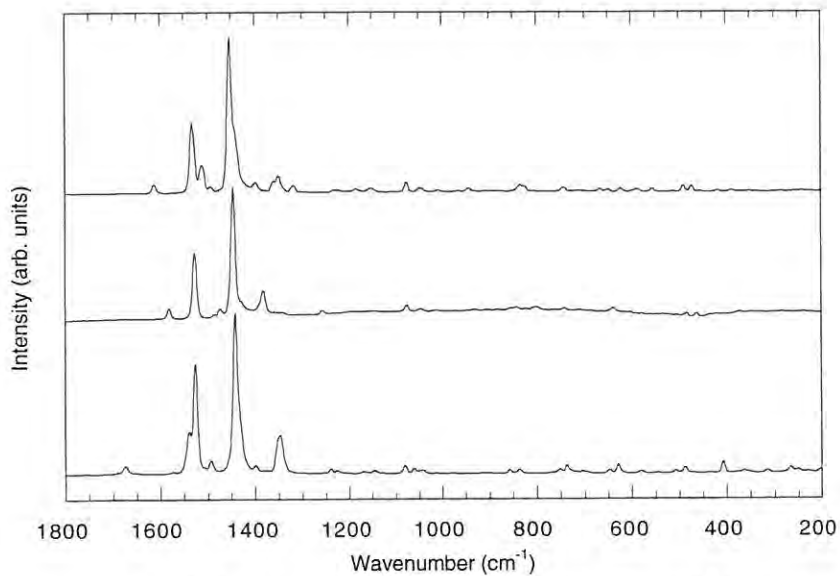


Figure 9.15 FT-Raman spectra of DTI (**4**), 1,3-dithienyl-4,5,6,7-tetradeuteroisothianaphthene (**36**) and TFDTI (**24**), respectively.

The UV-vis spectra of DTI (**4**) and TFDTI (**24**) were recorded in n-hexane. (Figure 9.17) For each compound a dilution series of six solutions was made in the range of 10^{-4} to 10^{-5} M. At these concentrations the equation of Lambert-Beer ($A = \epsilon c l$) may be used to calculate the molar extinction coefficient, ϵ . For this purpose the absorption intensity, A , was determined at the maxima present in the spectra, and plotted as a function of the concentration, c . On each set of six values a linear regression was performed. The value of ϵ can be obtained from the slope of the result of the linear regression. The correlation coefficient for each set is larger than 0.999. The $\lambda_{\max}$ and corresponding ϵ for the spectra recorded in n-hexane are summarised in Table 9.1

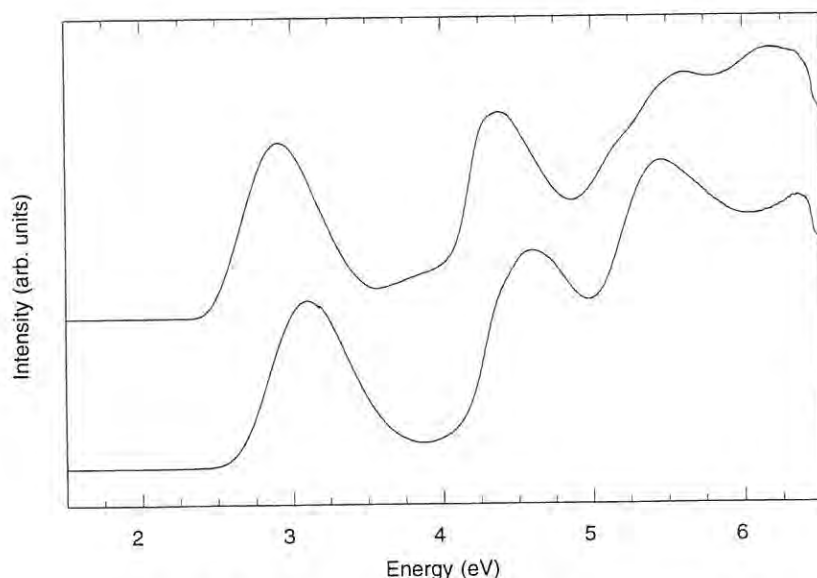


Figure 9.16 UV-vis spectra of DTI (**4**) and TFDTI (**24**), respectively, recorded in n-hexane.

Solvent: n-hexane	$\lambda_{\max}$ (nm)	E (eV)	ϵ
DTI (4)	426	2.91	14440
	283	4.38	16819
	220	5.62	19909
TFDTI (24)	400	3.10	12656
	269	4.60	16372
	227	5.45	23159

Table 9.1 UV-vis data of DTI (**4**) and TFDTI (**24**) recorded in n-hexane.

9.5 Poly(1,3-dithienylisothianaphthene)

9.5.1 Oxidative Polymerisation

The prototype of oxidative polymerisation consists in the use of a metal halide as oxidant. The most commonly used oxidant in the synthesis of conducting polymers is FeCl_3 . In a typical procedure^[67-70] the FeCl_3 was first carefully dried *in vacuo* at 100°C . Then dry nitrogen was introduced to the reaction vessel followed by phosphorus pentoxide and dried and distilled chloroform. The DTI (**4**) was added to the chloroform/ FeCl_3 suspension under vigorous stirring in a dry nitrogen atmosphere. The mixture was stirred for 48 h. After addition of methanol, a black precipitate was collected by filtration and transferred into a Soxhlet apparatus. This product was then successively extracted with methanol, THF and CHCl_3 .

Analysis of the residue from the methanol extraction did not indicate the presence of soluble oligomers or polymeric material. However, during extraction with THF and chloroform the solvents turned purple. A significant amount of a soluble dark purple compound could be isolated. When the THF and the chloroform fraction were compared, the chloroform fraction contained more of the purple compound. The product thus appeared to be easier to extract with chloroform as with THF. Analysis of the composition of both the THF and the chloroform fraction indicated no significant difference. Therefore, both fractions were combined and subjected to purification by column chromatography (silica, n-hexane(20)/chloroform(80)). The so obtained product was then precipitated from a chloroform solution by slowly adding n-hexane. The dark purple solid was collected by filtration. Mass spectroscopic analysis indicated that this compound was the 1,3-dithienylisothianaphthene dimer (**54**). (Figure 9.17)

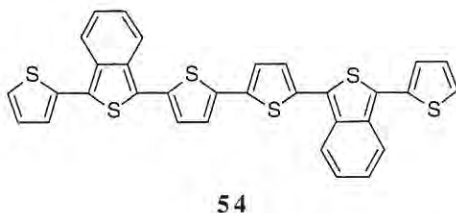


Figure 9.17 During oxidative polymerisation process of DTI (**4**) using FeCl_3 , important amounts of the corresponding dimer (**54**) are formed.

The ^{13}C NMR spectrum of this compound showed aromatic signals which were broadened to such an extent that detailed analysis of the spectrum was impossible. Since FeCl_3 was used as oxidising reagent for polymerisation of DTI (**4**), the dimeric compound (**54**) could contain still a small amount of iron and this paramagnetic material could be the origin of the broad peaks in the NMR spectrum. We therefore subjected a small amount of the product to an atomic absorption spectroscopic (AAS) analysis. This analysis indicated that up to 500 ppm of iron were present. The observation of broadened peaks in ^{13}C NMR spectroscopy has also been made by Pomerantz et al.^[71] in the case of a chloroform solution of poly(2,3-dihexylthieno[3,4-*c*]pyrazine). From ESR measurements they found indications that the material was paramagnetic, which could explain the observed peak broadening in their NMR spectra.

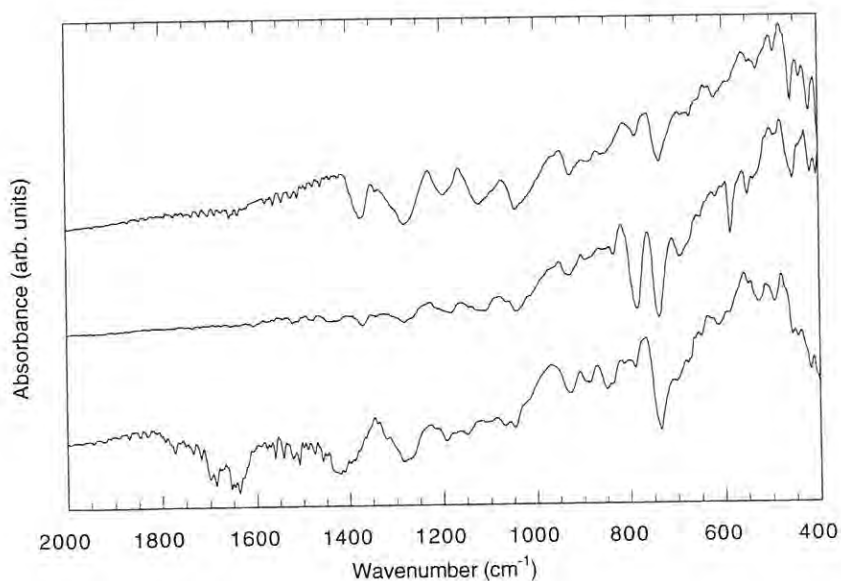


Figure 9.18 FT-IR spectra of the doped polymer, dedoped polymer and doped oligomer fraction (**54**) of poly(1,3-dithienylisothianaphene), respectively.

The black powder remaining after the successive extractions was next subjected to a dedoping process.^[4] The material (0.95 g) was suspended in a solution of 1 ml of hydrazine hydrate (85%) and 10 ml of methanol and heated till reflux. After 2 h the solution was allowed to cool down, the product collected by filtration and washed successively with methanol and ether. Finally, the remaining black powder was dried *in vacuo* for several hours.

Comparison of the IR spectra (Figure 9.18) of the product before dedoping and after the dedoping process showed that the signals originating from the dopant were almost completely removed. The IR spectrum of the purple oligomer fraction (**54**) shows some similarities with the spectrum of the doped polymer. Some of the bands which disappear by dedoping are apparently still slightly present in the oligomer fraction.

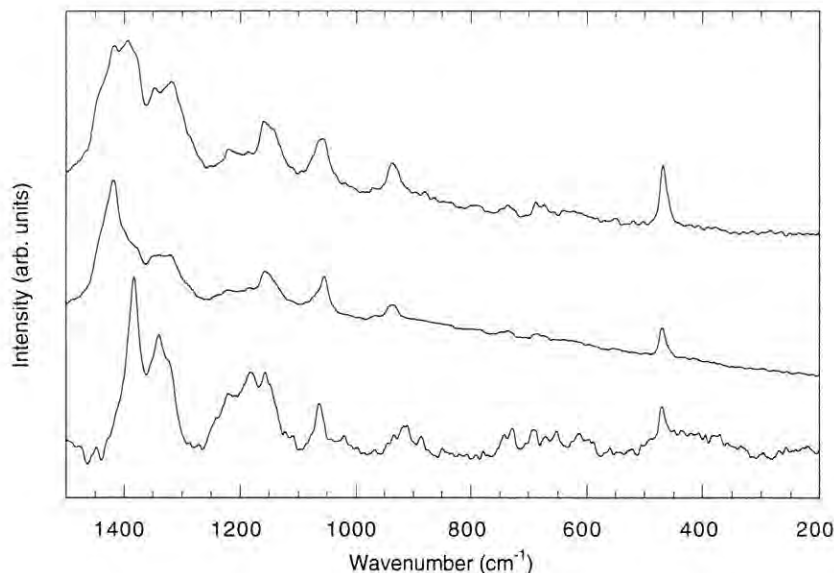


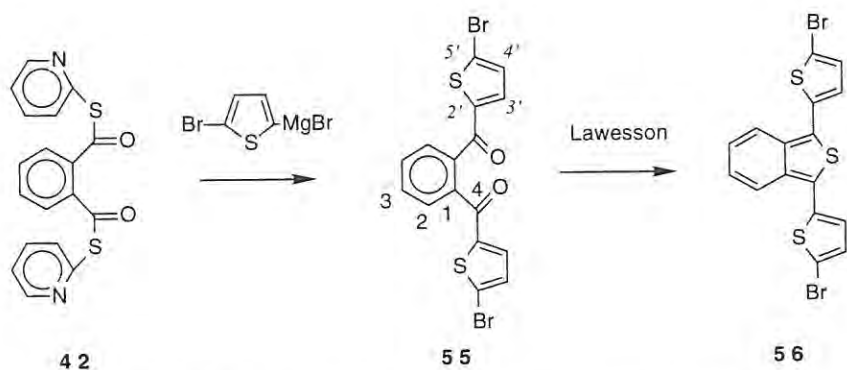
Figure 9.19 FT-Raman spectra of the doped polymer, dedoped polymer and doped oligomer fraction (**54**) of poly(1,3-dithienylisothianaphthene), respectively.

The FT-Raman spectrum (Figure 9.19) of the doped polymer shows signals at 1419, 1394, 1349, 1318, 1159, 1057, 937, 468 cm^{-1} . The band at 1159 cm^{-1} corresponds with the band at about 1164 cm^{-1} in the FT-Raman spectrum of pristine and doped PITN. (Figure 5.3) The signals at 1394, 1318, 1057 and 468 cm^{-1} also appear in the spectrum of doped PITN (1383, 1319, 1059, 466 cm^{-1}). Upon dedoping only small

changes occur. The signal at 1394 cm^{-1} disappears and the signals at 1349 and 1318 cm^{-1} decrease in relative intensity. The other smaller signals do not undergo any changes. The signal at 937 cm^{-1} in both the doped and dedoped spectra is not present in the FT-Raman spectra of PITN. The spectrum of the oligomer fraction shows an important difference to the spectrum of the dedoped material. The band at 1419 cm^{-1} is absent. The intense signal at 1388 cm^{-1} corresponds with the signal at 1394 cm^{-1} in the spectrum of the doped material. Both FT-IR and FT-Raman seem to indicate that the dimer (**54**) is doped. Since FeCl_3 was used for polymerisation purposes, the doping of the oligomer fraction could originate from FeCl_3 . This is in accordance with the inability to record NMR spectra.

9.5.2 Reductive Polymerisation

Although oxidative polymerisation results in polymerisation of DTI (**4**), some difficulties were experienced. First of all a large amount of a DTI dimer (**54**) was formed, indicating the oxidative polymerisation process is not very efficient. Furthermore, remaining oxidant prevents the recording of NMR spectra due to its paramagnetic character. Therefore, we investigated the possibility of applying reductive polymerisation methods. Mostly these methods are based on a nickel catalysed Grignard coupling of aromatic dihalides.^[72-89] In this type of reaction the aromatic ring system is not disturbed as in the case of oxidative polymerisations, resulting in a more efficient polymerisation. We therefore attempted the synthesis of 1,3-di(5'-bromothieryl)isothianaphthene (**55**). (Scheme 9.20)



Scheme 9.20 Synthesis of 1,3-di(5'-bromothieryl) isothianaphthene (**56**), a monomeric unit which can be used in nickel catalysed Grignard coupling reactions.

Based on our DTI synthesis method, we had to prepare the Grignard reagent of 2,5-dibromothiophene. Next the Grignard synthesis of the corresponding *ortho* diketone was performed in the usual way. The reaction of Lawesson's reagent with 1,2-di(5'-bromothienoyl) benzene should finally yield the monomeric unit, 1,3-di(5'-bromothienyl) isothianaphthene (**55**), to be used in the reductive polymerisation reaction.

For the preparation of the Grignard reagent one has to provide efficient mixing of the different reagents. For additional activation of the magnesium, the Grignard reagent of 2,5-dibromothiophene was prepared in an ultrasonic bath. Then the S-(2-pyridinyl) dithioester (**42**) was added to the Grignard reagent. After the usual work up and purification by means of column chromatography (silica/n-hexane) a greenish brown product was obtained in a yield of 41% . The characteristic IR band at 1625 cm⁻¹ indicated that the diketone had been formed. In proton NMR the presence of two doublets at 7.041 and 7.184 ppm clearly proved that we had made the dibrominated product (**55**), which was further confirmed by mass spectroscopy. The low yield can be explained by the fact that only about 50 % of the 2,5-dibromothiophene is transformed into the mono magnesium bromide.^[80] The ring closure to form the isothianaphthene ring system was performed by mixing 1,2-di(5'-bromothienoyl) benzene (**55**) with Lawesson's reagent in CH₂Cl₂ at room temperature. The CH₂Cl₂ was replaced by ethanol and refluxed for about 30 min. Water was added and the yellow fluorescent product was extracted with ether. TLC analysis of the reaction mixture indicated however that three fluorescent yellow products were formed. These products were separated by means of column chromatography. The main product appeared to be DTI (**4**). Since the bromines appeared to be removed during the ring closure, another method should be used to prepare the dibrominated DTI (**56**).

9.6 Conclusions

Since DTI derivatives could be of great interest for the development of semiconducting materials with tailor-made electronic properties as well as for spectroscopic and theoretical evaluation of structure-property relationships our aim was to develop an efficient synthesis which makes it possible to prepare other DTI derivatives.

Since an efficient method for the synthesis of DTI (**4**) was not available previously, we developed a highly specific and efficient synthesis route. In this method, the synthesis of *ortho* aryldiketones is the major bottleneck. A detailed evaluation of available starting compounds to be used in Grignard reactions was essential. For the synthesis of the 1,2-dithienoyl benzene (**43**) we investigated successively the Grignard reaction of 2-thienylmagnesiumbromide on phthaloyl dichloride (**40**), phthalic anhydride (**13**), thiophthalic anhydride (**14**), 1,2-(*S*-phenyl)-benzenedithioate (**41**) and 1,2-(*S*-(2-pyridinyl))-benzenedithioate (**42**).

On the one hand phthaloyl dichloride (**40**) appeared to be too reactive towards the reaction with 2-thienylmagnesiumbromide, but on the other hand the reaction on phthalic anhydride (**13**) and thiophthalic anhydride (**14**) yielded, besides small amounts of the 1,2-dithienoyl benzene (**43**), quantities of the isomeric 3,3-dithienyl-3*H*-isobenzofuran-1-one (**44**). In addition, the reactions on this compound were accompanied with some inconvenience such as the development of H₂S during workup, difficult mixing of the reaction products during addition of the Grignard reagent and the purification process was severely hindered by the formation of alcohols and monosubstituted products.

On the other hand the Grignard reaction on 1,2-(*S*-(2-pyridinyl))-benzenedithioate (**42**) yielded selectively almost pure *ortho* diketone (**43**). This result was attributed to the formation of a stable six membered organometallic complex trapping the enolate. In an analogous reaction on the 1,2-(*S*-phenyl)-benzenedithioate (**41**) according to the method of Cardellicchio et al.^[53] the enolate cannot be trapped, and the 3,3-di(*S*-phenyl)-3*H*-isobenzofuran-1-one (**45**) was formed.

Thorough analysis of the reaction products of the 1,2-(*S*-phenyl)-benzenedithioate thioester synthesis taught us a lot about the stability of 1,2-(*S*-phenyl)-benzenedithioates (**41**) compared with the isomeric lactone, 3,3-di(*S*-phenyl)-3*H*-isobenzofuran-1-one (**45**). From spectroscopic data and carefully analysing the reaction mixtures as a function of time it appeared that the thioester is first formed. In the presence of an excess of thiophenol the substitution of a proton at the 3 position of the lactone occurred. This indicates the presence of a stable radical, because thiophenol can act as a radical scavenger through proton transfer and disulphide formation. Moreover, at the 3 position the radical is not only stabilised by delocalisation in the aromatic ring system but it is also stabilised by delocalisation in the thiophenol group.

The synthesis of the deuterated (**36**) and fluorinated (**24**) DTI derivatives was successfully carried out. However, attempts of synthesising the 2,3-pyridine (**37**), 3,4-pyridine (**38**) and 2,3-pyrazine (**39**) derivatives failed. The introduction of nitrogens in the aromatic ring system seemed to interfere with the main principle on which the *ortho* diketone reaction sequence is based, namely the formation of a stabilised six membered intermediate which prevents the enolate from reacting with the neighbouring thioester group. In the case of the 2,3-pyridine the formation of the 3,3-dithienyl-3*H*-furo[5,6-*c*]pyridin-1-one structure (**47b**) is favoured due to the difference in reactivity of both carbonyl functional groups caused by the inherent asymmetry of the ring system as a consequence of the presence of only one nitrogen.

These observations agree to a certain extent with the results of Cama et al.^[90] They used the S-(2-pyridinyl) thioester method to synthesise aryl analogues of thienamycin. However when the Grignard reagent of 2-thiazole, tetrazole, benzthiazole or pyrimidine is used, it failed to react with the thioesters. It is striking to find that these Grignard reagents contain one or more nitrogens which upon reaction could possibly interfere with the stable six membered complex. Our results indicate that not only in the Grignard reagent but also in heteroaryl substrates, the presence of aromatic nitrogen nuclei will prevent the formation of ketones.

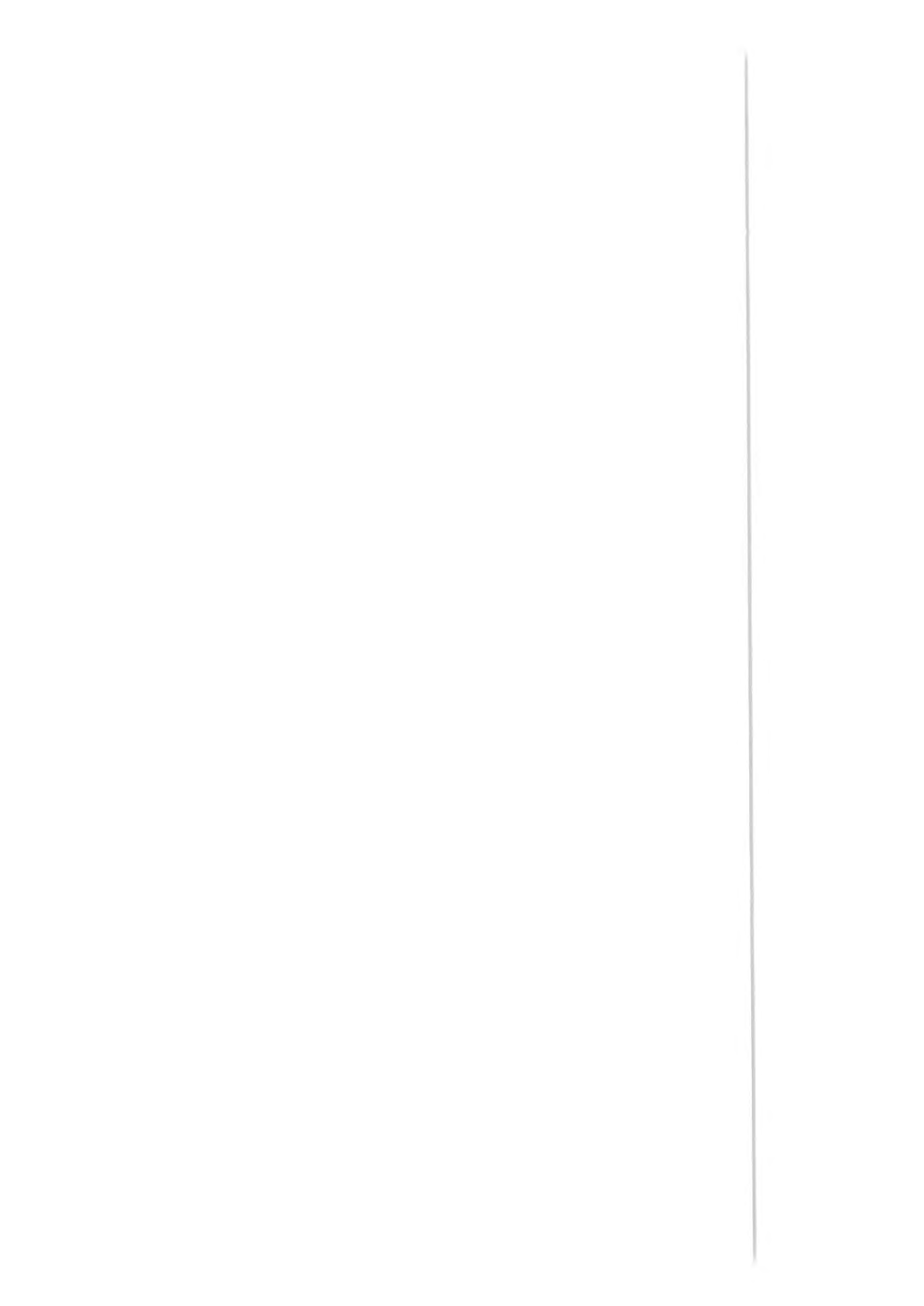
Finally, DTI (**4**) was polymerised oxidatively by means of FeCl₃. Besides the expected black polymer sizeable amounts of a purple product soluble in chloroform are also formed. Mass spectroscopic analysis indicated this product to be the DTI dimer (**54**). The polymer was dedoped by refluxing in a hydrazine solution. FT-IR indicated that remaining dopant from the polymerisation was removed. NMR analysis of the DTI dimer was hindered by broadening of the signals. AAS revealed the presence of iron. FT-IR and FT-Raman indicated that the dimer was probably doped. The doping of the dimer is likely due to the use of FeCl₃ for the polymerisation.

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Suggestions for Further Work

10.1 Introduction

In the first part of our research the structure of quinoid and aromatic PITN was investigated on the basis of an analysis of model compounds by means of a series of spectroscopic techniques such as, NMR, UV-VIS, XRD, IR, FT-Raman and *in situ* FT-Raman spectroscopy. In close connection with this research we attempted the analysis of fluorinated and nitrogen substituted derivatives of PITN. The second part was mainly devoted to the synthesis of 1,3-dithienylisothianaphthene and some of its derivatives, which can be used as monomeric units in the development of *formal* copolymers.

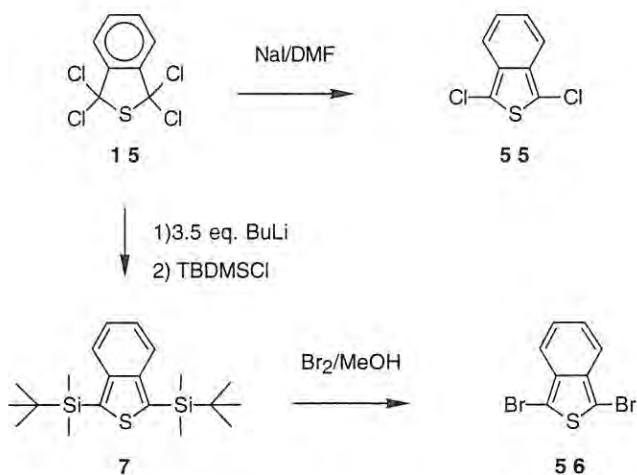
Ideas for further research can also be found at the fundamental level, i.e., understanding the relationship between the structure of PITN and its properties, as on the level of further development of *formal* copolymers. For both levels we shall outline some interesting aspects which can be investigated.

10.2 Synthesis of Aromatic PITN

As described in chapter 3, theoretical calculations indicate that the quinoid and aromatic forms of PITN appear to be almost isoenergetic (2.2 kcal/mole). Therefore, one could select the structure of the polymer depending on the chemical strategy chosen for the polymerisation.^[1] In this situation, the polymerisation mechanism and the nature of the monomer and of the end groups can direct the synthesis. Since the aromatic structure of PITN is predicted to possess a lower band gap as compared with the quinoid structure,

it is worthwhile to use different polymerisation techniques in order to verify these theoretical conclusions.

Until now all the monomers used in PITN syntheses contained end groups which favour the formation of a quinoid structure, namely 1,3-dihydroisothianaphthene, phthalide and phthalic anhydride. Even in the oxidative electrochemical polymerisation of the monomeric isothianaphthene the quinoid structure is readily accessible as electrons are removed from the isothianaphthene ring system, thereby creating a favourable situation for the formation of quinoid structures. Spectroscopic analysis of the materials so obtained indicate that they should possess a quinoid structure.^[1-8]

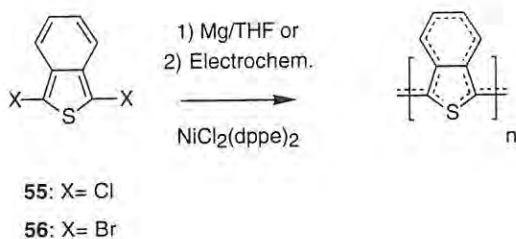


Scheme 10.1 The synthesis of 1,3-dichloroisothianaphthene (55) and a possible method to prepare 1,3-dibromoisothianaphthene (56).

The polycondensation of dihaloaryl compounds utilising transition metal catalysed C-C coupling first reported by Yamamoto et al.^[9-26] could be appropriate for the synthesis of aromatic PITN. Indeed the isothianaphthene ring system should not be disturbed by the polymerisation process and the inter ring bond should be formed by a transition metal catalysed dehalogenation polycondensation. Moreover, this method has been applied with success to a wide variety of compounds.^[27-34] The monomer needed to synthesise PITN using this polymerisation method is 1,3-dichloroisothianaphthene (55) or 1,3-dibromoisothianaphthene (56). Although the dibromo derivative (56) is best suited for this kind of polymerisation, it is however not accessible in a straightforward

way as is the dichloro derivative (**55**). Dichloroisothianaphthene (**55**) has been synthesised by Okuda et al.^[35] from 1,1,3,3-tetrachlorothiophthalan (**15**). (Scheme 10.1) On the other hand 1,3-dibromoisothianaphthene (**56**) could be obtained from a reaction of 1,3-bis(*tert*-butyldimethylsilyl)isothianaphthene (**7**) with Br₂.^[36] Alkyl chains could also be added to the isothianaphthene ring system to enhance solubility and facilitate spectroscopic analyses.

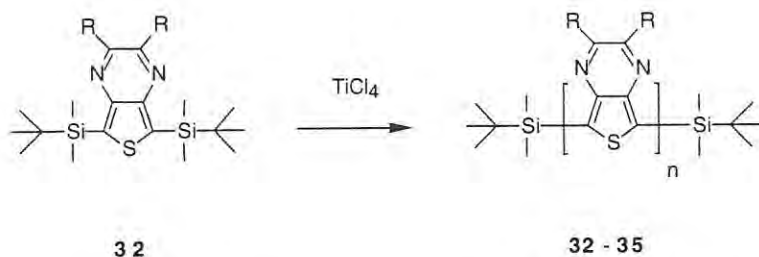
These two halogenated compounds could then be used in the polycondensation reaction as shown in Scheme 10.2.^[20, 27, 28] Spectroscopic analysis of the PITN so obtained by means of solid state NMR spectroscopy^[1, 6] and FT-Raman spectroscopy^[37] should enable us to determine if effectively aromatic PITN has been formed. Furthermore, these dihalogenated compounds could be used in a reductive electrochemical polymerisation and *in situ* FT-Raman spectroscopic analysis as described by Froyer et al.^[38-43] They synthesised poly(paraphenylene) electrochemically at a potential of -2.5V in the presence of NiCl₂(dppe)₂ using 1,4-dibromobenzene.



Scheme 10.2 Alternative synthesis of PITN by chemical or electrochemical Ni(II) complex catalysed dehalogenation polycondensation.

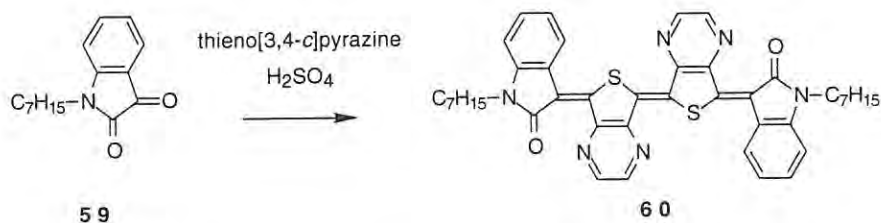
10.3 Analysis of Poly(thieno[3,4-*c*]pyrazine)

Theoretical^[44, 45] and experimental^[46, 47] results indicate poly(thieno[3,4-*c*]pyrazine) to be a promising low band gap polymer. We attempted the synthesis of aromatic model compounds, but the applied synthetic procedures did not permit us to obtain these compounds. Therefore we suggest another synthetic procedure for the synthesis of the monomer. This compound can then be used for the synthesis of the corresponding polymer as well as for the synthesis of necessary model compounds.



Scheme 10.4 1,3-(*tert*-butyldimethylsilyl)thieno[3,4-*c*]pyrazine, which could be used in oligomerisation and polymerisation reactions and as an intermediate in the synthesis of 1,3-dibromothieno[3,4-*c*]pyrazine to be used in reductive polymerisation reactions.

An efficient synthesis of quinoid isothianaphthene model compounds has not yet been established. For the synthesis of quinoid model compounds of thieno[3,4-*c*]pyrazine we suggest the interesting route for the synthesis of indophenine.^[58-63] This reaction has recently been revised by Tormos et al.^[64] who managed to obtain a soluble derivative by using *N*-heptylisatin (**59**). Indophenine is synthesised by mixing the isatin compound together with thiophene and sulphuric acid. To obtain the indophenine derivative of thieno[3,4-*c*]pyrazine (**60**), thiophene could be replaced by thieno[3,4-*c*]pyrazine. (Scheme 10.5)



Scheme 10.5 A quinoid model compound could be synthesised by replacing thiophene through thieno[3,4-*c*]pyrazine in the indophenine reaction.

10.4 Further Development of Formal Copolymers

As an efficient synthesis for the basic monomeric unit for the synthesis of *formal* copolymers, i.e., 1,3-dithienylisothianaphthene (**4**), has been developed, this method can

now be applied in the synthesis of more processable *formal* copolymers. The classical procedure for the enhancement of processability is by adding side chains onto the backbone. The problem to be solved is how to add side chains to the DTI unit. First of all, side chains can be put on the thiophene unit. Therefore one can use for example a 3-alkyl substituted thiophene Grignard reagent. However, side chains on the thiophene unit are expected to give rise to considerable steric interactions with the neighbouring units. When side chains are introduced onto the isothianaphthene ring on the 5 and/or 6 position, they are further removed from the backbone and it can be expected that they will give rise to less important disturbing steric interactions. We shall therefore focus on methods to introduce side chains onto the isothianaphthene ring of 1,3-dithienylisothianaphthene.

The most interesting approach towards the synthesis of substituted DTI units is to have at one's disposal a molecule allowing the introduction of different types of side chains. For the introduction of alkyl or aryl side chains one can make use of 5-chloro-1,3-dithienylisothianaphthene (**61**) or 5,6-dichloro-1,3-dithienylisothianaphthene (**62**). (Figure 10.1) The side chains can then be introduced using transition metal catalysed coupling reactions. These types of reactions have already been applied widely for the synthesis of oligomers and the introduction of side chains in thiophene.^[9-11, 31, 34, 57, 65-90]

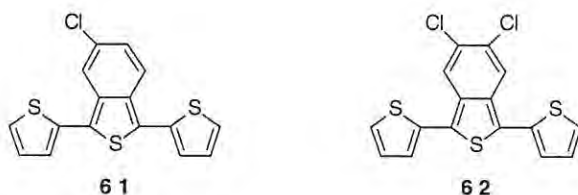
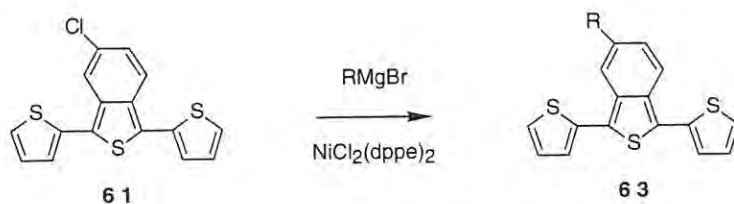


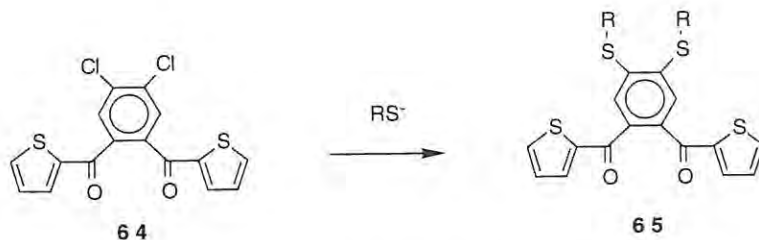
Figure 10.1 Two molecules which can be used for the introduction of different alkyl or aryl side chains by means of transition metal catalysed coupling reactions.

The starting compounds, 4-chlorophthalic acid and 4,5-dichlorophthalic acid are commercially available and could readily be used for the synthesis of the corresponding 1,3-dithienylisothianaphthene derivatives according to the synthesis scheme developed in chapter 9. Next the side chains could be introduced by preparing for example (Scheme 10.6) the Grignard reagent and adding a solution of the chlorinated DTI compound and a Ni catalyst such as $\text{NiCl}_2(\text{dppe})_2$.^[10, 31]



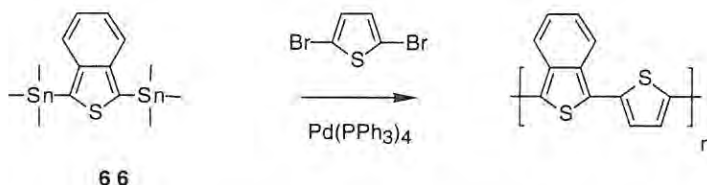
Scheme 10.6 Nickel catalyzed Grignard coupling reactions should allow the introduction of alkyl or aryl side chains.

Whereas the previous method may be well suited for the introduction of alkyl or aryl side chains, we would like to suggest a method for the introduction of thioether side chains. From the results of Wöhrle et al.^[91] and Kricheldorf et al.^[92] it appears that chlorine on aromatic ring systems can be replaced when good nucleophilic reagents such as thiolates are used. The reaction was carried out on 4,5-dichloro-1,2-dicyanobenzene and 4,5,6,7-tetrachlorophthalimides. These two ring systems have electron withdrawing substituents, namely cyano groups or a phthalimide group. The 1,2-thienoylbenzene, which is an important intermediate in the synthesis of the isothianaphthene ring system, possesses an analogous structure. Thus it would be interesting to verify if one could use thiolates to introduce onto 4-chloro or 4,5-dichloro-1,2-dithienoyl benzene (**64**), thioether substituents. (Scheme 10.7) If this reaction is possible a new series of isothianaphthene derivatives could become available for application in conducting polymers. The main advantage of this method is that the chlorinated 1,2-dithienoyl benzene (**64**) could be used as a starting material for obtaining a relatively easily accessible set of side chain containing DTI derivatives.



Scheme 10.7 This method should allow the introduction of thioether side chains.

Finally we would like to suggest an alternative method for the synthesis of copolymers. This method is again based on the transition metal catalysed coupling of halogenated aryl compounds.^[9, 65, 81] The palladium-catalysed cross-coupling polycondensation appears to be quite effective for the preparation of copolymers from distannyl aromatic compounds and dihalogenated aromatic compounds. Scheme 10.8 shows an example of this reaction in the synthesis of a copolymer containing alternating isothianaphthene and thiophene units. In combination with our method to synthesise DTI, the number of thiophene *versus* isothianaphthene units could be altered. The synthesis of 1,3-bis(trimethylstannyl)isothianaphthene (**66**) could be carried out according to the method of Okuda et al.^[35] for the synthesis of silylated analogues.



Scheme 10.8 An alternative synthesis of copolymers on the basis of palladium-catalysed cross-coupling polycondensation.

10.5 Conclusions

The aim of this chapter was to give a short survey of possibilities for further research. First of all we showed that it should be possible to verify if PITN with an aromatic structure can be synthesised. The transition metal catalysed coupling of dihalo isothianaphthenes seems to be the most promising method for this purpose. From the results of solid state NMR and *in situ* FT-Raman measurements it should be possible to determine whether the structure of the PITN so synthesised is aromatic or still quinoid.

Next we suggested a new approach for the synthesis of poly(thieno[3,4-*c*]pyrazine), a polymer which is predicted to possess interesting electronic properties. Methods for the synthesis of aromatic and quinoid model compounds was also described.

The solubility of DTI based polymers can be enhanced through the introduction of side chains onto 1,3-dithienylisothianaphthene. The strategy for this is to use a parent compound onto which side chains can be added. Again, transition metal catalysed coupling of alkyl or aryl chains offer a wide variety of possibilities. Another method could be the introduction of thioether side chains onto the 4-chloro (**61**) or 4,5-dichloro-1,2-dithienoyl benzene (**62**). Finally, an alternative route was proposed for the synthesis of copolymers using palladium-catalysed cross-coupling polycondensation from distannyl aromatic compounds and dihalogenated aromatic compounds.

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Nullum est jam dictum, quod non dictum sit prius
(Terentius, Eunuchus, Prologue 41)

General Conclusions

For the design of low bandgap polymers we investigated through a detailed analysis of literature to what extent substituents, end groups and the stability of π delocalisation influences the electronic properties such as the bandgap. In the case of PITN type polymers theoretical calculations predict that substituents will not alter the bandgap significantly. The main interest should rather be situated at the level of fine-tuning of the electronic characteristics for well defined applications and improving the properties during processing. The nature of the end groups seems to be only important for those polymers where the energy difference between the aromatic and quinoid structure is very small. For these polymers the structure and therefore the electronic properties could be controlled by appropriate synthesis methods. Variation of the π delocalisation appears to be the most important tool for altering the electronic properties in a significant way. A fully planar extended π system favours electron delocalisation across the polymer backbone and thereby lowers the bandgap and improves conductive properties. From classical Hückel Molecular Orbital theory and experimental data, there are some indications that a qualitative correlation may exist between the bandgap and the resonance stabilisation. Apparently a lower resonance stabilisation of an heterocyclic ring system coincides with a lower bandgap of the corresponding polymer. This qualitative correlation can be used as a rough guideline for further synthesis of low bandgap polymers but can by no means replace more sophisticated calculations. Additionally, the introduction of additional heteroatoms has just as great an influence on the resonance stability as on the geometric structure (lowering of steric interactions). Finally, by combining different aromatic ring systems, resulting in *formal* copolymers, the electronic

properties can be substantially altered and are in general situated in between those of the corresponding homopolymers.

Characterisation of aromatic isothianaphthene oligomers made it possible to establish a spectroscopic picture which can be considered as prototypic for "aromatic" poly(isothianaphthene). This spectroscopic analysis was performed by means of NMR, FT-Raman and UV-vis spectroscopy.

The ^{13}C NMR chemical shifts of the "central" carbon atoms of the aromatic oligomers were obtained from a full chemical shift assignment using 1D and 2D NMR experiments. For the comparison with PITN, only the carbons C3a, C4 and C5 of tetramer (**10**) are valuable since C3 shows almost the same shift in the aromatic and the quinoid model compound (**12**), synthesised by Hoogmartens. The shift of the three former carbons in PITN and in the quinoid model compound (**12**) correspond well while there is still no correspondence whatsoever between PITN and the aromatic tetramer (**10**). These results are in favour of previous conclusions by Hoogmartens et al.^[1] indicating that the structure of PITN possesses a strong quinoid character.

The FT-Raman spectrum of the tetramer (**10**) can be considered as a prototype for "aromatic" PITN since the length of the chain appeared to be large enough to minimise the effects of the end groups. From comparison of the FT-Raman spectra of PITN with the silylated aromatic tetramer (**10**) and the quinoid model compound (**12**) it could be concluded that the FT-Raman data of pristine PITN appeared to match almost exactly the data of the quinoid model compound (**12**). From this comprehensive analysis of the Raman spectra of model compounds, purposely synthesised to mimic the "quinoid" or "aromatic" structure, it is possible to reach the conclusion that the molecular structure of PITN in the electronic ground state is quinoid. This result also complements the results obtained from NMR spectroscopy.^[1-4]

The doping process of electrochemically synthesised PITN has also been followed by means of *in situ* FT-Raman spectroscopy ($\lambda_{\text{exc}} = 1064\text{nm}$). During the process of n-doping no changes in the FT-Raman spectrum could be observed. The process of p-doping, however, gives rise to additional Raman lines which become more important in function of increasing p-doping. Using the FT-Raman features of the "aromatic" and "quinoid" model compounds the structure of the doped material could not be associated with a pure aromatic nor a pure quinoid geometry. The identification of the origin of these new lines necessitates additional vibrational spectroscopic research.

Using the INDO/SCI formalism, the experimental optical spectra of aromatic isothianaphthene oligomers (**7** - **10**) have been analysed from monomer up to tetramer.

Two main absorption peaks were observed in the visible-near UV region. The low-energy absorption, corresponding to a $d \rightarrow d^*$ type transition from the HOMO level to the LUMO level, is shifted to lower energies when the chain length is increased. The extrapolations made from the HOMO—LUMO transitions of the oligomers to the band gap energy of aromatic PITN lead to a very small energy gap value of 0.63 eV for the planar system and a value of 1.55 eV for the 130° twisted infinite chain. The value calculated for the tilted system is in good agreement with the extrapolation of the first energy transition of the oligomers recorded in n-hexane, 1.94 eV. These results point out that in solution, the aromatic oligomers adopt a strongly non planar conformation, increasing significantly the HOMO—LUMO transition relative to that of a planar aromatic system. The second strong optical absorption peak is described by electronic excitations involving mostly $l \rightarrow d^*$ type transitions. The localised molecular orbitals (l) being less affected by the extent of conjugation than the delocalised levels (d), the position of the second peak evolves smoothly as the chain length increases, which is in good agreement with the features of the experimental spectra. These combination of experimental results and theoretical calculations therefore indicate that a substantial lowering of the band gap will occur in planar aromatic poly(isothianaphthene) systems.

Literature data shows that through control of the processability, materials with enhanced intrinsic conducting properties can be obtained. In the search for PITN derivatives with enhanced processability and stability, Brooke et al.^[5] synthesised poly(4,5,6,7-tetrafluoroisothianaphthene) (**19**), which is soluble in chlorinated and other organic solvents. To understand the effect of fluorine on the structure and the properties of this material, a detailed spectroscopic characterisation was started. At first, a series of aromatic tetrafluorinated isothianaphthene oligomers (**20** - **23**) were analysed by means of 1D and 2D NMR spectroscopic techniques to obtain an unambiguous full chemical shift assignment of the hydrogen, carbon and fluorine signals. The shifts of the "central" carbon atoms of these oligomers showed a clear convergence going from trimer (**22**) to tetramer (**23**). The chemical shift values of the "central" carbon atoms can therefore be considered as being representative of fluorinated poly(isothianaphthene) possessing an aromatic structure. Furthermore the analysis of a more simple model compound, 1,3-dithienyl-4,5,6,7-tetrafluoroisothianaphthene (**24**), indicates that from this model compound it is also possible to obtain a reliable indication of the chemical shift value of C4 and C5, despite the important structural and chemical changes induced by the fluorine nuclei. The characteristic convergence going from trimer to tetramer appeared also in FT-IR and FT-Raman spectroscopic data. Also on the level of FT-Raman spectroscopy the

spectrum of 1,3-dithienyl-4,5,6,7-tetrafluoroisothianaphthene showed the characteristic features of "aromatic" isothianaphthene units.

Comparison of the NMR and FT-IR data of the oligomers with the spectroscopic data of the polymer indicates that they point to an aromatic structure for the polymer. However, the FT-Raman spectrum of the polymer does not correspond with the typical features of the spectrum corresponding with "aromatic" ITN units, but rather with the spectrum of doped PITN. The explanation for this discrepancy is not obvious since there is a lack of data on the structure of quinoid PTFITN as on the structure determination of doped PITN.

Although this PITN derivative is surprisingly soluble, the band gap of this material has a value of about 2.1 eV.^[6] If the material possesses an aromatic structure, the fluorines probably induce non planarity such that inter ring π -conjugation is lowered to a considerable extent.

The replacement of carbon atoms in the ITN ring system by nitrogen atoms can have a considerable influence. From theoretical calculations it appeared that due to the weaker aromaticity of the nitrogen containing ring, it is more difficult to preserve a fully π delocalised character and the quinoid structure is less predominant in the N-derivatives compared with PITN. A second factor appeared to be the presence of non bonded S—N interactions which stabilise (destabilise) the aromatic (quinoid) structure. Finally, from the series of analysed aza derivatives the 4,5-diaza and 4,7-diaza polymers appear very promising: they present very small calculated energy gap values, 0.27 eV and 0.18 eV, respectively, provided they could be synthesised in the planar aromatic structure. An attempt was made to synthesise a series of aromatic 4,7-diaza oligomers based on the method of Okuda et al.^[7] However, it appeared that the chemistry used by Okuda et al. is not suitable for use with pyrazine derivatives.

From this analysis it appears that nitrogen containing PITN analogues present the possibility to obtain a fully planar aromatic system, which is predicted to be associated with a very low band gap, and to enhance processability due to the presence of aromatic nitrogen atoms. These materials can therefore be considered as very promising low band gap materials.

Since 1,3-dithienylisothianaphthene derivatives could be of great interest as much for the development of semiconducting *formal* copolymers with tailor-made electronic properties as for spectroscopic and theoretical evaluation of structure-properties

relationships our aim was first of all to develop an efficient synthesis, which makes it possible to prepare other 1,3-dithienylisothianaphthene derivatives.

We succeeded in the development of a highly specific and efficient synthesis route to 1,3-dithienylisothianaphthene (DTI, **4**). In this method the synthesis of *ortho* aryldiketones was the major bottleneck. A detailed evaluation of available starting compounds to be used in Grignard reactions was therefore essential. This evaluation led us to perform the Grignard reaction of 2-thiophenemagnesiumbromide on 1,2-(S-(2-pyridinyl))-benzenedithioate (**42**), yielding selectively almost pure *ortho* diketone (**43**). This result was attributed to the formation of a stable six membered organometallic complex trapping the enolate formed during the reaction.

The synthesis of the deuterated (**36**) and fluorinated (**24**) DTI derivatives was successfully carried out. However, attempts at synthesising the 2,3-pyridine (**37**), 3,4-pyridine (**38**) and 2,3-pyrazine (**39**) derivatives failed. The introduction of nitrogens in the aromatic ring system seemed to interfere with the formation of a stabilised six membered intermediate. In the case of the 2,3-pyridine the formation of the 3,3-dithienyl-3*H*-furo[5,6-*c*]pyridin-1-one structure (**47b**) is favoured due to the difference in reactivity of both carbonyl functional groups caused by the inherent asymmetry of the ring system as a consequence of the presence of only one nitrogen. These observations complete to a certain extent the results of Cama et al.^[8] which also used the S-(2-pyridinyl) thioester method to synthesise aryl analogues of thienamycin. When they used the Grignard reagent of 2-thiazole, tetrazole, benzthiazole or pyrimidine, it failed to react with the thioesters. It is striking to find that these Grignard reagents contain one or more nitrogens which upon reaction could possibly interfere with the stable six membered complex. Our results indicate that not only in the Grignard reagent but also in heteroaryl substrates, the presence of aromatic nitrogen nuclei will prevent the formation of ketones.

Finally, DTI was polymerised oxidatively by means of FeCl₃. The presence of important amounts of purple coloured DTI dimer (**54**), soluble in chloroform, indicated that another more efficient polymerisation should be used. Reductive polymerisation of 1,3-di(5'-bromothienyl)isothianaphthene was proposed as an alternative.

From our research it appeared that, based on a detailed NMR and FT-Raman analysis of oligomers and model compounds, the low band gap of PITN could be associated with the quinoid structure. However, a theoretical analysis of the UV-vis data of a series of aromatic isothianaphthene oligomers indicates that a substantial lowering of the band gap can be obtained in planar aromatic isothianaphthene systems.

A parallel investigation of PTFITN, a soluble isothianaphthene analogue, gave some indications that this polymer should possess an aromatic structure. The aromatic structure makes it possible that the fluorines probably induce non planarity such that inter ring π -conjugation is lowered to a considerable extent. This could explain the increased band gap of 2.1 eV observed by Swann et al.^[6]

Analysis of a series of aza-analogues of PITN revealed that in these materials it should be possible to combine a planar aromatic geometry with enhanced processability. The 4,5-diaza and 4,7-diaza isothianaphthene polymers can therefore be considered as very promising low band gap materials.

Finally, we showed that it is possible to combine the aromatic isothianaphthene ring system with another heterocycle such as thiophene in a *formal* copolymer. Through the development of a highly specific and efficient synthesis route to 1,3-dithienylisothianaphthene (DTI, **4**), we established the basis for the further synthesis and study of *formal* copolymers with tailor-made electronic properties.

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Experimental Section

12.1 Measurements

^1H , ^2H , ^{13}C and ^{19}F NMR spectra of the compounds were obtained with a Varian Unity 400 spectrometer. Most of the spectra were recorded in CDCl_3 at 30 °C, the chemical shifts of the carbon and the residual hydrogen being 77.0 and 7.24 ppm respectively (relative to tetramethylsilane) and which were used to reference the ppm scale. For *trans*-3,3'-bibenzo[*c*]thienylidene-1,1'-dione (**11**), we employed $\text{C}_2\text{D}_2\text{Cl}_4$ ($\delta\text{H} = 5.98$ and $\delta\text{C} = 73.7$ ppm relative to TMS) at 90 °C in place of CDCl_3 , because of the lack of solubility. The fluorine spectra were referenced externally against monofluorobenzene (35% in CFCl_3 with 12.5% CDCl_3 for lock) at -113.43 ppm which was referenced against CFCl_3 at 0 ppm.^[1, 2] The ^2H spectra were referenced externally against CDCl_3 at 7.24 ppm which was referenced against D_2O at 0 ppm. Assignments were made on the basis of the coupling patterns, the integration, one dimensional nuclear Overhauser effect (NOE), attached proton tests (APT), attached fluorine tests (AFT), selective irradiation experiments, two dimensional ^1H - ^1H COSY and ^{19}F - ^{19}F COSY experiments, two dimensional ^1H - ^{13}C heteronuclear correlation (HETCOR) experiments optimised for $J_{\text{CH}} = 140$ Hz and $J_{\text{CH}} = 8$ Hz and two dimensional ^{19}F - ^{13}C heteronuclear correlation (HETCOR) experiments optimised for $J_{\text{CF}} = 255$ Hz and $J_{\text{CF}} = 45$ Hz.

The IR spectra were recorded with a Philips Pye Unicam SP-300. The FT-IR and the FT-Raman data were obtained via a IFS 66 FT-IR spectrometer (excitation wavelength: 1064 nm) connected to a Bruker computer (ASPECT 1000) equipped with a Raman FRA 106 module. The mass spectra were obtained via a Finigan 1020 and a TSQ 70 apparatus. The UV-VIS spectra were recorded on a Perkin Elmer Lambda 5 (transmission mode) using uvasol quality n-hexane (Merck).

12.2 Synthetic Procedures

Solvents were dried and distilled prior to use. THF was distilled over sodium/benzophenone, acetonitrile was distilled from CaH_2 , dichloromethane was distilled from phosphorus pentoxide. All compounds were crystallised or distilled prior to use. Most of the products were purchased from Acros Chimica (previous Janssen Chimica). 3,4,5,6-Tetraduterophthaloyl dichloride (99.4 atom%) was purchased from Icon Services Inc. 3,4,5,6-Tetrafluorophthaloyl dichloride was purchased from Aldrich.

12.2.1 Synthesis of the Disilylated Aromatic Model Compounds

Thiophthalic anhydride (14)

40g (0.27 mole) phthalic anhydride was thoroughly mixed with 80g (0.33 mole) of sodium sulphide nonahydrate. The resulting liquid was stirred for 5 h. Addition of 100 mL of water gave a yellow solution which was added slowly to 2 L of HCl (5%). When the addition was completed, the mixture was stirred for an additional hour and filtered. The residue was dissolved in chloroform, washed with NaHCO_3 (1M) and water, and dried over magnesium sulphate. After crystallisation from chloroform/n-hexane, 35g of white thiophthalicanhydride crystals was obtained (yield 78%).

mp 105.5°C; FT-IR (KBr, ν , cm^{-1}): 1780, 1690, 1655, 1580, 1474, 1454, 1327, 1223, 949, 833, 783, 710, 455; MS (EI, m/e): 164 (M^+), 104 ($\text{M}^+ - \text{COS}$), 76 ($\text{M}^+ - (\text{CO})_2\text{S}$); ^1H NMR (CDCl_3 , 400 MHz, relative to TMS): 7.82 (dd, 2, $J=2.9/5.1$ Hz), 7.97 (dd, 2, $J=2.9/5.1$ Hz); ^{13}C NMR (CDCl_3 , 400 MHz, relative to TMS): 123.7 (CH), 135.0 (CH) 138.7 (C), 189.8 (CO).

1,1,3,3-Tetrachlorothiophthalan (15)

An intimate mixture of 24.6g (0.15 mole) thiophthalic anhydride and 78.0g (0.37 mole) phosphorus pentachloride was heated in an oil bath (150°C) for 15 h. Phosphorus oxychloride formed during the reaction was evaporated under reduced pressure. Toluene (10 mL) was added and removed under reduced pressure (2x). The residue was dissolved in chloroform and washed with NaHCO_3 (1M) and water. The organic phase was dried over magnesium sulphate and crystallised from n-hexane to yield 36.7g of white crystals (90%).

mp 111.5°C; FT-IR (KBr, ν , cm^{-1}): 2773, 2692, 2631, 1975, 1933, 1813, 1710, 1635, 1474, 1454, 1231, 1180, 1099, 887, 806, 700, 610, 440; MS (EI, m/e): 237 ($M^+ - \text{Cl}$), 202 ($M^+ - 2\text{Cl}$), 167 ($M^+ - 3\text{Cl}$); ^1H NMR (CDCl_3 , 400 MHz, relative to TMS): 7.63 (dd, 2, $J=3.1/6.0$ Hz), 7.78 (dd, 2, $J=3.1/6.0$ Hz); ^{13}C NMR (CDCl_3 , 400 MHz, relative to TMS): 123.8 (CH), 131.5 (CH), 142.0 (C), 92.6 (CCl_2).

1,3-Bis(*tert*-butyldimethylsilyl)isothianaphthene (7)

n-Butyl lithium (0.14 mole, 9g, 87.5mL/1.6M solution in *n*-hexane) was added dropwise to a stirred solution of 11g (0.04 mole) of 1,1,3,3-tetrachlorothiophthalan in 160 mL of THF at -78°C followed by the addition of 15.1g (0.1 mole) of *tert*-butyldimethylsilylchloride in 30 mL of THF. The mixture was allowed to warm to room temperature and stirred for an additional 30 min. It was then poured in ice-water, extracted into *n*-hexane and dried over magnesium sulphate. The obtained product was purified by column chromatography (silica, *n*-hexane) to give 13.7g of a yellow crystalline solid (95%). Further purification by crystallisation from chloroform/acetonitrile gave white crystals (yield 71%).

mp 78°C; FT-IR (KBr, ν , cm^{-1}): 3090, 2951, 2928, 2854, 2708, 1470, 1358, 1254, 1138, 1003, 964, 806, 768; FT-Raman (cm^{-1}): 3074 (m), 2957 (s), 2928 (s), 2900 (s), 2858 (s), 1512 (m), 1463 (m), 1448 (s), 1369 (s), 1358 (m), 1300 (m), 1200 (w), 1015 (m), 940 (w), 830 (w), 582 (m), 476 (m), 185 (w); MS (EI, m/e): 362 (M^+), 305 ($M^+ - \text{tert-butyl}$), 249, 233, 173, 159, 145, 131, 73, 57; ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 0.54 (s, 12, $\text{CH}_3\text{-Si}$), 0.98 (s, 18, $\text{CH}_3\text{-C}$), 7.11 (dd, 2, $J=2.9/6.7$ Hz, H5), 7.83 (dd, 2, $J=2.9/6.7$ Hz, H4); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): -3.9 (Si-CH_3), 18.2 ($\text{CH}_3\text{-C}$), 26.8 (C-CH_3), 135.0 (C3), 146.5 (C3a), 122.6 (C5), 124.0 (C4).

Oligomerisation

A solution of 6.1 mL (55.1 mmol) titanium tetrachloride in 60 mL dichloromethane was added all at once at room temperature to a solution of 10g (27.6 mmol) of 1,3-bis(*tert*-butyldimethylsilyl)isothianaphthene in 60 mL dichloromethane. After being stirred for max. 10h, the violet reaction mixture was poured into ice-water, extracted with ether and dried over magnesium sulphate. The residue from ether was subjected to column chromatography (silica, *n*-hexane) to give the dimer (0.55g), the trimer (0.34g) and the tetramer (0.24g). The resulting solids were further purified by crystallisation from chloroform/acetonitrile.

Dimer (8)

mp 145-147°C; FT-IR (KBr, ν , cm^{-1}): 3059, 2951, 2928, 2854, 1466, 1389, 1358, 1250, 1007, 976, 806, 744; FT-Raman (cm^{-1}): 3074 (w), 2957 (w), 2928 (w), 2900 (w), 2858 (w), 1517 (w), 1497 (s), 1449 (s), 1428 (w), 1372 (w), 1320 (m), 1185 (w), 889 (vw), 755 (w), 578 (w), 475 (m), 199 (w); MS (EI, m/e): 494 (M^+), 437 (M^+ - *tert*-butyl); ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 0.56 (s, 12, $\text{CH}_3\text{-Si}$), 1.02 (s, 18, $\text{CH}_3\text{-C}$), 7.10-7.18 (m, 4, H5 and H6), 7.76 (m, 2, H4), 7.86 (m, 2, H7); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): -3.9 (Si-CH_3), 18.2 ($\text{CH}_3\text{-C}$), 26.8 (C-CH_3), 129.2 (C3), 145.6 (C3a), 123.9 (C4), 123.7 (C5), 123.6 (C6), 122.0 (C7), 137.5 (C7a), 132.2 (C1).

Trimer (9)

FT-IR (KBr, ν , cm^{-1}): 3063, 2951, 2924, 2854, 1466, 1385, 1358, 1254, 1092, 1003, 980, 806, 768; FT-Raman (cm^{-1}): 3074 (vw), 2957 (vw), 2928 (vw), 2900 (vw), 2858 (vw), 1610 (vw), 1521 (vw), 1489 (m), 1448 (s), 1360 (w), 1331 (m), 1192 (w), 474 (w), 188 (w); MS (EI, m/e): 626 (M^+), 569 (M^+ - *tert*-butyl); ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 0.55 (s, 12, $\text{CH}_3\text{-Si}$), 1.02 (s, 18, $\text{CH}_3\text{-C}$), 7.14-7.18 (m, 6, H5[A,B] and H6[A]), 7.75 (m, 2, H4[A]), 7.86 (dd, 2, $J=3.0/7.0$ Hz, H4[B]), 7.94 (m, 2, H7[A]); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): -3.9 (Si-CH_3), 18.2 ($\text{CH}_3\text{-C}$), 26.8 (C-CH_3), 129.8 (C3[A]), 145.6 (C3a[A]), 124.0 (C4[A]), 123.8 (C5[A]), 123.9 (C6[A]), 121.9 (C7[A]), 137.6 (C7a[A]), 131.6 (C1[A]), 126.7 (C3[B]), 136.5 (C3a[B]), 121.9 (C4[B]), 124.7 (C5[B]).

Tetramer (10)

FT-IR (KBr, ν , cm^{-1}): 3063, 2951, 2924, 2854, 1466, 1408, 1358, 1254, 1007, 976, 802, 768; FT-Raman (cm^{-1}): 1641 (w), 1486 (w), 1444 (s), 1355 (w), 1333 (s), 1196 (w), 1151 (w), 977 (w), 892 (w), 749 (w), 470 (w), 185 (w); MS (EI, m/e): 758 (M^+), 701 (M^+ - *tert*-butyl); ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 0.55 (s, 12, $\text{CH}_3\text{-Si}$), 1.02 (s, 18, $\text{CH}_3\text{-C}$), 7.12-7.20 (m, 8, H5[A,B] and H6[A,B]), 7.76 (m, 2, H4[A]), 7.89 (m, 2, H4[B]), 7.99 (m, 4, H7[A,B]); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): -3.9 (Si-CH_3), 18.2 ($\text{CH}_3\text{-C}$), 26.8 (C-CH_3), 130.0 (C3[A]), 145.6 (C3a[A]), 124.0 (C4[A]), 123.8 (C5[A]), 123.9 (C6[A]), 121.9 (C7[A]), 137.7 (C7a[A]), 131.5 (C1[A]), 127.0 (C3[B]), 136.6* (C3a[B]), 122.0 (C4[B]), 124.9 (C5[B]), 125.0 (C6[B]), 121.9 (C7[B]), 136.7* (C7a[B]), 126.1 (C1[B]) (*: may be interchanged).

12.2.2 Quinoid Model Compounds

trans-3,3'-Bibenzo[*c*]thienylidene-1,1'-dione (11)

trans-3,3'-Bibenzo[*c*]thienylidene-1,1'-dione (**Q3**) was prepared according to the procedure described by Bird and Wong^[3] (yield 35-45%): Subl pt 350 °C; IR (KBr, ν , cm^{-1}) 1690, 1590, 1570, 1470, 1280, 1230, 1200, 915, 830, 765, 695; MS (m/e): 296, 280, 268, 252, 240, 232, 224, 204, 195, 176, 163, 152, 134, 120; ^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 90 °C, in ppm relative to TMS) 8.34 (d, 2, $J=7.5$ Hz, H4), 8.00 (d, 2, $J=7.5$ Hz, H7), 7.83 (t, 2, $J=7.5$ Hz, H5), 7.61 (t, 2, $J=7.5$ Hz, H6); ^{13}C NMR (100 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 90 °C, in ppm relative to TMS) 190.1 (C1), 142.3 (C3a), 134.3 (C7a), 133.8 (C5), 129.4 (C6), 128.3 (C3), 126.9 (C4), 124.4 (C7).

trans-3,3'-Bibenzo[*c*]thienylidene (12)

To a solution of 0.54 g (14.3 mmol) of NaBH_4 in 7.5 mL diglyme (dried by refluxing with CaH_2), stirred at room temperature in an atmosphere of N_2 , was added portion wise 1.18 g (4 mmol) *trans*-3,3'-bibenzo[*c*]thienylidene-1,1'-dione (**Q3**). To this mixture was added dropwise during 30 min a solution of boron trifluoride etherate in 3 mL of diglyme. The ratio of $\text{NaBH}_4:\text{BF}_3$ was 3:4, as required stoichiometrically for the formation of B_2H_6 . Stirring at room temperature was continued for 2 h. The reaction mixture was worked up by addition of ice water, followed by filtration, washing and drying under vacuum. Column chromatography of the crude product on silica gel using chloroform as eluant yielded **Q4** (45%) as a red crystalline product.

mp. 138 - 140 °C; IR (KBr, ν , cm^{-1}) 2920, 2040, 1590, 1470, 1440, 815, 755, 705; MS (m/e): 268, 235, 221, 202, 189, 134; ^1H NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) 8.24 (d, 2, $J=7.6$ Hz, H4), 7.39 (t, 2, $J=7.6$ Hz, H6 or H5), 7.35 (d, 2, $J=7.6$ Hz, H7), 7.25 (t, 2, $J=7.6$ Hz, H5 or H6), 4.51 (s, 4, H1); ^{13}C NMR (100 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) 141.0 (C7a), 140.4 (C3a), 127.4 (C3), 126.9 (C5 and C6), 125.2 (C4), 125.0 (C7), 38.0 (C1).

12.2.3 Fluorinated Aromatic Model Compounds

4,5,6,7-Tetrafluorobenzo[*c*]thiophene oligomers (20 - 23)

Oligomers were synthesised as reported by Brooke et al.^[4] by lithiation of the 4,5,6,7-tetrafluoroisothianaphthene monomer and coupling with copper(II)chloride followed by work up and separation by column chromatography.

4,5,6,7-tetrafluoroisothianaphthene (monomer) (20)

IR (KBr, ν , cm^{-1}): 3131, 1683, 1653, 1579, 1541, 1495, 1440, 1408, 1355, 1262, 1191, 1159, 1120, 1036, 992, 868, 763, 681, 625, 483; FT-Raman (ν , cm^{-1}): 3135, 1686, 1581, 1541, 1498, 1382, 1359, 1322, 1297, 1265, 1158, 1126, 990, 892, 874, 767, 748, 682, 631, 612, 486, 453, 404, 349, 296, 279, 228, 194, 153, 122, 86; ^1H NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) 7.82 (t, 2, $J = 1.5$ Hz, H3); ^{13}C NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) 115.55 (C3), 125.68(C3a), 136.66 (C5), 138.34 (C4); ^{19}F NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) -149.22 ($J = 1.5, 15.6$; F4), -162.99 ($J = 15.6$; F5)

Dimer (21)

IR (KBr, ν , cm^{-1}): 1671, 1641, 1570, 1508, 1489, 1429, 1409, 1372, 1349, 1248, 1219, 1160, 1135, 1077, 1055, 1037, 978, 958, 912, 853, 835, 802, 754, 728; FT-Raman (ν , cm^{-1}): 3134, 3111, 1685, 1584, 1547, 1491, 1445, 1356, 1249, 1230, 1193, 1138, 1120, 1048, 1024, 975, 943, 898, 761, 749, 720, 705, 648, 632, 534, 492, 461, 403, 375, 324, 295, 282, 239, 207, 188, 126, 81; ^1H NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) 8.00 (H3); ^{13}C NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) 117.51 (C3), 123.74 (C1), 123.92 (C7a), 126.60 (C3a), 136.68 (C5), 137.96 (C6), 138.01 (C4), 139.46 (C7); ^{19}F NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) -149.31 (F4), -150.10 (F7), -160.36 (F6), -162.06 (F5)

Trimer (22)

IR (KBr, ν , cm^{-1}): 3128, 2957, 2925, 2855, 1677, 1656, 1639, 1628, 1581, 1526, 1490, 1467, 1450, 1438, 1380, 1350, 1255, 1232, 1186, 1141, 1123, 1085, 1060, 1027, 995, 958, 930, 881, 760, 748, 717, 674, 646, 627, 525, 431; FT-Raman (ν , cm^{-1}): 1583, 1546, 1495, 1454, 1355, 186, 125; ^1H NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) 8.05 (H3(A)); ^{13}C NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) 118.10 (C3(A)), 122.81 (C1(A)), 124.06 (C7a(A)), 124.70 (C3a(B)), 125.37 (C3(B)), 126.72 (C3a(A)), 136.79 (C5(A)), 137.97 (C5(B)), 138.076 (C4(A)), 138.178 (C6(A)), 139.30 (C4(B)), 139.45 (C7(A)); ^{19}F NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) -148.97 (F4(A)), -149.41 (F4(B)), -149.70 (F7(A)), -159.666 (F6(A)), -159.672 (F5(B)), -161.66 (F5(A))

Tetramer (23)

IR (KBr, ν , cm^{-1}): 3112, 2920, 2851, 1681, 1579, 1526, 1489, 1352, 1260, 1234, 1182, 1135, 1058, 1031, 1000, 952, 911, 884, 802, 761, 711, 658, 627, 474; FT-Raman (ν , cm^{-1}): 3113, 1682, 1584, 1540, 1493, 1458, 1354, 1265, 1234, 1198,

1155, 1125, 1066, 988, 954, 892, 804, 764, 740, 691, 643, 628, 544, 491, 467, 440, 405, 384, 366, 327, 286, 271, 243, 189, 156, 117, 94; ^1H NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) 8.07 (H3(A)); ^{13}C NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) 118.310 (C3(A)), 122.560 (C1(A)), 124.082 (C7a(A)), 124.302 (C1(B)), 124.721 (C3a(B)), 124.778 (C7a(B)), 126.000 (C3(B)), 126.724 (C3a(A)), 136.800 (C5(A)), 138.011 (C5(B)), 138.078 (C4(A)), 138.140 (C6(B)), 138.217 (C6(A)), 139.261 (C4(B)), 139.338 (C7(B)), 139.428 (C7(A)); ^{19}F NMR (400 MHz, CDCl_3 , 30 °C, in ppm relative to TMS) -148.96 (F4(A)), -149.20 (F4(B)), -149.20 (F7(B)), -149.78 (F7(A)), -159.14 (F6(B)), -159.45 (F5(B)), -159.56 (F6(A)), -161.65 (F5(A))

12.2.4 Nitrogen Containing Aromatic Model Compounds

Pyrazine-2,3-dicarboxylic anhydride (29)

50 mL Acetic anhydride, which was dried on sodium and distilled prior to use, was added to 8.7g (0.052 mole) pyrazine-2,3-dicarboxylic acid. This mixture was then heated till all product was dissolved. The so obtained solution was then allowed to cool down resulting in the precipitation of pyrazine-2,3-dicarboxylic anhydride crystals. (Yield: 86%)

mp: 186°C; IR (KBr, ν , cm^{-1}): 1880, 1790, 1300, 1165, 1135, 725; MS (EI, m/e): 168 (M^+), 140, 108, 96, 80;

Pyrazine-2,3-dicarboxylic thioanhydride (30)

4.0 g (0.027 mole) Pyrazine-2,3-dicarboxylic anhydride was mixed intimately together with 8.0 g (0.033 mole) $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. This resulted in a pale yellow liquid, which after 3 h was diluted with water and stirred for an additional 30 min. This solution was then added slowly to a 5% HCl solution. The red precipitate which was formed during addition was filtered off and dried *in vacuo* above phosphorus pentoxide.

mp: 98°C; IR (KBr, ν , cm^{-1}): 1730, 1660, 1250; MS (EI, m/e): 166 (M^+), 106, 78;

Pyrazine-1,1,2,2-tetrachlorothiophthalan (31)

2.5g (0.015 mole) Pyrazine-2,3-dicarboxylic thioanhydride was heated together with 7.8g (0.037 mole) PCl_5 at 160°C for 15 h. After successive addition and evaporation of 10 mL of toluene (2x) a blackish liquid was obtained. This reaction mixture was next washed with NaHCO_3 (1M) and dried over magnesium sulphate.

12.2.5 1,3-Dithienylisothianaphthene and Related Compounds

o-Aryl dicarbonyl chlorides

A. 0.0084 mole *o*-aryldicarboxylic acid and 0.0252 mole (5.25g) phosphorus pentachloride were slowly heated to 180°C was reached (caution: HCl evolution at a temperature of about 60°C). The mixture was kept for 2 hours at 180°C under vigorous stirring and then allowed to cool down to room temperature. The remaining phosphorus pentachloride was removed by filtration of the liquid into a vacuum distillation apparatus. The reaction flask was washed with 10 mL toluene and the solvent was also filtered into the vacuum distillation apparatus. The purification by vacuum distillation yielded a liquid which was further used in the thioester synthesis.

B. A mixture of 18 mL toluene and 0.1 mole distilled SOCl_2 and 0.0084 mole *o*-aryldicarboxylic acid were refluxed for 1.5 hour. The solvent and remaining SOCl_2 were distilled off and the product was further purified by vacuum distillation.

2,3-Pyridinoyl dichloride

Yield: 1.56g (91%); bp. 140°C (4 mmHg); IR (NaCl, v, cm^{-1}): 3500, 3080, 1780, 1740, 1550, 1420, 1320, 1250, 1220, 1160, 1110, 970, 900, 860, 800, 770, 700, 640; MS (CI, m/e): 204 (MH^+), 168 (MH^+-Cl); ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.72 (dd; 1H; $J=4.78$, 7.99 Hz; H5), 8.32 (d; 1H; $J=1.51$, 8.03 Hz; H4), 8.84 (d; 1H; $J=1.53$, 4.79 Hz; H6); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 126.94 (C5), 128.96 (C3), 138.60 (C4), 149.46 (C2), 152.99 (C6), 166.25 (C8), 167.36 (C7)

2,3-Pyrazinoyl dichloride

Yield: 0.5g (29%); bp: 125°C (4 mmHg); IR (NaCl, v, cm^{-1}): 3500, 3040, 1780, 1730, 1550, 1530, 1380, 1260, 1240, 1140, 1050, 910, 860, 810, 730, 630; MS (EI, m/e): 205 (M^+), 169 (M^+-Cl), 113 ($\text{M}^+-\text{COCl}-\text{CO}$), 106 ($\text{M}^+-\text{COCl}-\text{Cl}$), 78 (M^+-2COCl); ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 8.91 (s; 2H; H6/H5); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 144.40 (C2/C3), 146.78 (C5/C6), 166.76 (C7/C8)

3,4-Pyridinoyl dichloride

Yield: 1.56 g (91%); bp: 145°C (4mmHg); IR (NaCl, v, cm^{-1}): 3500, 2940, 2840, 1780, 1660, 1560, 1440, 1410, 1200, 1110, 1050, 900, 750, 660; MS (EI, m/e): 205 (M^+), 169 (M^+-Cl), 140 (M^+-CO), 113 ($\text{M}^+-\text{COCl}-\text{CO}$), 106 ($\text{M}^+-\text{COCl}-\text{Cl}$), 78 (M^+-2COCl); ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.62 (d; 1H; $J=4.86$ Hz; H5), 8.83 (d; 1H; $J=4.89$ Hz; H6), 8.97 (s; 1H; H2); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 121.90 (C5), 125.78 (C3), 141.69 (C4), 150.06 (C2), 153.05 (C6), 166.80 (C7), 167.96 (C8).

3,4,5,6-Tetrafluorophthaloyl dichloride (27)

Yield: 2.2g (94%); bp: 180°C (5mmHg); IR (NaCl, v, cm^{-1}): 1770, 1490, 1390, 1205, 1100, 930, 910, 720; MS (CI, m/e): 275 (MH^+), 239, 221, 165; ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 120.06 (C), 143.6 (CF), 145.5 (CF), 161.5 (CO); ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to CFCl_3): -134.56, -144.82

3,4,5,6-Tetradeuterophthaloyl dichloride

Yield: g (84%); bp: 204°C (5mmHg) °C; IR (NaCl, v, cm^{-1}): 1780, 1750, 1550, 1390, 1290, 1220, 1160, 1140, 1030, 960, 890, 840, 820, 770, 750;

3,3-Di(S-phenyl)-3H-isobenzofuran-1-one (45)

A solution of 5mL triethylamine, 15 mL THF and 1.5 mL (0.0146 mole, 1.609g) thiophenol was stirred for 15 minutes at room temperature. A solution of 1 mL (0.0069 mole, 1.409g) phthaloyl dichloride in 10 mL THF was added. The reaction mixture was stirred for another 2 hours and was then worked up by adding 200 mL HCl (1%). After extraction with chloroform the combined fractions were washed with a NaOH (10%) solution and water and finally dried over magnesium sulphate. The product was purified by column chromatography (silica, chloroform/n-hexane) and crystallisation from hexane to yield 1.9g (79%).

mp: 101.9-102.3°C; IR (KBr, v, cm^{-1}): 1770, 1465, 1440, 1280, 1235, 1065, 915, 835, 740, 685; FT-Raman (cm^{-1}): 3147, 3088, 3058, 1779, 1606, 1582, 1467, 1284, 1243, 1191, 1158, 1087, 1027, 1002, 943, 917, 882, 841, 787, 745, 715, 704, 617, 584, 532, 492, 398, 379, 312, 292, 240, 218, 189, 154, 109, 88; MS (CI and EI, m/e): 351 ($\text{M}+1$), 306 ($\text{M}-\text{CO}_2$), 241 ($\text{M}-\text{SAr}$), 197 ($\text{M}-\text{CO}_2-\text{SAr}$), 109 (SAr), 104 (ArCO^+), 76 (Ar^+); ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.16 (t; 4H;

$J = 7.36$ Hz; $H3'$), 7.26 (t; 2H; $J = 7.48$ Hz; $H4'$), 7.32 (d; 1H; $J = 7.63$ Hz; $H6$), 7.38 (d; 4H; $J = 7.31$ Hz; $H2'$), 7.44 (d; 1H; $H7$), 7.64 (t; 1H; $J = 7.31$ Hz; $H5$), 7.71 (d; 1H; $J = 7.72$ Hz; $H4$); ^{13}C NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS): 99.1 ($C3$), 123.3 ($C4$), 124.5 ($C7$), 125.8 ($C7a$), 128.3 ($C1'$), 128.7 ($C3'$), 129.78 ($C6$), 129.82 ($C4'$), 134.2 ($C5$), 136.4 ($C2'$), 148.7 ($C3a$), 167.1 ($C1$)

3-(S-phenyl)-3H-isobenzofuran-1-one (46)

A solution of 100 mL of triethylamine and 18 mL (0.263 mole) of thiophenol was stirred for 15 minutes at room temperature. A solution of 6 mL (0.0414 mole) phthaloyl dichloride in 50 mL of THF was added. The reaction mixture was stirred for 48 hours at room temperature or 10 hours at 60°C and was then worked up by adding 200 mL of HCl (1%). After repeated extractions with chloroform the combined fractions were washed with NaOH (10%) and water and finally dried over magnesium sulphate. The product was purified by column chromatography (silica, chloroform/n-hexane) and crystallisation from hexane to yield 8.7 g (87%).

mp: 103.5–103.8°C; IR (KBr, ν , cm^{-1}): 1750 (ν_{COO} lacton), 1590, 1450, 1420, 1280, 1030, 1000, 940, 740, 720, 670, 1190; FT-Raman (cm^{-1}): 3148, 3065, 2957, 2883, 1756, 1602, 1585, 1470, 1439, 1339, 1291, 1237, 1199, 1181, 1160, 1129, 1090, 1056, 1027, 1016, 1003, 951, 884, 813, 794, 775, 730, 703, 680, 615, 575, 526, 493, 473, 426, 368, 299, 238, 222, 173, 129, 98; MS (EI, m/e): 242 (M^+), 133 ($M^+ - SAr$), 109 (SAr), 76 (Ar^+); 1H NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS): 6.71 (s; 1H; $H3$), 7.22 – 7.28 (m; 3H; $H3'$, $H4'$), 7.47 – 7.51 (m; 3H; $H6$, $H2'$), 7.69 (t; 1H; $J = 7.48$ Hz; $H4$), 7.64 (d; 1H; $J = 7.64$ Hz; $H5$), 7.77 (d; 1H; $J = 7.73$ Hz; $H7$); ^{13}C NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS): 86.4 ($C3$), 123.4 ($C4$), 125.3 ($C7$), 126.1 ($C7a$), 128.8 ($C4'$), 129.0 ($C3'$), 129.9 ($C6$), 130.2 ($C1'$), 133.6 ($C2'$), 134.2 ($C5$), 146.0 ($C3a$), 169.0 ($C1$)

1,2-(S-phenyl)-benzenedithioate (41)

A. A solution of 5 mL triethylamine, 15 mL THF and 1.5 mL (0.0146 mole, 1.609 g) thiophenol was stirred for 15 minutes at 0°C. A solution of 1 mL (0.0069 mole, 1.409 g) phthaloyl dichloride in 10 mL of THF was added. Immediately the reaction mixture was then worked up by adding 200 mL HCl (1%). After extraction with chloroform the combined fractions were washed with a NaOH (10%) solution and water and finally dried over magnesium sulphate. The product was purified by crystallisation from dichloromethane/diethyl ether to yield 1.8 g (77 %).

B. 5.8 mL (0.04 mole) phthaloyl dichloride was added dropwise at a temperature of 0°C to 8.2 mL (0.08 mole) thiophenol in a methanolate solution prepared by adding 1.74 g Na to 50 mL methanol. The precipitate was filtered off and washed with water and ice-cold methanol. Yield: 13.2 g (94%).

mp: 130.3–130.5°C; IR (KBr, ν , cm^{-1}): 1670 (ν_{COS}), 1570, 1485, 1445, 1095, 1210 (ν_{COSAr}), 1190 (ν_{COSAr}), 1120, 1030, 900, 780, 745 (doublet), 710, 690, 665; FT-Raman (cm^{-1}): 3145, 3108, 3061, 3024, 2995, 2953, 1685, 1588, 1572, 1478, 1442, 1302, 1276, 1211, 1196, 1176, 1161, 1089, 1045, 1025, 1002, 914, 874, 764, 706, 665, 637, 617, 591, 570, 510, 472, 417, 398, 366, 308, 286, 242, 220, 188, 174, 144, 116, 91; MS (EI, m/e): 351 (M^+), 241 ($M^+ - \text{SAr}$), 213 ($M^+ - \text{COSAr}$), 109 (SAr), 104 (ArCO^+), 76 (Ar^+); ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.42 (m; 6H; H3' , H4'), 7.52 (m; 4H; H2'), 7.60 (dd; 2H; $J = 3.2, 5.6$ Hz; H3), 7.82 (dd; 2H; $J = 3.2, 5.6$ Hz; H2); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 191.6 (C4), 137.1 (C1), 134.6 (C2'), 131.6 (C3), 129.6 (C4'), 129.2 (C3'), 128.3 (C2), 127.4 (C1')

1,2-(S-(2-pyridinyl))-benzenedithioate (42)

A solution of 5 mL of triethylamine, 50 mL of THF and 3.3 g (0.030 mole) 2-mercaptopyridine was stirred for 15 minutes at 0°C. A solution of 2.2 mL (0.015 mole) phthaloyl dichloride in 50 mL of THF was added all at once. Immediately the reaction was then quenched by adding 200 mL of HCl (1%). After extraction with chloroform the combined fractions were washed with 500 mL of NaOH (10%), 500 mL of NaHCO_3 (1M) and 500 of mL water. The chloroform solution was finally dried over magnesium sulphate. The product was purified by crystallisation from dichloromethane/diethyl ether to yield 4.4 g (84 %).

mp: 109.7°C; IR (KBr, ν , cm^{-1}): 1680, 1655, 1570, 1450, 1420, 1200, 1185, 1115, 900, 860, 765, 750, 690, 655; FT-Raman (cm^{-1}): 3145, 3126, 3066, 3053, 3018, 2994, 1692, 1665, 1591, 1573, 1478, 1454, 1422, 1304, 1284, 1210, 1169, 1152, 1121, 1084, 1046, 992, 911, 872, 772, 754, 727, 694, 660, 644, 618, 587, 570, 516, 484, 464, 442, 411, 344, 314, 294, 246, 219, 168, 105; MS (EI, m/e): 242 ($M^+ - \text{S-Ar}$), 214 ($M^+ - \text{COS-Ar}$); ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.27 (t; 2H; $J = 6.17$ Hz; H5'), 7.61 (dd; 2H; $J = 3.32, 5.77$ Hz; H3), 7.71 (td; 2H; $J = 1.86, 7.50$ Hz; H4'), 7.74 (dt; 2H; $J = 1.14, 7.38$ Hz; H3'), 7.84 (dd; 2H; $J = 3.23, 5.65$ Hz; H2), 8.59 (d; 2H; $J = 4.57$ Hz; H6'); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 123.7 (C5'), 128.5 (C2), 130.4 (C3'), 132.0 (C3), 136.8 (C1), 137.2 (C4'), 150.4 (C6'), 151.3 (C2'), 190.2 (C4)

1,2-(S-(2-pyridinyl))-3,4,5,6-tetradeuterobenzenedithioate

This compound was prepared according to the synthesis described for 1,2-(S-(2-pyridinyl))-benzenedithioate. Yield: 77%.

IR (KBr, ν , cm^{-1}): 1680, 1650, 1570, 1560, 1535, 1450, 1420, 1385, 1285, 1160, 1135, 1120, 1090, 1050, 1025, 995, 890, 850, 840, 820, 770, 760, 745, 730, 685, 680, 655, 615, 580, 480, 400; MS (EI, m/e): 356, 246, 218, 186, 158, 108, 78, 51

1,2-(S-(2-pyridinyl))-3,4,5,6-tetrafluorobenzenedithioate (27)

The reaction was carried out in a glove box under nitrogen atmosphere at an ambient temperature of 10°C due to the reactivity of the thioester and its sensitivity towards moisture. A sodium methanolate solution was prepared by adding at 0°C 0.015 mole (0.35g) Na to 50 mL methanol and 0.0168 mole (1.86g) 2-mercaptopyridine and this mixture was then cooled down to -78°C. A solution of 0.0084 mole (2.3g) 3,4,5,6-tetrafluorophthaloyl dichloride in 25 mL toluene was added dropwise under vigorous stirring. The precipitate was filtered off and rapidly washed with cold methanol (-78°C). Yield: 1.53g (43%)

mp: 71.5°C (decomposition); IR (KBr, ν , cm^{-1}): 1690, 1655, 1560, 1490, 1450, 1435, 1410, 1350, 1300, 1280, 1130, 1085, 980, 810, 790, 760, 740; FT-Raman (cm^{-1}): 3147, 3130, 3072, 3057, 2995, 2894, 1697, 1667, 1620, 1575, 1563, 1512, 1452, 1424, 1362, 1303, 1284, 1160, 1140, 1121, 1090, 1046, 990, 899, 820, 798, 752, 724, 686, 621, 587, 559, 488, 448, 411, 395, 365, 325, 310, 219, 206, 134, 109, 93; MS (EI, m/e): 424 (M^+), 333, 314, 305, 286, 258, 242, 223, 214, 195, 167, 148, 117; ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.30 ($J = 6.05, 4.84, 2.55$; $\text{H}5'$), 7.73 ($\text{H}4'$, $\text{H}3'$), 8.60 ($J = 4.71, 1.22$; $\text{H}6'$); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 121.67 ($\text{C}1$), 124.29 ($\text{C}5'$), 130.24 ($\text{C}3'$), 137.52 ($\text{C}4'$), 142.25 ($\text{C}3$), 144.94 ($\text{C}2$), 149.74 ($\text{C}2'$), 150.64 ($\text{C}6'$), 184.06 (CO); ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to CFCl_3): -135.81 ($\text{F}2$), -147.31 ($\text{F}3$)

2,3-(S-(2-pyridinyl))-pyridinedithioate (48)

A solution of 5mL of triethylamine, 15 mL of THF and 1.1 g (0.01 mole) 2-mercaptopyridine was stirred for 15 minutes at 0°C. A solution of 0.005 mole 2,3-pyridinoyl dichloride in 10 mL of diethyl ether was added. Immediately the reaction mixture was then worked up by adding 200 mL of HCl (1%). After extraction with chloroform the combined fractions were washed with 500 mL of NaOH (10%) and 500 mL of water. The chloroform solution was finally dried over magnesium sulphate. The

product was purified by crystallisation from dichloromethane/diethyl ether to yield 1.2g (68%).

mp: 145 °C; IR (KBr, ν , cm^{-1}): 1675, 1560, 1550, 1440, 1410, 1260, 1215, 1175, 1110, 920, 895, 815, 760, 715, 645; FT-Raman (cm^{-1}): 3127, 3084, 3053, 3012, 2995, 2896, 2848, 1789, 1685, 1645, 1575, 1563, 1452, 1426, 1281, 1261, 1238, 1217, 1179, 1152, 1122, 1085, 1070, 1048, 990, 921, 897, 817, 786, 739, 725, 660, 642, 620, 596, 579, 522, 492, 471, 438, 420, 345, 312, 292, 257, 218, 162, 128, 102; MS (EI, m/e): 353 (M^+), 243 (M^+ -S_{pyr}), 215 (M^+ -S_{pyr}-CO), 187 (M^+ -S_{pyr}-2CO), 105 (M^+ -2S_{pyr}-CO), 78 (M^+ -2S_{pyr}-2CO); ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.24-7.31 (2H; $\text{H}5'/\text{H}5''$), 7.614 (dd; 1H; $J = 4.70, 7.84$ Hz; $\text{H}5$), 7.67-7.79 (4H; $\text{H}3'/\text{H}3''/\text{H}4'/\text{H}4''$), 7.906 (dd; 1H; $J = 1.64, 7.80$ Hz; $\text{H}4$), 8.572 (dq; 1H; $J = 0.83, 1.80, 4.79$ Hz; $\text{H}6'$ or $\text{H}6''$), 8.646 (dq; 1H; $J = 0.88, 1.89, 4.84$ Hz; $\text{H}6'$ or $\text{H}6''$), 8.797 (dd; 1H; $J = 1.59, 4.71$ Hz; $\text{H}6$); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 123.58 ($\text{C}5'$ or $\text{C}5''$), 123.87 ($\text{C}5'$ or $\text{C}5''$), 127.21 ($\text{C}5$), 130.35 ($\text{C}3'$ or $\text{C}3''$), 130.74 ($\text{C}3'$ or $\text{C}3''$), 133.60 ($\text{C}3$), 135.80 ($\text{C}4$), 137.07 ($\text{C}4'$ or $\text{C}4''$), 137.39 ($\text{C}4'$ or $\text{C}4''$), 147.65 ($\text{C}2$), 150.39 ($\text{C}6$), 150.42 ($\text{C}6'$ or $\text{C}6''$), 150.53 ($\text{C}6'$ or $\text{C}6''$), 150.83 ($\text{C}2'$ or $\text{C}2''$), 151.67 ($\text{C}2'$ or $\text{C}2''$), 189.91 ($\text{C}8$), 189.93 ($\text{C}7$)

2,3-(S-(2-pyridinyl))-pyrazinedithioate (49)

Synthesis as described for 2,3-(S-(2-pyridinyl))-pyridinedithioate.

Yield 0.8g (46%); mp: 137.6°C; IR (KBr, ν , cm^{-1}): 1675, 1570, 1440, 1410, 1255, 1150, 1115, 1060, 980, 920, 875, 775, 745, 720, 430, 410; Raman (cm^{-1}): 2999, 2981, 2945, 2898, 2789, 2763, 2728, 2624, 2500, 1481, 1467, 1446, 1401, 1366, 1292, 1190, 1081, 1038, 906, 853, 811, 764, 464, 336, 282, 131; MS (EI, m/e): 244 (M -S_{pyr}), 216 (M -COS_{pyr}), 188, 156, 111, 78; ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.26-7.32 (m; 2H; $\text{H}5'$), 7.72-7.75 (m; 4H; $\text{H}4/\text{H}3'$), 8.605 (dt; 2H; $J = 1.34, 4.79$ Hz; $\text{H}6'$), 8.805 (s; 2H; $\text{H}6$); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 123.83 ($\text{C}5'$), 130.43 ($\text{C}3'$), 137.28 ($\text{C}4'$), 145.82 ($\text{C}5 \equiv \text{C}6$), 146.00 ($\text{C}2 \equiv \text{C}3$), 150.58 ($\text{C}6'$), 150.79 ($\text{C}2'$), 188.73 ($\text{C}7$)

2,3-(S-phenyl)-pyrazinedithioate (50)

Synthesis as described for 2,3-(S-(2-pyridinyl))-pyridinedithioate.

Yield 0.98g (57%); mp: 151.2-151.8°C; IR (KBr, ν , cm^{-1}): 1670, 1525, 1450, 1420, 1370, 1250, 1140, 1045, 1005, 920, 890, 865, 735, 690, 670; Raman (cm^{-1}): 3152, 3063, 2949, 2564, 2360, 2132, 1679, 1583, 1548, 1527, 1435, 1392, 1261, 1242, 1179, 1160, 1116, 1091, 1062, 1027, 1003, 937, 903, 807, 749, 707, 646, 616, 603, 518, 457, 428, 407, 365, 286, 220, 112; MS (EI, m/e): 243, 215, 187, 160, 133,

109, 77, 65; ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.40-7.45 (6H; $\text{H}3'$ and $\text{H}4'$), 7.52-7.55 (4H; $\text{H}2'$), 8.76 (s; 2H; $\text{H}5\equiv\text{H}6$); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 126.44 ($\text{C}1'$), 129.40 ($\text{C}3'$), 129.89 ($\text{C}4'$), 134.84 ($\text{C}2'$), 145.69 ($\text{C}5\equiv\text{C}6$), 146.37 ($\text{C}2\equiv\text{C}3$), 189.63 ($\text{C}7$)

3,3-Dithienyl-3H-isobenzofuran-1-one (44)

0.004 mole phthaloyl dichloride (0.6mL) and 1.276g AlCl_3 were mixed thoroughly for 5 minutes at 0°C . 0.012 mole thiophene (1mL) in 20 mL of dichloromethane was added slowly. The mixture was allowed to warm up to room temperature and was stirred for another 30 minutes. The reaction was worked up by pouring the mixture in 100 mL of ice and 10 mL of HCl (37%). The product was extracted with ether, dried over magnesium sulphate and purified by column chromatography (n-hexane/chloroform). Crystallisation resulted in white crystals with a yield of 0.76g (64%).

mp: 99.6°C ; IR (KBr, ν , cm^{-1}): 1760, 1590, 1450, 1415, 1345, 1280, 1255, 1235, 1205, 1085, 1070, 1060, 1030, 1005, 930, 845, 830, 740, 720, 700, 670; Raman (cm^{-1}): 3113, 3086, 3074, 3057, 1761, 1599, 1528, 1429, 1352, 1287, 1260, 1242, 1211, 1163, 1140, 1086, 1047, 1018, 940, 903, 854, 789, 748, 721, 668, 649, 631, 594, 571, 532, 485, 356, 324, 297, 276, 223, 211, 154, 91; MS (EI, m/e): 298 (M^+), 253 ($\text{M} - \text{CO}_2$), 221, 111; ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 6.937 (dd; 2H; $\text{J} = 3.69, 5.16$ Hz; $\text{H}4'$), 7.063 (dd; 2H; $\text{J} = 1.25, 3.64$ Hz; $\text{H}3'$), 7.293 (dd; 2H; $\text{J} = 1.25, 5.11$ Hz; $\text{H}5'$), 7.564 (t; 1H; $\text{J} = 1.15, 7.18, 7.56$ Hz; $\text{H}6$), 7.660 (d; 1H; $\text{J} = 1.11, 7.60$ Hz; $\text{H}4$), 7.713 (t; 1H; $\text{J} = 1.19, 7.10, 7.64$ Hz; $\text{H}5$), 7.901 (d; 1H; $\text{J} = 1.00, 7.43$ Hz; $\text{H}7$); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 86.26 ($\text{C}3$), 123.48 ($\text{C}4$), 124.80 ($\text{C}7\text{a}$), 125.87 ($\text{C}7$), 126.81 ($\text{C}4'$), 127.10 ($\text{C}5'$), 127.30 ($\text{C}3'$), 130.05 ($\text{C}6$), 134.57 ($\text{C}5$), 143.87 ($\text{C}2'$), 151.89 ($\text{C}3\text{a}$), 168.74 ($\text{C}1$).

1,2-dithienylbenzene (43)

2-Bromothiophene (4.5 mL - 46 mmol) in 50 mL of THF was added slowly to 1.2 g (46 mmol) of iodine activated magnesium in 50 mL of THF. After stirring for 3.5 h, this solution was slowly added to 7.95 g (23 mmol) of bis(*S*-(2-pyridinyl))benzenedithioate (4) in 150 mL of THF at 0°C . After stirring for another 30 minutes, the reaction was completed by adding 200 mL of a dilute hydrochloric acid solution (10%). The resulting mixture was extracted with diethyl ether. The diethyl ether solution was washed with 500 mL of NaOH (10%), 500 mL of NaHCO_3 (1M), and water and finally dried (magnesium sulphate). After evaporation of the solvent a light

brown product was obtained in a yield of 95%. This product can be used as such in further reactions. Crystallisation from chloroform/n-hexane resulted in white crystals.

mp 148-149 °C; IR (KBr, ν , cm^{-1}): 1620, 1585, 1570, 1510, 1410, 1350, 1340, 1280, 1260, 1220, 1150, 1045, 910, 880, 840, 820, 780, 725, 700, 650; Raman (cm^{-1}): 3106, 3092, 3074, 1644, 1593, 1574, 1515, 1412, 1351, 1301, 1230, 1212, 1153, 1079, 1040, 893, 875, 854, 832, 783, 750, 722, 678, 642, 571, 452, 374, 284, 245, 233, 208, 192, 172, 128, 107; MS (EI, m/e): 298 (M^+), 215 ($M^+ - \text{COAr}$), 187 ($M^+ - \text{COAr}$), 111 (COAr), 104, 76; ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.03 (dd, 2, $J=5.0/3.8$ Hz, H_4'), 7.44 (d, 2, $J=3.8$ Hz, H_3'), 7.60 (dd, 2, $J=5.4/3.4$ Hz, H_3), 7.63 (d, 2, $J=5.0$ Hz, H_5'), 7.70 (dd, 2, $J=5.4/3.4$ Hz, H_2); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 128.0 (C_4'), 129.2 (C_2), 130.6 (C_3), 134.9 (C_5'), 135.1 (C_3'), 139.3 (C_1), 144.0 (C_2'), 188.2 (C_4).

1,2-Dithienoyl -3,4,5,6-tetradeuterobenzene

Yield: 88%; IR (KBr, ν , cm^{-1}): 1620, 1545, 1510, 1410, 1350, 1330, 1280, 1255, 1220, 1195, 1105, 1060, 1020, 905, 895, 880, 850, 835, 815, 790, 735, 720, 700, 650, 600; MS (EI, m/e): 302, 273, 257, 219, 203, 191, 119, 111, 83

1,2-Dithienoyl-3,4,5,6-tetrafluorobenzene (28)

The Grignard reagent was prepared by adding 0.02 mole 2-bromothiophene (2mL) in 50 mL of THF to 0.02 mole of activated Mg (0.5g) together with a iodine crystal in 50 mL of THF. This mixture was heated under vigorous stirring for 3.5 hours. Then a solution of 0.01 mole crude tetrafluorothioester (4.2g) in 150 mL of THF was prepared and cooled down to 0°C. The Grignard reagent was added slowly to this solution. After the addition was completed the mixture was stirred for another 1.5 hours. The reaction was completed by adding 200 mL of HCl (10%). After extraction with diethyl ether the combined fractions were successively washed with 500mL of NaOH (10%), 500mL of NaHCO_3 (10%) and 500mL water. Further purification of the product can be done by direct crystallisation from CHCl_3 /n-hexane or by performing a column chromatographic purification (silica, CHCl_3 /n-hexane). Yield: 3.5g (95%)

mp: 118°C; IR (KBr, ν , cm^{-1}): 1620, 1510, 1470, 1410, 1375, 1350, 1310, 1240, 1320, 1090, 1080, 1060, 815, 795, 765, 730, 680; FT-Raman (ν , cm^{-1}): 3116, 3096, 2539, 1648, 1511, 1410, 1383, 1355, 1317, 1237, 1082, 1063, 941, 867, 804, 753, 672, 627, 567, 498, 472, 417, 366, 311, 232, 182, 139, 103; MS (EI, m/e): 370 (M^+), 325, 287, 271, 166, 111, 83; ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.09 (t; $J= 4.8, 1.1$; H_4'), 7.51 (dd; $J= 3.8, 0.9$; H_3'), 7.74 (dd; $J= 3.9, 5.1$; H_5');

^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 123.45 (C1), 128.60 (C4'), 136.17 (C3'), 136.85 (C5'), 141.57 (C3), 143.13 (C2'), 144.85 (C2), 180.54 (C4); ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to CFCl_3): -136.68 (F2), -150.35 (F3)

1,2-Di(5'-bromothiienoyl) benzene (55)

2,5-Dibromothiophene (4.5 mL - 46 mmol) in 50 mL THF was added slowly to 1.2 g (46 mmol) of iodine activated magnesium in 50 mL THF. During addition the mixture the flask was immersed in an ultrasonic bath to activate the magnesium more efficiently. After 3.5 hours, to this solution was slowly added at 0°C 4.2 g (23 mmol) of 1,2-(S-(2-pyridinyl))benzenedithioate in 150 mL of THF. After being stirred for another 30 minutes, the reaction was completed by adding 200 mL of a dilute hydrochloric acid solution (10%). The resulting mixture was extracted with diethyl ether. The diethyl ether solution was washed with 500 mL of NaOH (10%), 500 mL of NaHCO_3 (1M), water and finally dried (magnesium sulphate). After purification by means of column chromatography (silica/n-hexane) a greenish brown product was obtained in a yield of 41%.

mp: 169.2°C ; IR (KBr, ν , cm^{-1}): 1625, 1570, 1520, 1410, 1310, 1275, 1200, 1150, 1055, 975, 875, 840, 790, 780, 730, 700, 680, 665, 640, 540, 460; FT-Raman (cm^{-1}): 3100, 3084, 3062, 2540, 1655, 1588, 1519, 1412, 1317, 1209, 1150, 1061, 1040, 780, 736, 713, 683, 573, 384, 339, 257, 171, 144, 51; MS (EI, m/e): 456, 377, 333, 295, 268, 252, 189, 158, 104, 82; ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.041 (d; 2H; $J = 4.11$ Hz; H_4'), 7.184 (d; 2H; $J = 4.03$ Hz; H_3'), 7.60-7.63 (m; 2H; H_4), 7.66-7.69 (m; 2H; H_3); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 124.38 (C5'), 129.28 (C3), 130.90 (C4), 131.35 (C4'), 135.35 (C3'), 138.58 (C2), 145.31 (C2'), 187.09 (C7)

3,3-dithienyl-3H-furo[5,6-c]pyridin-1-on (47b)

Grignard reaction on 2,3-(S-(2-pyridinyl))-pyridinedithioate. 2-Bromothiophene (4.5 mL - 46 mmol) in 50 mL of THF was added slowly to 1.2 g (46 mmol) of iodine activated magnesium in 50 mL of THF. After stirring for 3.5 hours, this solution was slowly added to 8.12 g (23 mmol) 2,3-(S-(2-pyridinyl))pyridinedithioate in 150 mL of THF at 0°C . After being stirred for another 30 minutes, the reaction was completed by adding 200 mL of a dilute hydrochloric acid solution (10%). The resulting mixture was extracted with diethyl ether. The diethyl ether solution was washed with 500 mL of NaOH (10%), 500 mL of NaHCO_3 (1M), water and finally dried over magnesium

sulphate. Purification was performed by column chromatography (n-hexane/chloroform). Yield: 4.4g (64%).

mp: 142°C; IR (KBr, ν , cm^{-1}): 3090, 3050, 1760, 1500, 1580, 1475, 1420, 1350, 1300, 1280, 1250, 1240, 1190, 1180, 1140, 1120, 1080, 1050, 1040, 950, 900, 870, 850, 840, 790, 770, 730, 710, 600, 530, 490, 480, 400, 330; FT-Raman (cm^{-1}): 3315, 3105, 3082, 3058, 2937, 1770, 1604, 1589, 1529, 1430, 1352, 1311, 1288, 1264, 1240, 1194, 1144, 1121, 1077, 1038, 955, 908, 889, 854, 797, 747, 710, 688, 648, 625, 596, 542, 479, 326, 304, 280, 234, 212, 162, 111, 89; MS (EI, m/e): 299, 255, 222, 210, 160, 111, 77; ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 6.960 (dd; 2H; $J = 3.69, 5.09$ Hz; H_4'), 7.204 (dd; 2H; $J = 1.28, 3.66$ Hz; H_3'), 7.320 (dd; 2H; $J = 1.31, 5.12$ Hz; H_5'), 7.527 (dd; 1H; $J = 4.85, 7.76$ Hz; H_6), 8.224 (dd; 1H; $J = 1.59, 7.68$ Hz; H_7), 8.945 (dd; 1H; $J = 1.59, 4.81$ Hz; H_5); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 86.79 (C_3), 118.79 (C_7a), 124.80 (C_6), 126.94 (C_4'), 127.26 (C_5'), 127.46 (C_3'), 134.72 (C_4), 142.00 (C_2'), 155.87 (C_5), 166.86 (C_1), 169.43 (C_3a)

3,3-dithienyl-3*H*-furo[2,3-*c*]pyrazin-1-on (51)

Grignard reaction on 2,3-(S-(2-pyridinyl))-pyrazinedithioate. 2-Bromothiophene (4.5 mL - 46 mmol) in 50 mL of THF was added slowly to 1.2 g (46 mmol) of iodine activated magnesium in 50 mL of THF. After stirring for 3.5 hours, this solution was slowly added to 8.10 g (23 mmol) 2,3-(S-(2-pyridinyl))pyrazinedithioate in 150 mL of THF at 0°C. After being stirred for another 30 minutes, the reaction was completed by adding 200 mL of a dilute hydrochloric acid solution (10%). The resulting mixture was extracted with diethyl ether. The diethyl ether solution was washed with 500 mL of NaOH (10%), 500 mL of NaHCO_3 (1M), water and finally dried over magnesium sulphate. Purification was performed by column chromatography (n-hexane/chloroform). Yield: 5.0g (73%).

mp: 101.3°C; IR (KBr, ν , cm^{-1}): 1765, 1530, 1460, 1415, 1370, 1335, 1280, 1240, 1220, 1200, 1175, 1130, 1090, 1025, 900, 840, 785, 715, 705, 410; FT-Raman (cm^{-1}): 3113, 3089, 3078, 3064, 3030, 2061, 1787, 1775, 1595, 1541, 1431, 1349, 1298, 1235, 1179, 1075, 1043, 920, 856, 818, 751, 716, 694, 650, 627, 595, 538, 333, 283, 242, 220, 155, 114, 99; MS (EI, m/e): 300, 256, 223, 211, 177, 111; ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 6.95 (dd; 2H; $J = 3.7, 5.1$ Hz; H_4'), 7.17 (dd; 2H; $J = 1.3, 3.7$ Hz; H_3'), 7.33 (dd; 2H; $J = 1.3, 5.1$ Hz; H_5'), 8.88 (d; 1H; $J = 2.43$ Hz; H_5), 8.93 (d; 1H; $J = 2.44$ Hz; H_6); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 85.09 (C_3), 127.05 (C_4'), 127.65 (C_3' , C_5'), 137.44 (C_7a), 140.79 (C_2'), 148.19 (C_6), 149.10 (C_5), 163.33 (C_3a), 164.45 (C_1)

Grignard reaction on 2,3-(S-phenyl)-pyrazinedithioate.

2-Bromothiophene (4.5 mL - 46 mmol) in 50 mL of THF was added slowly to 1.2 g (46 mmol) of iodine activated magnesium in 50 mL of THF. After stirring for 3.5 hours, this solution was slowly added to 8.10 g (23 mmol) 2,3-(phenyl)pyrazinedithioate in 150 mL of THF at 0°C. After being stirred for another 30 minutes, the reaction was completed by adding 200 mL of a dilute hydrochloric acid solution (10%). The resulting mixture was extracted with diethyl ether. The diethyl ether solution was washed with 500 mL of NaOH (10%), 500 mL of NaHCO₃ (1M), water and finally dried over magnesium sulphate. Purification was performed by column chromatography (n-hexane/chloroform).

Compound (52)

Yield: 0.85g (8.6%); mp: 164.1-164.8°C; IR (KBr, ν , cm⁻¹): 1680, 1540, 1500, 1470, 1430, 1410, 1370, 1350, 1270, 1230, 1210, 1050, 980, 880, 790, 740, 720, 700, 680; MS (EI, m/e): 434, 325, 297, 271, 242, 185, 133, 109; ¹H NMR (CDCl₃, 400 MHz, in ppm relative to TMS): 7.107 (dd; 1H; J= 4.02, 5.06 Hz; H4'''), 7.45-7.50 (m; 6H; H4'/H4''/H3'/H3''), 7.53-7.59 (m; 4H; H2'/H2''), 7.619 (dd; 1H; J= 0.99, 4.98 Hz; H3'''), 7.985 (dd; 1H; J= 1.01, 3.99 Hz; H5'''), 9.145 (s; 1H; H6); ¹³C NMR (CDCl₃, 400 MHz, in ppm relative to TMS): 127.00 and 127.73 (C1' and C1''), 128.95 (C4'''), 129.40 and 129.44 (C3' and C3''), 129.79 and 129.91 (C4' and C4''), 132.78 (C5'''), 133.46 (C3'''), 134.93 and 134.97 (C2' and C2''), 139.48 (C2'''), 140.99 (C2), 141.28 (C3), 142.87 (C6), 148.69 (C5), 189.65 (C7), 191.66 (C8)

Compound (53)

Yield: 2.7g (31%); mp: 143.1-143.7°C; IR (KBr, ν , cm⁻¹): 3200, 1440, 1420, 1370, 1350, 1280, 1250, 1220, 1160, 1120, 1090, 1070, 1060, 1040, 980, 930, 900, 850, 840, 830, 770, 720, 690, 440; MS (EI, m/e): 384, 285, 256, 218, 211, 195, 162, 111;

2-Pyridinyl-2-mercaptothiophene

2-Bromothiophene (4.5mL - 46 mmol) in 50 mL of THF was added slowly to 1.2g (46 mmol) of iodine activated magnesium in 50 mL of THF. After stirring for 3.5 hours, this solution was slowly added to 8.13g (37 mmol) 2-pyridine disulphide in 150 mL of THF at 0°C. After being stirred for another 30 minutes, the reaction was completed by adding 200 mL of a dilute hydrochloric acid solution (10%). The resulting mixture was extracted with diethyl ether. The diethyl ether solution was washed with 500 mL of

NaOH (10%), 500 mL of NaHCO₃ (1M), water and finally dried over magnesium sulphate. Purification was performed by column chromatography (n-hexane/chloroform).

Yield: 6.28 g (88%); IR (KBr, ν , cm⁻¹): 3060, 3040, 2980, 2920, 1660, 1560, 1550, 1430, 1400, 1390, 1280, 1220, 1140, 1110, 1070, 1050, 1030, 1090, 1080, 850, 750, 690; MS (EI, m/e): 193, 149, 115, 83, 78; ¹H NMR (CDCl₃, 400 MHz, in ppm relative to TMS): 6.764 (dt; 1H; J= 0.95, 8.08 Hz; H3), 6.887 (ddd; 1H; J= 1.01, 1.03, 4.86, 7.42 Hz; H5), 7.033 (dd; 1H; J= 3.57, 5.37 Hz; H4'), 7.252 (dd; 1H; J= 1.25, 3.54 Hz; H3'), 7.357 (ddd; 1H; J= 1.88, 7.37, 8.05 Hz; H4), 7.462 (dd; 1H; J= 1.30, 5.37 Hz; H5'), 8.303 (ddd; 1H; J= 0.90, 1.88, 4.85 Hz; H6); ¹³C NMR (CDCl₃, 400 MHz, in ppm relative to TMS): 119.62 (C3), 119.73 (C5), 127.76 (C2'), 128.11 (C4'), 132.24 (C5'), 136.73 (C4), 137.03 (C3'), 148.98 (C6), 161.73 (C2)

1,3-Dithienylisothianaphthene (4)

A. To a solution of 0.58 g (2 mmol) 1,2-dithienylbenzene in 40 mL of dried acetonitrile was added 1.7 g (6.1 mmol) P₄S₁₀ and 2.0 g (24 mmol) sodium hydrogen carbonate. After stirring for four hours at a temperature of 30°C, 50 mL of water was added. The precipitate formed was filtered and dissolved in diethyl ether. After extraction of the remaining water solution with diethyl ether the combined fractions were dried (magnesium sulphate). Further fast purification was done through repeated crystallisations by adding n-hexane to a saturated chloroform solutions and combining the fractions containing the 1,3-dithienylisothianaphthene. A final purification was performed through column chromatography (silica, n-hexane/chloroform) and crystallisation from n-hexane/chloroform resulting in fluorescent orange crystals (52%).

B. A mixture of 0.0014 mole 1,2-dithienylbenzene (0.42g), 0.0014 mole Lawesson reagent (0.4g) and 50 mL of dichloromethane were stirred for 30 minutes at a temperature of 30°C. After evaporation of the dichloromethane 50 mL of ethanol was added and the mixture was refluxed for another 20 minutes. Finally 100 mL of water was added and the product was extracted with diethyl ether. The combined diethyl ether fractions were washed with 500 mL of NaOH(10%) and 500 mL of water and dried over magnesium sulphate. The product was further purified by repeated crystallisations. The ether was evaporated, the remaining solid was taken up in a minimum quantity of chloroform and precipitated by adding a large quantity of n-hexane. The solid was filtered and this procedure was repeated several times. All fractions containing almost pure product were then combined and subjected to a final column chromatographic purification (silica, n-hexane) (64%).

mp 96-97 °C; IR (KBr, ν , cm^{-1}): 1520, 1215, 1180, 1100, 1065, 1030, 995, 845, 830, 820, 720, 690, 550, 510, 485, 415; FT-Raman (cm^{-1}): 3099, 3066, 1611, 1531, 1511, 1492, 1452, 1398, 1349, 1317, 1231, 1184, 1152, 1075, 1047, 1007, 943, 833, 741, 665, 649, 623, 587, 555, 489, 471, 184, 98; MS (EI, m/e): 298 (M^+), 253, 221, 149, 132($M^+-2\text{Ar}$); ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.13 (dd, 2H, $J=3.0, 6.9$ Hz, H5 and H6), 7.14 (dd, 2H, $J=3.6, 5.2$ Hz, H4'), 7.34 (d, 2H, $J=3.6$ Hz, H3'), 7.36 (d, 2H, $J=5.2$ Hz, H5'), 7.94 (dd, 2H, $J=3.0, 6.9$ Hz, H4 and H7); ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 121.5 (C4), 124.8 (C5), 125.5 (C5'), 125.6 (C3'), 126.5 (C3), 127.9 (C4'), 135.4 (C3a), 135.7 (C2'); UV-Vis (λ_{max} , ϵ) in *n*-hexane: 426(14440), 283(16819), 220(19909).

1,3-dithienyl-4,5,6,7-tetradeuteroisothianaphthene (36)

Yield: 64%; mp: 95.6 - 96.0°C; IR (KBr, ν , cm^{-1}): 1525, 1425, 1405, 1245, 1225, 1210, 1140, 1080, 1050, 1015, 850, 830, 820, 800, 705, 695, 625, 575, 530, 365; FT-Raman (cm^{-1}): 3099, 3084, 3065, 1581, 1527, 1472, 1444, 1381, 1256, 1075, 1047, 931, 881, 843, 804, 741, 637, 483, 462, 370, 237, 176, 139, 101; MS (EI, m/e): 302, 268, 257, 225, 151; ^1H NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 7.138 (dd, 2H, $J=3.63, 5.15$ Hz, H4'), 7.341 (dd, 2H, $J=1.12, 3.62$ Hz, H3'), 7.366 (dd, 2H, $J=1.07, 5.04$ Hz, H5'); ^2H NMR (CHCl_3 , 400 MHz, in ppm relative to CDCl_3 at 7.24 ppm): 7.99, 7.18; ^{13}C NMR (CDCl_3 , 400 MHz, in ppm relative to TMS): 121.09 (C4), 124.26 (C5), 125.49 (C5'), 125.53 (C3'), 126.43 (C3), 127.87 (C4'), 135.19 (C3a), 135.61 (C2');

1,3-dithienyl-4,5,6,7-tetrafluoroisothianaphthene (24)

A mixture of 0.0014 mole 1,2-dithienoyl-3,4,5,6-tetrafluoro-benzene (0.5g), 0.0014 mole Lawesson reagent (0.4g) and 50 mL of dichloromethane were stirred for maximum one hour at 45°C. After evaporation of the dichloromethane 50 mL of ethanol was added and the mixture was refluxed for another 30 minutes. Finally 100 mL of water was added and the product was extracted with diethyl ether. The combined diethyl ether fractions were washed with 500 mL of NaOH(10%) and 500 mL of water and dried over magnesium sulphate. Finally a column chromatographic purification (silica, *n*-hexane) yielded 0.48g (95%).

mp: 184.6°C; IR (KBr, ν , cm^{-1}): 2920, 1660, 1560, 1470, 1415, 1365, 1340, 1260, 1215, 1125, 1080, 1040, 1020, 1010, 970, 955, 855, 800, 750, 695; FT-Raman (ν , cm^{-1}): 3118, 3070, 2959, 2655, 2568, 1674, 1539, 1526, 1493, 1441, 1398, 1347, 1240, 1225, 1167, 1145, 1080, 1061, 1042, 857, 836, 751, 737, 704, 647, 629, 580,

508, 487, 407, 364, 315, 266, 250, 201, 185, 110, 73; MS (EI, m/e): 370 (M^+), 203 ($M^+ - 2Ar$); 1H NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS): 7.11 (t; $J = 5.1, 1.0$; H_4'), 7.27 (dd; $J = 3.4, 1.4$; H_3'), 7.43 (dd; $J = 5.1, 3.6$; H_5'); ^{13}C NMR ($CDCl_3$, 400 MHz, in ppm relative to TMS): 121.78 (C_{3a}), 127.85 (C_4'), 127.85 (C_5'), 127.86 (C_3), 129.16 (C_3'), 132.70 (C_2'), 137.15 (C_5), 139.13 (C_4); ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to $CFCl_3$): -145.68 (F_4), -161.70 (F_5); UV-Vis (λ_{max} , ϵ) in *n*-hexane: 400(12656), 269(16372), 227(23159)

12.3 Single Crystal Structure Determination of Monomer (7) and Dimer (8)

The crystals used in the structure determination were obtained through slow evaporating of a n-hexane/acetonitrile two phase system. Data collection was performed on a Siemens P4-PC diffractometer (ω -scan mode) using graphite-monochromated Mo K α radiation (0.71073 Å). Three check reflections measured every 100 reflections showed no significant decrease in intensity. Structure analysis and refinement was performed using direct methods and full least-squares on F^2 using SHELXTL-93 with all non-hydrogen atoms anisotropic and hydrogen atoms with isotropic U 1.2 times U_{eq} of the parent atom. Siemens SHELXTL-PLUS was used for all other calculations and drawings. The list of atomic coordinates has been deposited with the Cambridge Crystallographic Data Centre.

(1) Monomer (7). Empirical formula= $C_{20}H_{34}SSi_2$; Formula Weight= 362.71; Temperature: 289(2) K; Wavelength= 0.71073 Å; Crystal system= Monoclinic; Space Group= P 2₁/N; Unit cell dimension= $a = 11.314(2)$ Å, $\alpha = 90^\circ$, $b = 7.764(2)$ Å, $\beta = 101.38(3)^\circ$, $c = 26.941(5)$ Å, $\gamma = 90^\circ$; Volume= $2320.0(8)$ Å³; $z = 4$; Density (calculated)= 1.038 Mg/m³; Absorption coefficient= 0.242 mm⁻¹; $F(000) = 792$; Crystal size= $0.30 \times 0.30 \times 0.20$ mm; θ range for data collection= 1.54 to 19.97° ; Index ranges= $0 \leq h \leq 10$, $0 \leq k \leq 7$, $-25 \leq l \leq 25$; Reflections collected= 2153; Independent reflections= 2153 ($R_{int} = 0.0000$); Absorption correction= Semi-empirical from ψ -scans; Maximum and minimum transmission= 0.995 and 0.887; Refinement method= Full-matrix least-squares on F^2 ; Data/restraints/parameters= 1682/0/233; Goodness-of-fit on $F^2 = 1.044$; Final R indices [$I > 2\sigma(I)$]= $R1 = 0.0703$, $\omega R2 = 0.1556$; R indices (all data)= $R1 = 0.1578$, $\omega R2 = 0.2048$; Extinction coefficient= $0.0016(6)$; Largest difference peak and hole= 0.678 and -0.241 eÅ⁻³;

(2) Dimer (8). Empirical formula= $C_{28}H_{38}S_2Si_2$; Formula weight= 494.88; Temperature= 289(2)K; Wavelength= 0.71073Å; Crystal system= Triclinic; Space group= P $\bar{1}$; Unit cell dimensions= $a = 7.484(4)$ Å, $\alpha = 68.51^\circ$, $b = 12.910(2)$ Å, $\beta = 83.60^\circ$, $c = 16.138(5)$ Å, $\gamma = 87.860(10)^\circ$; Volume= $1441.8(9)$ Å³; $Z = 2$; Density(calculated)= 1.140 Mg/cm³; Absorption coefficient= 0.282 mm⁻¹; $F(000) = 532$; Crystal size= $0.50 \times 0.50 \times 0.20$ mm; θ range for data collection= 1.36 to 23.25° ; Index

ranges= $-1 \leq h \leq 8$, $-13 \leq k \leq 13$, $-17 \leq l \leq 17$; Reflections collected= 5213; Independent reflections= 4122 ($R_{\text{int}} = 0.0306$); Absorption correction= Semi-empirical from ψ -scans; Maximum and minimum transmission= 0.875 and 0.940; Refinement method= Full-matrix least-squares on F^2 ; Data/restraints/parameters= 3942/0/318; Final R indices [$I > 2\sigma(I)$] = $R_1 = 0.0393$, $\omega R_2 = 0.0953$; R indices (all data)= $R_1 = 0.0910$, $\omega R_2 = 0.4531$; Extinction coefficient= 0.016(2); Largest difference peak and hole= 0.347 and -0.242 $\text{e}\text{\AA}^{-3}$.

S(1)-C(8)	1.700(6)	C(17)-C(20)	1.513(10)
C(1)-C(2)	1.415(7)	C(17)-C(19)	1.562(9)
C(2)-C(3)	1.409(7)	S(1)-C(1)	1.708(5)
C(3)-C(4)	1.354(7)	C(1)-Si(2)	1.859(6)
C(4)-C(5)	1.416(8)	C(2)-C(7)	1.434(7)
C(5)-C(6)	1.353(7)	C(8)-Si(1)	1.872(6)
C(6)-C(7)	1.408(7)	Si(1)-C(10)	1.836(6)
C(7)-C(8)	1.416(7)	C(11)-C(13)	1.516(8)
Si(1)-C(11)	1.766(7)	C(11)-C(14)	1.678(9)
Si(1)-C(9)	1.861(6)	Si(2)-C(17)	1.843(7)
C(11)-C(12)	1.519(9)	Si(2)-C(15)	1.859(6)
Si(2)-C(16)	1.852(7)	C(17)-C(18)	1.548(9)
C(8)-S(1)-C(1)	97.4(3)	C(2)-C(1)-S(1)	107.6(4)
C(2)-C(1)-Si(2)	132.8(4)	S(1)-C(1)-Si(2)	119.6(3)
C(3)-C(2)-C(1)	127.8(5)	C(3)-C(2)-C(7)	118.5(5)
C(1)-C(2)-C(7)	113.7(4)	C(4)-C(3)-C(2)	121.0(5)
C(3)-C(4)-C(5)	120.4(5)	C(6)-C(5)-C(4)	120.3(5)
C(5)-C(6)-C(7)	121.0(5)	C(8)-C(7)-C(6)	127.9(5)
C(8)-C(7)-C(2)	113.2(5)	C(6)-C(7)-C(2)	118.8(4)
C(7)-C(8)-S(1)	108.1(4)	C(7)-C(8)-Si(1)	132.1(4)
S(1)-C(8)-Si(1)	119.8(3)	C(11)-Si(1)-C(10)	113.4(3)
C(11)-Si(1)-C(9)	111.2(3)	C(10)-Si(1)-C(9)	107.1(3)
C(11)-Si(1)-C(8)	106.1(3)	C(10)-Si(1)-C(8)	110.9(3)
C(9)-Si(1)-C(8)	108.1(3)	C(13)-C(11)-C(12)	111.2(6)
C(13)-C(11)-C(14)	101.4(6)	C(12)-C(11)-C(14)	101.8(6)
C(13)-C(11)-Si(1)	116.3(5)	C(12)-C(11)-Si(1)	116.4(5)
C(14)-C(11)-Si(1)	107.4(5)		

Table 12.1 Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) of the isothianaphthene monomer (7).

S (1) - C (8)	1.719 (3)	S (1) - C (1)	1.721 (3)
S (2) - C (9)	1.714 (3)	S (2) - C (16)	1.717 (3)
Si (1) - C (17)	1.872 (4)	Si (1) - C (18)	1.875 (4)
Si (1) - C (8)	1.877 (3)	Si (1) - C (19)	1.901 (4)
Si (2) - C (24)	1.873 (4)	Si (2) - C (23)	1.874 (4)
Si (2) - C (16)	1.887 (3)	Si (2) - C (25)	1.895 (4)
C (1) - C (2)	1.393 (4)	C (1) - C (9)	1.471 (4)
C (2) - C (3)	1.430 (5)	C (2) - C (7)	1.446 (4)
C (3) - C (4)	1.350 (5)	C (4) - C (5)	1.425 (5)
C (5) - C (6)	1.364 (5)	C (6) - C (7)	1.424 (5)
C (7) - C (8)	1.412 (5)	C (9) - C (10)	1.393 (4)
C (10) - C (11)	1.422 (5)	C (10) - C (15)	1.444 (4)
C (11) - C (12)	1.356 (5)	C (12) - C (13)	1.425 (5)
C (13) - C (14)	1.363 (5)	C (14) - C (15)	1.431 (4)
C (15) - C (16)	1.415 (4)	C (19) - C (22)	1.536 (6)
C (19) - C (21)	1.547 (5)	C (19) - C (20)	1.549 (6)
C (25) - C (26)	1.531 (6)	C (25) - C (28)	1.536 (5)
C (25) - C (27)	1.537 (5)		
C (8) - S (1) - C (1)	95.5 (2)	C (9) - S (2) - C (16)	95.4 (2)
C (17) - Si (1) - C (18)	109.0 (2)	C (17) - Si (1) - C (8)	109.6 (2)
C (18) - Si (1) - C (8)	107.5 (2)	C (17) - Si (1) - C (19)	110.6 (2)
C (18) - Si (1) - C (19)	109.4 (2)	C (8) - Si (1) - C (19)	110.7 (2)
C (24) - Si (2) - C (23)	108.3 (2)	C (24) - Si (2) - C (16)	107.2 (2)
C (23) - Si (2) - C (16)	109.5 (2)	C (24) - Si (2) - C (25)	109.7 (2)
C (23) - Si (2) - C (25)	111.6 (2)	C (16) - Si (2) - C (25)	110.5 (2)
C (2) - C (1) - C (9)	128.5 (3)	C (2) - C (1) - S (1)	109.9 (2)
C (9) - C (1) - S (1)	121.5 (2)	C (1) - C (2) - C (3)	127.3 (3)
C (1) - C (2) - C (7)	112.5 (3)	C (3) - C (2) - C (7)	120.2 (3)
C (4) - C (3) - C (2)	119.5 (3)	C (3) - C (4) - C (5)	120.9 (4)
C (6) - C (5) - C (4)	121.4 (3)	C (5) - C (6) - C (7)	120.1 (3)
C (8) - C (7) - C (6)	128.5 (3)	C (8) - C (7) - C (2)	113.7 (3)
C (6) - C (7) - C (2)	117.8 (3)	C (7) - C (8) - S (1)	108.4 (2)
C (7) - C (8) - Si (1)	132.1 (2)	S (1) - C (8) - Si (1)	119.5 (2)
C (10) - C (9) - C (1)	129.0 (3)	C (10) - C (9) - S (2)	110.2 (2)
C (1) - C (9) - S (2)	120.8 (2)	C (9) - C (10) - C (11)	128.4 (3)
C (9) - C (10) - C (15)	112.4 (3)	C (11) - C (10) - C (15)	119.2 (3)
C (12) - C (11) - C (10)	120.6 (3)	C (11) - C (12) - C (13)	120.3 (4)
C (14) - C (13) - C (12)	121.6 (3)	C (13) - C (14) - C (15)	119.7 (3)
C (16) - C (15) - C (14)	127.9 (3)	C (16) - C (15) - C (10)	113.5 (3)
C (14) - C (15) - C (10)	118.6 (3)	C (15) - C (16) - S (2)	108.5 (2)
C (15) - C (16) - Si (2)	132.9 (2)	S (2) - C (16) - Si (2)	118.6 (2)
C (22) - C (19) - C (20)	109.4 (3)	C (22) - C (19) - C (20)	109.8 (4)
C (21) - C (19) - C (20)	109.1 (3)	C (22) - C (19) - Si (1)	109.4 (3)
C (21) - C (19) - Si (1)	109.2 (3)	C (20) - C (19) - Si (1)	109.9 (3)
C (26) - C (25) - C (28)	110.3 (4)	C (26) - C (25) - C (27)	109.2 (4)
C (28) - C (25) - C (27)	107.7 (3)	C (26) - C (25) - Si (2)	109.9 (3)
C (28) - C (25) - Si (2)	108.4 (2)	C (27) - C (25) - Si (2)	111.3 (3)

Table 12.2 Selected bond lengths (Å) and angles (°) of the isothianaphthene dimer (8).

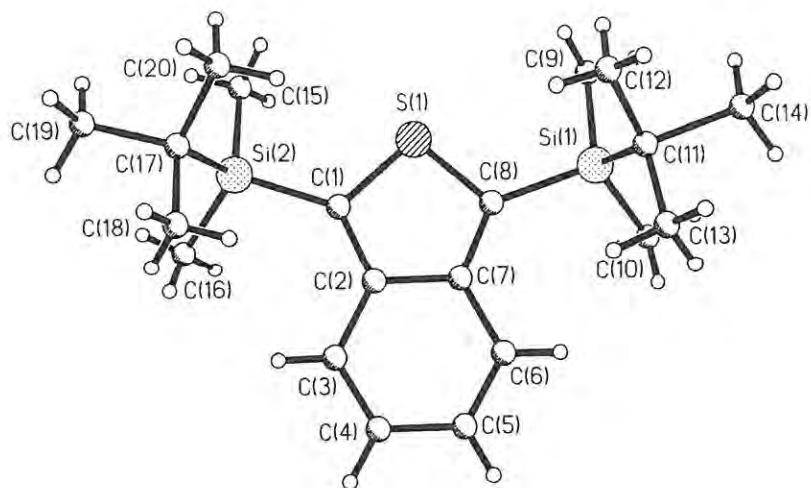


Figure 12.1 Numbering of carbon and silicon nuclei of the monomer (7).

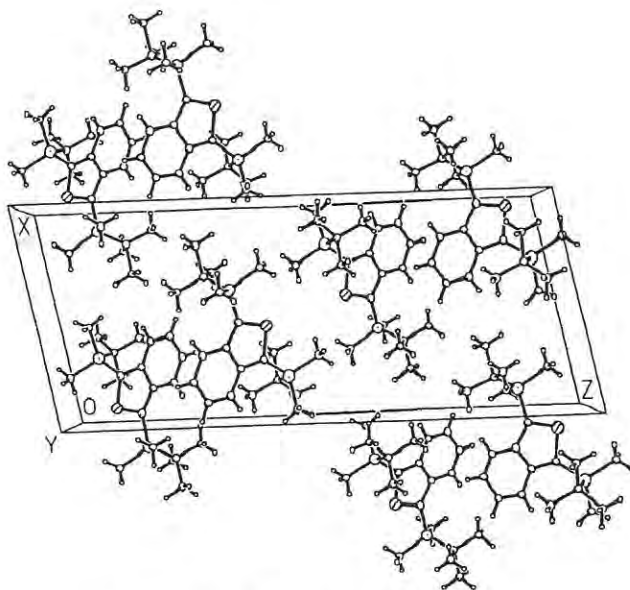


Figure 12.2 The unit cell of the monomer (7).

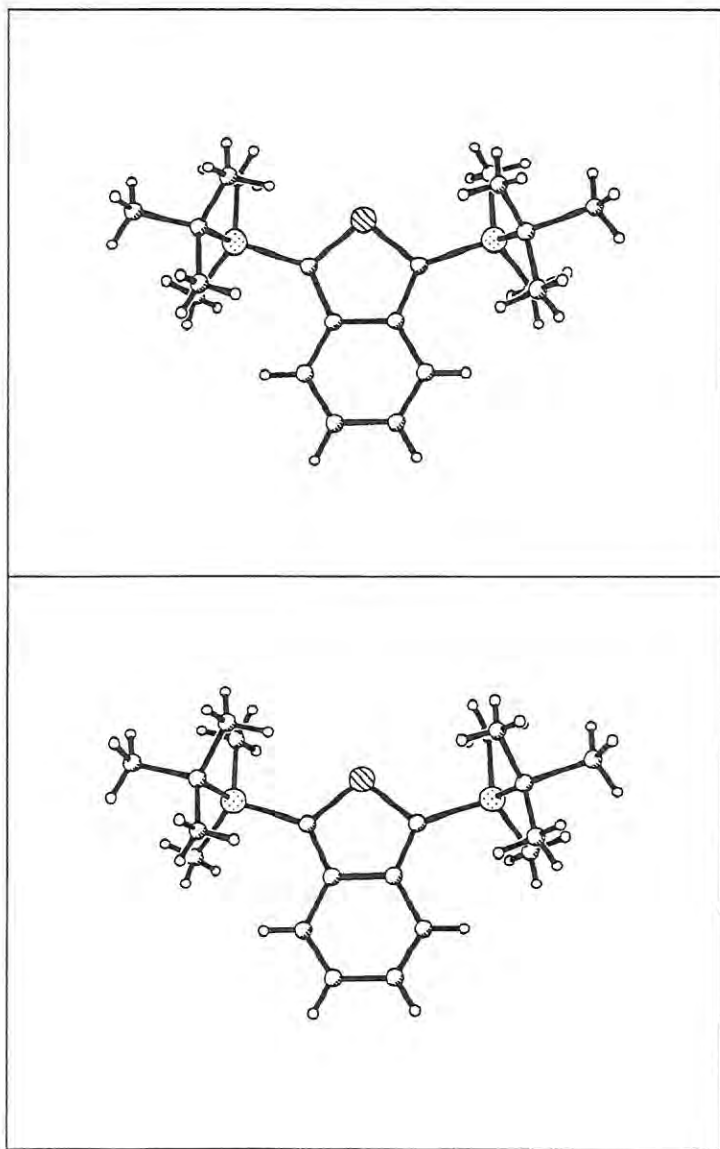


Figure 12.3 Stereoview of the monomer (7).

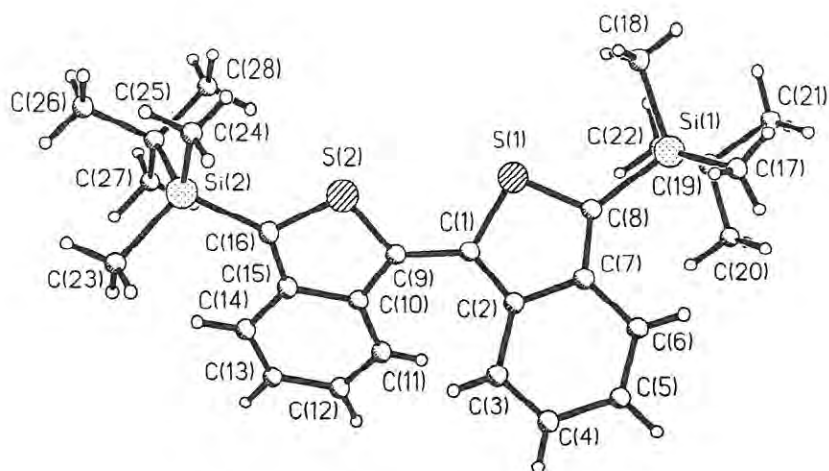


Figure 12.4 Numbering of carbon and silicon nuclei of the dimer (8).

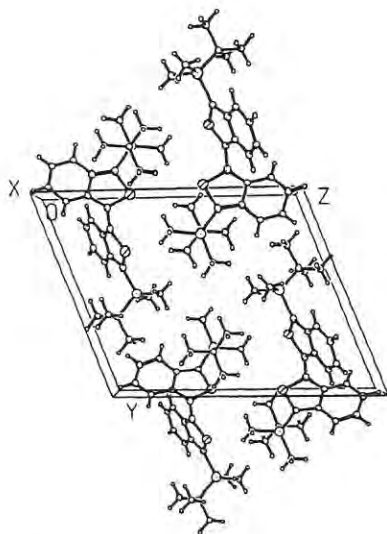


Figure 12.5 The unit cell of the dimer (8).

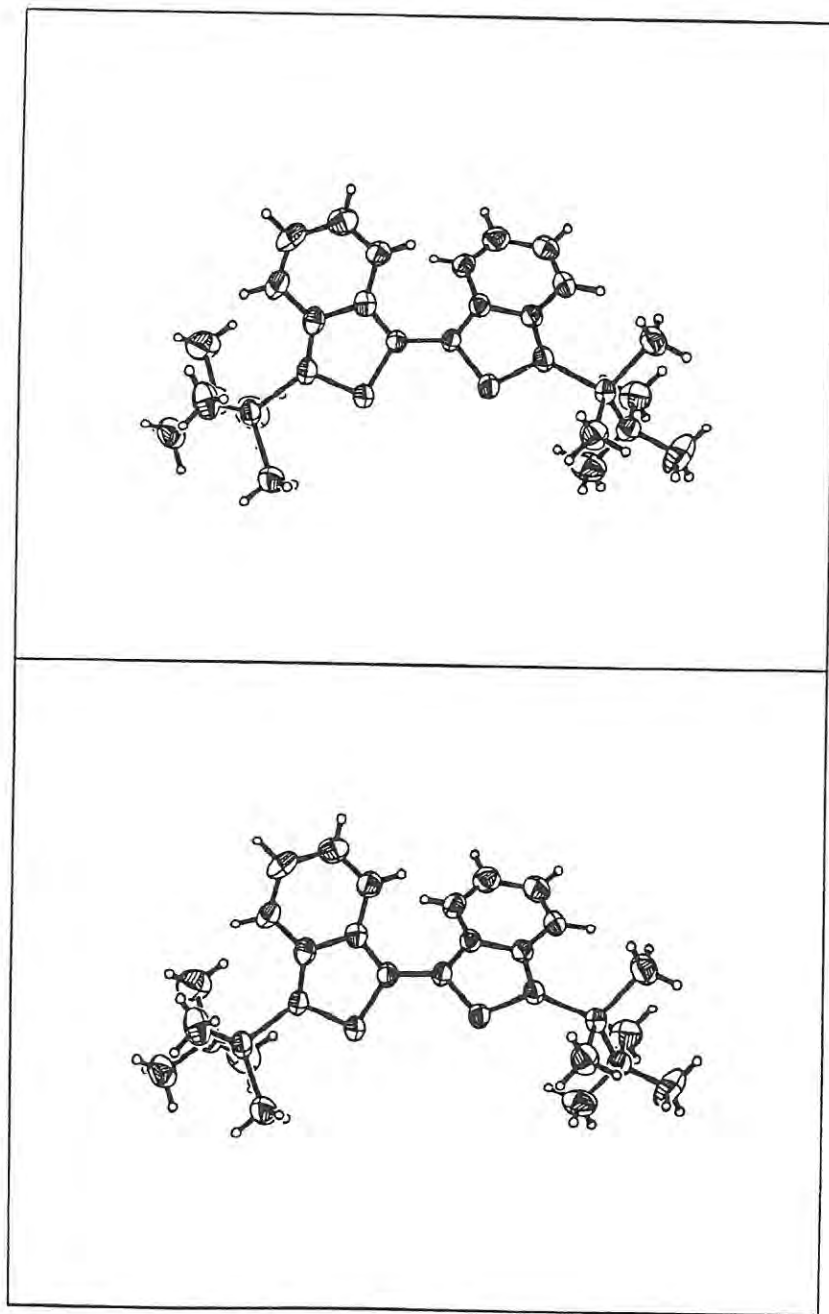


Figure 12.6 Stereoview of the monomer (7).

12.4 References

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Onderzoek van Aromatisch Poly(isothianafteen) en Analogen via de Struktuuranalyse van Oligomeren en Modelverbindingen

Polymere die aan de voorwaarden van echte intrinsieke organische geleiders voldoen blijken vrij zeldzaam te zijn. Tot op heden is poly(zwavelnitride) het enige polymeer dat metallische geleiding vertoont. Alhoewel poly(acetyleen) een ideaal materiaal lijkt om intrinsieke geleidbaarheid te vertonen, blijkt dat het een relatief grote bandafstand bezit ten gevolge van de Peierls distorsie. Niet gedopeerd poly(acetyleen) wordt bijgevolg slechts gekenmerkt door halfgeleider eigenschappen. In het geval van polyaromaten heeft men echter tevens te maken met de stabiliteit van aromatische en chinoidale structuren. Theoretische berekeningen voorspellen namelijk dat de bandafstand van halfgeleidende polyaromaten substantieel verkleind kan worden door chinoidale bijdragen aan de aromatische grondtoestand geometrie te stabiliseren. Dit werd experimenteel bevestigd door de synthese van poly(isothianafteen) PITN als zijnde een poly(thiofeen) (PT) derivaat waarbij een benzeen ring geplaatst werd op de β - β' binding.

Deze resultaten spoorden andere groepen er toe aan om op theoretisch vlak het effect van het verder stabiliseren van chinoidale bijdragen tot de grondtoestand geometrie te onderzoeken. Binnen het kader van het ontwikkelen van polymeren met een kleine bandafstand hebben de theoretische resultaten met betrekking tot PITN en andere verbindingen met additionele gesuperponeerde benzeenringen belangrijke gevolgen. Indien de redenering van Brédas consequent door getrokken wordt, dient men in het geval van PITN aromatische bijdragen tot de grondtoestand geometrie van PITN te stabiliseren. Het uiteindelijke doel zou erin bestaan the elektronische grondtoestand van het polymeer zodanig te beïnvloeden dat men de configuratie bekomt met de kleinste bandafstand.

Bijgevolg zijn structurele modificaties van geleidende polymeren zeer belangrijk bij het ontwerpen van intrinsiek geleidende polymeren. Door gebruik van hetero-atomen of

specifieke anti- of niet-aromatische structuren kan de grondtoestand energie van polyaromaten in de ene of de andere richting gemanipuleerd worden.

Het doel van hoofdstuk 3 bestond erin na te gaan op welke manier het mogelijk is door structurele modificaties polymeren te ontwikkelen met een kleine bandafstand. Daartoe werd op basis van een gedetailleerd literatuur onderzoek na gegaan in welke mate substituenten, eindgroepen en de stabiliteit van het gedelokaliseerd π -systeem elektronische eigenschappen zoals de bandafstand beïnvloeden.

In het geval van PITN-achtige polymeren voorspellen theoretische berekeningen dat substituenten weinig invloeden zullen hebben op de bandafstand. Het grootste belang van substituenten zou eerder gesitueerd moeten worden op het niveau van het afstemmen van de elektronische karakteristieken op welbepaalde toepassingen en ten einde de verwerkbaarheid te verbeteren.

De aard van de eindgroepen lijkt alleen belangrijk voor deze polymeren waarbij het energie verschil tussen the aromatische structuur en de chinoidale structuur vrij klein is. Bij deze polymeren zou de structuur en bijgevolg ook de elektronische eigenschappen gecontroleerd kunnen worden door middel van een aangepaste synthese.

Variatie van de π delokalisatie lijkt het meest belangrijke middel te zijn om de elektronische eigenschappen op een significante wijze te veranderen. Een volledig planair π systeem bevordert de electron delokalisatie langsheen de polymeerketen. Hierdoor verbeteren tevens de geleidende eigenschappen. Op basis van de klassieke Hückel Moleculaire Orbitaal theorie en experimentele gegevens blijken er aanwijzingen te bestaan voor een kwalitatieve correlatie tussen de bandafstand en de resonantie stabilisatie. Blijkbaar valt een kleinere resonantie stabilisatie van een heterocyclisch ringsysteem samen met een kleinere bandafstand in het polymeer. Deze kwalitatieve relatie zou gebruikt kunnen worden als een ruwe leidraad bij verdere synthese van polymeren met een kleine bandafstand, maar kan in geen geval meer gesofistikeerde berekeningen vervangen. De introductie van heteroatomen in het aromatisch ringsysteem kan bovendien niet alleen een invloed hebben op de resonantie stabilisatie maar ook op de uiteindelijke geometrische structuur door het verminderen van sterische interacties. Tenslotte kunnen de elektronische eigenschappen substantieel beïnvloed worden door het combineren van verschillende aromatische ringsystemen. De uiteindelijke eigenschappen van dergelijke *formele* copolymeren zijn dan het resultaat van de combinatie van de eigenschappen van de overeenkomstige homopolymeren.

Karakterisatie van aromatische isothianafteen oligomeren liet toe een spectroscopisch beeld op te stellen dat zou beschouwd kunnen worden als typisch voor

"aromatisch" PITN. Deze spectroscopische analyse is gebaseerd op NMR, FT-Raman en UV-vis spectroscopie.

Ten einde de geometrische structuur van onoplosbaar PITN te analyseren bepaalden Hoogmartens et al.^[1] de ^{13}C chemische shift van de vier niet-equivalente koolstofatomen, C3, C3a, C4 en C5 op basis van een ^{13}C CP/MAS NMR pulssekwentie. Deze gegevens werden vervolgens vergeleken met de gegevens van model verbindingen met ofwel een aromatische ofwel een chinoidale structuur. De "eerste orde" model verbindingen (2) en (5) bleken niet geschikt te zijn voor vergelijking met de gegevens van het polymeer aangezien de isothianafteen systemen niet deel uitmaakten van een uitgebreid geconjugeerd π systeem. De simulatie van de structuur van PITN werd verbeterd in de "tweede orde" model verbindingen (3) en (6). Wat betreft de aromatische model verbinding bleek er hoegenaamd geen overeenkomst te bestaan met het polymeer. De chemische shifts C3a en C5 van de chinoidale model verbinding komen echter vrij goed overeen met de waarden bekomen voor PITN. Het waargenomen verschil voor C3 en C4 kan verklaard worden door het feit dat de shiften van deze koolstofatomen in PITN ook beïnvloed worden door het zwavel atoom van de naburige isothianafteen eenheden. Deze situatie werd niet in rekening gebracht in de "tweede orde" model verbindingen aangezien er geen zwavelatomen aanwezig zijn in de zijgroepen. Dit verplichte ons er toe "derde orde" model verbindingen te bereiden waarin de chemische omgeving van C3 en C4 vergelijkbaar is met deze van het polymeer.

Bij de aromatische "derde orde" model verbinding (4) bleek dat de ^{13}C chemische shifts van C3a, C4 en C5 vrijwel niet beïnvloed worden in vergelijking met de "tweede orde" model verbinding (3). Dit betekent dat het S atoom in de naburige ring geen significante invloed heeft op de chemische shift van C4. In contrast hiermee, induceert het zwavel atoom van de naburige ring(en) een verandering in de chemische shift van C3 van ongeveer 8 ppm. Deze "derde orde" model verbinding blijkt een vrij goed model te zijn voor aromatisch PITN aangezien de ^{13}C data bovendien sterk vergelijkbaar zijn met deze van de centrale ring in een gesilyleerd aromatisch tetrameer (10).

In de "derde orde" chinoidale model (12) heeft het S atoom een belangrijke invloed op de shift van C3 in vergelijking met de "tweede orde" model verbinding (6). In tegenstelling met de aromatische verbindingen ondergaat de shift van C4 een belangrijke verandering. Bijgevolg is de interactie tussen waterstofatoom H4 en het naburige S atoom, — voornamelijk afgezwakt in de aromatische model verbindingen door interring rotatie —, intenser bij de chinoidale model verbindingen.

Voor vergelijking met PITN zijn echter slechts de koolstofatomen C3a, C4 en C5 van het aromatisch tetrameer (10) en chinoidaal model (12) geschikt aangezien C3 in beide verbindingen bijna dezelfde shift vertoont. De shift van de drie koolstofatomen

C3a, C4 en C5 vertonen een sterke overeenkomst bij vergelijking van PITN en de chinoidale model verbinding (12). Er is echter hoegenaamd geen overeenkomst tussen PITN en het aromatische tetrameer (10). Deze resultaten bevestigen de eerdere besluiten van Hoogmartens et al.^[2] dat de structuur van PITN in belangrijke mate een chinoidaal karakter bezit. Er dient echter op gewezen te worden dat ten gevolge van het kleine theoretisch afgeleide energieverschil van ongeveer 2 kcal/mol per repeterende eenheid tussen de chinoidale en de aromatische vorm, de structuur van PITN eerder door de polymerisatie chemie bepaald kan worden dan door het energie verschil tussen twee alternatieve structuren. De synthese van de aromatische oligomeren (7 - 10) kan beschouwd worden als een illustratie van dit principe.

Uit de vergelijking van de FT-Raman spectra van de serie gesilyleerde aromatische oligomeren (7 - 10) kon besloten worden dat het spectrum van het tetrameer beschouwd kan worden als prototype van "aromatisch" PITN. Inderdaad, de lengte van de keten bleek lang genoeg om effecten afkomstig van eindgroepen te minimaliseren. Uit de vergelijking van 1,3-difenylisothianafteen (3), 1,3-dithienylisothianafteen (4) en het gesilyleerde aromatische tetrameer (10) konden drie FT-Raman lijnen geïdentificeerd worden als zijnde karakteristiek voor isothianafteen eenheden met een aromatische structuur. Deze lijnen bevinden zich bij 1486 cm^{-1} , 1444 cm^{-1} en 1333 cm^{-1} . De FT-Raman gegevens van niet gedopeerd PITN blijken echter volledig overeen te stemmen met de gegevens van de chinoidale model verbinding (12). Op basis van deze analyse van de Raman spectra van model verbindingen, gesynthetiseerd met het oog op het nabootsen van de chinoidale en aromatische structuur, is het mogelijk tot het besluit te komen dat de moleculaire structuur van PITN in de niet gedopeerde toestand chinoidaal is. Dit is de eerste maal dat vanuit vibrationele spectroscopie experimenteel bewijs aangebracht wordt voor de chinoidale grondtoestand van een polymeer met een kleine bandafstand. Deze resultaten bevestigen tevens de resultaten bekomen uit NMR spectroscopie.

Ook het doperings proces van electrochemisch bereid PITN werd gevolgd door middel van *in situ* FT-Raman spectroscopie ($\lambda_{\text{exc}} = 1064\text{ nm}$). Tijdens het n-doperings proces kon geen verandering van het FT-Raman spectrum waargenomen worden. Bij het p-doperings proces verschenen echter bijkomende FT-Raman lijnen bij 1402 cm^{-1} , 1384 cm^{-1} , 1192 cm^{-1} , 1059 cm^{-1} en 464 cm^{-1} . De intensiteit van deze lijnen nam toe bij toenemende p-dopering. Vergelijking met de karakteristieke Raman gegevens bekomen uit aromatische en chinoidale model verbindingen liet echter niet toe tot een eenduidige uitspraak te komen of het gedopeerde materiaal nu een aromatische dan wel een

chinoidale structuur zou bezitten. De identificatie van deze bijkomende lijnen vereist bijkomend vibrationeel onderzoek.

De experimenteel bekomen UV-vis spectra van de aromatische oligomeren (7 - 10) werden geanalyseerd gebruikmakende van het INDO/SCI formalisme. Twee belangrijke absorptie banden werden berekend. De absorptie bij lagere energie, overeenkomend met een $d \rightarrow d^*$ type transitie van het HOMO niveau naar het LUMO niveau, schuift op naar kleinere energieën bij toenemende ketenlengte. Extrapolatie van de HOMO—LUMO transities van de oligomeren naar de bandafstand energie van aromatisch PITN leidt tot een zeer kleine band afstand van 0.63 eV in het geval van het planaire systeem. In het geval van een dihedrale hoek tussen twee naburige ringsystemen van 130° werd een waarde van 1.55 eV bekomen. De waarde bekomen voor het systeem met een grote dihedrale hoek is in vrij goede overeenstemming met de extrapolatie van de eerste energie overgang bij 1.94 eV van de oligomeren opgenomen in n-hexaan. Deze resultaten wijzen erop dat de aromatische oligomeren in oplossing een sterk niet planaire conformatie aannemen waardoor de HOMO—LUMO transities aanzienlijk toenemen in vergelijking met deze van een planair aromatisch systeem. De tweede optische absorptie band wordt beschreven door electronische overgangen van het $l \rightarrow d^*$ type. De gelocaliseerde (l) orbitalen worden minder beïnvloed door de mate van interring conjugatie dan de gedelocaliseerde (d) niveau's. Hierdoor ondergaat de tweede piek bijna geen verschuiving bij toenemende ketenlengte. Dit is in goede overeenstemming met de experimenteel opgenomen spectra.

Bij het onderzoek naar PITN derivaten die beter verwerkbaar zijn en die een grotere stabiliteit bezitten, werd door Brooke et al.^[3] poly(4,5,6,7-tetrafluoroisothianafteen) (PTFITN) (19) gesynthetiseerd. Dit materiaal is verbazingwekkend goed oplosbaar in gechloreerde en andere organische solventen. Om het effect van fluor op de structuur en eigenschappen van dit materiaal beter te begrijpen werd een gedetailleerde spectroscopische studie aangevangen. Op de eerste plaats werd een reeks aromatische gefluoreerde isothianafteen oligomeren (20 - 23) geanalyseerd door middel van 1D en 2D NMR spectroscopische technieken om tot een eenduidige chemische shift toewijzing te kunnen komen van de waterstof, koolstof en fluor signalen. De shifts van de "centrale" koolstofatomen van deze oligomeren vertonen een duidelijke convergentie vanaf het trimeer (22) naar het tetrameer (23). De chemische shift waarden van de "centrale" koolstof atomen van het tetrameer kunnen bijgevolg beschouwd worden als zijnde representatief voor PTFITN met een aromatische structuur. Analyse van een eenvoudigere model verbinding, namelijk 1,3-dithienyl-4,5,6,7-tetrafluoroisothianafteen

(24), wijst erop dat het mogelijk is op basis van deze model verbinding betrouwbare aanwijzingen te bekomen voor de chemische shift waarden van C4 en C5, ondanks de belangrijke structurele en chemische verschillen.

De karakteristieke convergentie van trimeer naar tetrameer werd tevens waargenomen bij de FT-IR en FT-Raman analyse. Ook op niveau van FT-Raman spectroscopie bleek model verbinding (24) reeds karakteristieken te vertonen van aromatische isothianafteen eenheden.

Vergelijking van de NMR en FT-IR data van de oligomeren met deze van het polymeer gaven aan dat het polymeer een aromatische structuur zou bezitten. Het FT-Raman spectrum van het polymeer komt echter niet overeen met de typische kenmerken van "aromatische" isothianafteen eenheden maar eerder met dat van gedopeerd PITN. De verklaring van deze afwijking is niet voor de hand liggend aangezien er een gebrek is aan nadere gegevens zowel over de structuur van chinoidaal PTFITN als wat betreft de structuur van gedopeerd PITN.

Op basis van theoretische berekeningen bleek dat het vervangen van koolstofatomen door stikstofatomen op twee niveau's de relatieve stabiliteiten beïnvloed van aromatische en chinoidale structuren. Op de eerste plaats is het moeilijker om het volledig π gedelokaliseerd karakter te bewaren ten gevolge van een kleinere aromaticiteit van het stikstofatoom bevattende ring systeem waardoor de chinoidale structuur minder overheerst in vergelijking met het klassieke PITN. De aanwezigheid van niet bindende S—N interacties bleek een tweede faktor te zijn die de aromatische (chinoidale) structuur stabiliseert (destabiliseert). Tenslotte bleek uit de analyse van een serie aza derivaten dat de 4,5-diaza en de 4,7-diaza polymeren veelbelovend zouden zijn. Zij zouden een zeer kleine band afstand bezitten van ongeveer 0.27 eV en 0.18 eV, respectievelijk, indien zij gesynthetiseerd kunnen worden met een planaire aromatische structuur. Er werd bovendien een poging ondernomen om een serie aromatische 4,7-diaza oligomeren te bereiden op basis van de methode van Okuda et al.^[4] De chemie aangewend bij deze methode bleek echter niet geschikt voor gebruik bij pyrazine analogen. Bijgevolg werden de inspanningen op synthetisch vlak verder toegespitst op de bereiding van de stikstof derivaten van 1,3-dithienylisothianafteen.

Aangezien 1,3-dithienylisothianafteen derivaten van groot belang kunnen zijn zowel voor de ontwikkeling van halfgeleider materialen met op maat gemaakte elektronische eigenschappen als voor spectroscopische en theoretische evaluatie van structuur-eigenschap relaties, was ons doel in dit deel een efficiënte synthese te ontwikkelen voor de bereiding van 1,3-dithienylisothianafteen (DTI) (4) en zijn derivaten.

Bij de synthese van dit type verbinding bleek dat de synthese van *ortho* diketonen de belangrijkste struikelblok was. Een doorgedreven evaluatie van beschikbare beginprodukten was bijgevolg een essentieel onderdeel van dit onderzoek. Voor de synthese van het 1,2-dithienoyl benzeen (**43**) onderzochten we het gebruik van ftaloyl dichloride (**40**), ftaalzuur anhydride (**13**), thioftaalzuur anhydride (**14**), 1,2-(S-phenyl)-benzenedithioate (**41**) en 1,2-(S-(2-pyridinyl))-benzenedithioate (**42**).

Enerzijds bleek dat ftaloyl dichloride (**40**) te reactief was voor gebruik in Grignard reacties met 2-thienylmagnesiumbromide, maar aan de andere kant leverde het gebruik van ftaalzuur anhydride (**13**) en thioftaalzuur anhydride (**14**) naast kleine hoeveelheden 1,2-dithienoylbenzeen ook belangrijke hoeveelheden van het isomere 3,3-dithienyl-3*H*-isobenzofuran-1-one (**44**). Bovendien gingen de reacties met gebruik van ftaalzuur anhydride (**13**) en thioftaalzuur anhydride (**14**) gepaard met de ontwikkeling van enorme hoeveelheden H₂S en door vorming van een neerslag was het moeilijk de reagentia efficiënt te vermengen tijdens de toevoeging van het Grignard reagens. Tenslotte werd het zuiverings proces sterk gehinderd door de aanwezigheid van sterk gekleurde alcoholen en monogesubstitueerde tussen produkten.

De Grignard reactie op 1,2-(S-(2-pyridinyl))-benzenedithioate (**42**) bleek echter selectief bijna zuiver *ortho* diketon (**43**) op te leveren. Dit resultaat werd toegeschreven aan de vorming van een zesring vorming organometaal complex waarin het intermediair enolaat gevangen werd. In een analoge reactie op het 1,2-(S-phenyl)-benzenedithioate (**41**) naar de methode van Cardellicchio et al.^[5] kan het enolaat niet gevangen worden en werd het 3,3-di(S-phenyl)-3*H*-isobenzofuran-1-one (**45**) gevormd.

Gedetailleerde analyse van de reactieprodukten van de 1,2-(S-phenyl)-benzenedithioate synthese leerde ons heel wat meer over de stabiliteit van 1,2-(S-phenyl)-benzenedithioate (**41**) in vergelijking met het isomere lacton 3,3-di(S-phenyl)-3*H*-isobenzofuran-1-one (**45**). Uit spectroscopische analyse en zorgvuldige analyse van de reactie produkten in functie van de tijd bleek dat het thioester (**41**) eerst gevormd werd. In de aanwezigheid van een overmaat aan thiofenol gebeurde op positie 3 van het isomere lacton (**45**) een substitutie van een S-phenyl groep door een waterstofatoom. Dit duidt op de aanwezigheid van een gestabiliseerd radikaal aangezien thiofenol kan optreden als radikaalvanger door proton transfer en de vorming van het overeenkomstige disulfide. Op de positie 3 is het radikaal bovendien niet alleen gestabiliseerd door delokalisatie in het aromatisch ringsysteem, maar ook door delokalisatie in de thiofenol groep.

De synthese van het gedeutereerde (**36**) en gefluoreerde (**24**) DTI derivaat werd met succes uitgevoerd. We zijn er echter niet in geslaagd om het 2,3-pyridine (**37**), 3,4-pyridine (**38**) en 2,3-pyrazine (**39**) derivaat te bereiden. Het invoeren van stikstofatomen in het aromatisch ringsysteem bleek te interfereren met de vorming van het zesring

vorming organometaal complex waardoor het intermediair gevormde enolaat met de naburige functionele thioester groep kan reageren. In het geval van 2,3-pyridine bleek dat de vorming van het 3,3-dithienyl-3H-furo[5,6-c]pyridin-1-one (**47b**) bevoordeeld werd door het verschil in reactiviteit tussen beide carbonyl koolstofatomen als gevolg van de inherente assymetrie van het aromatisch ringsysteem door de aanwezigheid van slechts één stikstofaatom.

Deze waarnemingen vervolledigen in zekere mate de resultaten van Cama et al.^[6] Deze onderzoekers stelden vast dat bij de S(2-pyridinyl) thioester methode geen ketonen gevormd werden bij gebruik van de Grignard reagentia van 2-thiazole, tetrazole, benzthiazole of pyrimidine. Het valt op dat al deze Grignard reagentia één of meerdere stikstofatomen bevatten die zouden kunnen interfereren met de vorming van het zesring vorming organometaal complex. Onze resultaten wijzen erop dat niet alleen in de Grignard reagentia maar ook in het heteroaryl substraat, de aanwezigheid van stikstofatomen de vorming van ketonen zal verhinderen.

Tenslotte werd DTI oxidatief gepolymeriseerd met FeCl₃. Naast het te verwachten zwarte polymeer werden tevens belangrijke hoeveelheden van een in chloroform oplosbaar paars produkt gevormd. Op basis van massaspectroscopie bleek dat dit produkt het DTI dimeer (**54**) moest zijn. Het polymeer werd gededopeerd door refluxen in een hydrazine oplossing. Uit FT-IR bleek dat resterend dopant verwijderd was.

NMR analyse van het dimeer werd verhinderd door sterke piek verbreding. Op basis van AAS werd aanwijzing gevonden voor de aanwezigheid van ijzer. Ook FT-IR en FT-Raman duiden erop dat het dimeer gedopeerd zou zijn.

Uit dit onderzoekswerk is gebleken dat op basis van een grondige NMR en FT-Raman analyse op basis van oligomeren en model verbindingen, de kleine bandafstand van PITN geassocieerd kan worden met een chinoidale structuur. Een theoretische analyse van de UV-vis data van een reeks aromatische isothianafteen oligomeren geeft aan dat een substantiële verkleining van de bandafstand bekomen kan worden in planaire aromatische isothianafteen systemen.

In een parallel onderzoek van PTFITN, een oplosbaar gefluoreerd PITN derivaat, werden aanwijzingen bekomen dat dit polymeer een aromatische structuur zou bezitten. De aanwezigheid van de fluoratomen in combinatie met een aromatische structuur kunnen bijgevolg de ketenoverspannende π conjugatie in zulke mate verhinderen dat een grotere bandafstand van 2.1 eV bekomen wordt.

Analyse van een serie aza analogen van PITN bracht aan het licht dat het mogelijk zou moeten zijn in deze materialen een planaire geometrie te combineren met een

verbeterde verwerkbaarheid. De 4,5-diaza en 4,7-diaza isothianafteen polymeren kunnen bijgevolg beschouwd worden als veel belovende materialen met een kleine bandafstand.

Tenslotte toonden we aan dat het mogelijk is aromatisch isothianafteen ringsystemen te combineren met andere heterocyclische structuren, zoals thiofeen, ter vorming van een *formeel* copolymeer. Via het op punt stellen van een zeer specifieke en efficiënte synthese van 1,3-dithienylisothianafteen (4) werd de basis gelegd voor verdere ontwikkeling en onderzoek naar *formeel* copolymeren met op maat gemaakte elektronische eigenschappen.

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Appendix

Ten einde de latijnse spreuken aan het begin van ieder hoofdstuk beter naar waarde te kunnen schatten, wordt hierna de vertaling gegeven zoals ze voorkomt in werk 'Veni, vidi, vici' samengesteld door G. Vanden Berghe (Uitgeverij Lannoo).

Quidquid agunt homines votum, timor, ira, voluptas, gaudia, discursus, nostri farrago libelli est.

Alles wat de mensen doen, hun hartewens, angst, woede, lust, hun vreugden en wispelturigheden vormen de bonte inhoud van ons boekje.

Arcadium petis, immensam petis!

Gij grijpt naar Arcadia, gij grijpt naar iets onmetelijks

Ab ovo usque ad mala

Van het ei tot de appels

Aevo rarissima nostro simplicitas

In onze tijd is eenvoud uiterst zeldzaam

Credimus ut cognoscamus, non cognoscimus ut credamus

Wij geloven om te begrijpen, wij begrijpen niet om te geloven

Ex oriente lux

Uit het Oosten komt het licht

Nullum magnum ingenium sine mixtura dementiae fuit

Nooit bestond er een grote begaafdheid zonder een scheut waanzin

Apparent rari nantes in gurgite vasto

Zeldzame zwemmers verschijnen in de onmetelijke maalstroom

Quid si etiam jucunda memoria est praeteritorum memoria?

Wat als zelfs de herinnering aan voorbije tegenslagen ons aangenaam is?

Quid novi ex africa?

Wat nieuws komt er uit Afrika?

Nullum est jam dictum, quod non dictum sit prius

Er valt niets meer te zeggen dat al niet eerder is gezegd

Non olet

Het stinkt niet

Credo quia absurdum

Ik geloof omdat dit volstrekt onredelijk is

Sunt bona, sunt quaedam mediocra, sunt mala plura, quae legis hic: aliter non fit,

Avite, liber.

Onder wat je hier leest, bevinden zich voortreffelijke dingen, een aantal dooddoeners en heel wat onnozelheden: er bestaat geen andere manier, Avitus, om een boek als dit te maken.

*Sunt bona, sunt quaedam mediocra, sunt mala plura,
quae legis hic: aliter non fit, Avite, liber.*
(Martialis, Epigrammes 1,17,1)

