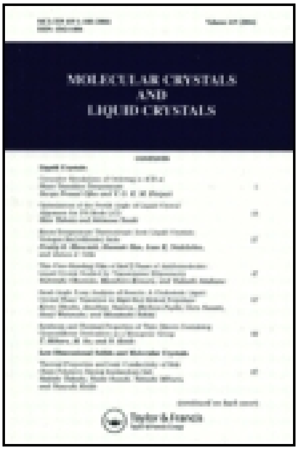

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Solid State Conformation and Crystal Packing of Methyl-Substituted Quaterthiophenes

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Solid State Conformation and Crystal Packing of Methyl-Substituted Quaterthiophenes

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The solid state structures of a series of methyl substituted neutral quaterthiophenes have been analysed. Structures have been retrieved from the Cambridge Structural Database and investigated in terms of crystal cohesion and intermolecular interactions. In these thiophene oligomers, it can be shown that crystal packing efficiency and optimisation of S---S, C-H---S and C-H---π interactions constitute the driving force for their solid state geometry and configuration. A detailed discussion of their packing arrangement is reported and shown to be based on either a herringbone or π-π stacking of thiophene units.

Keywords: Intermolecular Interactions; Thiophene; Crystal Packing; Conformation; Herringbone; π-π stacking

INTRODUCTION

Thiophene polymers have been extensively investigated over the last decade for their promising optoelectronic properties, and applications have been found, for example, in light-emitting diodes and field effect transistors.[1] The electronic behaviour of these polymers arises principally from the delocalisation of electrons along the aromatic backbone and the presence of highly polarisable sulfur atoms. The presence of coplanarity or torsional distortion about the bonds between rings in the solid state is of particular significance since it determines the extent of intramolecular π-electron delocalisation in these materials.[2] In gen-

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* Correspondence Author.

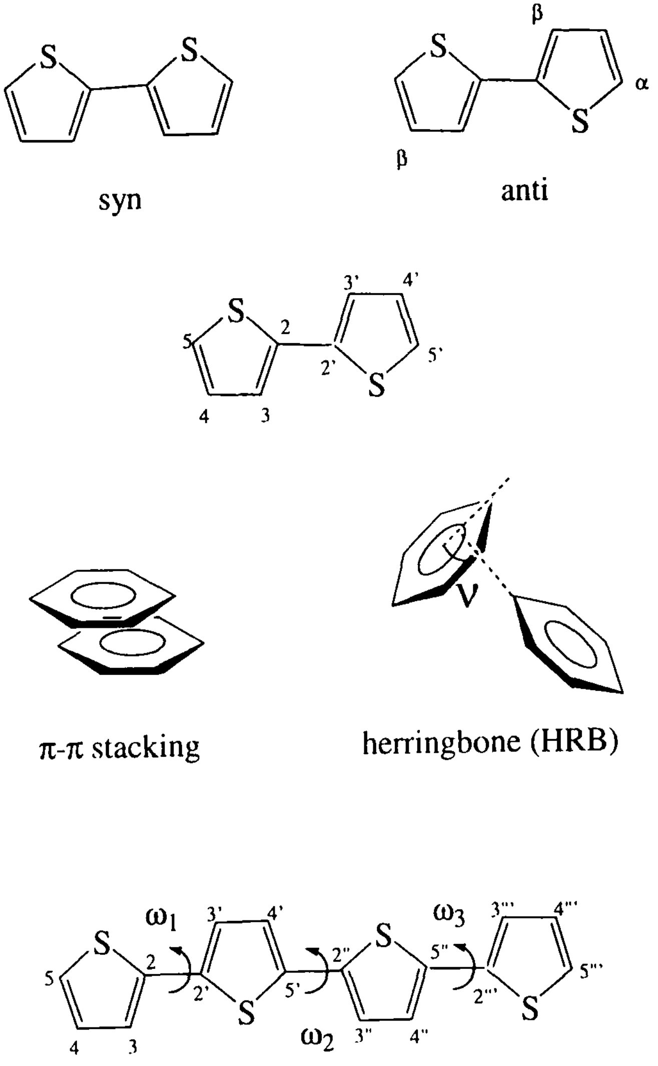
eral, a coplanar backbone leads to a denser packing and more π electron delocalisation, which are both favourable conditions for the optimisation of optoelectronic properties in these thiophene oligomers, and torsional deviation from this causes π-conjugation to decrease as a cosine function of the angle of distortion.[3]

However, it is now thought that the solid state organisation of these polymers also plays a key role in influencing their luminescence and charge transport behaviour, and, as a result, there is increasing interest in a detailed knowledge and understanding of the interchain interactions between nearest neighbour molecules in the solid state.[4–9] Detailed structural information on thiophene polymers is not easily obtained, although a few have been studied and their structures characterised to some extent.[10–13] Attention has, therefore, been directed towards thiophene oligomers,[14–17] which not only serve as model compounds for studying structural-electronic relationships in the corresponding polymers but also show promise in themselves as potential materials for device applications.[18–21]

Recent work has concentrated on investigating the effect of alkyl substitution on the structure and properties of oligothiophenes.[22–26] Functionalisation with alkyl chains makes oligothiophenes generally more soluble and processable, but sometimes causes an unfavourable change in the molecular planarity and in the stacking arrangements of the rings.

Using ab initio calculations, Aleman *et al.* have shown that unsubstituted bithiophene favours an anti twisted conformation of rings in the isolated molecule, whereas in the solid state the anti planar arrangement is preferred.[27] The energy barriers for anti planar-syn planar interconversion are estimated to be *ca.* 1.7 kcal mol^{-1} for unsubstituted bithiophene in the gaseous phase while the presence of methyl substituents, e.g. in the 3,3′-position (see Scheme 1 for definitions), increases this value to a range of 6.0 to 12.0 kcal mol^{-1}. The two main structural motifs which characterise delocalised π-electron systems are: π-π stacking, where two planar rings interact closely in an offset parallel way, and the herringbone (HRB) pattern, which involves a T-shaped ring arrangement.[28] These two packing types are illustrated in Scheme 1. The presence of sulfur atoms introduces intermolecular interactions such as S---S and C-H---S, which are energetically quite weak (of the order of 1 kcal mol^{-1}) but still capable of influencing the solid state packing.[29,30]

In solution both substituted and unsubstituted oligothiophenes are usually found to be non coplanar.[31] In the solid state, unsubstituted oligothiophenes tend to be coplanar and to pack with the HRB motif.[32,33–40] In the alkyl substituted ones, the aromatic rings can still exhibit π-π or HRB type stacking, though with varying degrees of distortion from coplanarity.



SCHEME 1

In this paper we explore further this effect of substitution on a series of neutral quaterthiophenes (**1–7**) for which both structural and optoelectronic information is available (see Table I and Scheme 2).[31,39–47] These compounds represent a homogeneous class for which structures have all been determined at room temperature and with comparable refinement accuracy. In some of these structures (**4**,**6**) there is also crystallographic disorder, and in one case (**1**,**2**) polymorphism.

TABLE I Refcodes and chemical names of the oligothiophenes in Scheme 2

Compound	*CSD refcode*	*Chemical name*	*Ref.*
1–2	PEWXAQ	2,2’:5’,2:5″,2‴-tetrathiophene	39,40
3	SOTCEJ	5,5‴-dimethyl-2,2’:5’,2″:5″,2‴-tetrathiophene	41
4	PIKGIZ	4’,3″-dimethyl-2,2’:5’,2″:5″,2‴-tetrathiophene	43
5	VUWTEM	4,4’,3″,4‴-tetramethyl-2,2’:5’,2″:5″,2‴-tetrathiophene	42
6	PIKGUL	3,4’,3″,3‴-tetramethyl-2,2’:5’,2″:5″,2‴-tetrathiophene	43
7	PIKGOF	3,3’,4″,3‴-tetramethyl-2,2’:5’,2″:5″,2‴-tetrathiophene	43

We have carried out a detailed analysis of the crystal structure of these quaterthiophenes, with a view to understanding the factors leading to their solid state conformation and arrangement. In particular we have examined such features as torsional distortion in going from solution to solid, short inter and intramolecular distances, cohesion factors, stacking patterns and other characteristics that contribute to the overall structural organisation of the crystal.

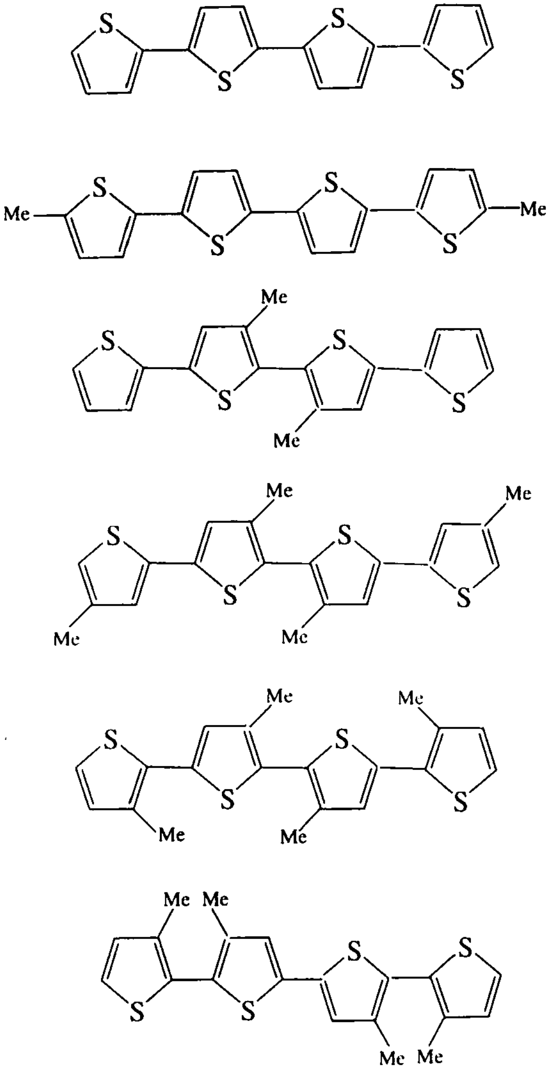
METHOD

The atomic coordinates and cell parameters of these quaterthiophenes were obtained from the Cambridge Structural Database (CSD).[48] All structural parameters were calculated with C-H distances normalised to neutron diffraction average values (1.08 Å). Crystal structures were investigated with the aid of graphics software,[49] and the program PLATON[50] was used to analyse for intermolecular interactions. Potential energy calculations were carried out using a semiempirical approach,[51] based on an atom-atom potential energy method[52] in which the energy terms are calculated as:

$$\text{packing potential energy (p.p.e.)} = \Sigma_j \Sigma_i [A \exp(-Br_{ij}) - Cr_{ij}{}^{-6}]$$

where r_{ij} represents an intermolecular distance, and the indices i and j in the summation run, respectively, over all atoms of the reference molecule and of the surrounding symmetry-related molecules (cut off at 10 Å). The coefficients in the potential-energy function were taken from a compilation by Filippini *et al.*[53] In the presence of structural disorder (molecules **4**,**6**), calculations have been carried out on ordered models, retaining the prevailing conformation of the disordered fragment.

These potential energy calculations can be used as an energy probe to locate the most important intermolecular interactions within the crystal. In particular we can isolate an interaction between nearest neighbour molecules and relate the



1-2

3

4

5

6

7

SCHEME 2

energy of this interaction to the type of packing in the crystal. For the purposes of the following discussion we shall call this the nearest neighbour molecule-molecule interaction (NMI) energy. This energy is useful for comparing intermolecular energies within a crystal, but as it is dependent on the number and type of atoms in the molecule it cannot be used directly to compare NMI energies between different crystals.

The packing coefficient is calculated as:

$$\text{packing coefficient (p.c.)} = Z\ V_{\text{mol}}/V_{\text{cell}}$$

where Z is the number of molecules in the unit cell, and the molecular volume (V_{mol}) is calculated using the integration method.[54]

Molecular mechanics calculations were carried out on molecule **5** with the Cerius^2 software package.[55] The initial geometry was taken from the X-ray data and optimised using a universal force field (UFF).[56]

RESULTS AND DISCUSSION

The neutral quaterthiophenes **1–7** reported in Scheme 2 exhibit some interesting changes when going from solution to the solid state. Table II lists values of the average twisting angle for these thiophenes in solution, estimated from the energy of the first absorption peak in the UV spectrum (λ_{max}),[57] compared with the same angle found in the solid state.

None of these oligomers are coplanar in solution,[31,42] with a distortion angle varying from 44 to 56°. In the solid, oligomers **1, 2, 3** and **5** become coplanar or nearly so. The others, **4, 6, 7** remain distorted in the solid, but the degree or type of distortion has changed. Oligomer **7**, for example, has an anti arrangement in solution, but in the solid it prefers a syn arrangement of adjacent methyl groups.

TABLE II Average twisting angles in solution and solid state of quaterthiophenes

Compound	*Solution*			*Solid state*		
	λ_{max}[a] *(nm)*	*E (eV)*	θ_{av} *(°)*[b]	ω_1*(°)*[c]	ω_2*(°)*	ω_3*(°)*
1	386	3.21	46	0.9	0	0.9
2	–	–	–	0.7	1.3	0.9
3	394	3.15	44	0	0	0
4	346	3.58	54	3.9	55.3	12.6
5	348	3.56	53	3.4	0	3.4
6	340	3.65	56	11.8	28.8	21.3
7	346	3.58	54	54.2	0	54.2

a. From ref. [31,42,44]
b. Calculated according to ref. [57]
c. See Scheme 1 for definition.

The total packing potential energies (p.p.e.), packing coefficients (p.c.) and molecular volumes (V_{mol}) for all the available structures are given in Table III.

From the packing coefficients we can see that planar quaterthiophenes usually form denser crystals, as would be expected, e.g. the coplanar oligomer **5** has a p.c. of 0.73 whereas for the distorted molecule **7** it is 0.67. In crystals such as these where the packing forces are predominantly of the van der Waals type, a higher packing coefficient corresponds to an energetically more cohesive crystal, and therefore represents a more stable solid state configuration.[58]

The crystal arrangements of each quaterthiophene have also been characterised in terms of the most cohesive NMIs (see Table IV).

TABLE III Atom-atom potential energy calculations on crystalline quaterthiophenes

Compound	*p.c.*	*p.p.e. (kcal mol^{-1})*	*V_{mol} (Å^3)*
1	0.73	−79.5	267
2	0.73	−79.9	267
3	0.72	−87.3	295
4	0.69	−76.8	295
5	0.73	−88.0	329
6	0.71	−90.4	329
7	0.67	−84.1	316

TABLE IV Most important inter- and intramolecular interactions in crystalline quaterthiophenes **1–7**

Compound	*S---S (Å)*	*C-H---S (Å)*	*C-H---π (Å) HRB*	*π---π (Å)*
1	–	–	2.77	–
2	–	–	2.74	–
3	–	–	2.78	–
4	–	–	2.84	4.09
5	–	–	–	4.31
6	–	2.8	–	–
7	3.45 (intra)	–	H_8---π 2.80 H_3---C_8 2.79 H_3---C_9 2.98	3.78

The single crystal structure of 2,2′:5′,2:5″,2‴-tetrathiophene has been recently determined simultaneously by two different groups.[39,40] This unsubstituted quaterthiophene crystallises in two forms depending on growth conditions, the "high-temperature" crystal (**1**, space group $P2_1/a$, $Z = 2$) and the "low-temperature" polymorph (**2**, space group $P2_1/c$, $Z = 4$). Interestingly, previous semi-empirical calculations by Gavezzotti predicted the crystal structure of **1**,[32] while a structure determination from polycrystalline material revealed the second polymorph **2**.[36] In both of these structures the oligomer is nearly coplanar (twisting angles of 0.9° for **1**, 0.7 and 1.3° for **2**), in contrast with its twisted conformation in solution (see Table II), and both have an HRB packing arrangement, but with a slight difference in the orientation of nearest neighbour molecules interacting via C-H---π contacts ($\nu = 56°$ in 1, $\nu = 63°$ in 2). In fact, the packing coefficients and total p.p.e. values calculated for **1** and **2** are very similar, as shown in Table III. The most important NMIs are again of the HRB type (see Figure 1), with energies of -11.8 kcal mol^{-1} and -12.0 kcal mol^{-1}, and H---π distances of 2.77 Å, and 2.74 Å respectively, (where H---π is the intermolecular distance between a hydrogen atom and the centre of an aromatic ring).

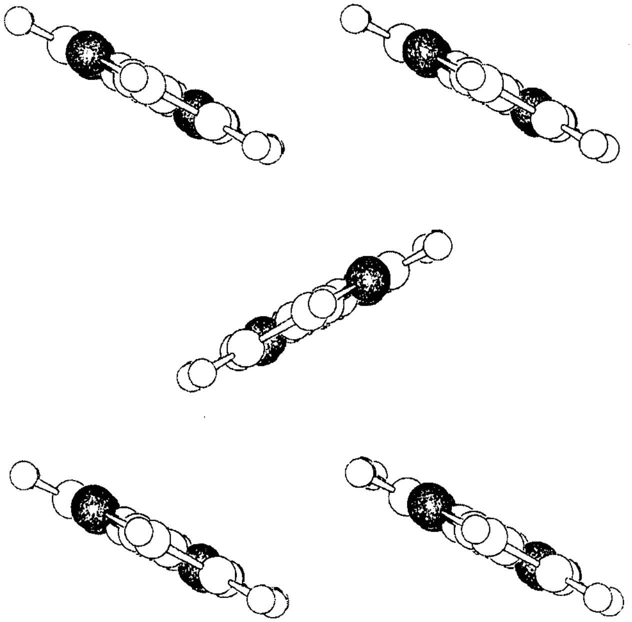


FIGURE 1 Five molecules of **1** (2,2′:5′,2:5″,2‴-tetrathiophene) arranged in a herringbone (HRB) fashion with H---π distances of 2.77 Å. (Filled circles are sulphur atoms, smaller white circles are hydrogen atoms)

The introduction of two methyl groups at the α-position in **3** does not affect the molecular and crystal structure very much in that both are very similar to those found in **1**and **2**, with the crystal packing still dominated by an HRB interaction (NMI energy of -13.7 kcal mol^{-1}). This similarity is also reflected in the electronic properties.[22]

Molecule **4** has two methyl groups at the 4′ and 3″ positions respectively. In the solid there is a torsion of the two inner rings of 55.3°, probably due to the steric hindrance of the methyl groups (see also molecular mechanics calculations below), while the two outer adjacent thiophene rings are nearly coplanar and disordered over two conformations (the main conformation having 88% occupancy). A similar twisting (54°) has been estimated in solution, as seen from Table II. These two sets of coplanar rings stack in the crystal via a combination of HRB and π-π stacking types (Figure 2) with comparable NMI energies of -13.3 kcal mol^{-1} and -12.4 kcal mol^{-1}; in this way the crystal has achieved a p.c. of 0.69 and a p.p.e. of -76.8 kcal mol^{-1}.

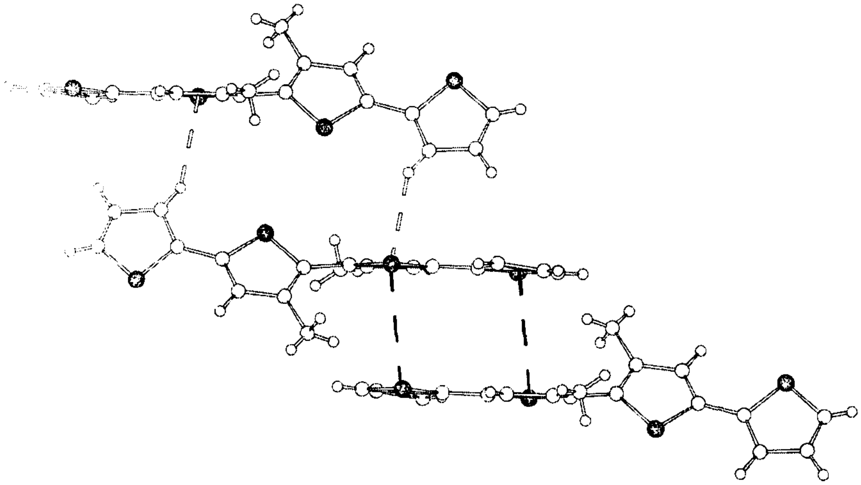


FIGURE 2 Combined HRB and π-π stacking interactions in crystalline **4** (4′,3″-dimethyl-2,2′:5′,2″:5″,2‴-tetrathiophene) with π-π distances (black broken lines) of 4.09 Å and H--- π distances (white broken lines) of 2.84 Å. (Filled circles are sulphur atoms, smaller white circles are hydrogen atoms)

In molecule **5**, the substitution pattern changes, with two more methyl groups added at the 4,4‴ sites on the oligomer backbone. In solution, this molecule also has a torsion of about 53°, as in **4**, but in contrast to **4**, the torsion decreases in the solid so that the molecules become essentially coplanar, and a different type of packing is found. In this case the HRB arrangement gives way entirely to a π-π type of stacking of the nearly coplanar rings. Figure 3 illustrates the π-π offset of about 3.3 Å which is in keeping with the prediction by Hunter and Sanders of a major offset in π-π stacking when π-σ attractions dominate[28a]. The potential energy calculations show that this is the strongest intermolecular interaction in the crystal, with an NMI energy of -18.9 kcal mol^{-1}, leading to very efficient crystal packing (p.c. = 0.73) and an overall p.p.e value of –88.0 kcal mol^{-1} (see Table III).

Molecular mechanics calculations have been used to evaluate the steric hindrance of the inner ring methyl group in this oligomer. The planar molecule determined experimentally by X-rays was used as the starting geometry for the optimisation. The final calculated molecular geometry shows a torsional angle between the inner thiophenes of ca. 56°, while the outer rings remain coplanar with respect to the inner ones (i.e. a geometry similar to **4**). The van der Waals energy difference between the calculated (twisted) and the experimental (planar) molecular geometry of **5** accounts for 5.7 kcal mol^{-1}, an estimation of the steric repulsion of the side methyl substituents within this planar molecule.

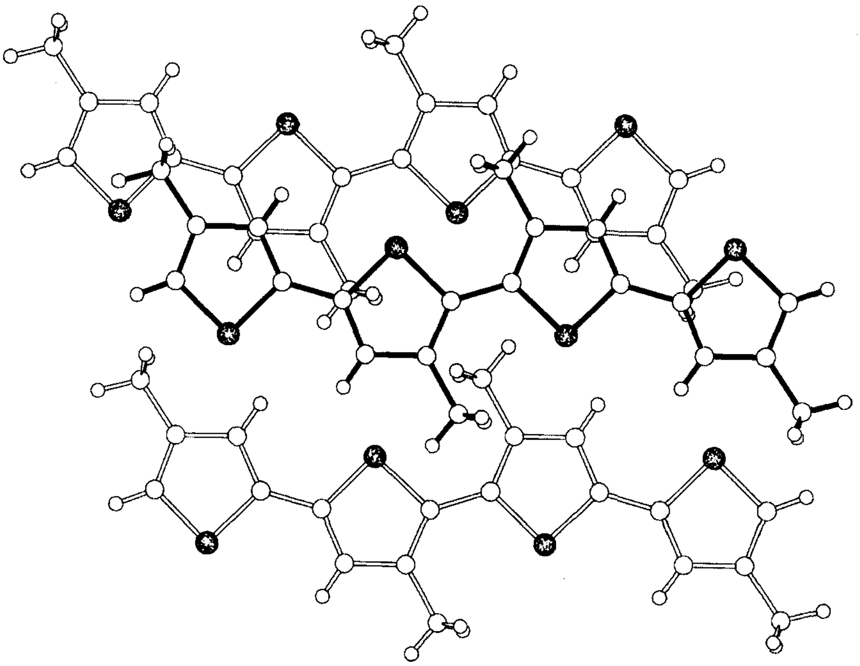


FIGURE 3 Projection onto the *ab*-plane showing the offset π-π stacking in **5** (4,4′,3′,4′-tetramethyl-2,2′:5′,2″:5″,2‴-tetrathiophene). (Filled circles are sulphur atoms, smaller white circles are hydrogen atoms)

In other words, by becoming coplanar in the solid and by adopting a π-π type of stacking, the crystal has overcome the steric repulsive forces of the methyl groups and has gained a significant amount of cohesive energy.

In molecule **6**, the extra two methyl groups are now at sites 3 and 3‴. In solution, the torsion of the inner rings is again similar to **4** (about 56°), but in the

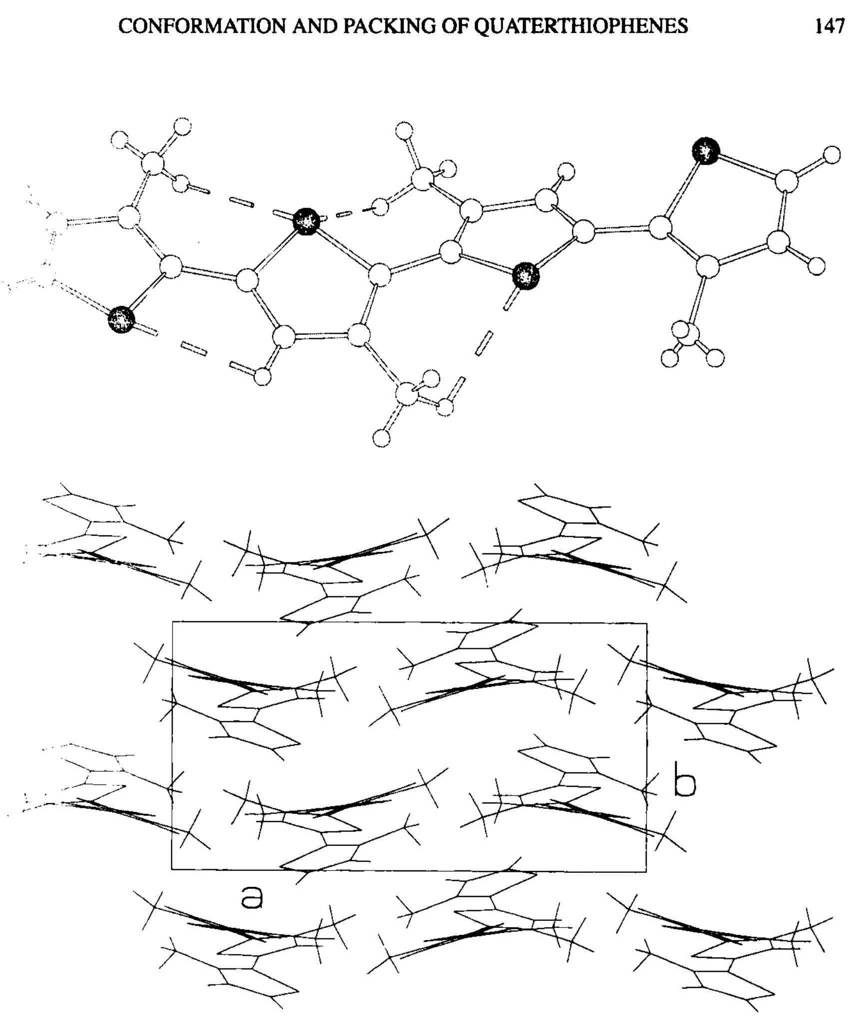


FIGURE 4 (a) Molecular geometry of **6** (3,4′,3″,3‴-tetramethyl-2,2′:5′,2″:5″,2‴-tetrathiophene) showing short C-H---S intramolecular contacts of ca. 2.8 Å. (Filled circles are sulphur atoms, smaller white circles are hydrogen atoms). (b) Pseudo π-π stacking organisation of **6** in the solid state

solid yet another molecular conformation is found, this time with three different inter-ring angles of 11.8°, 28.8° and 21.3°. One ring is also disordered, with 84% in its main orientation. Short C-H---S intramolecular contacts are found between the β-methyl substituents and sulfur atoms of the adjacent rings, as illustrated in Figure 4a, of the order of 2.8 Å. More accurate ab initio calculations would be needed to shed light on whether the actual solid state conformation of **6** is driven by steric hindrance of the methyl groups or by a cohesive C-H---S "hydrogen bonding" type of interaction, or both.

In spite of the molecular distortion, the molecules are still able to pack with a pseudo π-π type of stacking (Figure 4b), with a significant NMI energy along the stacking direction (-16.3 kcal mol^{-1}) and an overall packing coefficient of 0.71 and a p.p.e energy of –90.4 kcal mol^{-1}.

An intriguing case is offered by molecule **7**, which has the same methyl substitution as **6** on the outer rings but with 3′,4″ substitution on the inner rings. In solution the rings have an anti conformation as shown from NMR studies and as predicted by force field calculations,[31] with an average twist again of about 54°. The situation in the solid however, is very different. Here the inner rings are exactly coplanar, and the external rings have a non-coplanar syn conformation, with an angle of twist of 54.2°. This conformation also brings the outer bulky methyl substituents into a syn arrangement. The reason for this seemingly unfavourable situation is the presence of both intramolecular interactions of the type S---S (S---S = 3.45 Å) and intermolecular interactions of the type C-H---S (H---S = 2.90 Å) and C-H---π (H---π = 2.80 Å). This arrangement leads to a pseudo HRB type of stacking, with a strong cohesive NMI (E = -11.3 kcal mol^{-1}). The C-H---ring interactions contributing to this NMI include a symmetric H---π bond with a distance of 2.80 Å, and a non-symmetric one, with $C\text{-}H_3\text{---}C_8$ and $C\text{-}H_3\text{---}C_9$ distances of 2.79 Å and 2.98 Å respectively (see Figure 5a). Another important NMI in the crystal (E = –8.2 kcal mol^{-1}) exploits the planarity of one of the outer rings which interact via π-π stacking along the *c*-axis, giving an intermolecular ring-ring distance of 3.78 Å. This distance is comparable to the π-π stacking distance estimated for regioregular poly(3-hexylthiophene).[12] Figure 5b shows how molecules of **7** are organised in the solid state via this type of stacking.

CONCLUSIONS

In this study we have shown how the presence and positions of methyl groups influence the conformation and crystal packing of a series of seven neutral quaterthiophenes. The solid state planarity of these substituted quaterthiophenes is the result of an interplay between steric constraints and intra or intermolecular interactions. In this context the difference between the structures in the solid state and those found in solution can be explained. For example, the seemingly unfavorable syn arrangement of adjacent methyl groups in crystalline oligomer **7** is the result of an optimisation of S---S, C-H---S and C-H---π interactions, and the coplanarity in crystalline oligomer **5** is the result of very efficient crystal packing via π---π interactions which allows a gain in overall energy even at the expense of a certain amount of internal steric constraint. The most important inter- and

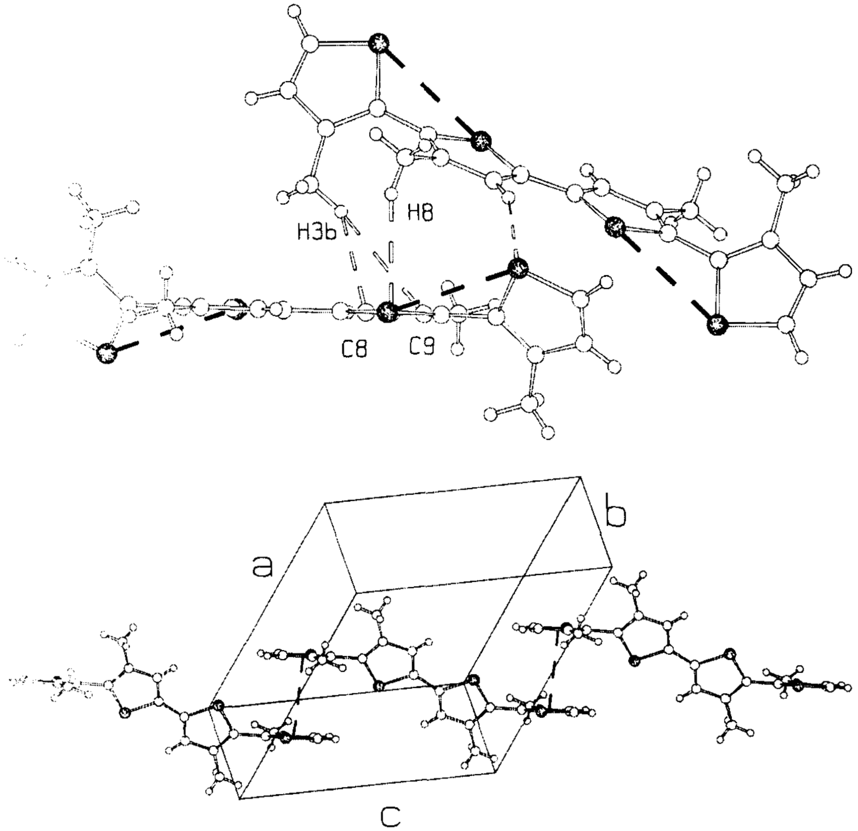


FIGURE 5 (a) Intramolecular S---S interactions (black broken lines) and hydrogen bonded intermolecular interactions (white broken lines). associated with the most cohesive NMIs of 7 (3,3′,4″,3‴-tetramethyl-2,2′:5′,2″:5″,2‴-tetrathiophene). H---S distances are 2.90 Å, and H_8---π, H_3---C_8 and H_3---C_9 distances are 2.80, 2.79 and 2.98 Å, respectively. (b) View of oligomer 7 showing the next strongest NMI. Broken lines refer to π-π distances of 3.78 Å. (Filled circles are sulphur atoms, smaller white circles are hydrogen atoms)

intramolecular solid state interactions in all seven crystals analysed in this work are summarised in Table IV.

This study provides a useful insight into the solid state organisation of these thiophene-based systems and will facilitate the formulation of realistic structural models for the corresponding thiophene polymers.

Acknowledgements

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