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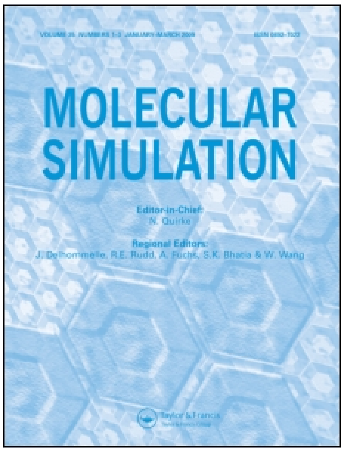

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An Atomistic Investigation of Helical Polythiophene

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AN ATOMISTIC INVESTIGATION OF HELICAL POLYTHIOPHENE

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An atomistic lattice simulation method invoking bonded, nonbonded and torsional interactions has been used to simulate infinitely long polythiophene helices both as single chains and in a hexagonal lattice. It is shown that while the lowest energy of the polymer is for the all-planar *anti* conformation (torsional angle $\phi = 0°$), the helical structure becomes stabilised at $\phi \approx 170°$, provided the variation of the π-component of the torsional energy allows for an energy barrier separating the planar forms ($\phi = 0°$, $180°$) of at least 0.3 eV, indicating a significant quinoid component, which might result from doping. When the chains form a hexagonal lattice ($a \approx 13.0$ Å) the helical pitch increases from 7.1 to 11.4 Å as adjacent helices partially 'interleave'.

KEY WORDS: Polythiophene, lattice simulation, helix, conformation.

1 INTRODUCTION

Electron microscopy has revealed the presence of helical conformations in several polymer samples, usually in isolated chains, i.e. not in a crystalline environment [1–5]. The same methods [4–6] sometimes confirm the findings of diffraction studies [6–8] in describing polymer materials as microcrystallites dispersed in amorphous regions. While the crystalline regions have usually been identified with polymer chains in *planar* configurations [7], electron microscopy studies [4–5] sometimes combined with diffraction methods [6, 8], show that the crystalline regions in some polymers also contain helical chains.

Usually the sample heterogeneity and the small sizes of the microcrystallites limit the precision of the structural studies. Even where investigators have succeeded in obtaining diffraction data that have been interpreted to provide lattice structures, the *different* structures sometimes afforded by investigations on nominally the *same* materials suggest that either (*a*) the interpretations of the diffractograms are ambiguous or (*b*) the dominant lattice structure in the sample is sensitive to sample preparation. For some of these polymers, atomistic lattice simulation studies have proved to be of value in simulating probable structures [9–11]. The fact that these lattice simulation methods sometimes predict the existence of some of the apparently 'conflicting' structures obtained from experiment suggests that some conducting polymers, at least, may exhibit polymorphism.

Electrochemically synthesized polythiophene possesses a primary structure in which the aromatic rings are linked mainly in the α, α' positions [12, 13]. Diffraction studies [14, 15] on these structures show that there are two *planar* polythiophene chains per monoclinic unit cell, with the C_4H_2S rings adopting the alternating disposition depicted in Figure 1 (a). This chain is described as being in the *anti* conformation, and when discussing polythiophene structures we shall define the torsional angle ϕ between adjacent rings as that measured from this conformation. Thus the *anti* conformation is is specified by $\phi = 0°$, and the sterically-precluded *syn* conformation of Figure 1 (b) by $\phi = 180°$.

Garnier *et al.* [6, 8] used a combination of electron microscopy and diffraction methods to investigate β-methylpolythiophene, doped to a level of 50% with the trifluoromethylsulphonate anion, as a result of which they proposed a hexagonal lattice of polymer helices. The coils had an overall width of 19 Å and a pitch (the separation of adjacent loops in the coil) of 7.1 Å. The translation repeat segment of length 12–14 Å contained two loops of the chain. The hexagonal lattice distance $a = 9.5$ Å separates the axes of the nearest-neighbour helices.

In a later scanning tunnelling microscopy (STM) investigation [5], Yang *et al.* found helical structures of similar dimensions in unsubstituted polythiophene and polypyrrole doped with a variety of p-dopant anions. They found a pitch of 8 Å and a width of 18 Å for polythiophene (5 Å and 15 Å for polypyrrole). The authors also interpreted some STM images as being due to superhelices.

Using various semi-empirical methods to calculate conformational profiles of polythiophene and poly-β-methylthiophene single chains, Cui and Kertesz [17] found that the unsubstituted polymer had a stable all-planar (*anti*) structure, i.e. a zero torsional angle ϕ, and a higher-energy coil at $\phi = 144°$ with a large width. In poly-β-methylthiophene the substituent displaces the energy minimum at $\phi = 0°$ to one defining a small-width helix with $\phi = 20°$; the large-width helix shown by the unsubstituted polymer is retained, with the torsional angle shifted by only 2° to $\phi = 146°$. The latter fact is consistent with the observation made above in the discussion of the electron microscopy/diffraction work, namely, that small substituents seem to have minor effects on helical parameters in structures that are near the *syn* conformation.

Few theoretical investigations have been reported on the characteristics of helical polymer chain *lattices*: therefore in this work we should like to examine the factors that decide the structural parameters of the helices in a lattice environment. For example, it would be desirable to know whether or not the planarity derived from the data on the polythiophene lattice in some of the diffraction studies arises from the stabilisation of the planar chain by π-electron delocalisation, or whether it is due to inter-chain forces. What, on the other hand, would be the dominant configuration of the chain in an amorphous state or in a solute or melt? Zerbi and co-workers performed ir and nmr investigations on the dimer and trimer oligomers of thiophene and of pyrrole in the gaseous and liquid phases. Their conclusions, that were also supported by a series of semi-empirical quantum chemical calculations, were that the thiophene and pyrrole units possess a tendency to twist around the inter-ring bonds [16]. Although planar chains have been shown to exist in pristine polythiophene lattices, the tendency of solid

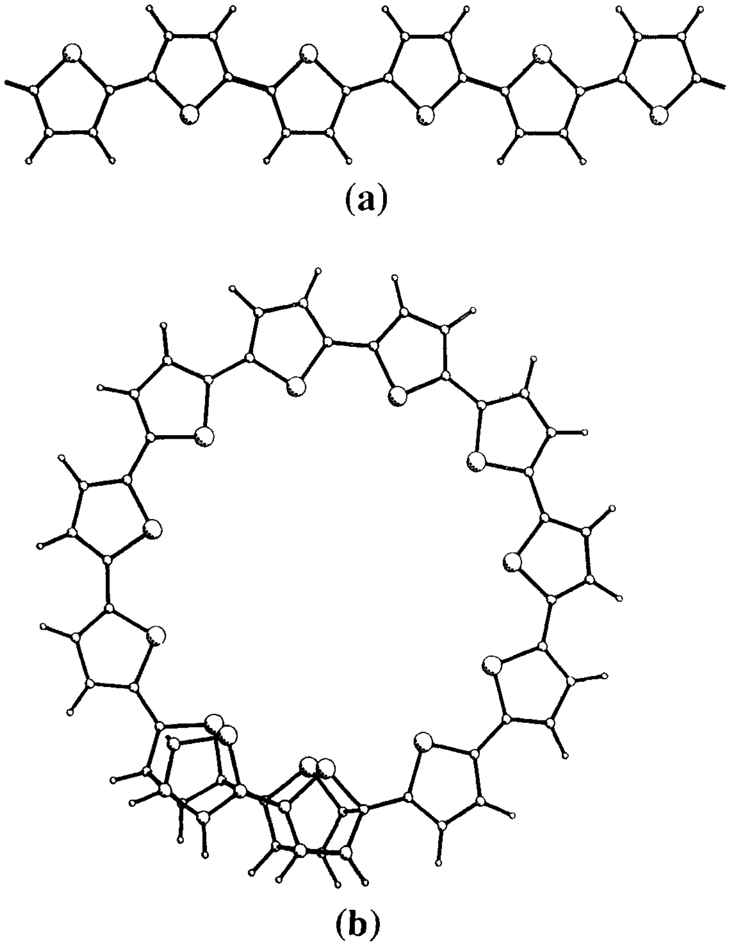

Figure 1 The primary structure of α, α'-linked polythiophene. The torsional angle ϕ around the inter-ring C—C bond is defined as that in which $\phi = 0°$ describes the all-*anti* conformation (**a**) and $\phi = 180°$ the sterically impossible all-*syn* structure (**b**).

polymer samples to exhibit polymorphism (see discussion in refs. 9 and 11) leads to the expectation that samples may, in addition, contain regions in which the polymer chains assume non-planar conformations, as indeed is indicated by the electron microscopy studies.

2 CHAIN MODEL AND METHOD OF CALCULATION

2.1 Helical chains

As the torsional angle ϕ in polythiophene in the *anti* conformation increases from 0° the chain passes through a series of helical conformations which are characterised by a *pitch*, a *width* and (except for short chains), a *repeat length*. These structural parameters are illustrated in Figure 2. When ϕ is 180° the conformation is again planar, with the rings in *syn* positions, but since the ends of the chain would superimpose for a length of 11–12 rings, shown in Figure 1(b), a torsional angle of precisely 180° is precluded.

It is expected that the stabilities of helical polythiophene would be influenced by contributions such as the following:

(1) Non-bonded repulsions between pairs of nearest-neighbour sulphur atoms at chain conformations near the $\phi = 180°$ *syn* form. In the 180° limit the S atoms would approach to 3.2 Å, which is less than their van der Waals diameter of 3.7 Å.
(2) Repulsions between segments on the same chain that are separated by 11 rings or more when ϕ is close to 180°.
(3) The loss of π-orbital stability or 'chain conjugation' upon departing from the all-planar conformations.
(4) The lowering of the energy of the chain by the 'stacking' configuration of aromatic rings in adjacent loops of the coils when ϕ approaches 180°. Stabilising stacking contributions to the energy are found in certain hydrocarbon lattices and in graphite.
(5) Interactions with other helical chains. There is a possibility that adjacent chains could approach sufficiently closely for their loops to 'interleave'.
(6) Substituents on the aromatic ring. These would normally lead to non-bonded repulsions (in the absence of groups that take part in hydrogen bonding such as those that stabilise helices in peptides and proteins).
(7) Interactions involving the dopant ions that are introduced in order to confer electrical conductivity on the polymer material.

The helices found in the reported electron microscopy/diffraction investigations on polythiophene and polypyrrole [5, 6, 8] have torsional angles ϕ close to 180°, showing chain conformations close to the *syn* arrangement of adjacent rings. Although the values found for the pitch (5 to 8 Å) are greater than the 3.35 Å between the lamellae in graphite or the nucleotide bases in the DNA helix (probably because of repulsions such

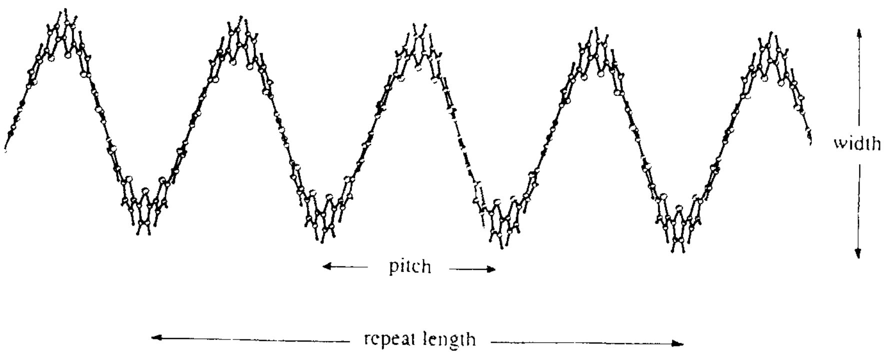

Figure 2 A length of helical polythiophene defining the terms *width*, *pitch* and *repeat length*. The helix is that defined by $\phi = 169.75°$ in Table 1, and its repeat segment contains 3 turns and 32 monomer units.

as those described in (1) and (2) above), we shall nevertheless refer to the arrangement of the thiophene rings in adjacent loops as 'stacked'. Since the TEM/diffraction investiations conducted on methyl-substituted polythiophene revealed a pitch of *ca.* 7 Å while STM on unsubstituted polythiophene gave *ca.* 8 Å, it would appear that the rôle played by the methyl group in increasing the pitch from the stacked-ring value may be a minor one.

Because structural parameters of the helical chains might be affected by interchain interactions (point (5) above), it is necessary that the system chosen for the calculation should include more than one polymer chain. We resolve the ensuing conflict between system size and computational accuracy by selecting an atomistic simulation method that, calling on periodic boundary conditions, may be applied to a crystal lattice. For the work to be presented here we have used the lattice simulation program CASCADE [18], which calculates the lattice energy employing two-, three-and four-body atom potentials (describing non-bonding interactions, deformations of bonds and bond angles, and intramolecular torsions) as well as atomic Coulomb interactions. These potentials, which usually involve the assumption of analytic forms such as Buckingham, Lennard-Jones, Morse, harmonic etc., have been described and listed by several authors [9–11, 19–22]. The energy may then be minimised with respect to the structure of the unit cell by a variational technique to produce an optimum structure and chain geometry. The potentials have been developed in such a way as to reproduce a larger number of experimentally measured molecular structures, and have subsequently been observed to provide a good agreement with the features of several polymer lattices. Their use in a previous atomistic simulation investigation of the lattice structure of polythiophene gave results in agreement with those of diffraction studies [14, 15]. Below, that simulation work will be referred to as I.

2.2 *Molecular geometry*

The bond lengths and bond angles used to describe the chain geometry of polythiophene are those used in I. In that work the absence of measurements on polythiophene made it necessary to use the bond lengths and angles derived by Mintmire *et al.* from a MNDO treatment of the polymer [23]. This quantum chemical method is generally accepted as reliable for molecular geometries, and the results compare quite well with measurements derived from diffraction investigations on solid dithiophene.

2.3 *Atomistic potentials: inter-ring torsion*

The sources of most of the atom-pair and atom-triad potentials have been described in I. One difference in the present work is the treatment of the inter-ring torsion which, although clearly of importance in an investigation of helical structures, is unfortunately difficult to specify reliably. We shall assume that it can be described by the periodic form

$$V(\phi)=(v/2)[1-\cos(2\phi)] \tag{1}$$

so that v is the height of the energy barrier involved in a torsional rotation about the inter-ring bond. $V(\phi)$ is not the *actual* energy change that is invoked by the torsion:

a part of that quantity would of course be provided by the atom-pair potentials describing interactions between non-bonded atom pairs whose separations vary during the torsional motion, e.g. the pairs S...S, H...H and S...H. This energy variation would clearly not possess a two-fold periodicity in the $0° \leqslant \phi \leqslant 360°$ range, and so v in eq. (1) should be defined as the result of the two-fold 'making and breaking' of the formal π-electron conjugation during the torsion, with v the energy barrier for this process. As a guide to the selection of the v parameter we selected the values contained in the DREIDING force field proposed by Mayo *et al.*, [22] which include the following cases of interest to the present case:

carbon-carbon bond		v (eV)
$\mathrm{C}{=}\mathrm{C}$	olefinic	1.95
$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$	aromatic	1.09
$\mathrm{C}{-}\mathrm{C}$	'sp^2 single'	0.22

The third entry refers to a bond of low π-bond order such as C_2—C_3 in butadiene or the interphenyl bond in diphenyl, C_6H_5—C_6H_5. Clearly it might also be used for polythiophene. Two factors press for caution in the use of these figures, particularly that relating to the 'single' C—C bond. Firstly, torsional potentials culled from the force fields used by different workers to describe corresponding C—C torsions show little agreement. Secondly, we must bear in mind that if the polymer is in its oxidised (i.e. conducting) state due to the action of p-dopants, then polaron-or bipolaron-chain distortions would be expected to produce a significant quinoidal contribution to the electronic structure of the chain [24, 25]. As a result of the dopant-induced bonding pattern shown in Figure 3 the inter-ring bond may acquire a high π-bond order. A recent ESR/visible spectroscopic investigation of polythiophene oligomers showed that chains greater than certain lengths may spontaneously acquire polarons or bipolarons without the action of dopants [26].

Clearly, the acquisition of quinoidal character by the chain would favour two structures:

(a) planar chains in which ϕ is zero, thus defining an *anti* sequence of rings, and
(b) chains in which ϕ is nearly 180°, resulting in a helix of small pitch. This conformation allows the thiophene rings to form a nearly parallel, approximately stacked arrangement.

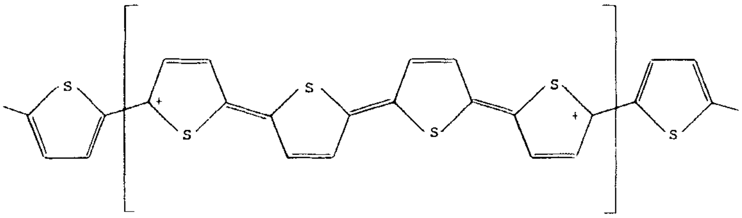

Figure 3 The interaction between the polythiophene chain and an oxidising dopant species results in a transfer of electronic charge between the two component systems. The effect is accompanied by a polaron or (as shown here) a dipolaron distortion, resulting in a quinodial bonding pattern in the doped regions. As a result, the chain possesses enhanced olefinic character in the inter-ring C—C bond.

We have seen that both (a) and (b) have been identified in polythiophene, but that while the planar structure (a) was assumed by the pristine polymer [14, 15], the sample in which the helical conformation (b) was identified was highly doped [6, 8]. Thus, although the doping-induced quinoidal character favours both structures, it is less necessary in (a) since a comparison of structure investigations on oligomers of thiophene in the crystalline [14, 15] and fluid [16] states show that planar configurations are in any case favoured by lattice forces. The formation of the (B) structure must be aided by the acquisition of olefinic character by the inter-ring bonds.

In our investigations the uncertainties associated with the estimation of v were avoided by performing sets of calculations in which the value of v was varied over a suitable range in order to observe the effect of π-conjugation on the stabilisation of the helical structures.

3 RESULTS

3.1 *Generation of translationally-periodic helices*

Starting from a planar (all-*anti*) polythiophene chain with the geometry defined in Section 2.2, the program HELIX [27] was used to apply torsional rotations ϕ to the inter-ring bonds and to examine the resulting chain for translational periodicity within a given number of monomer units. In this way a chain sequence that would form the basis of unit cell of an infinite lattice was generated. Results of this calculation for helical chains showing translational periodicity within 50 thiophene rings are displayed in Table 1. Of course there is no requirement for helical chains in the actual polymer to exhibit translational periodicity, but such structures have had to be assumed in order to apply the periodic boundary conditions in the method which we use to treat lattices. Provided the repeat unit used for the calculation can be made sufficiently large this should not be a serious restriction, and the table shows that there is a sufficiently high occurrence of helices to monitor the effect of changing the torsional angle in the $0° \leqslant \phi < 180°$ range.

3.2 *Helix structures*

(a) One-dimensional lattice (single chain) In the initial calculations a large unit cell was considered so as to define a 'one-dimensional lattice' consisting of an isolated, infinitely long helical chain.

The lattice energies and hence the energy per thiophene ring, E_r, were calculated for the various translationally-periodic helical chains with the torsional angles ϕ that are listed in Table 1. Because of uncertainty regarding the most suitable v parameter to use in the torsional potential expression of equation (1), the effects of several values in the range $0 \leqslant v \leqslant 2.0\,\text{eV}$ suggested by the DREIDING force field [22] were explored, and the results plotted against ϕ in Figure 4.

The most stable conformer is found always to be the planar chain for which $\phi = 0°$. As v increases the set of energy curves reveals a threshold energy barrier at $v \approx 0.3\,\text{eV}$,

Table 1 Structural parameters of some helical conformations of polythiophene possessing translational periodicity. ϕ is the inter-ring torsional angle.

ϕ (*deg.*)	*Repeat length* (*Å*)	*Repeat segment* *No. of rings*	*No. of turns*	*Width* (*Å*)	*Pitch* (*Å*)
6.46	112.50	29	14	4.70	8.04
9.86	73.69	19	9	4.71	8.19
20.83	34.87	9	4	4.74	8.72
33.10	65.73	17	7	4.80	9.39
40.80	88.76	23	9	4.85	9.86
62.73	11.48	3	1	5.09	11.48
83.99	67.76	18	5	5.53	13.55
94.79	14.86	4	1	5.87	14.86
99.45	77.43	21	5	6.06	15.49
114.72	17.80	5	1	6.90	17.80
119.86	55.99	16	3	7.30	18.66
128.68	20.16	6	1	8.17	20.16
136.90	85.73	27	4	9.27	21.43
139.35	21.74	7	1	9.670	21.74
143.92	44.31	15	2	10.50	22.16
152.12	43.99	17	2	12.33	22.00
155.95	21.27	9	1	13.33	21.27
161.04	58.05	29	3	14.75	19.35
163.69	17.81	10	1	15.50	17.81
169.75	38.20	32	3	17.07	12.73
171.00	102.75	97	9	17.34	11.42
174.06	7.85	11	1	17.89	7.85
177.33	25.34	78	7	18.25	3.62
178.40	13.07	67	6	18.31	2.18

above which the '$\phi \approx 180°$ helices also become stabilised, to an energy which is 0.20 eV higher than that of the $\phi = 0°$ structures. This implies that the stacking-like arrangement of the thiophene rings in the latter structures is unable to stabilise the helices without the aid of the dopant-induced quinoid contribution that enhances the π bond order of the inter-ring bonds. This is consistent with the observation of helical structures only for highly-doped polythiophene, while planar chain lattices can be formed by the pristine polymer. At torsional angles $\phi > 177.4°$ the energy curves for all the v values rise sharply as the stacking separation d (pitch) becomes less than ~ 3.5 Å. Figure 4(b) shows that although the energy curves pass through a very shallow minimum at $\phi = 177.33°$ (where d would indeed correspond to the stacking distance in graphite [28] and DNA bases [29]), their flatness between 175° and 177.4° suggests a considerable conformational freedom in this ϕ range.

The effect of the v parameter was then examined on the structure of the helices with torsional angles ϕ near to 180°. The molecular geometries were optimised by allowing the structure to relax fully in a set of energy variation calculations for different values of v (0, 0.2, 0.5, 1.0, 1.5 and 2.0 eV). The relaxation seems to favour the initial structure with a torsional angle $\phi = 174.06°$, and a pitch of 7.85 Å. Those with larger torsional angles, that would lead to a pitch corresponding to the graphitic stacking distance $d \approx 3.5$ Å could not be stabilised.

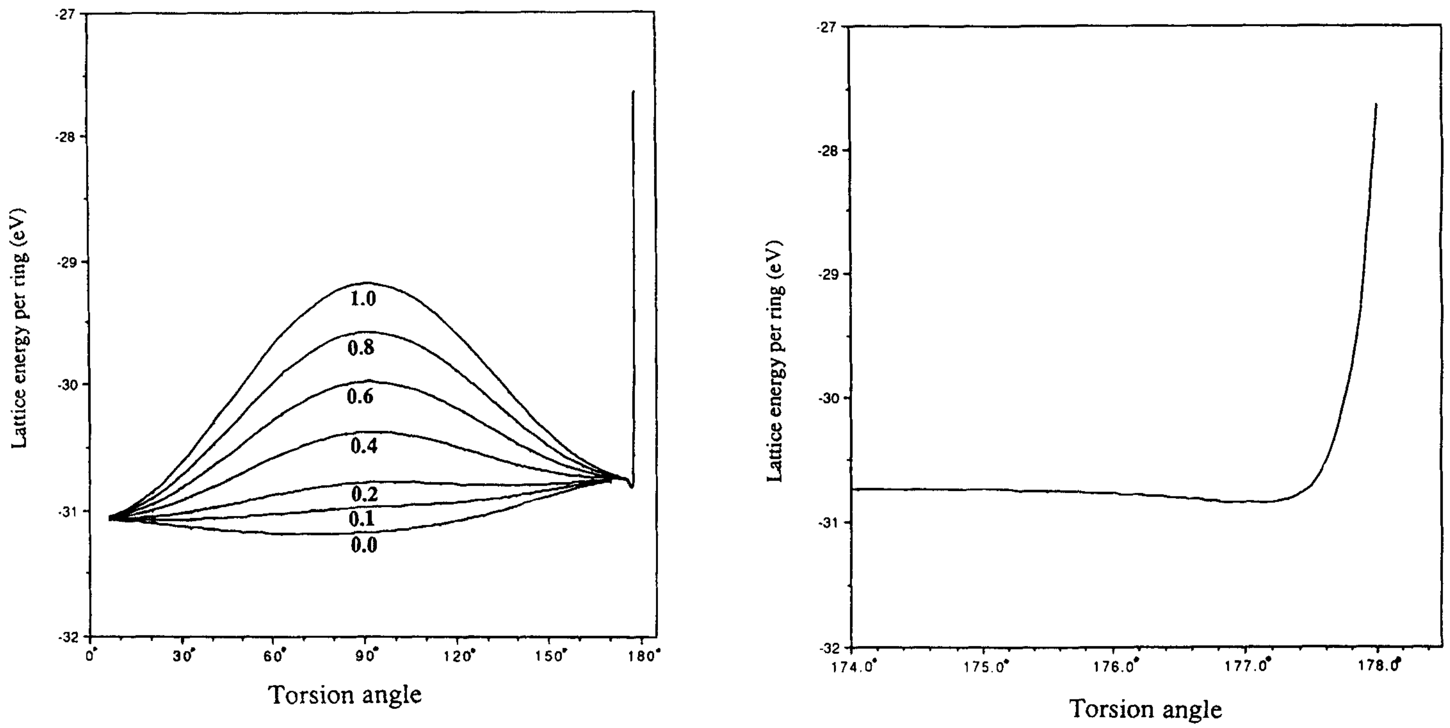

Figure 4 The 'lattice' energy per thiophene ring as a function of the torsional angle ϕ between the ring segments. The family of curves in (**a**) are for the indicated values of the π-bond torsional parameter v defined by equation (1) and the text. In the (**b**) figure the ϕ axis is expanded to reveal the 'blip' in (**a**) when ϕ approaches 180° and the energy barrier at this limit, where the curves are practically independent of v.

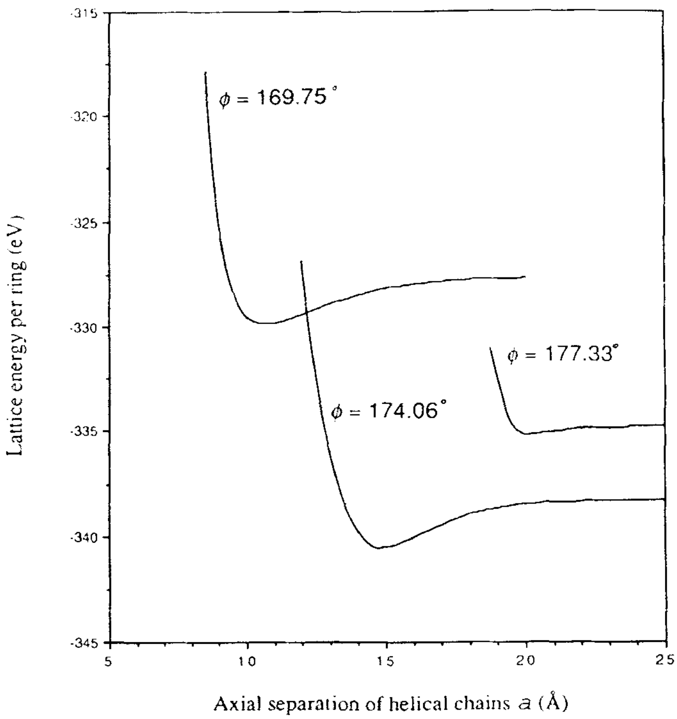

Figure 5 The lattice energy of the unrelaxed hexagonal lattice showing its variation with axial separation *a* (the length of the lattice vector) for the three most stable helical polythiophene lattices in Table 1.

Provided v is sufficiently large to stabilise the helix, the final structure was found to be rather insensitive to the value of v chosen. Because the torsional angle $\phi = 174.06°$ defines a structure close to the all-*syn* form, the relaxation produces practically no change on the width of the helix; however as it results in dropping the strict observance of the screw-axis symmetry condition, the various torsional angles ϕ in the unit cell show a slight, but uniform oscillation between 176.20° and 176.53°. The $\phi = 174.06°$ structure in Table 1 (calculated from the assumed molecular geometry, which dictated a pitch of 7.85 Å) relaxed to one with a pitch of 7.1–7.2 Å. This value might at first appear to be in excellent accord with the 7.1 Å derived from the diffraction studies of Garnier *et al.* [6, 8]; it must be remembered, however, that the polymer structure investigated in that work differs somewhat from the one described in this sub-section. The experimental investigation was on a lattice in which the interactions between neighbouring chains could significantly affect the helical parameters, whereas the model being considered at present is that of a *single* polythiophene helical chain. In addition, we are not considering the effect of the $SO_3CF_3^-$ dopant ions or the methyl ring substituent that were associated with the polymer chains in the diffraction investigation.

(b) Three-dimensional lattice For our trial lattice we chose the hexagonal structure derived by Garnier *et al.* [6, 8], in which each helical chain was surrounded at equal

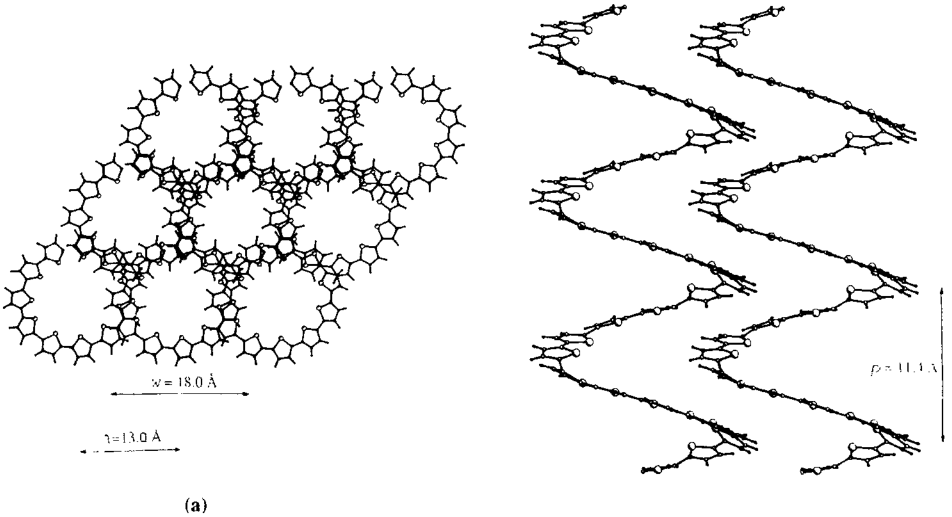

Figure 6 The lowest-energy relaxed lattice structure of helical polythiophene projected on planes (**a**) normal to, and (**b**) containing, the helical axes, showing the cell length *a*, the external width *w* and the pitch *p* of the helices. In (**a**) three cell lengths along each axis have been taken to show the almost hexagonal environment of each chain. The pair of adjacent chains in (**b**) has been included to show the extent of their 'interleaving'.

interaxial distances *a* by six similar chains. Without, as yet, allowing the lattice to relax to its minimum energy, the relative stabilities of the three-dimensional lattices determined in this way show slight differences from those of the *single-chain* lattices reported in (a) above. The most stable helix is now that with $\phi = 174.06°$. The family of curves in Figure 5 includes the three most stable chain conformations found, and shows the dependence of the lattice energy per thiophene ring on the inter-axial distance *a*. The most stable conformation of all ($\phi = 174.06°$) shows a minimum at $a = 14.8$ Å. Since the width of the helix is 17.9 Å, the separation *a* of the chains indicates that the strands of adjacent helical chains with these distance parameters would be expected to partially interleave. A possible consequence of this is an expansion of the repeat segment along the axial direction of the helical chain. It is therefore important to allow the lattice to relax as was described in (a) above for the single chain.

The result of the relaxation simulation is a lattice in which the hexagonal symmetry of the initial condition is almost preserved: the cell vectors are directed at an angle of 123°, and they have lengths $a = 13.2$ and $a' = 12.8$ Å. The torsional angles around the inter-ring C—C bonds show a greater variation than in the relaxed single chain, ranging non-uniformly between the limits 167.7° and 179.0°. The relaxed lattice structure is depicted in Figure 6, in which neighbouring cells have been included to show the approximately hexagonal environment of each helical chain.

The hexagonal lattice vector length $a = 13.0$ Å compared with the helical width $w = 18$ Å implies, as shown in Figure 6, that adjacent helices partially interleave. This was found also in the rigid-lattice calculations described above, but it will be observed that the adjustment of the atomic positions associated with the relaxation of the lattice results in a shortening of *a* from 14.8 to 13.0 Å, thereby allowing the chains to approach each other more closely. Probably as a result of the interleaving, the pitch of the helical chains increases from 7.1 Å for the isolated chain to 11.4 Å. A consequence of this structure is the non-availability of sites for dopant species *between* the helices. The dopants would have to occupy positions either in the axial cavities or between the helical turns.

4 CONCLUSIONS AND DISCUSSION

The present investigation has been on the 'inherent' abilities of polythiophene to form helices as a single chain and also as a lattice of such chains, without explicit inclusion of dopant species. In this respect it parallels the quantum chemical studies of Cui and Kertesz [17] on single polymer chains, who found tendencies to form both all-planar *anti* structures and also *syn*-like helical conformations. Thus, atomistic lattice simulation of polythiophene using standard interatomic potentials predicts both (*i*) a planar all-*anti* conformation of polythiophene (**I**) that is consistent with diffraction studies [14, 15] and (*ii*) a higher-energy polymorph consisting of helices,both in single chains and also in a lattice, which is also supported by experiment [6, 8].

We found that in the absence of other polythiophene chains a single helix is stable when the torsional angle ϕ around the inter-ring C—C bond is about 174°, resulting in a pitch of 7.1 Å, and a width of 17.9 Å. The stability is dependent on the possession, by the inter-ring carbon-carbon bond, of a substantial degree of 'double bond' character. In a conducting polymer, this could be caused by polaron distortions of the polythiophene chain resulting from chain-dopant interaction. The transfer of electronic charge between the polymer and the dopant species results in the imposition of quinoid bonding patterns on π-conjugated molecular chains [24, 25], which would indeed be expected to decrease the ease of torsion about the inter-ring carbon-carbon bonds.

The single-chain results are in reasonable agreement with the helical structures found in scanning tunnelling microscopy studies of BF_4^--doped polythiophene, from which pitch and width values of 8 and 15–18 Å respectively were derived [5]. The inclusion of the dopant species between the helical coils as proposed by the authors of the scanning tunnelling microscopy work might account for the slightly larger pitch found in their investigations.

The lattice simulations led to a structure in which the helical chains showed axial separations of 13 Å and a pitch of 11.4 Å. The larger value of the pitch in the hexagonal lattice, compared with that in the single helix, is interpreted as a consequence of 'interleaving' of the helical stands in adjacent coils. Surprisingly, a smaller pitch is reported from the X-ray diffraction studies of Garnier *et al.* [6, 8] than in the tunnelling microscopy findings on the single helices—7.1 Å (compared with 8 Å from the single helical chains) which is just the average value we derived for the *single* helical chain. If the structural parameters of the $CF_3SO_3^-$-doped methylpolythiophene depends only on the host polymer system, it is difficult to see why the expected interleaving of strands does not lead to an increase in the value of the pitch. It is possible that the large trifluoromethylsulphonate dopant ions are located between neighbouring helices, thereby serving as spacers to prevent the interleaving expected by the host chains. In this case the pitch would indeed be expected to be that (7–8 Å) found and calculated for the isolated helices.

It has already been pointed out that the lattice structure presented in this work does not provide sites for the dopant ions between adjacent chains. They would have to occupy positions either between the helical strands or within the axial cavity of the helix (rather like helicenes—coils of angularly fused benzenoid [30] and heteroaromatic [31] rings—wrap themselves around guest ions). According to the structures presented in this work, the former location would offer an intercalation region characterised by a space of 7 Å in the single chain and by $(1/2) \times 11 = 5.5$ Å in the hexagonal lattice, allowing for the interleaving of adjacent helices. The axial cavity region is more spacious, consisting of a hollow tube with width 11 Å; however the sites favoured by the dopants are decided by their interactions with the host polymer which must maintain the essential charge transfer, and might therefore require a close association with the strands of the polymer.

The question of the sites and migration route of the dopants is of importance in an understanding of the electric-field induced redox changes in electronic devices such as the charging-discharging cycle of batteries containing doped polythiophene electrodes. The host-dopant interactions and the rôle played by the dopant ions in helical polythiophene in deciding the structures of the single chain and of the lattice, as well as their migration through the lattice of the conducting polymer, will form the subject of future work.

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