

Atomistic Investigation of Thermochromism in a Poly(3-alkylthiophene)

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In an attempt to explain the mechanism of thermochromism in poly(3-alkylthiophene)s we conducted lattice energy and Monte Carlo calculations to investigate the conformational structures and conformational energy profiles of the butyl side chains. The results reveal barriers of 0.3–0.6 eV (agreeing with the range found experimentally) and predict stable lattice structures in which the butyl side chains are in low-lying well-defined gauche and cis conformations as well as the lowest energy trans. If a thiophene ring is displaced from its regular position in which it is coplanar with its neighbors and the lattice is then allowed to relax to its minimum energy structure, the ring returns to coplanarity only if its alkyl side chain is in an all-trans conformation. If on the other hand the alkyl bears a gauche or a cis linkage, the ring takes up one of a number of out-of-plane distortions coupled with torsions of several degrees around the bonds linking it with its neighbors. A series of ab initio quantum chemical calculations was conducted to establish the type of distortions of the polythiophene backbone that would reveal the observed thermochromism. One of these is a torsion around the inter-ring bonds; another is a booklike folding of the rings, both of which (among others) were predicted by the lattice relaxation calculations.

1. Introduction

As well as possessing the electrical properties that are associated with polymers having π -conjugated backbones, polythiophenes in which the ring is substituted at a position β to the sulfur atom constitute a group of electroactive polymers of special interest. First the blocking of the thiophene ring's 3 position precludes the occasional ring coupling at this site during the polymerization which would diminish the structural periodicity of the polymer chain and hence lead to a lower electrical conductivity.¹ Moreover, if the substituent is a flexible alkyl or alkoxy chain, the resulting polymers are found to be fusible,² to be soluble in common solvents,³ to form Langmuir–Blodgett films with optical and electrical properties,^{4–6} and to exhibit solvatochromism and thermochromism;^{7–9} that is, they show spectral shifts on changing the solvent or temperature. The absence of these properties in unsubstituted polythiophene suggests that they owe their origin to the substituent groups which constitute flexible side chains. It is the stiffness of the conjugated chains that is responsible for the insolubilities and infusibilities of materials such as polyacetylene and polythiophene, but the main-chain rigidity that is present also in the substituted polythiophenes is here offset by the flexibility of the side chains, whose conformational entropy facilitates the fusibility of the polymers and the process of solution.

A series of such polymers of current interest are the poly(3-alkylthiophene)s (P3ATs), whose thermochromism,^{7–14} electrical properties,^{15–19} and crystal structures^{20–31} have been the subject of several investigations. However the precise role of the alkyl chains in the thermochromism is not clear. It is usually assumed that the energy of the thermally induced conformational changes (conformons) effected in the alkyl groups is transferred to the thiophene main chain.¹⁰ The consequent (either localized or extended) deviation from planarity of the conjugated backbone is thought to lead to an increase in the gap between the

electronic valence and conduction bands and hence to a blue-shift in the electronic transitions involving these bands. There is indeed structural evidence that a temperature increase causes P3AT to lose the planarity of the thiophene backbone by undergoing conformational torsions about bonds linking the thiophene rings.³² The resulting loss of π conjugation produces a wider HOMO–LUMO energy gap and hence a blue-shift in the UV–visible spectrum. In alkoxy-substituted polythiophenes Roux and Leclerc calculated¹³ that the shift corresponded to a torsion of the thiophene rings of as much as 45° when the material was heated to 150 °C. However whether such conformation changes can occur free from the association of other distortions has yet to be demonstrated.

To examine the validity of the common supposition that the thermochromism is a consequence of main chain torsions, we must first examine the “primary” structure of the polymer. The predominant configuration of the thiophene units in P3AT materials is, as in polythiophene, one in which the thiophene rings are linked in the anti arrangement; that is, it has a structure in which the orientation of the rings alternates along the chain as shown in Figure 1. The conformation of the main chain in P3AT is important in a discussion in which distortions of the π conjugation plane are invoked to explain thermochromism. According to the bond angles measured in oligothiophenes, there are two directions associated with the C–C bonds linking the thiophene rings. As these make a mutual angle of 160°, any molecular torsion around these bonds would result in a drastic modification of the regular structure in which the polymer is aligned along the *c* axis.³³ It would appear that the only simple ways in which torsions around these bonds can occur while ensuring regularity along the chain direction would be one of the following. In the first, a torsion about just *one* of the inter-ring bonds labeled * in Figure 1 could be combined with an out-of-plane distortion of the thiophene ring. In the second, *both* * C–C bonds might bend sufficiently to come into line (i.e. increase their mutual angle from 160° to 180°), so that the

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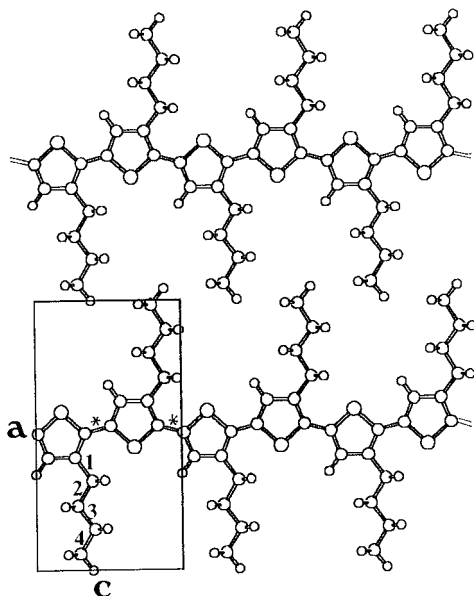


Figure 1. Two adjacent, coplanar P3AT chains according to diffraction^{20,22–24} investigations. Chains in a parallel plane at $1/2b$ have been omitted to show the interdigitation of the alkyl side chains and the angle between the inter-ring bonds that are labeled *.

thiophene ring between them could twist around the new common axis. Wang et al.³⁴ in their tight-binding semiempirical calculations on single polythiophene chains concluded that such distortions would impose high energies (~ 2 eV per monomer) and considered the possibility of helical conformations that would be formed by the application of *constant* torsional angles around the inter-ring bonds. They showed that such changes would be expected to increase the bandgap of the polymer. But although there is both experimental and theoretical evidence for the stability of helical structures in both methyl-substituted^{35,36} and unsubstituted^{37,38} polythiophenes, it is difficult to conceive of *reversible* thermal effects accomplishing such a highly activated transition in which the main polymer chain would be oriented in quite a different direction from its original one, while maintaining the observed crystallinity of the material.²²

In this work we investigate the distortions in P3AT chains using the atomistic lattice simulation method, which has been successfully applied in recent years to describe π -conjugated polymer lattices,^{39–41} particularly torsions in lattices of various types of conjugated chains.^{38,42} In ref 33 and in a preliminary report of the present work⁴³ we showed that the method can also be usefully applied to investigate both features of P3AT chains described above, namely the conformational freedoms and the response of the conjugated backbone to thermal energy.

2. Method of Calculation

The atomistic lattice simulation method is well-known both in its original form^{44,45} and as applied to lattices of hydrocarbon chains.^{38–42} We need therefore only describe its general outline as a calculation of lattice energy, with the inclusion of periodic boundary conditions, from a trial structure defined by a set of atoms in a unit cell and a set of two-, three-, and four-body interatomic potential functions. The two-body terms include the Coulombic energy $q_i q_j / (4\pi\epsilon_0 r_{ij})$ arising from the partial charges q_i and q_j on atoms i and j at the separation r_{ij} . It also includes the interactions between bonded atoms for which in the present case we employ Morse functions of the type

$$V(r) = A[1 - e^{-B(r-r_0)}]^2 - A \quad (1)$$

where r is the separation of the atom pair whose equilibrium bond length is r_0 , A is approximately the dissociation energy of the bond, and B depends on A and on the stretching force constant k of the bond according to $B = \sqrt{k/2A}$. Finally the two-body terms include the interactions between nonbonded atoms separated by a distance r , for which we use functions (atom-pair “potentials”) of the Buckingham form

$$V(r) = A e^{-r/\rho} - Cr^{-6} \quad (2)$$

The three-body functions describe the directional properties of the bonding potentials. The energy required to change the bond angle from its equilibrium value θ_0 to a deformed angle θ is given by the harmonic bond angle bending function

$$V(\theta) = \frac{1}{2}\kappa(\theta - \theta_0)^2 \quad (3)$$

where κ is the bending force constant. Finally, a four-body function is introduced to help describe the energy changes incurred when two parts of a molecule undergo relative torsion through an angle ϕ :

$$V(\phi) = v_0 \cos[1 - \cos(n\phi)] \quad (4)$$

where n is the number of cycles of $V(\phi)$ in a complete revolution. It is important to point out that $V(\phi)$ accounts for only that part of the torsional energy that is associated with the π and σ components of the electronic system. Contributions from the varying nonbonded interactions as the interatomic distances between atoms on different rings change with ϕ are already included in (2). The parameter v_0 then becomes the energy barrier incurred by the elimination of the pure π bond when ϕ is swept to 90° .

For the parameters in eqs 1–3 we used those tested for polythiophene,⁴⁰ which were shown also³³ to be in accord with diffraction structures on P3ATs by Kawai and co-workers.^{20,22–24} Because of the near-zero torsional angles found between the monomer units of electroactive polymers, it is difficult to fix the v_0 parameter in eq 4 from experiment. We therefore followed the procedure described in our earlier work on P3AT lattices³³ of transporting the value optimized in our calculations on the biphenyl lattice⁴² and used to simulate single chains and lattices of helical polythiophene.³⁸

The calculation of the lattice energy and its minimization by the subsequent relaxation of the structures was performed by the perfect-lattice segments of the atomistic lattice simulation codes GULP.⁴⁶ This program has options of various methods to minimize the lattice energy, which can sometimes prove useful if the energy wells on the potential surface depart from harmonic. However in common with all energy minimization methods, there is no guarantee that without repeating the procedure from a large set of initial structures the method will locate the global energy minimum.

The motions of chain segments in polymers can occur readily at normal temperatures, often giving rise to conformational states with thermally accessible energies. Although polymorphism in the solid state is therefore not unexpected in polymers containing alkyl chains, it may occur also in rigid conjugated polymers such as polyacetylene, polyparaphenylene, and polythiophene. This is revealed by the finding of crystal structures,^{47–52} supported by lattice simulation studies,^{39,40} in which the two parallel polymer chains in the unit cell can be mutually oriented at more than one angle between their carbon planes. The “setting-angle polymorphism” suggests that whole-chain rotation of these narrow polymers may be activated in the conditions which are obtained during the polymer synthesis. Since polymer lattices are prone to polymorphism, caution must

be exercised when energy minimization methods are used as a basis for the optimization of structures. These methods rely on the curvature of the multidimensional energy surface to locate energy minima, which do not necessarily include the desired global minimum.

We attempted to counter the problem of confinement to local energy minima by using a Monte Carlo method in conjunction with the energy minimization procedure inherent in GULP. In the former method the bond lengths and bond angles of the polymer were kept at their equilibrium values, but by the use of a Monte Carlo program specially written for the P3AT lattice it was hoped that the applications of random changes to torsional angles in the alkyl side chains would allow accessibility to their lowest energy conformations. For this reason the temperature was taken to be 0 K. Sets of random torsional angles were applied with the maximum permitted value "tormax" decreasing to half its previous value until it reached 0.25° . The halving of the tormax parameter was made only after one thousand successive tries had produced no energy decrease. Another advantage of the Monte Carlo approach is its lack of sensitivity to instabilities in the lattice relaxation path under conditions of high steric energy.

3. Structures

3.1. Molecular and Crystal Structure. The crystal structure used for the simulation calculations is based on that provided by diffraction investigations,^{20,22–24} in which two chains are aligned along the c axis of an orthorhombic unit cell with parameters $a = 13.18$, $b = 7.52$, $c = 7.77$ Å. The thiophene rings constituting the main chain are coplanar, and the alkyl side chains are in a trans (fully extended) conformation, with their carbon atoms also occupying the same plane as that of the main chain. The alkyl side chains are approximately parallel and are at right angles to the main chain, so that the alkyl groups on one polymer chain are directed toward the spaces between the alkyls on a coplanar adjacent polymer chain, as shown in Figure 1. If, as is the case in the Kawai structure, the tips of the alkyl chains on one polymer protrude into the spaces between the alkyl chains of a coplanar, adjacent polymer, the resulting arrangement of the side chains is referred to as "interdigitation".

Of the other reported P3AT crystal structures, that defined by the monoclinic cell of Mårdalen et al. >(containing one polymer chain)⁵³ is similar to that of Kawai and co-workers. Although we do not consider it in this work, we should like to call attention also to the "abutted chain" structure described by Winokur et al.^{28–31} in which each alkyl side chain, although in a planar (all-trans) conformation, is uniformly twisted about the C–C bond attaching it to the thiophene ring, resulting in a nonplanarity of the polymer backbone with its side chains. In this arrangement of the alkyl chains interdigitation is precluded and correlated torsional motion in the side chains of neighboring coplanar polymers should be absent. In a very recent X-ray diffraction⁵⁴ reported by the Osaka group, Tashiro et al. tested four lattice models and concluded that discrepancies with the observed diffractograms are minimized for a layer structure in which the carbon planes are inclined to the crystalline a axis. Because of the lack of accord on the details of the P3AT lattice structure by various workers, we selected the simplest one, in which the polymers are in the ac plane.

In the results of diffraction investigations leading to structures in which the side-chain carbon atoms are found to be coplanar with the main chain there is a small discrepancy in the measured value of the cell parameter a . Kawai and co-workers^{20,22–24} find $a = 13.18$ Å, while Gustafsson et al.⁵⁵ give $a = 12.7$ Å. The a distance determines the degree of interdigitation of the

butyl chains on coplanar adjacent polymers. In a recent paper³³ we showed that the approach of the polymer chains in this direction gives rise to a number of minima, some of which we associated with interdigitation of the alkyl chains. In the present work we use our own energy-optimized value $a = 14.2$ Å, which is the lowest point of a rather shallow, multim minima energy well. The remaining lattice parameters provided by our energy minimization of the all-planar polymer conformation and which are also used in this work are $b = 7.40$ and $c = 7.98$ Å; these are in reasonable agreement with those found from the diffraction studies already quoted^{20,22–24} ($b = 7.56$ and $c = 7.76$ Å). Obtaining correct values for a and b requires the use of accurate nonbonded atom-pair potentials, whereas the c parameter is of course dictated by the molecular geometry taken for the thiophene ring.

3.2. The Alkyl Side Chain. Our choice of the butyl group to investigate side-chain motion in P3AT was the result of striking a balance between, on one hand, taking chains that were sufficiently long to exhibit thermochromism and, on the other, longer chains demanding excessive computing times. The problem concerning the latter is aggravated by two additional factors that characterize the calculations being described. First, in the energy-minimizing method (that used by GULP), the increasing conformational freedom as the alkyl chain becomes longer implies a correspondingly greater risk of identifying a local energy minimum as the global minimum. As this problem can only be countered by allowing the lattice to relax from several initial structures with slightly different conformations, it is clear that this approach is impracticable for long alkyl chains. Second, to eliminate the possibility of simulating the same rotational motion for all the alkyl chains, we represented the lattice structure by a "supercell" consisting of more than one crystallographic unit cell. Torsional motions could thus be investigated in a single alkyl chain in such a way that ensured that the immediately neighboring alkyls relaxed in response to the imposed conformational motion of the selected chain.

The butyl side chain's C–C bonds about which we consider torsion are numbered from the thiophene ring as shown in Figure 1. The most facile torsional motion is expected to be that around link 4, i.e., that associated with the "internal rotation" of the chain's terminal CH_3 group. Here the carbon skeleton of the alkyl side chain remains stationary, and consequently the motion should require little or no increase in conformational volume, as would be the case for torsion around other C–C bonds.

The thermal motions of the side-chain atoms are based upon lattice torsional modes that involve the whole alkyl chain (and in principle the polymer backbone also). However the restriction to torsion around the C–C bonds increases so severely as we go from the terminal methyl toward the thiophene ring that it may be a useful simplification to consider the rotations around each of the various C–C bonds separately. Using the lattice simulation method, this was done by twisting the free end of the butyl chain by an angle ϕ around a selected C–C bond in poly(3-butylthiophene) (P3BT). The four atoms defining the dihedral angle ϕ were then frozen, i.e. held stationary while all the other atoms in the unit cell (including the remaining ones in the same alkyl chain) relaxed around this set of atoms. The same approach was employed in the Monte Carlo method, which we improved over the calculation presented in our preliminary report⁴⁶ by allowing all the atoms of the selected butyl chain to relax except the four defining the torsion.

4. Side-Chain Torsions

4.1. Lattice Energy Minimization Method. The unit cell upon which we based our simulations contains two polymer chains A and B aligned along the c axis, the planes of whose

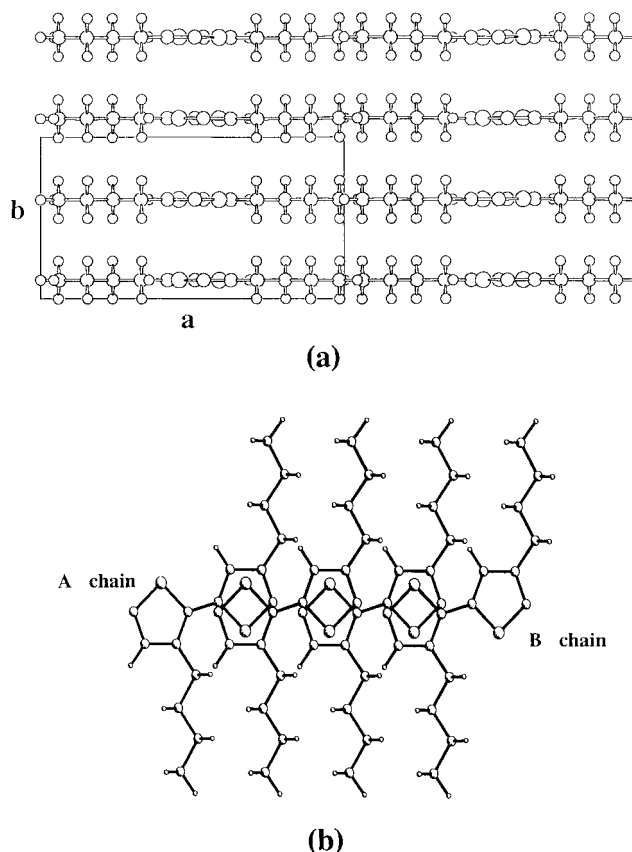


Figure 2. Two chains in the unit cell viewed along (a) the c axis, which is also the direction of the polymer main chain. The B chain is shown separated from the A chain by $1/2b$. (b) Lattice viewed along the a axis showing the two superimposed chains, with the rings in a "staggered" relationship.

main chains are parallel to ac , as shown in Figure 2. The lattice therefore consists of a layer structure in which each polymer chain forms a column of chains ABAB... stacked along the b axis with a separation of $1/2b = 3.88 \text{ \AA}$. The diffraction results describe chains A and B as being shifted by approximately half a repeat segment of the anti chain (3.88 \AA), so that when viewed along b the thiophene rings present a "staggered" relationship, as shown in Figure 2b. In addition to the two neighboring B chains above and below its plane, each A chain lies between its two nearest coplanar translational images at separations $\pm|a|$ decided by the length of the alkyl side chain (here butyl, where $a = 14.25 \text{ \AA}$). It is the geometric arrangement in these coplanar chains that gives rise to that type of interaction of the alkyl side groups, resulting in the possibility of interdigitation (Figure 1). We conducted our calculations on a $1 \times 1 \times 2$ supercell by doubling the length of the cell along the c axis so that it contains four thiophene rings per chain rather than two as in the crystallographic cell. This precludes the restrictions resulting from identical relaxations for adjacent butyl groups on the same main chain.

Figure 3 shows the energy profiles calculated (plotted with the same scale) when torsions were imposed around the various C—C links constituting the butyl group, numbered as in Figure 1. The figure shows the lattice energy calculated when all the atoms were permitted to relax except the four atoms used to define the torsion. Data points to construct the profiles were taken in the range $0^\circ < \phi < 360^\circ$, but because of the point group symmetry of the unit cell the curves for the portion 180° – 360° were near-reflections of those from 0° – 180° . In plotting the energy profiles the points in the former range have been folded into the 0° – 180° range to supplement those of the latter. The lines joining the plotted points serve as a guide to the eye

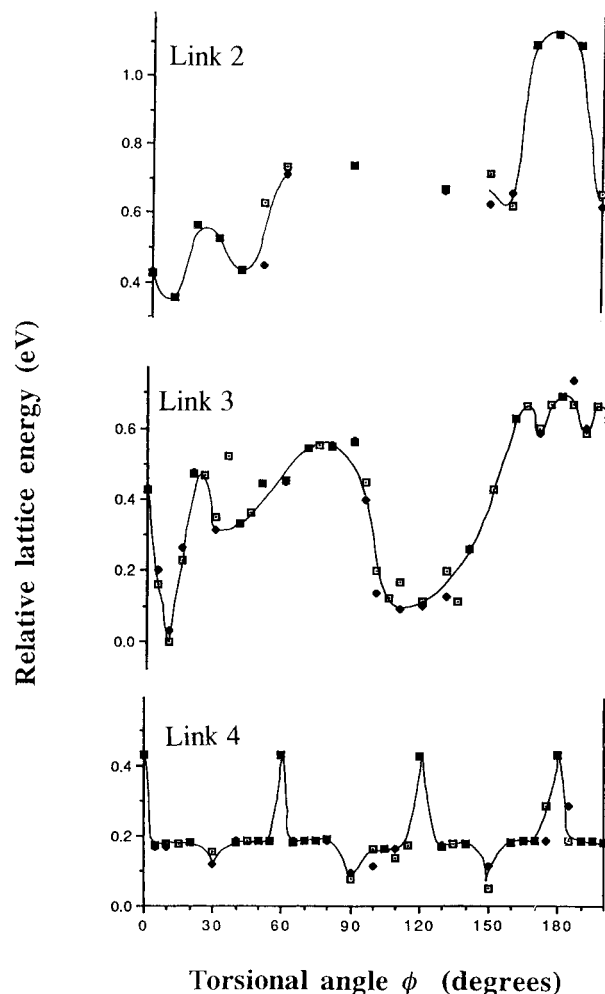


Figure 3. Energy profiles, as obtained by lattice energy minimization, when a torsion ϕ is applied to one butyl chain along links 2, 3, and 4 (see text), allowing the lattice to relax. The three are plotted with the same scale so as to allow a comparison of the energy barriers. The uncertainty in the link 2 profile is discussed in the text. Here and in Figure 4 the two plotting symbols refer to plots from 0° to 180° and from 180° to 360° (the symmetry of the unit cell allows the latter plots to be "folded" into the 0° – 180° range).

to distinguish the three sets of points and have no theoretical significance.

The torsion around link 4, the terminal C—C bond in the side chain, corresponding to the methyl group internal rotation is shown to be characterized by a low-energy barrier (approximately 0.2 eV), and the profile shows the necessary 120° periodicity along ϕ . In fact the curve repeats the "spiked" maximum every 60° , the origin of which is not clear and, since they are not supported by other energy points, may be a spurious effect resulting from a trapping of the lattice in local energy minima at these conformations. The 0.1 eV dips in the curve, however, appear to be genuine. The profile describing the ethyl group's rotation (link 3) has two barriers of 0.45 and 0.60 eV . It shows a well-defined minimum at $\phi = 120^\circ$, indicating the stability of the gauche conformation about this C—C bond. An examination of the atomic coordinates in the thiophene rings showed that throughout the ϕ range each ring remained planar and also coplanar with its neighbors.

It is difficult to make estimates of the barrier of the propyl group (around link 2); the degree of scatter of the plotted points indicates that the lattice has relaxed to a number of unconnected *relative* energy-minimum polymorphs rather than to the more structurally significant *global* minimum. The missing portion of the profile for the torsion around link 2 is a consequence of

the tendency of the minimization methods to lead to lattice instability under conditions of high steric strain. The minimization method did not tolerate torsions of greater than 20° around link 1; no energy profile for this torsion therefore appears in Figure 3.

Interestingly, the lowest minima of profiles for links 2 and 3 are at ϕ values close to 10° , where the energy falls sharply from peaks at 0° . This implies that the side chains adopt conformations that deviate slightly from strictly trans ($\phi = 0^\circ$). The profiles of links 2 and 3 in Figure 3 also show small energy minima fairly close to the cis conformation ($\phi = 180^\circ$). The smallness of these wells might suggest that the corresponding conformations are of minor importance, but we shall see in the next section that they are supported by the results of other calculations. If they are indeed significant then the near-trans and the near-cis wells imply that the side chains adopt conformations that are nearly (rather than perfectly) planar.

4.2. Monte Carlo Calculations. Since the bond lengths and bond angles in the alkyl groups are not permitted to change during the Monte Carlo relaxations, this method can be applied to conditions where the steric strain is too high for the full lattice energy minimization methods to operate successfully. Because of the smaller number of optimizable structural parameters in comparison with those in the lattice energy minimization method, a larger $2 \times 2 \times 2$ cell was selected in order to provide as realistic an environment as was practicable for the rotational motion. We initially tested the reliability of the random-torsion approach by generating the relaxed lattice with several different number "seeds". The resulting sets of calculated energies were very similar, as we showed in the Monte Carlo energy plots for link 3 in our earlier paper.⁴³

The energy profiles in Figure 4 reveal a clearer trend than those that were obtained using the lattice energy minimization method. The torsion around link 4, i.e., the rotation of the terminal CH_3 group, which, of the four torsions considered, requires the smallest space, occurs with an energy barrier of only about 0.1 eV and, except for the necessary 120° periodicity, does not show the features (spiked barriers) of the energy minimization calculation in section 4.1. The profiles reveal the requirement of progressively larger amounts of free volume as we pass to link 3 by showing energy barriers of 0.6 eV (and subsidiary barriers of 0.4 and 0.3 eV) and for link 2 two barriers of 0.5 and nearly 1.3 eV. The shape of the energy profile for link 3 shows a distinct minimum at $\phi = 120^\circ$ corresponding to a *gauche* conformation about this C–C bond and a less well-defined one at 165° near the cis conformation. Rotation around link 2 passes through a relative minimum near $\phi = 90^\circ$. Complete (360°) rotations around links 3 and 2 would require overcoming barriers of 1.0 and 1.8 eV, respectively.

For the torsion around link 1, the profile (shown in the inset in Figure 4) progresses, via two subsidiary peaks of 7 and 15 eV at 60° and 140° , to a very high, sharp barrier at $\phi = 150^\circ$. Near the syn conformation of link 1 at 170° the curve falls rapidly to a relative energy minimum just 2 eV higher than the global minimum at the trans position. Although the high barrier precludes the direct accessibility of the syn from the trans conformation by torsion, a syn linkage produced during the polymerization, for example, might be stabilized by the lattice.

Experimentally it is difficult to identify a measured energy barrier with torsion around a particular alkyl C–C bond in P3ATs. However it is interesting that in their conductivity relaxation investigations of chain motions in P3BTs in the glassy and melt states, Chen and Liao detected energy barriers of 0.38 and 0.74 eV.⁵⁶ These values are in accord with the barriers we calculate for torsional motion around link 3 using both the lattice energy minimization (0.45 and 0.60 eV) and Monte Carlo (0.3,

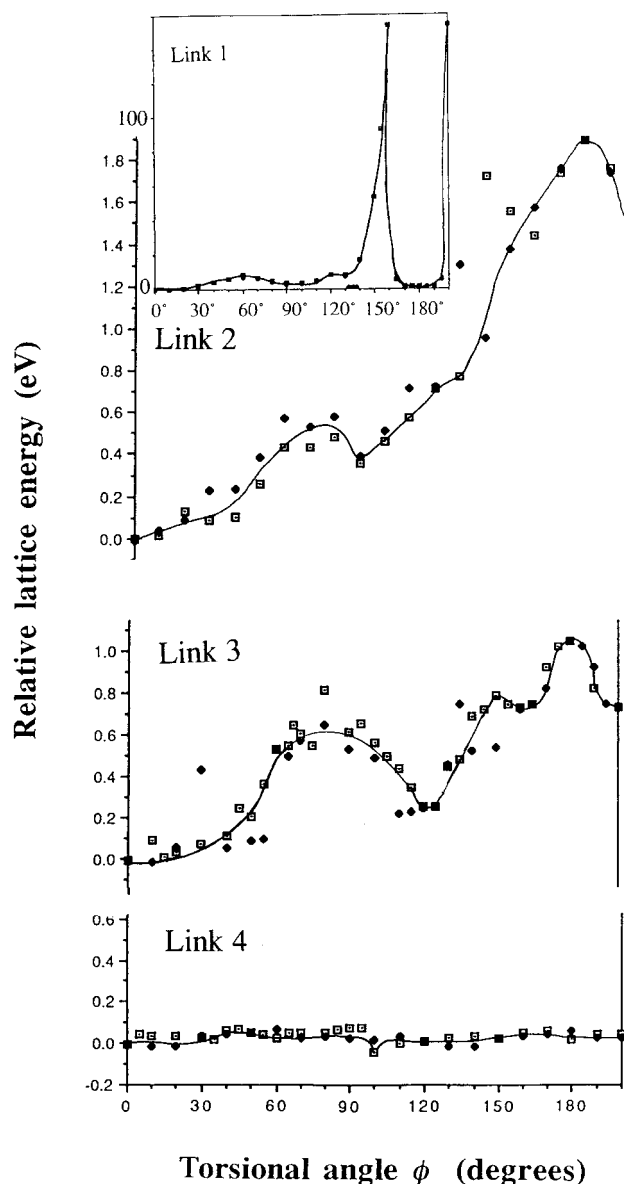


Figure 4. Energy profiles, as obtained by a Monte Carlo calculation, when a torsion ϕ is applied to one butyl chain along links 1, 2, 3, and 4 (see text), allowing the other links in all butyl chains to relax. Equal energy scales are used for plotting except for link 1, whose profile is shown as an inset.

0.4, and 0.60 eV) methods. These are also consistent with the 0.45 eV activation energy attributed to methyl reorientation from proton magnetic resonance relaxation times in solid-state alkanes.⁵⁷ The profiles, particularly those for link 4 torsions, also show the presence of minor barriers on the order of 0.1 eV. It would be hard to identify these with certainty with experimental measurements, but it is perhaps worth noting that spin–lattice relaxation times from NMR investigations have postulated barriers of 1–3 kcal mol⁻¹ (0.04–0.13 eV) in P3AT samples with long P3AT side chains.⁵⁸

The energy profiles obtained by our Monte Carlo method show that the lowest minima are always at $\phi = 0^\circ$, and not 10° as for some cases in the energy minimization method. The slight deviation from strict planarity may be a consequence of the greater degree of lattice relaxation inherent in the energy minimization than can be allowed for in the Monte Carlo. However we should like to call attention to the prediction by both methods of not only the clear energy wells at the *gauche* conformations but also the small minima close to the cis conformations. That in the high-energy torsion around link 1 has already been referred to, and for link 3, the motion of the

TABLE 1: Unrelaxed Lattice Energies (eV) of Poly(3-butylthiophene) ($1 \times 1 \times 2$ Cell) in Which Torsions φ_1 and φ_2 Have Been Imposed on Link 3 of Adjacent Butyl Side Chains. The Lattice Energies Are Relative to That of the Most Stable (All-Trans) Unrelaxed Conformation of Side Chains

φ_1	φ_2								
	100°	110°	120°	130°	140°	150°	160°	170°	180°
100°	1.6319								
110°	1.6417	1.6516							
120°	1.5329	1.5428	1.4336						
130°	1.4388	1.4487	1.3392	1.2443					
140°	1.4488	1.4589	1.3493	1.2540	1.2630				
150°	1.5282	1.5388	1.4294	1.3337	1.3422	1.4207			
160°	1.5544	1.5656	1.4567	1.3612	1.3692	1.4772	1.4731		
170°	1.5018	1.5138	1.4056	1.3106	1.3187	1.3962	1.4216	1.3695	
180°	1.4683	1.4809	1.3736	1.2793	1.2878	1.3652	1.3901	1.3375	1.3050

ethyl group, there is a well-defined minimum at $\phi = 165^\circ$. This is consistent with the conclusions of the near-cis conformations made at the end of our discussion of the energy minimization method.

5. Torsions with Complete Lattice Relaxations

5.1. The Low-Energy Alkyl Conformations. In the lattice energy minimization calculations described in section 4.1 and in the Monte Carlo approach of section 4.2 all the atoms constituting the lattice were relaxed except those four that defined the imposed torsions in the alkyl chains. This was necessary so as to explore the conformation space for stable “rotamers” and to estimate the barriers separating them. To confirm the stability of the lattice containing the gauche conformations found for the butyl side chains, torsions were again imposed on these linkages, but the entire lattice was now permitted to relax, *including* the atoms associated with the butyl torsions.

For this purpose we made use of our findings reported in section 4.1: because of the low-energy torsional motion of the terminal methyl group (link 4) and the highly hindered rotation around links 1 and 2, we decided to investigate the steric effects in the region containing the overlapping of the alkyl chains by imposing torsions on just link 3 of adjacent chains. The purpose of this particular investigation is to confirm the existence of stable lattices in which the side chains contain a near-gauche linkage, as suggested by the calculations of the previous subsections, and also to examine the possibility of simple torsional correlations between neighboring side chains.

Figure 2 shows that the methyl tip of each alkyl side chain on a given polymer lies between two similar terminal methyl groups belonging to a polymer which is adjacent and coplanar to the polymer in question. In the most regular conformation of the diffraction-determined lattice structure—that in which the side chains are fully extended (all-trans)—the carbon atoms of the terminal methyls on adjacent coplanar polymer are at distances of 4.03 Å. If we consider the corresponding methyl carbons on the closest polymer chains which are not in the same plane (chains A and B in the same cell), we find two separations of 5.24 and 5.41 Å. The next separation is between the methyl carbon and its translational images at $\pm c$ (where $c = 7.76$ Å) along the direction of the main polymer chain. Because of the difficulty of presenting the results of applying torsions between so many interacting butyl chains, we decided to restrict the independently applied torsions to the pair of butyl groups with the smallest inter-methyl separation in the fully extended structure (4.03 Å).

To get a clear picture of the possibility of torsional correlations between neighboring butyl chains, we first calculated the lattice energies when conformational torsions were imposed on the pair of butyl groups just defined *without* allowing the lattice to relax. In this series of calculations the torsional angles φ_1 and φ_2 were

independently swept through 360° , but for conciseness we have included in Table 1 just those in the ranges of interest in our quest for the stabilization of gauche structures, $100^\circ < (\varphi_1, \varphi_2) < 180^\circ$. They show clear energy minima when both φ_1 and φ_2 are 130° , which describe conformations close to gauche for each chain, and indicate that the stability of this conformation is independent of the conformation of the corresponding linkage in the neighboring chain. The (φ_1, φ_2) energy surface is reflected along the 180° lines, consequently the secondary energy minima evident along these lines constitute energy troughs in the surface. In other words, consistent with the results of the calculations described in section 4, not only the gauche conformations but also the cis are expected to form structures with almost the same stabilities.

When the lattices were subjected to complete relaxation from a large number of starting (φ_1, φ_2) structures in the ranges given in the previous paragraph, the only stable lattices found are those whose parameters are listed in Table 2. The lattice energies are relative to the energy of the most stable (all-trans) fully relaxed conformation of side chains, which will henceforth be referred to as the “global minimum” structure. The results give conformations which are mainly in the gauche region (100 – 150°), but interestingly, and consistent with the results of Table 1, we find that an important effect of the lattice relaxation is now to stabilize one gauche ($\varphi_1 \approx 140^\circ$) and one near-cis conformation ($\varphi_2 \approx 170^\circ$).

A comparison of the dimensions of the unit cells of the lattice structures obtained with those of the “perfect” lattice for which $a = 14.28$, $b = 7.39$, and $c = 7.98$ Å shows that a result of the side-chain torsions is an expansion of the lattice in both directions perpendicular to the main chain (particularly along b axis) and a contraction along the main chain, the c axis. In all the relaxed structures the cell angles α , β , and γ retained their closely orthorhombic 90° values and the main chain retained its planarity.

5.2. Out-of-Plane Displacements of the Thiophene Rings.

The imposition of conformational torsions on the butyl side chains has just been demonstrated to produce stable lattices in which the thiophene units of the polymer backbone remained coplanar. It is generally supposed, however, that the molecular mechanisms leading to thermochromism involve nonplanar distortions of the π -conjugated chain. If this is correct, then

TABLE 2: Relaxed Structures Obtained from the Imposition of a Large Number of Conformational Torsions on the Side Chains in P3BT ($1 \times 1 \times 2$ Cell) in Order of Increasing Lattice Energy. The Lattice Energies Are Relative to the Global Minimum Structure (See Text)

energy (eV)	φ_1	φ_2	a (Å)	b (Å)	c (Å)
2.4226	140°	170°	14.34	7.62	2×7.83
2.5938	120°	150°	14.32	7.62	2×7.81
3.0089	140°	101°	14.30	7.62	2×7.80
3.0264	101°	120°	14.32	7.62	2×7.81

TABLE 3: Application of Main-Chain Distortion I to the P3BT $1 \times 1 \times 2$ Cell Lattice with Side-Chain Conformational Torsions (φ_1, φ_2). The Thiophene Rings Have Alternating Displacements of d along the $\pm b$ Axis

d (Å) ^a	E (eV) ^b	j_1	j_2	description of structures after relaxation
0.20	2.0464 2.0650 2.3416	140° 149° 130°	170° 160° 150°	The imposed $\pm b$ axis displacements are lost by rings containing all-trans alkyl chains. Distortion from planarity occur in the thiophene rings, especially at atoms in the 2 and 5 positions.
0.25	1.9192 1.9336 2.0184	140° 112° 133°	180° 122° 140°	Again, those rings with no imposed conformational torsions return to near coplanarity, while those with non-trans alkyl chains retain their displacements along $\pm b$. These rings also start to twist ($\sim 5^\circ$) out of their former planes.
0.30	1.8282 2.2766 2.3392	140° 149° 131°	141° 170° 140°	This d value leads to relaxation to the lowest energy deformed lattice. The thiophene rings bearing the twisted alkyl groups distort from planarity as for $d = 0.25$ Å, but in addition the plane of the 3 bonds around thiophene's 3 position (the site of attachment of the side chain) is lost, as the C–C bond to the C ₄ H ₉ bearing the torsions is bent by $\sim 10^\circ$ out of the ring plane.
0.35	3.3606 4.0876	130° 101°	170° 159°	These two, the only stable lattices found, are of much higher energy than those of the other distortions in this series. Their structures are similar to those described for the $d = 0.30$ distortion.

^a For $d > 0.35$ Å no stable lattices were found. ^b The lattice energies E are relative to that of the global minimum structure, in which the main chains are planar and the side chains are in all-trans conformations.

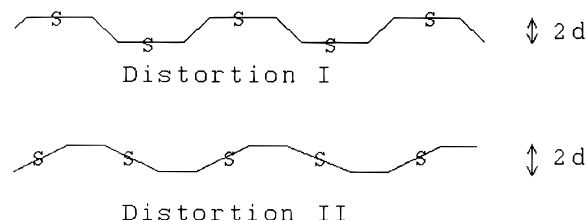
the relaxation simulated by the lattice energy minimization described in sections 4.1 and 5.1 has not located the trajectory on the potential energy surface that conveys the conformational steric energy to the main chain. Now if access to the trajectory requires the system to undergo a transition from one stable lattice to another, then it must surmount an energy barrier. Clearly, such a change could not occur by any relaxation procedure that is based on energy minimization.

We tried to overcome the problem by exploring selected portions of the potential energy surface of the lattice that lead to a distorted main chain, while the butyl side chains bore imposed conformational torsions. In section 1 we presented arguments concerning the difficulty of maintaining lattice regularity if the polymer is twisted around the inter-ring C–C bonds, unless additional distortions are incurred. Again exploring the (φ_1, φ_2) conformational space of a pair of adjacent butyl chains, we imposed simple periodic distortions on the polymer by applying displacements to portions of the main chain alternately along the positive and negative b axis direction. In this way the repeat distance of the polymer chain, but not its regularity, might be altered along the crystalline c axis. From the application of such simple distortions of the main chain it was hoped that any distortions of lower symmetry favored by the lattice would be indicated by the structures to which the lattice then relaxed.

In the simplest main-chain distortions, alternating displacements of $+d$ and $-d$ were applied along the crystalline b axis to either the thiophene rings or to the inter-ring C–C bonds. In the scheme shown below the butyl side chains are omitted for clarity. The polythiophene chain is viewed along the a axis, and the lines bisected by the S atoms represent the thiophene rings. In **I** successive thiophene rings are displaced into two parallel planes along $\pm b$, while in **II** the rings are alternately folded in opposite directions in such a way that the ring planes form a zigzag when viewed along a . The end-to-end extent of

the distortion of the conjugation plane in each case is $2d$. As in the other lattice energy minimization calculations, a $1 \times 1 \times 2$ cell was used which allowed the distortions to repeat after four rings. The imposition of the (φ_1, φ_2) conformational torsions in just *two* of the butyl side chains (leaving six butyls in the all-trans conformation) ensures the loss of the internal symmetry of the chain segments in the supercell, thus providing a greater number of degrees of freedom to the relaxation than would be the case for the simple crystallographic unit cell.

The calculations showed that distortions **I** and **II** produced acceptable lattices only if the distortion parameter d did not exceed 0.35 Å. Above this value attempts to relax the structure



led to convergence failure or to lattice instability. In general the sweeping of the pair of torsional angles (φ_1, φ_2) over their subspace sometimes produced several stable lattices, of which Tables 3 and 4 contain only the lower lying polymorphs. Their energies (relative to that of the global minimum energy lattice), the side-chain conformational torsions φ_1 and φ_2 , and a descriptive summary of the relaxed structures are included in the tables for the three values of the d parameter that describes the extent of the distortion of the main chain. Probably the most stable lattice in each case (data written in bold type) is the most significant, and the others are included mainly to indicate their energy separations from that of the minimum. The structure description in the final column on the whole applies

TABLE 4: Application of Main-Chain Distortion II to the P3BT $1 \times 1 \times 2$ Cell Lattice with Side-Chain Conformational Torsions (φ_1, φ_2). The Planes of the Thiophene Rings Fold by an Amount d in Alternating Directions So As to Zigzag along the $\pm b$ Axis

d (Å) ^a	E (eV) ^b	φ_1	φ_2	description of structures after relaxation
0.20	2.1344 2.68	121° 121°	170° 149°	(For $d = 0.20$ and $d = 0.25$): In common with the distortion I results for low d values, the most stable lattices are those in which one butyl chain is in a gauche and the other is in a trans conformation. One difference between these structures and those of distortion I is that for distortion II <i>all</i> the rings (including the six whose side chains do <i>not</i> bear conformational torsions) retain their imposed distortions on lattice relaxation. A second is the retention of ring planarity.
0.25	2.2898 2.3746 2.5840 3.3246	149° 140° 131° 110°	159° 149° 149° 169°	
0.30	2.0019 2.8561 2.8786 2.8929	148° 149° 99° 139°	179° 180° 139° 169°	

^a For $d > 0.30$ a no stable lattices were found. ^b The lattice energies E are relative to that of the global minimum structure.

to all the lattices shown that are associated with the same d parameter and not just to the most stable one.

A comparison of the energy of the most stable lattice for each d value shows that with one exception these lattices become more stable as d increases from 0 to 0.30 Å. Thereafter the energies increase sharply, but above $d = 0.35$ Å no stable lattices are found. This result probably indicates that the optimum volume required by the conformational torsions in the alkyl side chains is provided when the main-chain segments are displaced by ± 0.30 Å along b , but that any further displacement rapidly results in excessive repulsions between adjacent polymer chains.

We found that *unless* nonplanar (φ_1, φ_2) torsions were imposed on the butyl side chains, then lattice relaxation caused the $\pm b$ axis displacement of the polythiophene main chain to vanish. Also, an examination of the atomic coordinates of the eight thiophene rings relaxed from distortion I structures showed that the six rings whose side chains were *not* subjected to conformational torsions tended to lose their $\pm b$ axis displacements and to return to near-coplanarity. Now if the preservation of the nonplanar distortion of the π conjugation plane is dependent on side-chain conformational torsions, it would seem reasonable to infer the existence of a causal link between the (thermally produced) conformational torsions and the main-chain distortions. The fact that a distortion from the main chain's planarity requires the imposition of displacements on the thiophene rings rather than a downhill relaxation from the planar structure implies the presence of an energy barrier between the polymorphs. It is difficult to devise a method of investigating this barrier by a lattice minimization calculation, but we have seen that the calculations described here can reveal the presence of structures that are separated by energy barriers.

Although no explicit torsions were imposed on the inter-ring C—C bonds for the reasons already discussed, it is interesting that lattices relaxed from "distortion I" structures do reveal small ($\sim 5^\circ$) torsions about these bonds, coupled however with out-of-plane displacements of atoms of the thiophene rings. It will be recalled that this was one of the two conditions that were described in section 1 for the generation of ring torsions that would be expected to preserve the regularity of the lattice. The relaxed lattices do not show any sign of the bond-bending distortions that would bring the * links (Figure 1) into line, which was the alternative possibility that we discussed as a mechanism to create ring torsion.

5.3. Torsional Displacements. The finding of out-of-plane distortions and twisting deformations of the thiophene rings in section 5.2 is interesting as it implies that the explanation of the thermochromism of P3ATs may be different from the simple description that involves ring torsions *alone*. We have argued that the lack of a common axis linking the thiophene rings to their neighbors precludes the possibility that such torsions are the sole structural changes occurring in the lattice. If the ring torsions are indeed an important feature of the thermochromism, then they must occur in conjunction with out-of-plane distortions of the kind described. This suggests that the distortion of the main chain, which is caused by the gauche-type conformations in the side chain, should also be investigated by imposing *torsions* on the thiophene rings in order to determine their response to lattice relaxation. This is a complementary investigation to that involving the imposition of b -axis displacements in section 5.2.

To impose a torsion on a thiophene ring, it is necessary first to "align" it by bending the C—C bonds that link it to its immediate neighbors until these bonds are collinear. The 3-butylthiophene unit was therefore displaced along the a axis, retaining the lengths of the inter-ring bonds and increasing the length of the cell along the c axis. For practical reasons (to

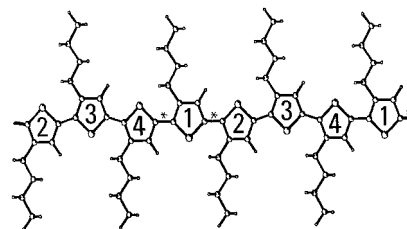


Figure 5. Conformations imposed when one thiophene ring in each chain in the unit cell is "aligned" to create a torsional axis by bending the inter-ring bonds labeled *. Only ring 1 in the A chain is shown; in the B chain a similar alignment occurs in ring 8.

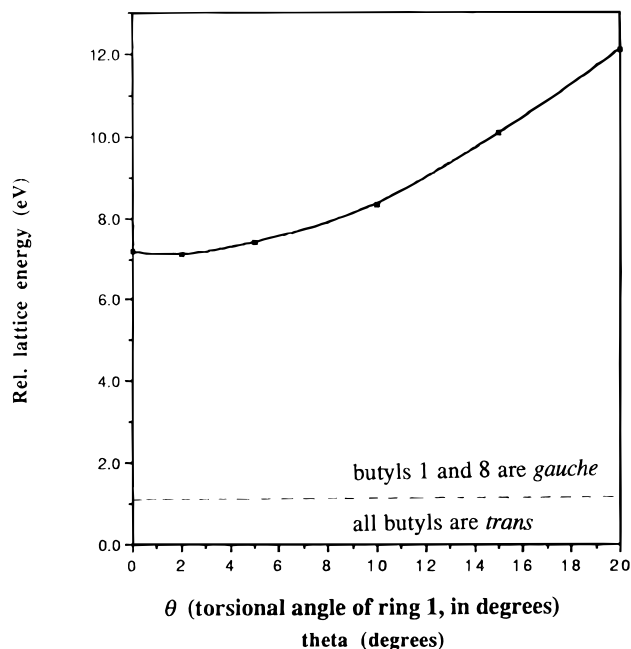


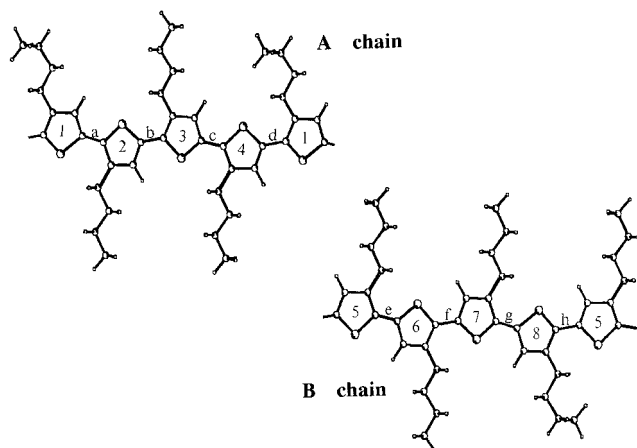
Figure 6. Energy changes incurred by the lattice when link 3 gauche conformations are imposed on two butyl chains (1.06 eV), and when subsequently rings are aligned according to Figure 5 and subjected to torsions (see text).

avoid incommensurate structures) we decided to retain the use of a $1 \times 1 \times 2$ cell, allowing both polymers in the unit cell to have equal periodicities along the c axis; the alignment described was then performed on one of the four thiophene rings in each of the two polymer chains in the cell. These rings are called 1 and 8, and Figure 5 shows one such chain where the bonds between rings 1 and 2, and between 1 and 4, have been aligned along c to form a rotational axis. We decided to investigate the effect of a single gauche conformation on each side chain in the unit cell and therefore applied a $\phi = 120^\circ$ torsion on the third C—C bond (as before) in the butyl chains of thiophene rings 1 and 8. Using ϕ and θ to describe torsional angles in the alkyl side chains and in the polymer backbone, respectively, torsions were then imposed on these rings: that on ring 8 was kept constant at $\theta_8 = 10^\circ$, while the one on ring 1 was swept through the range $0 < \theta_1 < 20^\circ$.

Analogous to the preliminary relaxation calculation described for the of b axis displacements in section 5.2, a similar one was performed that ascertained that when the side chains had no nonplanar conformations (the butyl groups were all trans) and after applying small torsions θ_1 and θ_8 (less than about 10°), the main chains relaxed to their all-planar structures. It is instructive to examine the energetics of imposing the torsion prior to permitting the lattice to relax. Figure 6 shows the energy cost first of imposing gauche conformations on the butyl groups attached to thiophene rings 1 and 8, second of "aligning" these rings as described above to as to provide each of them

TABLE 5: Distortions and Relative Energies in Fully Relaxed P3BT $1 \times 1 \times 2$ Lattice in Which Torsions Are Applied to Two Thiophene Rings Which Have Side Chains Bearing Gauche Conformations. The Main Part of the Table Lists the Torsional Angles (deg) in the Inter-ring Bonds *a–h* in Figure 7, and the Lattice Energies Are Relative to that of the Global Minimum Structure Defined Above

lattice:	0	1	2	3	4	5	6
relative energy (eV):	(all trans)	1.5705	1.4868	1.9923	2.8207	2.0409	3.1110
applied torsion θ_1 :	0.0000	0°	2°	5°	10°	15°	20°
bond							
<i>a</i>	0.0	3.8	3.1	27.0	14.3	23.2	39.7
<i>b</i>	0.0	2.9	2.5	2.9	5.8	6.7	1.9
<i>c</i>	0.0	2.1	3.9	1.2	4.6	4.8	8.9
<i>d</i>	0.0	1.9	20.5	22.0	6.0	23.5	30.7
<i>e</i>	0.0	2.3	2.9	11.0	21.7	1.6	8.4
<i>f</i>	0.0	1.1	1.3	2.4	3.7	5.1	2.5
<i>g</i>	0.0	3.8	10.9	7.7	0.5	3.9	6.4
<i>h</i>	0.0	5.3	16.0	20.4	13.8	3.2	2.2

**Figure 7.** Labeling scheme used to identify the inter-ring bonds in the $1 \times 1 \times 2$ lattice used to investigate distortions in the polythiophene main chain that are shown in Table 5. The A and B chains are separated for clarity.

with a torsional axis, and third, having put a 10° torsion on ring 8, to rotate ring 1 through an angle θ_1 up to 20° . When we consider the relaxation of the lattice, the torsional curve in Figure 6 is unrealistic since such calculations make no provision for the additional conformational changes that must occur in the butyl chain of ring 1 as the ring rotates against the force field of neighboring polymer chains (the actual curve would be flatter than the one shown). But Figure 6 shows the relatively small energy cost of creating two gauche conformations (1.1 eV prior to relaxation) compared with the much more severe one to “align” the two rings (6.1 eV), followed by the rather gentle energy response to the rotation of the thiophene ring. This suggests that unless the thiophene ring is permitted to distort, then its torsion is energetically unfeasible.

When the lattice was permitted to relax after imposing the ring torsions described, a number of stable structures were obtained. A representative listing of six lower lying lattices are compiled in Table 5. Regular trends of the response to relaxation from the θ_1 torsions are not obvious in the data, but all the lattices are characterized by out-of-plane deformations and torsion of the thiophene rings, particularly (but not exclusively) as a result of *b* axis displacements of the sulfur atoms. In Figure 7 and Table 5 the torsional angle between each pair of thiophene rings in Table 5 was calculated from the dihedral angle defined by the $C_\beta-C_\alpha-C_\alpha'-C_\beta'$ quartet of atoms in Figure 7. Although the distortions are greatest at those rings whose side chains bear gauche conformations (bond pairs [*a*, *d*] and [*e*, *h*]), Table 5 shows that the deformation is communicated to the other rings also, which exhibit torsions from 2° to 40° .

To summarize the findings of this and the previous subsection, the calculations affirm the possibility that polymer chains

bearing gauche and cis conformations in their side chains can acquire main-chain distortions and that the link between the two kinds of distortion involves an intramolecular transmission of energy. A more precise description of the main-chain distortions would probably require relaxations to be conducted using larger $n_1 \times n_2 \times n_3$ supercells than those considered in the present work, but we have demonstrated that simple main-chain distortions along the *b* axis give rise to a series of relaxed, distorted lattices with low-lying energies. An examination of the chain structures of these lattices shows that some thiophene rings have lost their planarity and assumed significant torsions around the bonds linking these rings to their neighbors. Both these features would be expected to decrease the π conjugation of the main chain and possibly therefore increase the π valence-to-conduction bandgap.

6. Electronic Structure Calculations

The acquisition of conformational torsions in the side chains can lead to geometry changes in the main chain. These may be described as out-of-plane distortions of the thiophene units coupled with a twisting around their inter-ring bonds. Various quantum chemical calculations on thiophene oligomers lead one to expect that the deviations from planarity of the main chain associated with the twisting of the rings would result in an increase in the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied one (LUMO), and this has been confirmed by UV spectroscopy. We must now examine whether the other geometry changes found in section 5 could also contribute to the spectral changes.

For this purpose we conducted ab initio electronic structure calculations on the tetrathiophene oligomer using a 3-21G basis set. Having performed preliminary calculations on some butyl-substituted oligomers to establish that the molecular orbitals in the “frontier” region (and which are presumably involved in the electronic transitions associated with the thermochromism) are mainly of a π character, we continued the investigation on the unsubstituted molecule. By simplifying the molecular model in this way, longer chains may be used to represent the polymer in an electronic structure calculation. Nevertheless, the restriction of the calculation on such a large molecular system to a Hartree–Fock level allowed only a treatment of the electronic ground state of the oligomers. Accurate spectroscopic transition energies would require a reliable description of higher electronic states, but because of the large size of the molecules with which we are concerned, probably the only quantities that we can hope to predict with any reliability is the *direction* of the energy gap’s shift in response to the distortion of the chain.

The calculations showed that in each case the HOMO possessed nodal planes bisecting the inter-ring bonds, whereas the nodal patterns of the LUMO were almost the exact opposite of those of the HOMOs. We do not need to place reliance on

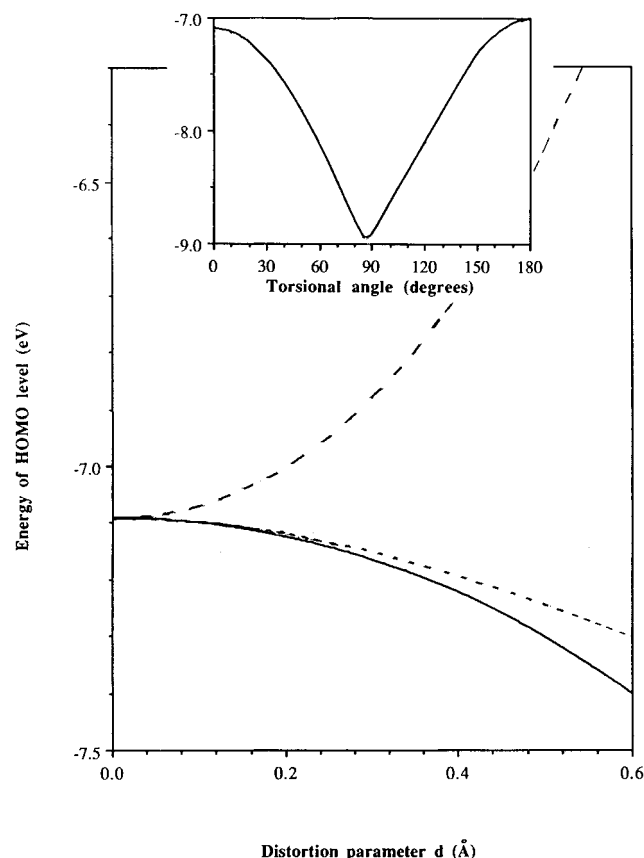


Figure 8. Response of the highest occupied molecular orbital energy level of a tetrathiophene molecule to various degrees d of the three types of out-of-plane deformations discussed in the text as obtained from 3-21G ab initio calculations: (---) distortion I, (···) distortion II, (—) helical torsion. Inset: HOMO level for the complete range of helical angle $0^\circ < \varphi < 180^\circ$.

the calculated values of the LUMO energies, which are probably overestimated by the Hartree–Fock method because of the neglect of electron correlation; we simply note that the energy shifts in the HOMO and LUMO resulting from geometry changes occur in opposite directions. We therefore monitored the effect on the HOMO–LUMO gap of the application of various types of distortion to the tetrathiophene chain. This is seen in Figure 8, in which the energies of the HOMO are plotted as a function of the distortion parameter d . For cases in which sections of the polythiophene chain are displaced, as described for distortions I and II of section 5.2, the d parameter has the same definition as before; when uniform torsions are applied to the inter-ring C–C bond (to form a helix), d is taken as the perpendicular distance of the sulfur atom of one ring from the plane of its neighbor. The inset in Figure 8 shows that the maximum HOMO shift is about 2 eV if the distortion were to be continued until the helical angle φ is 90° , while in the cis conformation ($\varphi = 180^\circ$) the HOMO level is close to that for the trans ($\varphi = 0^\circ$). The same inset implies that the imposition of $1/2 \times 30^\circ$ to $1/2 \times 60^\circ$ torsions on each inter-ring bond in the chain would produce spectral shifts consistent with those (0.5–1.0 eV) observed^{10,13} in P3ATs. (The factor $1/2$ is included as we suppose that the symmetry-related LUMO level representing the lower edge of the conduction band rises by approximately the same rate as that by which the HOMO is depressed.) In the interpretation of their photoelectron spectra of poly(3-hexylthiophene) with the aid of valence-effective-Hamiltonian calculations,¹⁰ Salaneck et al. derived the existence of inter-ring torsional angles of 45° and 60° . Angles close to 45° were also reported by Roux and Leclerc¹³ from quantum chemical and differential scanning calorimetry. Our 15 – 30° range of tor-

sional angles is smaller, but it is consistent with the $\theta < 40^\circ$ range appearing in Table 5 describing the relaxed, lower lying distorted lattices described in section 5.3, which, it must be emphasized, are combined with other out-of-plane distortion elements of the polymers.

Because of the arbitrariness in the definition of d , no inferences are drawn about the relative magnitudes of the HOMO shifts produced by the three types of distortion; we must look only at the directions of the energy changes. These fall into two groups. In the first, the distortion of the main chain consists of (a) torsions of the rings around their inter-ring bonds (leading to nonplanar oligomer chains) and (b) a folding of the chain so as to produce a zigzag arrangement of the thiophene planes as in distortion II. In both a and b the HOMO is stabilized by the distortion, thus increasing the HOMO–LUMO energy gap in accordance with the direction of the observed thermochromism. In the second group the planes of the thiophene rings are displaced in directions normal to the rings so as to produce structures similar to those in distortion I of section 5.2. These distortions destabilize the energy of the HOMO, resulting in a HOMO–LUMO energy gap that decreases with increasing d , thereby leading to a thermochromism that is in the opposite sense to that observed. It would thus appear that the chain deformations that occur should be closer to II than to I according to the simple distortions that we selected for this study.

It is not easy to rationalize the shifts of the HOMOs in terms of a qualitative discussion of the effect of geometry changes on the interactions of the atomic orbitals. It is tempting to explain the increasing HOMO–LUMO gap with torsional rotation θ around the inter-ring bond as a diminishing overlap integral of the carbon ($2p_y$, $2p_y$) atomic orbital pair forming the π bond. This is sometimes assumed to show a $\cos^2 \theta$ dependence, which would certainly appear to stabilize the antisymmetric π molecular orbital constituting the HOMO and lead to an increased energy gap. However the separation of the atomic orbitals forming the π MOs from those forming the σ MOs is unlikely to be valid when the conjugation plane is lost. In fact the π overlap integral formed by the ($2p_y$, $2p_y$) pair also (initially) decreases with increasing deformation d for distortion I, while that for distortion II increases. Such oversimplified arguments would lead to thermochromic effects whose trends are opposite those of the quantum chemical calculations.

We conclude that the main-chain distortions that effectively increase the energy gap considered are those that are associated with a twisting of the thiophene units around the inter-ring bonds and, to a smaller extent, structures in which the thiophene rings undergo the booklike folding of distortion II. It would appear that those in which the rings are displaced to form parallel planes do not lead to the type of thermochromism that is experimentally observed. The isolated thiophene oligomer chain considered in this section is of course free to take up simple inter-ring torsional conformations, which we argued are not possible in the polymer lattice. In such materials the torsions must be combined with additional distortions such as those that were demonstrated in section 5.

7. Conclusions

Using both lattice energy minimization and Monte Carlo methods, we have shown that the poly(3-butylthiophene) lattice can support several low-energy structures in which the alkyl chains are in gauche and cis (as well as trans) conformations. The Monte Carlo approach was most useful for finding stable conformations and energy profiles involving motions of flexible molecular components, in particular the alkyl side chains, where (a) the presence of a large number of polymorphic forms results

in difficulty in accessing the global minimum conformations, and (b) high-energy sections of the energy profiles can lead to lattice instabilities. As a result we calculated torsional energy barriers of 0.3–0.6 eV that were in accord with experiment.

The conjugated polythiophene backbone was stiffer than the alkyl side chains and therefore less susceptible to the large number of shallow energy wells associated with the alkyl chains. Its conformational changes could more easily be investigated using the lattice energy minimization method. Full-lattice relaxations from different torsional conformations in the side chains confirmed the stabilities of near-gauche and some cis conformations suggested by the energy-profile calculations. When the polymer backbone was distorted by shifting the positions of the thiophene rings either by displacement along the $\pm b$ axis (distortion **I**) or by folding (distortion **II**), or else by a combination of a axis displacements and inter-ring torsions (section 5.3), then the thiophene rings relaxed to main-chain distorted structures *only if* the alkyl chains on those particular rings bore non-trans configurations. This suggests that distortion of the main-chain is aided by the presence of a side-chain conformation that is not the lowest energy one. Since the gauche and cis conformations are usually supposed to be thermally accessible, it would be reasonable to claim that the distortions described in section 5 could indeed be generated by the transmission of energy from thermally induced sources stored in the alkyl side chains, resulting in deformations of the π -conjugated polymer backbone that can cause the observed dilation of the frontier bandgap.

In more specific investigations of energy transfer in P3ATs it would be interesting to examine the role played by the (disputed) degree of interdigitation of the alkyl chains, such as in the lattice structures proposed by Winokur et al.^{28–31} and by the recent work of Tashiro et al.,⁵⁴ where the alkyls interleave to a minimal extent. The absence of interdigitation would reduce *inter-* but not *intrapolymer* transfer of steric energy to the conjugated backbone; we have shown that a lattice environment of the alkyl chains appears not to diminish the innate stabilities of their trans and gauche conformations. This would not be expected to change in other lattice structures. A more detailed theoretical investigation of the mechanism of energy transfer in these systems has been started using various methods including quantum chemistry and molecular dynamics.

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