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Abstract
Two conductive polymers are selected for static lattice and molecular dynamics methods to determine the possibilities of 'fine tuning' them in order to achieve desired bandgaps. These are poly-*para*-phenylene (PPP), consisting of a π-conjugated backbone only, and the thermochromic polymer poly(3-alkylthiophene) (P3AT), which additionally contains flexible side chains. Conformational changes in both polymers indicate that pressures of $\sim$6–7 GPa planarize the main chains. With a sterically hindering atom F in the *ortho* site of PPP, conformations a few degrees from planarity may be achieved at about 20 GPa. The response of the C–H and C–F bonds to pressure is also described. In the P3AT polymer molecular dynamics predicts that above 10 GPa not only does planarization of the main chain occur but the spontaneous 'tilting' observed in the alkyl side chains is also reduced.

1. Introduction

One of the factors responsible for the electrical and optical properties of π-conjugated polymers is the planarity of their backbones. The properties may sometimes be changed by imposing 'internal' effects such as the substitution of hydrogen atoms by larger atoms or groups or 'external' effects such as pressure or temperature, both of which often lead to a modification of the torsional configuration of the backbone. For example the intramolecular steric consequences of substituting the hydrogen atoms in phenylene oligomers [1] and probably poly-*para*-phenylene (PPP) by fluorine leads to a loss of planarity, and to altered electro-optical properties such as lower conductivities. Out-of-plane buckling of the backbone results in reduced overlap of the 2p atomic orbitals forming the π MOs, thereby changing the electronic energy bandgap. One way of encouraging the formation of planar chains is to apply external pressure or to compress the polymer material by other means.

The present work describes the imposition of stress on polymer lattices, either in one direction or isotropically. By examining how the chain atoms respond to such a stress, an understanding may be gained of the behaviour of the material at an atomic level.

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Experimentally it is known that the application of hydrostatic (isotropic) pressure on conductive polymers leads to increased electrical conductivities [2] and to spectral shifts [3], and that these changes are reversible.

Because it may be both oxidized and reduced (e.g. by iodine or by alkali metals) poly-*para*-phenylene has, like polyacetylene, long been considered as an electronics device and as a candidate for use in solid state batteries [4]. Chains may assume planar conformations as a response not only to external compression but also to their crystalline environment (often described as exerting 'lattice forces'). The phenylene oligomers, particularly biphenyl, have been shown to demonstrate this effect. In the vapour state [5] and in solution [6] the latter molecule has a dihedral angle of about 40° between the phenyl rings. But in the crystal, biphenyl, the *para*-linked phenylene oligomers and probably also poly-*para*-phenylene all show a *time-averaged* planarity [7]. Atomistic simulations suggest that the application of even moderate compression in any direction perpendicular to the long axis converts the double-well potential profile into a single well, i.e. planarizes the molecule [8].

The electronic bandgap is also invoked to explain the thermochromism of the poly(3-alkylthiophenes) (P3ATs). By raising the temperature of the material, thermally induced torsions occurring in the main chain produce a dilation of the energy gap. The resulting blue shift of the electronic transitions associated with these bands is held to be responsible for the observed thermochromism. The absorption peak reverts to its original low frequency either on cooling or by applying hydrostatic pressure [9].

2. Methodology

2.1. Methods of calculation

The codes used for the static lattice atomistic simulations were GULP [10] and the molecular dynamics were performed by DL_POLY [11]. The application of static atomistic lattice simulation or 'molecular mechanics' (MM) and molecular dynamics (MD) to periodic polymer systems, together with the atomistic potentials, atomic charges and Ewald summations have been previously described [12, 13]. For the non-bonded interactions involving the carbon and hydrogen atoms we retain the Williams IV potentials, which a recent study [14] has shown to be superior to other functions as a fit to good-quality *ab initio* calculations particularly for internuclear distances shorter than equilibrium separations, that are required to describe the high-pressure conditions relevant to the present work.

The variation of pressure is effected *either* by controlling the parameters of the unit cell (or simulation box) *or* by using the available options in the codes concerned to apply hydrostatic pressures directly to the simulated system. In the MM calculations steps had to be taken to address the problem of entrapment in local energy wells. This was done [15] by starting from a range of initial structures, usually chosen from a set of different structure parameters such as cell axes, setting angles and inter-ring torsional angles. For the pressure simulations, the problem was tackled by the method of 'successive relaxations', which will be described below.

2.2. Molecular and lattice structures

The published structures of PPP contain two chains in a P_{gg} orthorhombic unit cell, each chain containing just one phenyl ring per cell [16]; as a result such a model requires the polymer to be planar ($\varphi = 0°$). However since the hydrogen atoms in adjacent rings are separated by about 1.8 Å, which is less than twice their van der Waals radius of 1.2 Å, the model should
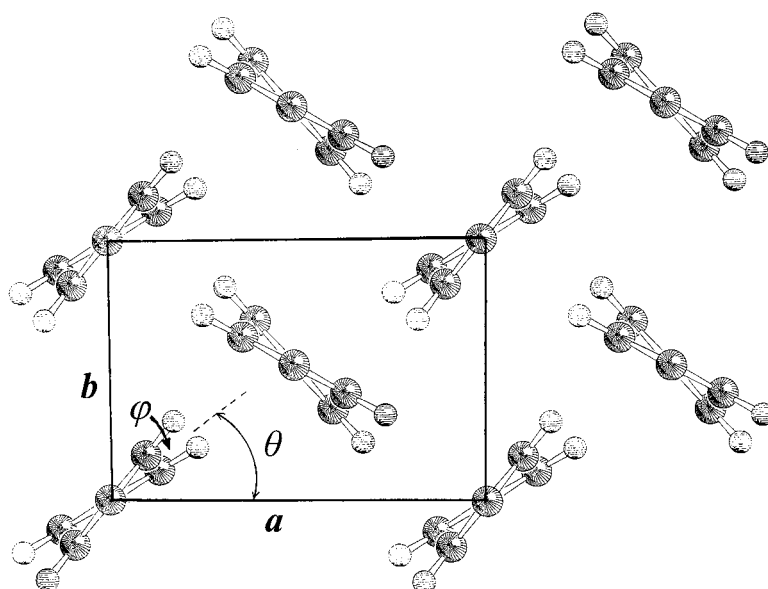
Figure 1. The poly-*para*-phenylene chain in the P_{gg} lattice structure [16] viewed along the chain direction (*c* axis). The figure defines the ring torsional angle φ and the chain setting angle θ.

allow for the possibility of a twisting of the phenyl units. We therefore doubled the length of the unit cell along the *c* axis and imposed a series of torsional angles between the phenyl rings, thereby generating a PPP chain in which the phenyl rings twist alternately by $+\frac{1}{2}\varphi$ and $-\frac{1}{2}\varphi$ (figure 1).

The structure assumed for the poly(3-alkylthiophene) lattice was essentially that of Kawai and coworkers [17]. In this the alkylthiophene units that comprise the polymer chain are linked 'head to tail' in a zigzag *anti* conformation. Two polymer chains, aligned along *c*, occupy a stacked arrangement along the *b* axis of a nearly orthorhombic unit cell in which the conjugation planes of the main chains are parallel to *ac*. The two chains are displaced by half a bithiophene unit (i.e. $\frac{1}{2}c$) along the *c* axis. As a result, adjacent pairs of thiophene rings have a *staggered* configuration when viewed along their stacking axis *b*. The alkyl side chains are all *trans* and are attached to the 3 position of the thiophene rings, each alkylthiophene unit being attached 'head to tail'. The resulting bithiophene translational repeat unit is shown in figure 2, which identifies the bond torsion angles $\varphi_1, \ldots, \varphi_5$ which are referred to in this work. These angles are defined in the sense that a value of $0°$ in $\varphi_2, \ldots, \varphi_4$ in the side chain implies that the respective C–C bond is *trans* (*cis* would be $180°$). The φ_5 torsional angle is defined by the condition that when $\varphi_5 = 0°$ the conformation of the thiophene units is *anti* as illustrated in figure 2. Figure 3 shows that with this configuration the alkyl groups on adjacent chains in the *ac* plane *interdigitate*, i.e. each alkyl is directed towards the gap between alkyl groups in an adjacent polymer chain. However other x-ray groups make a different interpretation of their P3AT diffractograms. Winokur and coworkers describe the polymer lattice in which, although the conjugated main chains are planar and the alkyl chains are all *trans* (fully extended), the planes of the side chains are different from that of the main chain to which they are attached [18]. In other words, while the torsional angles $\varphi_2, \ldots, \varphi_5$ (defined in figure 2) are still close to zero, φ_1 is about 75–85°, which means that the common plane of the main chain and side chains in figure 3 is eliminated by a considerable rotation of each alkyl group around its link to
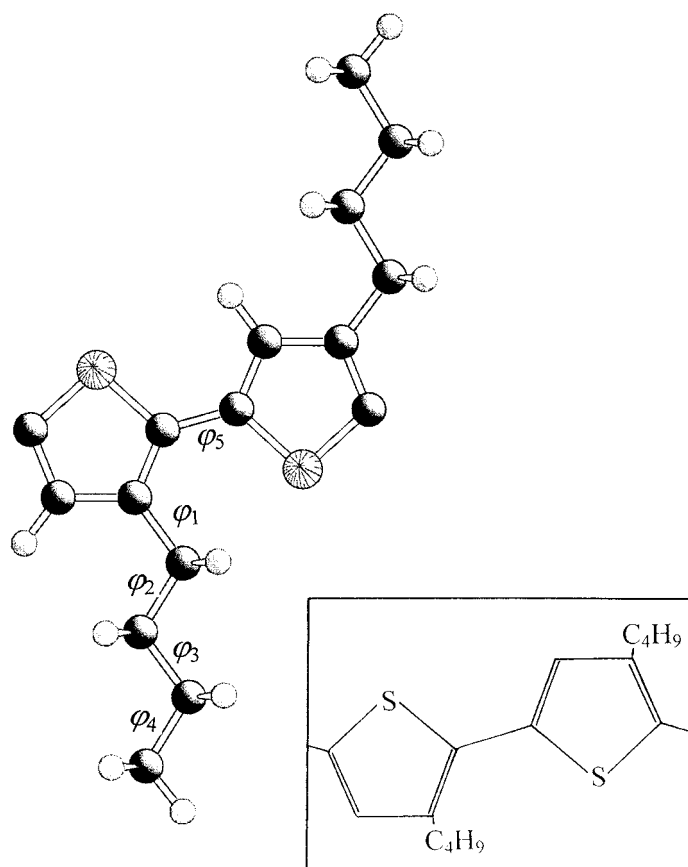
Figure 2. The P3AT bithiophene translational repeat unit defining the torsional angles in poly(3-butylthiophene) that are referred to in the text. Inset: chemical structure.

the thiophene ring. In addition the polymer chains make a small setting angle with the cell's *a* axis.

In a P3AT structure by Proń *et al* [19] the side chains are coplanar with the polythiophene backbone as in the structure of Kawai *et al* [17], but the orthorhombic unit cell contains a single polymer chain. A consequence of this is that unlike the case in the other two structures, in the stacking arrangement of the polymers, the thiophene rings are necessarily eclipsed rather than staggered.

The diversity in the reported structures has been partly resolved by findings that suggest that the actual conformations of the side chains in a polymer sample depend on experimental conditions [20]. This implies that any sample may contain more than one structural phase. In a recent MM and MD investigation of the present polymer poly(3-butylthiophene), P3BT, we showed that the alkyl side chain has a *tendency* (not always realized) to undergo a torsion φ_1 around the C–C bond linking it to the thiophene ring [21]. As a structural mechanism of the thermochromic distortion in the crystalline regions another report [22] proposes a thermally induced elimination of the $\frac{1}{2}c$ shift of alternate chains along *b* that was described at the beginning of this subsection. The sliding of these chains brings the thiophene stacked along *b* into an eclipsed arrangement effectively creating a one-chain cell. The complete translational
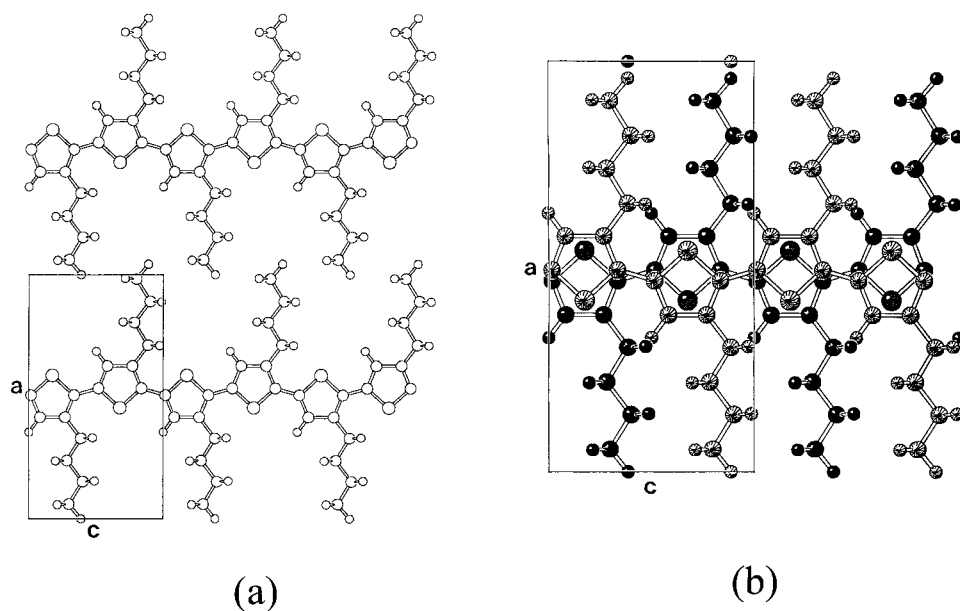
(a)

(b)

Figure 3. The poly(3-butylthiophene) structure according to [17]. In (a) two adjacent chains are shown to illustrate the interdigitation of the alkyl chains. In part (b), showing the lattice viewed along the stacking direction (b axis), the two stacked chains are distinguished by different shading.

periodicity of the polymer chains along b permits a thermally-induced 'dovetailing' of the torsions in the crystalline phase, resulting in thermochromism. Such a structure avoids the concomitant severe decrease in crystal density that would be found in a 'staggered' structure. Conditions of preparation might cause this structure to occur in some crystalline regions of the polymer even at temperatures below the thermochromic transition; this could explain the diffraction investigations which propose an orthorhombic unit cell containing a single polymer chain [19].

3. Results

3.1. Poly-para-phenylene lattices

For each value of interphenyl angle φ the lattice was fully relaxed, and on the basis of using different starting structures to avoid local energy minima we describe the most probable lattice as the one with the lowest energy that could be found. The orthorhombic cell parameters for this double-cell structure are essentially equal to those which we determined from the single cell [23] ($a = 8.07$, $b = 5.30$, $c = 8.07$ Å; setting angles $47.8°$ and $57.4°$) but the dihedral (torsional) angle between successive rings for the lowest-energy structure was found to be $\varphi = 9.5°$. Both chains in the unit cell show this value of $|\varphi|$, but the lattice energy was slightly lower for the configuration in which one chain had positive, and the other negative, φ. The inter-ring torsion in PPP has not been measured, but our calculated value is close to the $10.2°$ twist found [7] in biphenyl at 22 K.

Compressions were then applied to the lattice along the a and b axes separately. In order, as far as possible, to avoid the problem of entrapment in a local energy-well, which could be serious in any investigation that sets out to derive conclusions from an energy profile, the
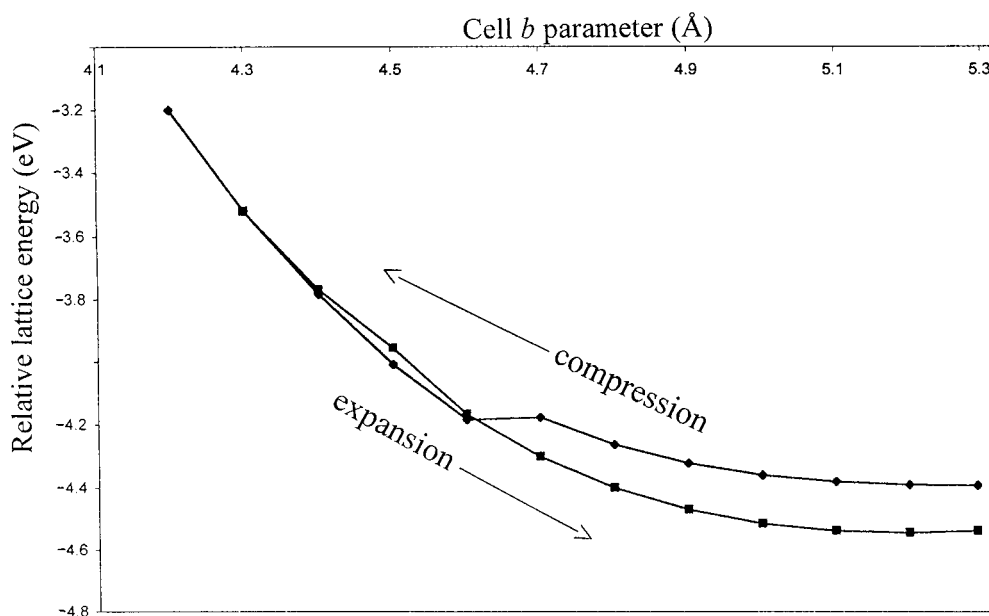
Cell *b* parameter (Å)

Figure 4. The lattice energy of poly-*para*-phenylene on compression (●) and subsequent expansion (■) along the *b* axis.

following procedure was adopted. Each structure resulting from relaxation to achieve energy minimization at one pressure was used as an input structure for the lattice corresponding to the next pressure (a value of *a* or *b* diminished by 0.1 Å). This method of successive relaxations imposes less strain on the energy minimization procedure to locate the global minimum.

Figure 4 shows the lattice energy when the unit cell is compressed along the *b* axis. The kink in the compression curve between *b* = 4.6 and 4.7 Å indicates that in the course of the energy minimization the lattice has encountered a local energy well, in which it has become stuck. After 'recovery' no further entrapments occur, and the expansion curve shows a smooth decrease of what we may assume to be a series of global-minimum energy values back to normal pressures. The kink is reminiscent of the stick–slip behaviour found and calculated in systems to which pressure is applied [24]. It corresponds to a local melting of the lattice, which, after the imposition of increasing stimulus, abruptly re-freezes. In order to try to ensure that the relaxations have attained their global minima for the appropriate conditions, in this and in subsequent calculations the lattice was compressed until the energy minimization calculation failed to produce a stable structure. The lattice was then expanded back to zero pressure, and if necessary the process re-cycled until the compression and expansion curves showed no obvious gradient discontinuities. From the slope of the energy with decreasing *b* and the area of the *ac* face of the unit cell, pressures in the region shown were calculated to be up to 7.2 GPa (1 GPa = 10 kbar).

Figures 5(a) and (b) show how the lattice energy and the dihedral angle between adjacent rings vary when the lattice parameter *a* is changed. Temporary entrapment in a local energy well is testified by the short-lived rise of *φ* with decreasing *a* at 4.6–4.7 Å, matched with a gradient discontinuity in lattice energy at the same *a*. The pressure attained for the conditions in the left-hand part of the figure was calculated to be 6.6 GPa by the method described above.
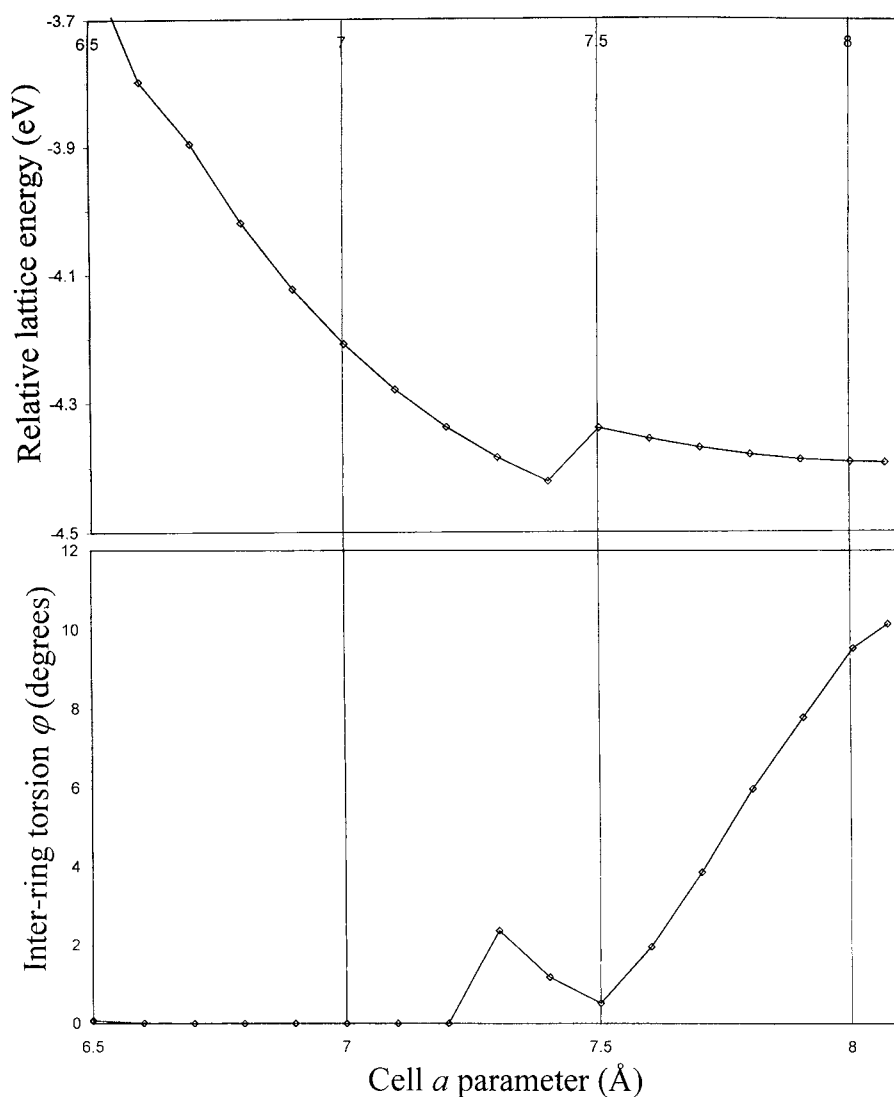
Figure 5. The upper and lower graph are plotted with a common abscissa—the length of the cell parameter a of poly-*para*-phenylene. They show the effect of axial compression on the lattice energy and the inter-ring torsional angle φ of PPP.

The similarity of the pressures calculated for both the a and b directions, which are perpendicular to the main chain, follows from the chain setting angles $\pm\theta$, where θ is 45–60°, which ensure that there is a substantial component of polymer area perpendicular to the directions of the applied compression. If, as in the case of at least some proposed lattice structures of P3ATs, the setting angles are zero [17, 19], then there is only one direction that is efficacious [15] in producing chain planarity—that which is perpendicular to the conjugated plane of the polymer backbone. Both prediction and experiment show that the response of the lattice is highly anisotropic [25–27]. However the results suggest that application of compression along a and b separately does indeed describe the response of the lattice to the application of hydrostatic pressures, in which the forces on the polymer chains are isotropic.
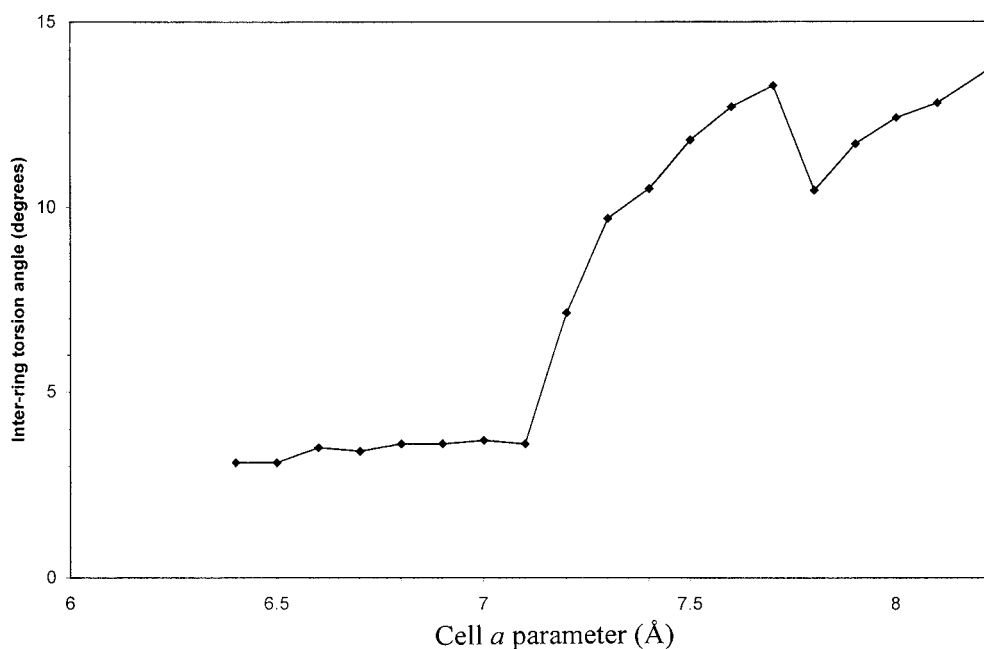
Figure 6. The compression of partially fluorinated poly-*para*-phenylene along the lattice *a* direction. The phenyl rings are brought to within 3° of a coplanar configuration.

The results may be compared with empirical measurements. Infrared and Raman studies in which pressures up to 20 GPa were applied to PPP describe shifts of the absorption edge to lower frequency [28]. These are consistent with a narrowed bandgap, indicative of increased planarity of the chains. However a new Raman band appeared at the highest pressures, which is supposed to be a consequence of increased interchain coupling. Another study [29] monitoring the photoluminescence of PPP when pressures of up to 6 GPa were applied describes a red shift. Further increase of pressure produces a blue shift, which is interpreted as the result of interchain coupling which then dilates the bandgap. However a recent Raman study to monitor the response of the oligomer *para*-hexaphenyl (structurally similar to PPP) reports only an increasing planarity of the chains up to similar pressures [30].

In order to gauge the sensitivity of the inter-ring torsion to a small change in the size of the *ortho* atoms in the ring we next considered a PPP polymer lattice in which the hydrogen atoms in *alternate* rings are substituted by fluorine. In an all-planar deformation-free polymer, the H . . . F atom pairs in adjacent rings would be separated by about 1.7 Å. Since this distance is considerably less than the fluorine atom's van der Waals diameter of 2.7 Å, a significant amount of twisting is expected. An investigation on this polymer along the same lines as that described for unsubstituted PPP using a near-orthorhombic P_{gg} two-chain cell leads to the lattice parameters $a = 8.24, b = 5.12, c = 8.82$ Å, with chain setting angles of 43.9° and 55.4° and inter-ring torsions of 11.4°. The torsion curve in figure 6 (for compression/expansion along *a*, but effects along *b* give an equivalent result) shows that in comparison with unsubstituted PPP considerably greater pressures are required to reduce the twisting of the chains. With compressions of 20 and 65 GPa along *a* and *b* respectively (calculated from the slope of the energy curve, as described above) the carbon atoms of the phenyl rings retain their planarity, while the torsions in successive rings decrease to 3° and 5°.

It is also interesting to examine the structural effect of the pressure on other aspects of the chains. In particular, how do those atoms that are responsible for the twisting (H and F) react to the lattice stress? Do they produce a change in bond angle and remain in the plane of the ring or do they buckle by out-of-plane displacements? An examination of the atomic coordinates in the structures of PPP and its fluorinated derivative shows that when viewed along the chain direction the hydrogen atoms on the two sides of the unsubstituted PPP ring undergo a 20° out of plane bending in opposite directions, and that the effect alternates along the chain. In other words, if the right-hand hydrogens in one ring are folded 'up' (+20°) while those on the left are folded 'down' (−20°), in the next ring the pattern is 'down' on the right and 'up' on the left. In the partially fluorinated polymer, although the F atoms showed rather small displacements, the H atoms were quite severely bent (by about 40°) out of the plane of their phenyl ring. The unsubstituted phenyl ring itself suffered small out-of-plane distortions mainly by a booklike folding of about 4° about the polymer axis.

3.2. Poly(3-butylthiophene): the static lattice

As well as the possibility of property-tuning associated with electrical conductivity as in PPP, the application of pressure to P3BT has an additional feature of interest as it is observed to modify the polymer's thermochromism (section 2.2).

In order to perform the pressure studies we used the all-planar, interdigitated structure of Kawai and coworkers [17], which has two chains in the unit cell, and considered four thiophene units in each chain since this sequence is the simplest one that can give rise to a strain-free periodic pattern of torsions [22]. However, in accordance with the description in section 1.3, and in order to avoid the unacceptable fall in crystal density above the thermochromic temperature, half the chains were shifted by $\frac{1}{2}c$ as proposed by Corish *et al* [22]. It is interesting to observe whether the lattice, after relaxation from the series of pressure conditions, retains the Kawai structure [17] or perhaps adopts other features such as that of the Winokur structure [18] described in section 2.2.

In an earlier work to consider the interaction between the alkyls on different polymer chains, compression was applied along the *a* and *b* axes of P3ATs [25]. From the energy profiles obtained it was concluded that in agreement with empirical measurements [26, 27] P3ATs were substantially more compressible along *a* than along *b* The maxima and minima in the energy profile as a function of *a*, with pressures in between of about 1 GPa, were interpreted as involving structural changes (probably conformational) while compression of an order of magnitude higher along *b* caused no such ripples in the energy profile. As far as we are aware all measured lattice structures of P3ATs reported in the current literature describe the polymer chains as stacked along the *b* axis (or in some cases stacked with slight tilt angles to this direction). For the purpose of examining the feasibility of using pressure to produce chain planarity, therefore, it will be sufficient to supply compression along *b*.

The torsional angles φ_1 to φ_5 defined in figure 2 were calculated with the lattice compressed along *b*. Although the four butyl side chains in the unit cell do not show identical sets of conformations after the lattice relaxations, they are quite similar, and the selection of one of them as a representative alkyl involves no loss of information. The responses of the five torsional angles to compression are displayed in figure 7, where it should be noted that since the application of the $\frac{1}{2}c$ shift to half the chains converts the two-chain unit cell to a one-chain cell, the value of *b* now refers to the latter, and measures the stacking separation of the polymer chains.

An important result is that concerning the conformation of the butyl chain, for which φ_2, φ_3 and φ_4 show values less than 10°, indicating that this chain has retained its initial all-*trans* conformation. However φ_1, which measures the rotation of the side chain around the bond
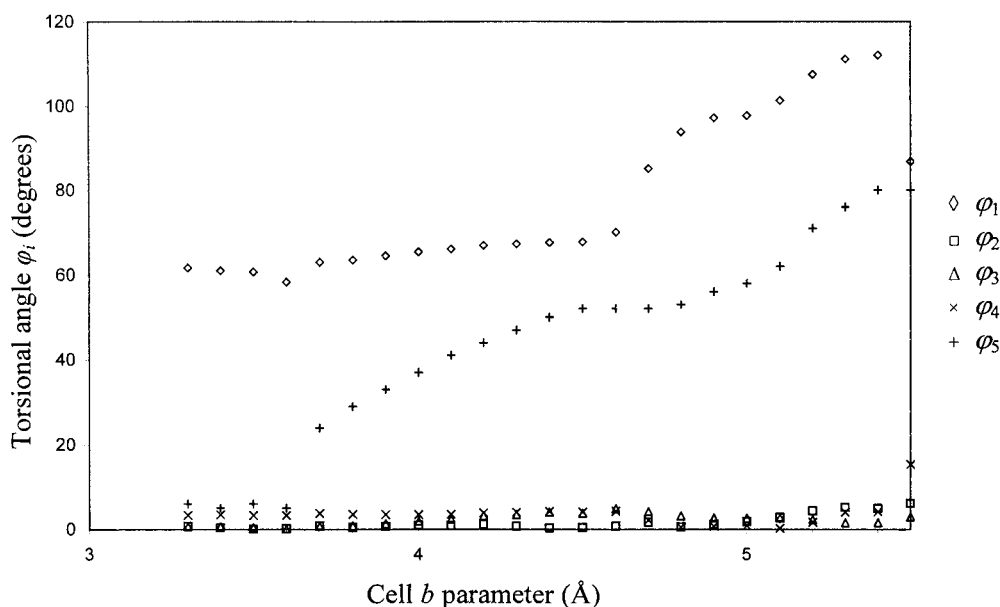
Figure 7. How poly(3-butylthiophene)'s five torsional angles defined in figure 2 respond to compression along the *b* axis in a static lattice (MM) calculation. The pressure increases from right to left in the figure.

securing it to the thiophene ring, shows a large angle which the compression abruptly reduces to 60° at $b = 4.7$ Å (where the pressure is still essentially atmospheric) after which it stays practically constant. This torsion of the all-*trans* alkyl chain out of the plane of the polymer backbone is consistent with the results of a combined MM and MD study of P3BT at zero pressure [21], both techniques predicting the same torsion. The existence of this torsion, and its stability to pressure, both support the tilted side chains proposed by Prosa *et al* [18] in the structure described in section 2.2.

The large values of the φ_5 torsions are a consequence of the $\frac{1}{2}c$ shift of half the chains relative to their original positions: we showed in earlier work [22] that this thermally motivated shift, implying a change from staggered to eclipsed stacking, produces a *spontaneous* inter-ring torsion $\varphi_5 \approx 60$–70°, and hence the thermochromic transition. This angle diminishes with decreasing cell dimension until at $b = 3.6$ Å (40 GPa) it drops sharply to below 10°. We may conclude that the application of pressure would be expected to lead to an increased planarity of the conjugated main chain, but does not bring the planes of the alkyl side chains into that of the main chain. Experimental investigations suggest that the application of 8 GPa planarizes the polymer backbone of poly(3-hexylthiophene) as its thermochromism [31] is thereby completely inhibited.

3.3. Poly(3-butylthiophene): MD and thermochromism

The part of the work relating to P3BT has focused attention on two conformational aspects of the polymer. One is the inter-ring twist (φ_5) in the main chain, which is believed to be a direct cause of the thermochromism. The second is the angle of tilt (φ_1) of the plane of the butyl group to that of the main chain, which addresses the question of the configuration of the side chains (hitherto not definitively resolved by empirical methods). The results of the
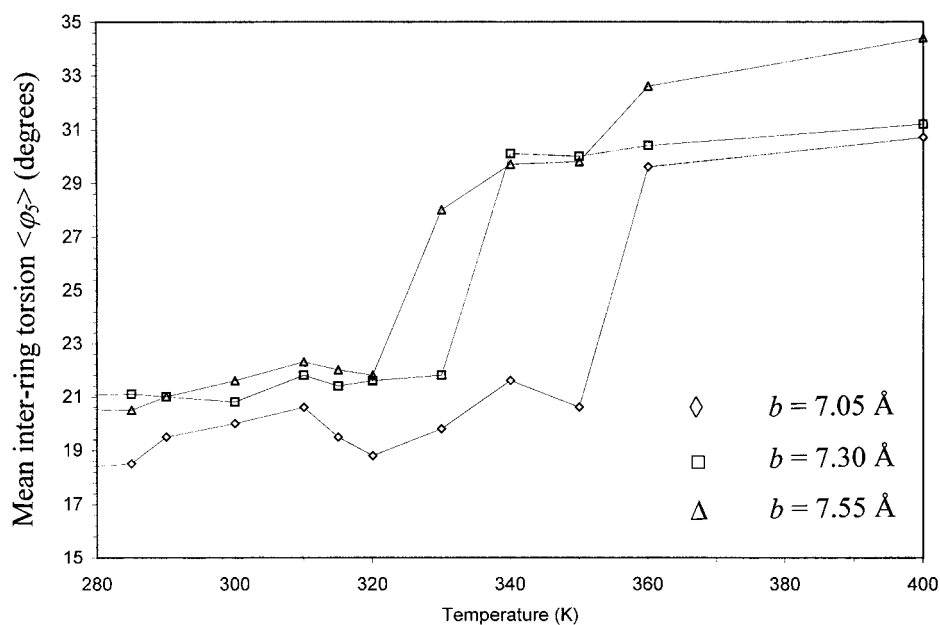
Figure 8. The mean torsional angle $\langle\varphi_5\rangle$ between the rings in P3BT as a function of temperature, for three values of cell parameter b, in a molecular dynamics calculation. (The lines are merely to identify isobaric plots.) As the pressure increases with decreasing b, the thermochromic transition is deferred to higher temperature.

MM simulation suggest that it would be interesting to perform a similar investigation using molecular dynamics.

A recent MD investigation of the mechanism of the thermochromism of P3ATs [21] showed that the average values of the five angles φ_1 to φ_5 underwent changes as the temperature of the chains increased. The time-averaged values $\langle\varphi_2\rangle$ and $\langle\varphi_3\rangle$ were centred at $0°$, indicating that the side chains largely retained their all-*trans* conformations; the orientation of the terminal methyl groups produced $\langle\varphi_4\rangle$ peaks at its equivalent sites, and $\langle\varphi_1\rangle$, describing the bond linking the side chain to the thiophene ring, had values of $60–70°$, indicating a Winokur-like tilting of the side chains [18] (cf sections 2.2 and 3.2). When the chain-averaged values of some of the $\langle\varphi_i\rangle$ were plotted against temperature, they showed discontinuities at 330 K. Below this temperature the value of $\langle\varphi_5\rangle$ in particular is appreciably constant at $20°$, indicating a fairly planar main chain conformation. However between 330 and 340 K it shows an abrupt steplike increase of about $10°$ of torsion, which would imply a dilated electronic energy bandgap and a shift of the spectral absorption band.

In the light of the results described in sections 3.1 and 3.2 it would be interesting to use a similar approach to investigate the effect of pressure on the thermochromic transition. For this purpose we investigated the molecular dynamics of a simulation box that was a $2 \times 2 \times 2$ supercell relative to the Kawai crystallographic cell [17], and which contained eight chains and a total of 32 butylthiophene units. The system was subjected to an NPT thermostat when a series of hydrostatic (isotropic) pressures and temperatures were to be specified directly for the simulation. An NVT thermostat was used when the dynamics were to occur at pressures which, as for the MM calculations, were to be defined by the size of the unit cell (or simulation box). After thermal equilibration the dynamics were run, and the necessary statistics accumulated, over a period of 10^5 timesteps (0.1 ns).
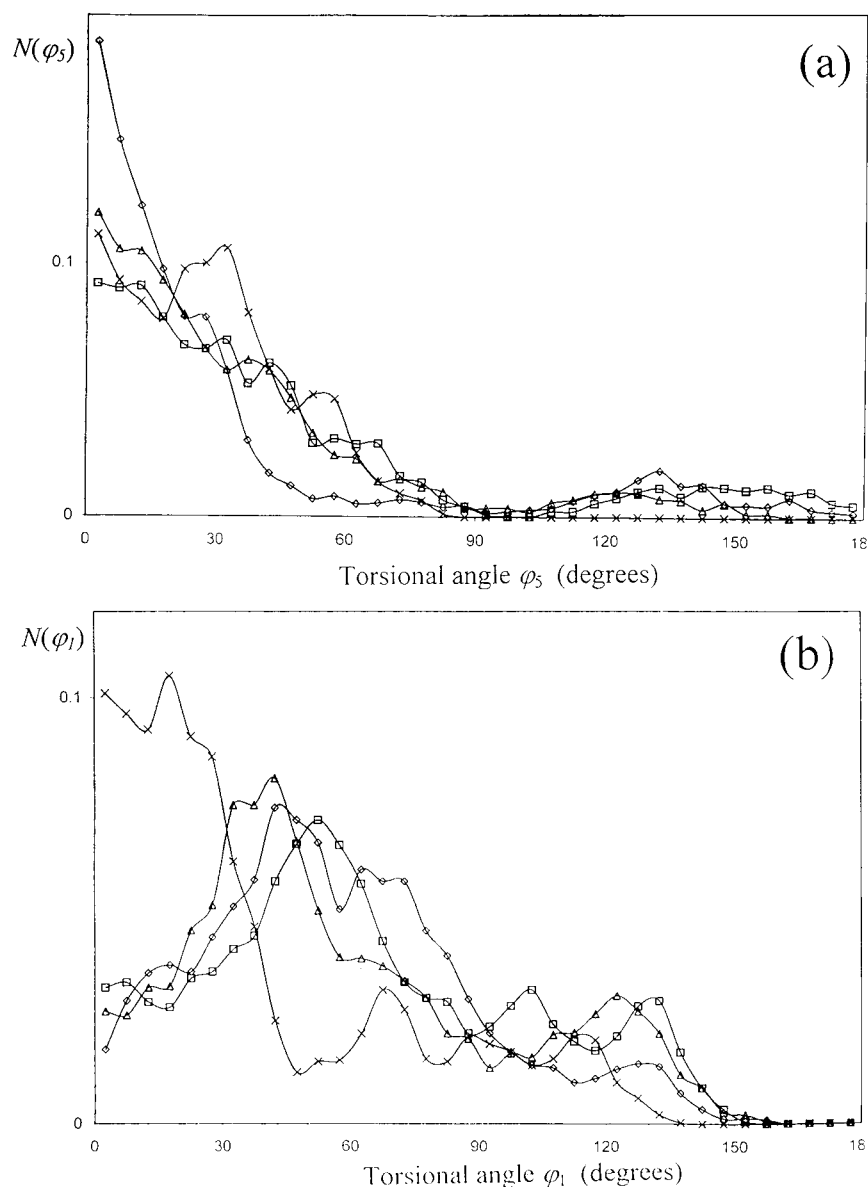
Figure 9. The mean frequency distribution of (a) the inter-ring torsional angle φ_5 and (b) the torsion φ_1 around the C–C bond between main chain and side chain in P3BT. Plotting symbols: –◇– (0 GPa), –□– (0.1 GPa), –△– (1 GPa), –×– (10 GPa).

In figure 8 the mean torsional angles $\langle \varphi_5 \rangle$ about the inter-thiophene C–C bond taken over the 32 inter-thiophene bonds in the simulation box are plotted against temperature for three compressions along **b**. Although the simulation box is a supercell, for comparison with the results in section 3.2 the values of b in the figure refer to the basic crystallographic unit cell [17]. A discontinuous change in mean inter-ring torsion angle produces step-like increases in $\langle \varphi_5 \rangle$ for the three pressure conditions imposed. This twisting of the conjugated backbone would widen the energy gap between the π valence and conduction
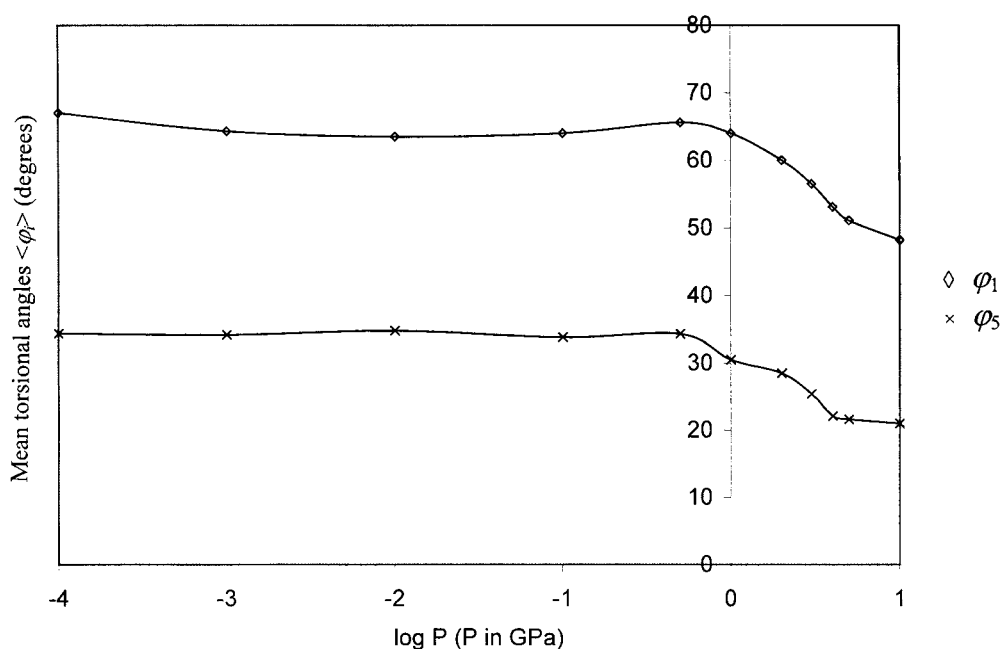
Figure 10. The mean values of torsional angles φ_5 and φ_1 (defined in figure 9) in P3BT as a function of hydrostatic pressure.

bands, and allows the prediction of an important structural change involved in thermochromism. The curves show that increasing the pressure causes the onset of the main-chain torsion to be deferred to higher temperatures, thereby providing a means to 'fine tune' the thermochromism.

Another gauge of the inter-ring torsion φ_5 is to calculate its mean frequency distribution (MFD) over the same canonical system as that just described to calculate its mean value $\langle \varphi_5 \rangle$. Figure 9(a) shows the MFD of φ_5 accumulated at 360 K, which is above the temperature range 330–340 K in which the MD predicts a thermochromic transition, at a series of hydrostatic pressures. While the thermal randomizing effects of temperature do not make the results as clear-cut as the apparently unequivocal ones found from the MM treatment of the same system, they contain important information. This is that the abrupt shift in $\langle \varphi_5 \rangle$ shown in figure 8 to occur at the thermochromic transition is far from being a uniform twisting of a previously planar chain and its suppression by the application of pressure. For all the imposed pressures the major peak in the frequency distribution of φ_5 is centred at $0°$. While pressure has no effect on the position of this maximum, and rather a random one on its height, the result of imposing the highest pressure is to create a new peak at $30°$ and to eliminate the broad peak which at low pressures is centred at $135°$. A clearer effect is on the smaller peak which at low pressures is centred at $135°$ and whose existence indicates that although the thiophene rings do not spend much time in a perpendicular position ($\varphi_5 = 90°$) or forming a *syn* link in the main chain ($\varphi_5 = 180°$), they do have a finite probability of undergoing torsions to conformations with intermediate φ_5. We believe that the strains and conformational disorder thereby imposed on the backbone also contribute to the widening of the energy gap and thereby to the thermochromism.

A similar MFD plot of φ_1 in figure 9(b) also at 360 K shows a major peak in the distribution centred at about $50°$, almost consistent with that found at $60°$ in the MM studies. The molecular

Table 1. The effects of pressure on the structures of the polymers according to MM and/or MD simulations. (MD is applied to P3BT only.)

		PPP	fluoro-PPP	P3BT
Main chain	Low P	$\varphi_5 = 9.5°$ Coplanar ring atoms	$\varphi_5 = 11.4°$ Coplanar ring atoms	MM: Both $\varphi_5 = 0°$ and $60°$ are stable. Temp. effect? See text and [22] Slight distortion of rings MD: φ_5 shows temperature dependence (thermochromism, see text)
	High P	$\varphi_5 = 0°$ (7 GPa) C–H bonds bent $20°$ out of the ring plane	$\varphi_5 = 4°$ (20 GPa) C–F almost collinear with ring; C–H bent $40°$ out of ring plane. Slight 'folding' distortion of ring plane	MM: φ_5 decreases from $60°$ to below $20°$. At 40 GPa $\varphi_5 = 5°$ Small ring distortion is maintained MD: The thermochromic change in φ_5 is suppressed resulting in $\langle\varphi_5\rangle \approx 20°$
Side chains		—	—	MM: Just above atmos. pressure φ_1 decreases to $60°$ (Winnokur struct.) Remains const. at higher P. Other links approx. *trans* MD: $\langle\varphi_1\rangle \approx 50°$, but at $P = 10$ GPa it decreases to a small value

dynamics, also therefore, indicate a tendency for a Winokur-like [18] tilting of the butyl side chains out of the plane of the main chain to occur at most of the imposed pressures. However the $0°$-centred $\langle\varphi_1\rangle$ peak at the highest pressure imposed (10 GPa) predicts that at a sufficiently high pressure the Winokur torsion is eliminated, resulting in all-planar polymer chains.

Another attempt to elucidate the MD data relating to the two P3AT structural features stated at the beginning of this subsection is to plot the torsions directly against the applied pressure. We saw in figures 8 and 9 that by 360 K the mean main-chain torsional angle $\langle\varphi_5\rangle$ had just undergone an abrupt $10°$ increase. When the mean torsional angles $\langle\varphi_1\rangle$ and $\langle\varphi_5\rangle$ at 360 K are plotted against applied pressure as in figure 10 the results clearly show that while the post-thermochromic torsions are held up to just under 1 GPa, above this pressure both types of torsion decrease by 10–$20°$. This means that sufficiently high pressures not only increase the planarity of the polymer backbone, but also partially offset the Winokur tilting of the side chains. The latter effect is not supported by the MM calculations in section 3.2, suggesting the requirement of thermal activation.

4. Conclusions

The reduction of the polymer backbone angle φ_5 described in the forgoing sections, and the summarized results in table 1, testify to the effectiveness of the application of pressure to increase the planarity of the main chains of the π-conjugated polymer backbones discussed in this work, poly-*para*-phenylene and poly(3-butylthiophene). This is the conclusion of both the molecular mechanics (static lattice) and molecular dynamics approaches, whose results

are largely (often even quantitatively) consistent. One instance where this is not the case is the response of the side chain to pressure: MM retains the 'Winokur folding' while MD predicts that the highest pressure considered (10 GPa) may almost bring the alkyl chains into the plane of the main chain.

Of course there is no certainty that the ability to planarize a chain by severely constricting the space available to the polymer chains will always reduce the energy bandgap. Chain dimerization or other effects associated with the increasing degree of interaction between chains may lead to a widening of the gap [32, 29]. It is hoped that electronic structure calculations which are currently being conducted on P3ATs and other polymers will help to provide answers to this question.

Acknowledgments

References

[1] Saitoh H, Saito K, Yamamura Y, Matsuyama H, Kikuchi K and Ikemoto I 1994 *Solid State Commun.* **91** 89
[2] Yoshino K, Nakao K, Onoda M and Sugimoto R-I 1988 *Solid State Commun.* **68** 513
   Isotalo H, Ahlskog M and Stubb H 1992 *Synth. Met.* **48** 313
[3] Yoshino K, Nakao K and Onoda M 1989 *Japan. J. Appl. Phys.* **28** L332
   Kaniowski T, Niziol S, Sanetra J, Trznadel M and Proń A 1998 *Synth. Met.* **94** 111
[4] Endo M, Kim C, Karaki T, Fujino T, Matthews M J, Brown S D M and Dresslhaus M S 1998 *Synth. Met.* **98** 17
   Lacaze P C, Aeiyach S and Lacroix J C 1997 *Handbook of Organic Conductive Molecules* vol 2, ed H S Nalwa (Chichester: Wiley) p 205
[5] Almenningen A, Bastiansen O, Fernholdt L, Cyvin B N, Cyvin S J and Samdal S 1985 *J. Mol. Struct.* **128** 59
[6] Suzuki S 1959 *Bull. Chem. Soc. Japan* **32** 1340
[7] Charbonneau G P and Délugeard Y 1977 *Acta Crystallogr.* B **33** 1586
   Cailleau H Baudour J-L and Zeyen C M E 1979 *Acta Crystallogr.* B **35** 426
[8] Corish J, Morton-Blake D A, O'Donoghue F, Baudour J-L, Bénière F and Toudic B 1995 *J. Mol. Struct. (Theochem.)* **358** 29
[9] Yoshino K, Nakao K, Onoda M and Sugimoto R-I 1989 *J. Phys.: Condens. Matter* **1** 1009
   Mårdalen J, Cerenius Y and Häggkvist P 1995 *J. Phys.: Condens. Matter* **7** 3501
[10] Gale J D 1997 *J. Chem. Soc. Faraday Trans.* **93** 629
[11] Smith W and Forester T R 1996 *J. Mol. Graph.* **14** 136
[12] See for example Morton-Blake D A and Corish J 1996 Atomistic simulation investigations of electroactive polymers *Electroactive Polymer Electrochemistry* ed M E G Lyons (New York: Plenum) and references therein
[13] Corish J, Morton-Blake D A,Veluri K and Bénière F 1993 *J. Mol. Struct. (Theochem.)* **283** 121
[14] Hayes J B and Greer J C *PhD Thesis* University of Dublin
[15] Corish J, Morton-Blake D A, Feeley D E, Bénière F and Marchetti M 1997 *J. Phys. Chem.* B **101** 10 075
[16] Kovačić P, Feldmann M, Kovačić J P and Lando J P 1968 *J. Appl. Polym. Sci.* **12** 1735
   Stamm M and Hocker J 1983 *J. Physique Coll.* **44** C3 (suppl. 6) 667
   Stamm M, Fink J and Tieke B 1985 *Mol. Cryst. Liq. Cryst.* **118** 281
[17] Kawai T, Nakazono M, Sugimoto R and Yoshino K 1992 *Japan. J. Appl. Phys.* **61** 3400
[18] Prosa T J, Winokur M J, Moulton J, Smith P and Heeger A J 1991 *Macromolecules* **25** 4364
[19] Łuzny W and Proń A 1996 *Synth. Met.* **79** 37
   Łuzny W, Niżioł S, Zagorska M and Proń A 1993 *Synth. Met.* **55** 359
[20] Prosa T J, Winokur M J and McCullough R D 1996 *Macromolecules* **29** 3654
[21] Xie H, O'Dwyer S, Corish J and Morton-Blake D A 2000 *Synth. Met.* at press
[22] Xie H, Corish J, Morton-Blake D A and Aasmundtveit K E 2000 *Synth. Met.* **113** 65
[23] Corish J, Hanratty V C A, Morton-Blake D A, Bénière F and Morin A 1990 *J. Mol. Struct. (Theochem.)* **207** 41

[24] Corish J and Morton-Blake D A 1998 *Mol. Simul.* **21** 41
[25] Corish J, Morton-Blake D A, Bénière F and Lantoine M 1996 *J. Chem. Soc. Faraday Trans.* **92** 671
[26] Samuelsen E J, Mårdalen J, Konestabo O R, Hanfland M and Lorenzen M 1999 *Synth. Met.* **101** 98
[27] Mårdalen J, Samuelsen E J and Lorenzen M 1998 *J. Phys.: Condens. Matter* **10** 7145
[28] Hanfland M, Brillante A, Syassen K, Stamm M and Fink J 1989 *J. Chem. Phys.* **90** 1930
[29] Hu B, Zhang X Y, Zhou Y X, Jin C Q and Zhang J S 1991 *Phys. Rev.* B **43** 14 001
[30] Guha S, Graupner W, Resel R, Chandrasekhar M, Chandrasekhar H R, Glaser R and Leising G 1999 *Synth. Met.* **101** 180
[31] Hess B C, Kanner G S and Vardeny Z 1993 *Phys. Rev.* B **47** 1407
[32] Iwasaki K, Fujimoto H and Matzusaki S 1994 *Synth. Met.* **63** 101