

Structural study of two conducting polymers: poly(pyrrole) and poly(thiophene)

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Structural modelling of two relatively stable conducting polymers, poly(thiophene) and poly(pyrrole), has been carried out using a number of theoretical modelling tools. These have included determination of optimized valence molecular geometry; conformational properties of single isolated chains and their crystalline packing arrangements; and finally a correlation of theoretically predicted structures with experimentally determined properties. While confirming most observed results reported data indicate the possibility of extensive polymorphism for both polymers and provide a number of starting structures for complete crystal structure determination using limited X-ray or electron diffraction data.

(Keywords: structural model; conducting polymer; poly(pyrrole); poly(thiophene))

INTRODUCTION

A considerable amount of effort has been spent in an attempt to understand the electronic properties of conducting polymers¹. It is expected that these studies will not only establish clearly the molecular basis for the electrical properties of these novel materials but will also help in designing new ones. Evidently, electronic properties are directly linked to the chemical bonding topology, the electron distribution and the spatial arrangement of the atoms that constitute the system. The paracrystalline nature of polymeric systems often renders such basic structural information elusive and difficult to obtain by conventional techniques, e.g. X-ray and electron diffraction. It is under these circumstances that a combination of theoretical and experimental methods may prove invaluable in gaining a more thorough understanding of the correlation between electronic and structural properties of conducting polymers. Indeed, investigations along these lines for the prototype conducting polymer poly(acetylene) have been very fruitful. For example, definitive structural characterization could be carried out with limited diffraction (X-ray and electron) data by judicious modelling and packing calculations carried out on these acetylenic systems².

A large number of conductive polymers have been identified since the demonstration of electrical conductivity in poly(acetylene). Polyheterocycles form one of these important classes of materials. Extensive research carried out on these polymers indicate them to be the most stable class of conductive polymers³. In addition, researchers at GTE and other laboratories⁴ have determined methods which increase the processability of these materials. There is, however, still considerable debate regarding the chain organization and morphology.

In this paper we have outlined a series of steps to determine the structural characteristics of two conducting polymers belonging to this class, poly(pyrrole) and poly(thiophene) (henceforth referred to as PP and PT, respectively). At the end of the analysis, ideally, a complete and thorough structural description will be

available. The steps of the analysis include the determination of: (1) the valence molecular geometry; (2) the conformational properties of a single isolated chain; (3) the possible crystal packing arrangements of the low energy conformations identified in step (2); and (4) the correlation between theoretically predicted structures and experimentally determined properties.

Several theoretical methods are employed in this study. The object is to use an accessible method that is both reliable and computationally feasible. To determine the reliability of a particular method, it is necessary to evaluate the degree of accuracy required such that the uncertainty of a particular result does not obscure a coherent and logical explanation.

In this paper we investigate the structural and electronic properties of PP and PT. Both these polymers have been electrochemically polymerized. The materials are reasonably conducting ($1-100 \Omega^{-1} \text{ cm}^{-1}$) and are the most stable among the known conducting polymer systems. The polymers are poorly crystalline as synthesized electrochemically. Hence, the theoretical approach presented here seems all the more applicable.

METHODOLOGY

Intramolecular energy calculations

The total energy of a single chain may be partitioned into steric repulsive-dispersive, electrostatic and torsional components within the fixed valence geometry molecular mechanics methodology⁵. Steric interactions are represented by a Lennard-Jones 6-12 potential function; the electrostatic potentials are calculated via a simple Coulombic term; and the torsional barrier is fitted to approximate the difference between the total potential energy barrier from rotation about the polymer backbone and the energy calculated within a particular model.

Pair-wise interactions of atoms within a single chain were properly weighted and counted using a method developed by Tripathy *et al.*⁶⁻⁸. It was assumed that there were two rotational degrees of freedom along the polymer backbone. Thus, there are two geometrically unique

molecular segments in the chain, which each consist of a single ring for PP and PT. It is the interaction of these two segments with their neighbours that constitutes the relative energy of a particular conformation. As is shown in *Figure 1*, the atoms within rings 1 and 2 interact with the atoms of rings {2,3,4,5} and {3,4,5,6}, respectively. The interaction of rings 3 and 5 with their neighbours need not be considered since the environment surrounding these two rings is identical to that found for ring 1. Similarly, rings 4 and 6 are equivalent to ring 2 and thus may also be neglected. This method thus excludes redundant interactions and accurately models the periodic nature of a long polymer chain.

All interactions within four nearest neighbours are included for both PP and PT in a complete conformational analysis. The bonds which connect the rings assume values between -180 and $+180$ degrees with a grid size of 5 degrees. The resulting energies of the 5184 conformations per polymer are plotted as a function of bond rotations. A fixed dielectric of 4 was used for the electrostatic contribution.

Intermolecular interactions

The relative crystal packing energy is the potential energy realized by a single repeat segment of a polymer chain, given a periodic array of polymer chains. The potential energy is found by summing over all inter-atom pair-wise interactions between atoms located in the central polymer chain segment and all those atoms that form the other chains. Unfortunately, evaluating all pair-wise interactions for a representative bundle of chains is a time consuming process that often necessitates the use of more approximate methods. A method developed by Tripathy *et al.*⁹ represents these interactions as infinite series sums, which are then transformed to more rapidly converging representations.

The crystal packing energy is subsequently minimized as a function of the unit cell variables (the cell edges and angles) and the chain setting angle, which is the angle between the molecular plane and the crystal *b*-axis. By constraining some of the lattice variables to constants, i.e. assuming that a lower symmetry class exists, the time required for the minimization process is reduced to a reasonable level.

Only orthorhombic, hexagonal and monoclinic space groups are examined in this work. The monoclinic and hexagonal lattices have polymer chains aligned with their helical axis coincident with the crystal *c*-axis and are located at the four corners of the unit cell. The polymer chains with unit crystal coordinates $(0,0,z)$ and $(0,b,z)$ have a chain setting angle ϕ , while the remaining two chains, located at $(a,0,z)$ and (a,b,z) , have chain setting angles equal to ϕ plus 180 degrees. The orthorhombic lattice, on the other hand, has a chain located at the centre of the unit cell, whose chain setting angle is the supplement of the chain setting angle of the chains located at the corners of the unit cell.

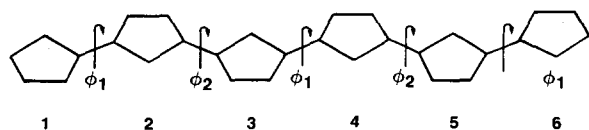


Figure 1 General polymer chain structure depicting the numbering sequence used to describe the intrachain interactions

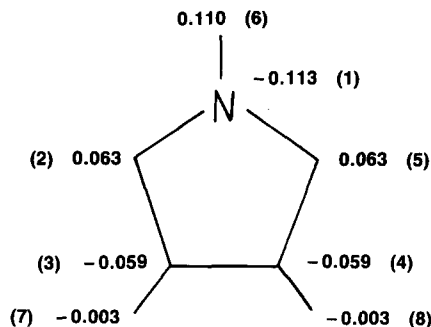


Figure 2 Numbering scheme and partial atomic charges of poly(thiophene) repeat

Table 1 Valence geometry of poly(thiophene)

Bond	<i>d</i> (Å)	Bond angle	θ (degrees)
1-2	1.71	5-1-2	92.2
2-3	1.37	1-2-3	111.5
3-4	1.42	2-3-4	112.5
4-5	1.37	3-4-5	112.5
5-1	1.71	4-5-1	111.5
3-6	1.08	6-3-2	125.0
4-7	1.08	7-4-5	125.0
5-8	1.48	8-5-1	125.0

Several randomly chosen sets are used as starting points in the chain packing analyses of the orthorhombic and monoclinic/hexagonal cells. (The hexagonal lattice is a special case of the monoclinic cell). Lennard-Jones 6-12 potential energy parameters developed by Hopfinger⁵ and Scheraga¹⁰ have been used throughout in this study. The Hopfinger set is known to be 'softer' than the Scheraga values for aromatic systems, perhaps resulting in the occurrence of tighter packing organizations. Yet with a softer set, one has a stronger probability of identifying all possible crystalline packing possibilities. Once a rough set of optimum packing geometries are realized, further refining is sought by using these points as starting points for a further series of minimization.

All calculations were carried out on a GTE Laboratories VAX 11/780 using the computational facilities of the CHEMLAB-II^{1b} software environment.

RESULTS

Valence geometry

The valence geometry of PT is assumed to be similar to that found in model compounds thiophene and diethienyl¹¹ and is shown in *Figure 2*. The values of the bond lengths and angles are listed in *Table 1*. The C-H bond lengths and C-C-H bond angles are assumed to be the same as those found in benzene. The bond angle formed by the atoms that link the thiophene rings (atoms 1, 5 and 8 in *Figure 2*) were chosen by assuming that the bond vector 5-8 bisects the angle formed by atoms 1, 5 and 4. An MNDO (modified neglect of diatomic differential overlap)¹² geometric optimization of the tetramer is also reported, in which the bond lengths and angles within the inner two rings are independent variables. The valence geometry of the optimized structure is shown in *Table 2*.

The valence geometry of PP has received much attention in the literature, and a wide range of values have been reported¹³⁻¹⁶, henceforth referred to as structures A, B, C and D, respectively. Since no good solvent has

been found for PP and it displays a low degree of crystallinity, conclusive structural analyses of the polymer sample are difficult. Thus, the use of low molecular weight model compounds has been necessary. The methods employed in these structural determinations include microwave spectroscopy of the monomer¹³, geometric optimization of the tetramer within a restricted Hartree-Fock SCF-LCAO-MO methodology¹⁴; electron diffraction studies of the dimer¹⁵; and X-ray diffraction studies of the monomer, dimer and trimer of pyrrole¹⁶. PP is shown in Figure 3 while the previously reported geometries are listed in Tables 3 and 4. The bond length of the link between chains for structure A was found via a MNDO¹² optimization. Extensive analysis carried out by Dewar and coworkers¹² have demonstrated the reliability and limitations of MNDO for geometry minimizations.

The positions and relative stabilities of the single chain conformational energy minima are affected negligibly by variations in the valence geometry. Thus, in the molecular mechanics framework, exact description of the valence geometry is not a rigid requirement. Clearly, this is not the case for calculations involving electronic structure, since the valence geometry is more strongly coupled to the electronic properties. To understand better the valence geometry, the energies of the proposed structures were calculated using the MNDO¹² approximation. The relative energies per monomer are shown in Table 5. All the energies appearing in Table 5 are the result of calculations performed on a dimer.

It is evident from this table that the geometries reported by Bredas¹⁴ and Bak¹³ are both energetically feasible. The structures suggested based on diffraction experiments^{15,16} have higher energies and appear to be energetically less probable geometries. The main differences between structures B(14) and D(16) concern the values assigned to the C-N-C and N-C-C bond angles. Structure D(16) has lower values for both of these angles and results in a more compact and apparently strained geometry. It is known that MNDO does not accurately predict the relative stabilities of heteroatomic

Table 2 Optimized valence geometry of poly(thiophene)

Bond	<i>d</i> (Å)	Bond angle	θ (degrees)
1-2	1.71	5-1-2	94.7
2-3	1.38	1-2-3	110.5
3-4	1.44	2-3-4	112.0
4-5	1.38	3-4-5	112.7
5-1	1.70	4-5-1	110.1
3-6	1.08	6-3-2	125.0
4-7	1.08	7-4-5	125.0
5-8	1.45	8-5-1	122.8

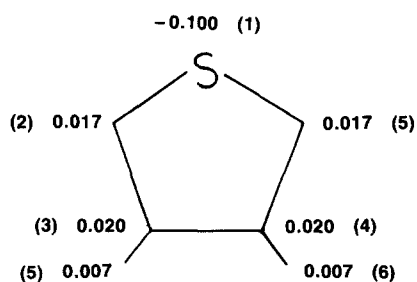


Figure 3 Numbering scheme and partial atomic charges of poly(pyrrole) repeat

Table 3 Bond lengths of poly(pyrrole)

Bond	Structure			
	A (Å)	B (Å)	C (Å)	D (Å)
1-2	1.39	1.39	1.42	1.38
2-3	1.37	1.36	1.35	1.35
3-4	1.43	1.42	1.44	1.41
4-5	1.37	1.36	1.35	1.35
5-1	1.39	1.39	1.42	1.38
1-6	0.99	0.99	1.04	1.15
5-9	1.47	1.47	1.50	1.44
3-7	1.08	1.08	1.09	0.84
4-8	1.08	1.08	1.09	0.84

Table 4 Bond angles of poly(pyrrole)

Angle	Structure			
	A	B	C	D
5-1-2	109.0	109.3	105.0	107.4
1-2-3	108.0	107.5	110.0	108.6
2-3-4	107.5	107.8	107.5	107.7
3-4-5	107.5	107.8	107.5	107.7
4-5-1	108.0	107.5	110.0	108.6
6-2-1	125.5	125.4	127.5	126.3
2-3-7	125.8	126.1	125.9	131.4
8-4-5	125.8	121.2	125.0	121.2
9-5-1	121.0	126.1	125.9	131.4

Table 5 Relative stabilities of proposed pyrrole structures: MNDO values

Structure	<i>E</i> (kcal mol ⁻¹)	<i>E</i> (kcal mol ⁻¹)
A	-17856.9	0.0
B	-17356.2	0.7
C	-17843.0	13.9
D	-17762.5	94.4

ringed systems¹², but as the difference in energies is so large, structure D(16) has some definite shortcomings. In all molecular mechanics calculations, the valence geometry proposed by Bak *et al.*¹³ was used.

To optimize further the valence geometry of pyrrole, the structures of Bredas¹⁴ and Bak¹³ were incorporated as starting points in a MNDO geometric optimization. Calculations were performed on a tetramer, with only the two inner rings undergoing optimization. These calculations produced negligible modifications of the bond lengths for the Bredas model¹⁴ and only slight alterations of the Bak structure. The bond angles of the Bak¹³ ring were more strongly modified.

The Bak¹³ and Bredas¹⁴ optimized structures have nearly identical energies and thus a further refinement of the molecular geometry is not possible with this method.

Electron charge distribution

The partial atomic charges were computed via the CNDO/2 method¹⁷. This semi-empirical MO method gives reasonable partial atomic charges without consuming much computer time. Calculations performed on dimers of PP and PT show that the partial charges are not a function of the relative orientation of the ring planes. Thus, a good approximation for the charge distribution is determined by performing calculations on successively larger planar oligomers.

The partial atomic charges rapidly converge to a value that accurately models an infinite polymer chain. Figures 2 and 3 show the converged partial charges of PT and PP, respectively.

A comparison of these CNDO/2 calculated values and those obtained by other semi-empirical and ab initio methods¹⁸ reveals that, although there is a quantitative difference in the partial charges, a clear qualitative picture remains intact. For example, all methods show the nitrogen atom to be the most electronegative member of the ring while the beta carbon is more negative than the alpha carbon. As a further check of the reliability of CNDO/2 results, identical calculations were performed using the MNDO method. There is only a small difference between the MNDO and CNDO/2 results. The quantitative discrepancy between the various methods is not a serious consequence, since only qualitative information is being extracted from the molecular mechanics calculations that will incorporate these particular results.

Torsional barriers

An important element in the intramolecular conformational analysis is the form of the torsional potential energy barrier. Calculations based solely on the steric repulsive-dispersive forces often lead to an erroneously low barrier. Also, the symmetry of the function may be incorrect, resulting from the neglect of non-steric factors, such as the spatial arrangement of the bonding and non-bonding electrons.

Two main approaches have been used in evaluating the intrinsic torsional barrier. Experimentally determined values, which are most frequently obtained from microwave spectra on small model molecules, are used when available. An acceptable model compound must have both the same symmetry and bonding characteristics as the polymer. When an appropriate experimental model is not available, quantum mechanical calculations are then used as a substitute.

The results for PP and PT as calculated by the CNDO/2¹⁷ method are shown in Figures 4 and 5 respectively. The reference state was arbitrarily chosen as an alternating structure for both PP and PT, i.e. ϕ equals zero when the heteroatoms of adjacent rings point in

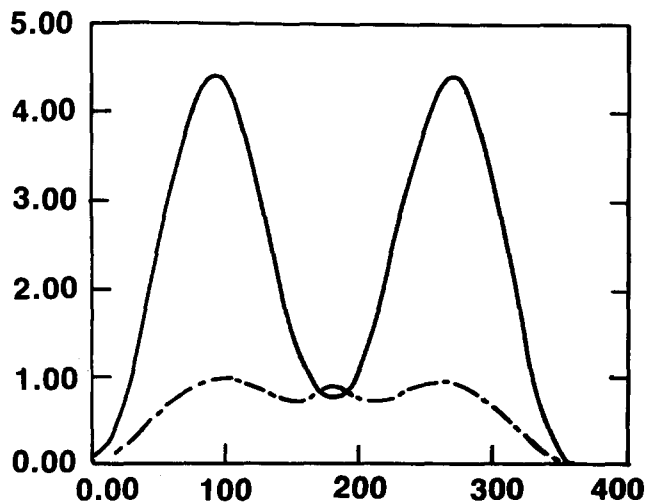


Figure 4 CNDO/2 (solid line) and MM (broken line) calculated rotational energy barriers for poly(pyrrrole)

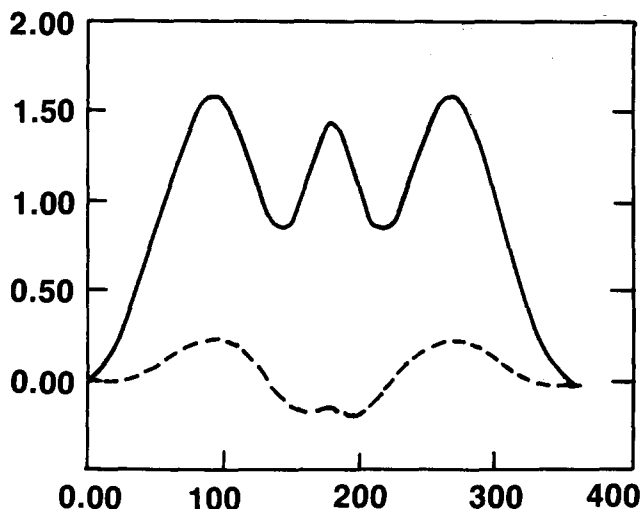


Figure 5 CNDO/2 (solid line) and MM (broken line) calculated rotational energy barriers for poly(thiophene)

opposite directions. Clearly, the barriers as predicted by the CNDO/2 and molecular mechanics methods are different. The difference between the two will be corrected by the incorporation of a torsional function.

The calculated rotational barriers have the correct form that is expected from physical intuition, i.e. there should be an energy barrier to non-planar structures and the *cis* conformer should have a higher energy than the *trans* form, resulting from the repulsive interactions of the beta hydrogens on adjacent rings. This hydrogen-hydrogen repulsive interaction is greater for PT than for PP. Although the *trans-cis* barrier as calculated by CNDO/2 is greater by approximately 2.8 kcal mol⁻¹ for PP than for PT, the *cis* conformer is of comparable energy to the *trans* form of PP, while PT shows the *cis* conformer to be about 1.3 kcal mol⁻¹ higher than the *trans* form.

The same series of calculations were carried out using the MNDO¹² method. Calculations on the dimers of PP and PT predict the off-planar conformation to have a lower energy than the planar form, i.e. the MNDO results conflict with those found from CNDO/2. At this point, it was necessary to combine experimental data, physical intuition and a good knowledge of the methods and their limitations to resolve this apparent dilemma.

Two main factors contribute to the rotational barrier of a system: (1) an increase in energy from the loss of delocalization of the π electrons and favourable π - π overlap as the degree of non-planarity is increased, and (2) a reduction in the energy from the decrease of possible steric repulsive interactions between rings¹⁹. To determine how accurately MNDO and CNDO/2 predict the first effect, calculations on the *trans-cis* transformation of butadiene were carried out. Experimentally, the barrier to rotation is approximately 4.9 kcal mol⁻¹ while the *trans* form is more stable than the *cis* form by about 2 kcal mol⁻¹.²⁰ The barrier calculated with MNDO is only 0.5 kcal mol⁻¹ while CNDO/2 predicts the non-planar form to be more stable. Not only does the MNDO method seriously underestimate the gain in energy from the loss in conjugation, but the CNDO/2 and MNDO results once again are in conflict with one another.

The CNDO/2 and MNDO results on the model compound butadiene suggest that the calculated

CNDO/2 barriers for PP and PT are fortuitously correct in a qualitative sense, if the intuitive description previously described is accepted. Although the calculated symmetries for the rotational barriers appear correct, the height of the barrier is uncertain. CNDO/2 calculated torsional barriers are 3.5 and 1.85 kcal mol⁻¹, respectively, for PP and PT.

Recently, Bredas *et al.*²¹ calculated at the *ab initio* HF-STO-3G (minimal basis set) level the *trans-cis* barrier to be approximately 4 kcal mol⁻¹ for PP and PT. The calculations were performed on a dimer with only the inter-ring bond variable in the energy minimization. For PP, the *ab initio* and CNDO/2 results agree fairly well, although there is a discrepancy concerning the relative stability of the *cis* structure. CNDO/2 predicts the energies of the *cis* and *trans* structure of PP to be nearly equal while *ab initio* shows the *cis* form to be approximately 2.5 kcal mol⁻¹ less stable than *trans*. The *ab initio* and CNDO/2 energies agree very well for rotations less than 90 degrees. Thus, the barrier to perturbations about the lowest energy *trans* conformer are the same for both methods. Since this study is concerned with the identification of the most probable structure and the relative occurrence of non-ideal structures, the cruder, but less CPU time-consuming CNDO/2 method does provide a reasonable estimate of the important conformational features.

The CNDO/2 and *ab initio* results for PT are not in as good an agreement as found for PP, although they are in good qualitative agreement near the global minimum. The major differences are: (1) the CNDO/2 *trans-cis* energy barrier is approximately 2.5 kcal mol⁻¹ less than found with STO-3G; (2) the *cis* form of PT is a local maximum for CNDO/2, but is a local minimum for the *ab initio* calculations. Since the symmetry of the CNDO/2 energy barrier is similar to that of the corresponding barrier calculated by molecular mechanics, which includes only steric and electrostatic interactions, it appears that CNDO/2 more accurately models the steric and electrostatic component, but is deficient when modelling the orbital interactions for sulphur-containing hetero-cyclic compounds. Again, since we are primarily concerned with only the global minimum structure and the barrier to small perturbations from that structure, the use of the CNDO/2 results does not present a significant problem since the CNDO/2 and *ab initio* results are similar in this region.

In addition, Radom and Pople²² proved that it is necessary to carry out a nearly complete optimization of the molecular geometry at each step of the bond rotation. By varying only the length of the single bond which connects the rings and not allowing for bond angle deformation, the *ab initio* calculated barrier may not be quantitatively correct either.

In summary, since this aspect of the study is only concerned with identifying the global and local minima, the possible underestimation of the rotational barrier does not have any serious effect on calculations. Given the crudity of the CNDO/2 method, it is reassuring to see the fairly good agreement with the more reliable *ab initio* results. Uncertainties may arise when trying to evaluate the probability of non-planar chain segments occurring in a crystalline phase, but extra factors arising from intermolecular interactions would also need to be included.

Conformational energetics of a single chain

The basic characteristics of the conformational energies strongly reflect the functional form of the torsional energy barrier. This is a direct consequence of the large difference in magnitude between the total conformational energy and that arising from only steric and electrostatic interactions. The conformational energy maps are shown in Figures 6 and 7 for PP and PT, respectively.

PP and PT both show the planar conjugated structure to be the most stable. The resistance to non-planar conformations is higher for PP, which reflects its higher and steeper torsional barrier. PP and PT show local minima in the region of $\phi_1 = \phi_2 = \pm 90$ with an energy that is about 3 kcal mol⁻¹ above the global minimum. PT exhibits more rotational freedom about these local minima fluctuations of ± 50 degrees cost only 3 kcal mol⁻¹ for PT, but result in a destabilization of about 6 kcal mol⁻¹ for PP. The other main difference

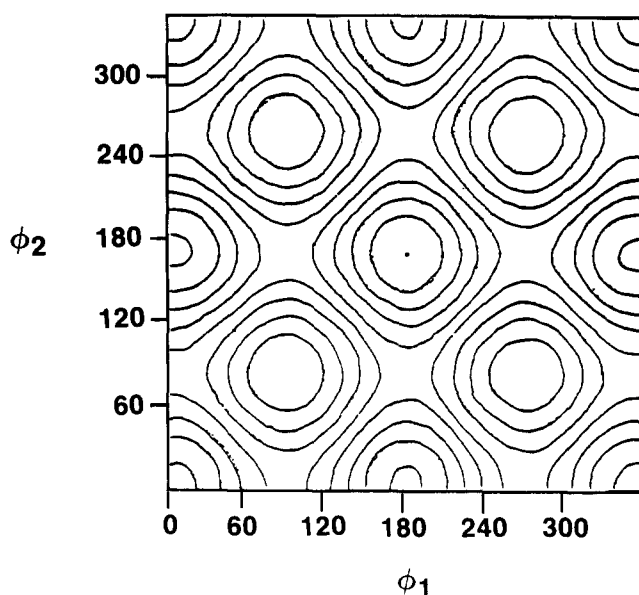


Figure 6 Conformational energy map of poly(pyrrrole). Energies are in kcal mol⁻¹ per repeat. 1 kcal mol⁻¹ per contour level

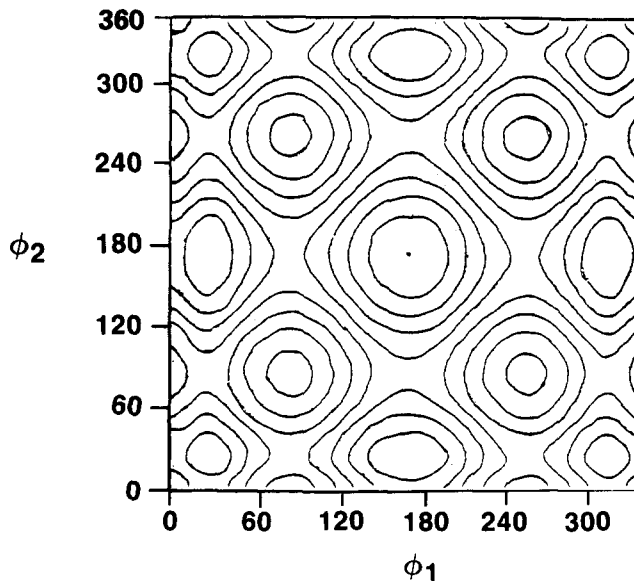


Figure 7 Conformational energy map of poly(thiophene). Energies are in kcal mol⁻¹ per repeat. 0.5 kcal mol⁻¹ per contour level

between the two polymers concerns the feasibility of the other planar structure, whereby all the heteroatoms of the ring (nitrogen for PP and sulphur in PT) are on the same side of the chain. This particular linearly curved conformation is a local minimum for PP and is within about 2 kcal mol⁻¹ of the global minimum. PT has a local minimum that is slightly off-planar from this alternate planar form. An examination of the torsional barriers shown in Figures 4 and 5 clearly demonstrates this basic difference between PP and PT. For subsequent crystal packing calculation, a planar geometry was adopted where the adjacent heteroatoms are on opposite sides of the backbone.

Crystal packing calculations

A large set of randomly chosen starting points were used to determine possible crystal packing arrangements. Each starting point consists of a set of variable lattice values. Energy minimizations were carried out while constraining the chains to either a monoclinic or orthorhombic lattice. Potential energy parameters of both Hopfinger⁵ and Scheraga¹⁰ were used. The resulting minimized lattices and energies corresponding to each starting point are shown in Tables 6 and 7 and 8 and 9 for PP and PT, respectively. The chain setting angles (CSA) shown in these Tables are defined as the angle between the molecular plane and the cartesian coordinate Y-axis. The repeat distances for PP and PT are 7.21 Å and 7.84 Å, respectively.

The distribution of minimized lattice energies is much narrower when using the 'harder' potential of Scheraga¹⁰ in contrast to those found with the Hopfinger⁵ potentials (Tables 6-9). A direct comparison of the absolute energy values found with different potential sets is not relevant; only relative stabilities within each set are physically meaningful. If only the Scheraga values are used, it would be difficult to determine the best possible lattice, since the spread of energies is small (about 2 kcal mol⁻¹). In contrast, the lattice energies found using the Hopfinger values have a much wider range. A comparison of the spatially non-degenerate low energy lattices found within each potential set reveals that no new information is gained by the inclusion of the other set. That is, the resulting low energy lattices found are independent of the choice of potential energy parameters employed; only the relative stabilities of the different packing arrangements are dependent on the exact form of the potential function.

Within each set of minimized lattices shown in Tables 6-9, there are several spatially equivalent structures, i.e. they share common broad characteristics. A further series of minimizations were carried out using the remaining non-degenerate lattices as starting points. Each starting point was chosen using values for the lattice variables that were close to the values found for the non-degenerate structures. Only a slight refinement of the lattice energy is found in this step.

To assess the sensitivity of the lattice energy to modifications in the relationship between the chain setting angles within a unit cell, a series of calculations were carried out in which the (ϕ , 180 - ϕ) (orthorhombic) and (ϕ , 180 + ϕ) (monoclinic) constraints were relaxed. For the orthorhombic case, the setting angle assigned to the chains at the corners of the unit cell and to the chain located at the centre of the cell were allowed to vary independently. For the monoclinic cell, the setting angles for all the chains were set equal to each other although the setting angles were still treated as a single variable. It is found that PP is much more sensitive than PT for the monoclinic case as is evidenced by a larger decrease in energy. The PP lattice is further stabilized by an additional 7 kcal mol⁻¹ when all the chains have equal or independent chain setting angles for the monoclinic and orthorhombic cells, respectively. On the other hand, PT exhibits a smaller stabilization for both symmetries. These results verify that rotations about the chain helical axis are energetically feasible, and slight deviations from

Table 7 Orthorhombic poly(pyrrole)

Starting			Ending			Energy (kcal mol ⁻¹)
A	B	CSA	A	B	CSA	
12.00	6.00	62.0	11.13	2.82	66.0	-42.84
9.00	7.00	123.0	9.92	3.00	58.0	-43.03
10.00	9.00	26.0	9.26	3.11	53.8	-43.69
4.00	6.00	154.0	4.50	6.50	65.7	-36.67
8.00	5.00	125.0	9.06	3.19	52.5	-43.96
13.00	4.00	170.0	7.85	3.57	41.9	-44.65
4.00	9.00	121.0	8.40	3.36	45.9	-44.32
9.00	4.00	47.0	7.91	3.53	42.7	-44.67
4.00	4.00	105.0	7.44	3.90	86.0	-32.44
13.00	7.00	68.0	2.69	6.61	12.6	-39.66
4.00	6.00	9.0	7.65	3.61	40.6	-44.63
11.00	4.00	11.0	11.00	4.01	44.7	-22.65
4.00	3.00	28.0	7.32	5.64	46.7	-16.77

Table 6 Monoclinic poly(pyrrole)

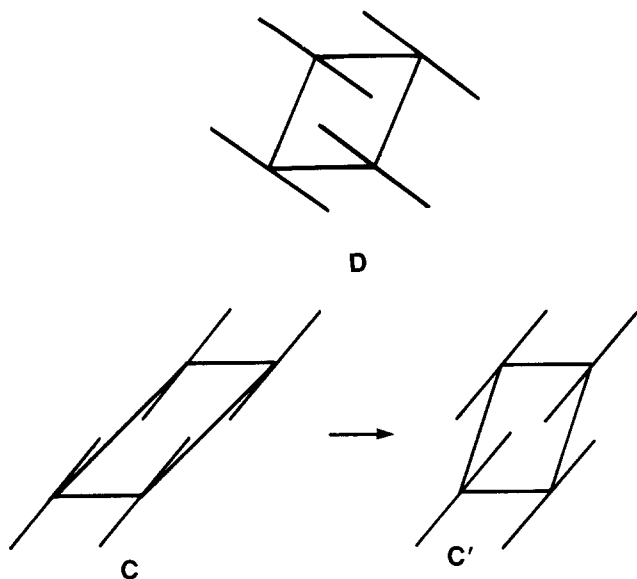
Starting				Ending				Energy (kcal mol ⁻¹)
A	B	γ	CSA	A	B	γ	CSA	
12.00	4.00	62.0	125.0	7.86	2.80	50.1	152.8	-47.95
14.00	5.00	73.0	174.0	4.37	4.21	63.6	125.0	-46.87
7.00	7.00	80.0	153.0	4.41	4.26	82.0	159.6	-38.83
4.00	7.00	59.0	152.0	3.73	6.70	52.2	159.5	-29.89
12.00	5.00	60.0	15.0	2.76	6.65	60.4	26.4	-47.06
11.00	10.00	57.0	40.0	6.98	3.70	38.3	89.1	-47.53
4.00	4.00	70.0	125.0	2.62	6.88	66.4	165.1	-49.76
7.00	10.00	58.0	39.0	4.97	6.69	29.7	62.5	-44.67
6.00	7.00	79.0	10.0	7.14	4.49	31.3	86.1	-47.81
3.00	5.00	93.0	19.0	3.78	4.44	64.7	49.1	-50.35
3.00	8.00	91.0	137.0	2.57	7.34	60.3	175.4	-51.08
6.00	9.00	100.0	147.0	3.40	6.76	41.4	137.6	-51.34
3.00	14.00	118.0	54.0	4.68	5.09	44.1	59.9	-43.01

Table 8 Monoclinic poly(thiophene)

Starting				Ending				Energy (kcal mol ⁻¹)
A	B	γ	CSA	A	B	γ	CSA	
7.00	9.00	70.0	88.0	6.08	3.12	67.1	39.4	-41.46
9.00	12.00	104.0	170.0	5.08	5.92	31.9	66.4	-45.55
9.00	12.00	84.0	179.0	5.12	6.02	30.3	113.7	-45.99
8.00	13.00	126.0	116.0	2.87	7.86	49.1	167.9	-39.71
4.00	9.00	98.0	68.0	3.33	6.04	53.9	30.7	-44.18
9.00	6.00	76.0	25.0	5.59	3.00	93.0	110.3	-42.28
12.00	10.00	72.0	54.0	5.34	3.14	82.2	67.7	-42.88
12.00	7.00	75.0	128.0	2.88	7.77	45.7	9.8	-44.16
4.00	7.00	79.0	109.0	6.57	4.79	33.3	95.5	-37.21
14.00	10.00	110.0	22.0	3.16	5.95	57.0	25.5	-45.77

Table 9 Orthorhombic poly(thiophene)

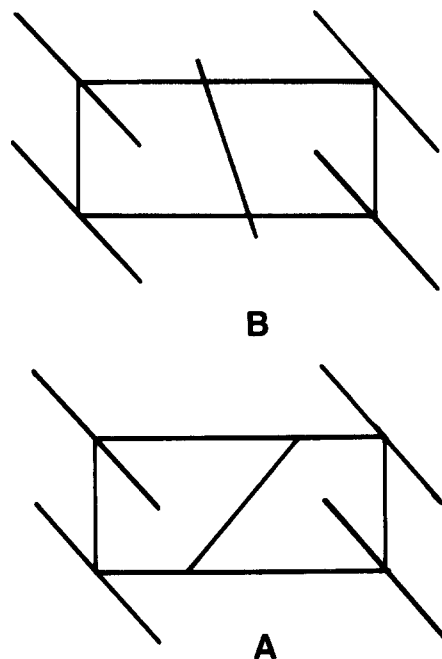
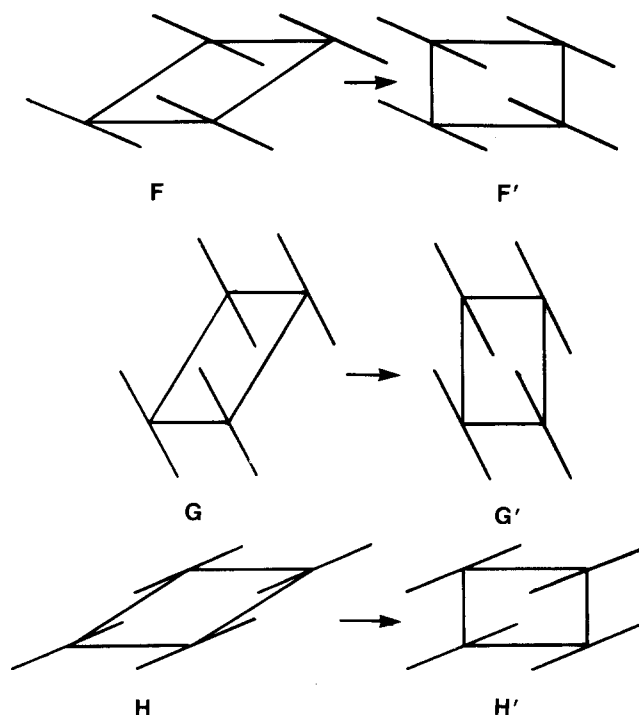
Starting			Ending			Energy (kcal mol ⁻¹)
A	B	CSA	A	B	CSA	
12.00	6.00	62.0	11.25	3.68	64.3	-11.75
5.00	9.00	4.0	5.90	5.19	19.7	-27.90
6.00	5.00	97.0	5.05	6.17	68.6	-28.53
6.00	5.00	63.0	6.10	5.38	85.3	-22.68
4.00	8.00	41.0	10.14	2.98	68.9	-38.26
8.00	7.00	45.0	7.67	5.70	46.4	-14.45
5.00	9.00	35.0	2.96	6.73	13.6	-30.86
7.00	6.00	51.0	9.32	3.09	61.1	-35.72
9.00	4.00	31.0	10.01	3.00	67.6	-38.18
7.00	9.00	13.0	5.85	5.29	19.3	-27.85
7.00	4.00	54.0	5.97	5.19	20.5	-27.93

**Figure 8** Monoclinic unit cells of poly(pyrrrole)

the ideal case may occur with marked frequency in the crystal.

The most energetically feasible structures are shown in *Figures 8 and 9 and 10 and 11* for PP and PT, respectively. The corresponding lattice values are shown in *Tables 10 and 11*. The chain setting angles are with respect to the *b* crystal cell edge in *Tables 10 and 11*. Some of the unit cells listed in *Tables 10 and 11* may be equally represented by lattices that are more in line with standard usage. These transformed unit cells are also shown in *Figures 8-11* and in *Tables 10 and 11*.

PP and PT share common packing characteristics, which is not surprising since both have similar molecular

**Figure 9** Orthorhombic unit cells of poly(pyrrrole)**Figure 10** Monoclinic unit cells of poly(thiophene)

geometries, i.e. both are planar or nearly planar polymer chains consisting of 5-membered heterocyclic rings. The planarity of the polymer chains allows for favourable π - π interchain interactions within the unit cell which significantly stabilize the system.

Electronic band structure calculations

Conformational energy calculations of single isolated chains of PP and PT suggest that the planar alternating conformer has the lowest energy and thus appears to be the most probable form present in the crystalline state. It is believed that non-planar 'defects' may also exist, but molecular mechanics calculations are not a sufficiently sensitive probe unambiguously to determine the probability that these defects occur. The electronic band structure, on the other hand, is sensitive to the spatial arrangement of the constituent atoms and thus may be analysed to this end.

Valence effective Hamiltonian (VEH) quantum mechanical calculations²³ were performed on planar and slightly non-planar conformers of PP and PT to determine the sensitivity of the band structure to chain conformation. If the electronic properties of the non-planar forms are within range of the experimentally observed values, then non-planar conformations cannot be ruled out as possible crystalline structures.

The calculations were performed on chains that have alternating bond rotations of 5 and 10 degrees along with the planar conformation. Even though the reliability of the VEH method diminishes as the degree of non-planarity increases, this extent of non-planarity is sufficiently small to ensure confidence in the results²⁴. The basis set and atomic potential parameters used are the

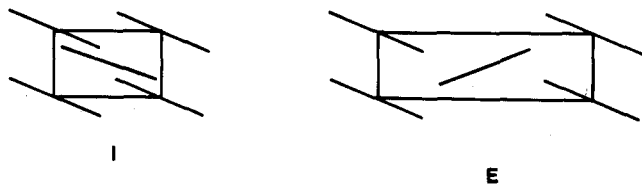


Figure 11 Orthorhombic unit cells of poly(thiophene)

Table 10 Poly(pyrrole) unit cells

Structure	A	B	γ	CSA1	CSA2	Energy (kcal mol ⁻¹)
A(1)	4.00	4.03	63.41	84.90	—	-59.08
B(1)	3.28 (3.28)	6.61 (4.73)	42.2 (70.0)	185.8 (158.2)	—	-58.70
C(2)	8.21	3.54	90.0	43.5	38.0	-51.39
D	7.85	3.56	90.0	42.0	138.0	-44.68

(1): all chains have equal setting angles
 (2): two independent chain setting angles per unit cell
 Transformed unit cells in parentheses

Table 11 Poly(thiophene) unit cells

Structure	A	B	γ	CSA1	CSA2	Energy (kcal mol ⁻¹)
E(1)	4.99 (4.99)	5.81 (3.03)	31.5 (90.6)	171.0 (111.8)	—	-47.64
F(1)	3.16 (3.16)	5.95 (4.97)	56.6 (88.6)	59.5 (27.5)	—	-46.56
G	5.08 (5.08)	5.91 (3.12)	31.9 (91.1)	124.5 (65.2)	—	-46.31
H	10.13	2.98	90.0	68.7	111.3	-38.30

(1): all chains have equal setting angles
 (2): two independent chain setting angles per unit cell
 Transformed unit cells in parentheses

same as found in previous studies^{25,26}. The valence geometry of PP was taken from both Bak¹³ and Bredas¹⁴, while the geometry suggested by Wachters¹¹ was used for PT.

The calculated band gaps (E_g), band widths (BW) and Koopman ionization potentials (IP) for PP and PT are listed in Tables 12 and 13, respectively. As is clearly evident, slightly non-planar periodic segments do not induce large changes in the band structure. The changes calculated are all well within the uncertainty of the experimentally observed values.

Recent calculations by Bredas *et al.*²¹ also examined the electronic properties as a function of non-planarity for values of 0, 20, 40, 60 and 90 degrees. As expected, as the degree of non-planarity increases the band gap and ionization potential increase while the band gap decreases. Since the VEH method was parameterized for nearly planar structures, the calculated electronic properties for the nearly planar structures should be more reliable than those calculated for the highly non-planar systems examined by Bredas²⁵ since the latter are outside the domain of the molecules employed in the parameterization process.

As is reported by Bredas *et al.*²⁵, a slight change in the

Table 12 VEH poly(pyrrole)—Bak structure

Angle (degrees)	E_g (eV)	BW (eV)	IP (eV)
0	3.870	3.497	4.089
5	3.875	3.494	4.095
10	3.889	3.483	4.106

Table 13 VEH poly(thiophene)

Angle (degrees)	E_g (eV)	BW (eV)	IP (eV)
0	1.855	2.074	5.179
5	1.865	2.065	5.185
10	1.895	2.038	5.203

bond length which connects the pyrrole rings (from 1.45 to 1.49 Å) also causes similar changes in the band structure. These calculations suggest that planar as well as slightly non-planar conformations can exist within the crystalline state with no significant alteration of the electronic properties.

SUMMARY

A series of calculations were performed in an attempt further to understand the structural characteristics of poly(pyrrole) and poly(thiophene). The levels of structural organization addressed concerned the molecular valence geometry, the probable conformations of the polymer chain and possible crystalline packing arrangements.

Planar and slightly non-planar (5–10 degrees) conformations are consistent with energetic and electronic band structure factors. A number of possible crystal structures were proposed that may subsequently be used as starting structures in conjunction with limited X-ray or electron diffraction information to arrive at the final structures in an unambiguous manner. Clearly while all the proposed structures are energetically feasible, other kinetic and thermodynamic factors not included explicitly in this analysis may favour one form over the other. It could also be very instructive further to investigate the packing of these lattices while simultaneously accommodating the various dopant species that have been investigated.

ACKNOWLEDGEMENT

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