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Conformational and electronic band structure analysis of a new type of high performance polybenzothiazole polymers

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The energy-band structure and preferred (minimum energy) conformation of the recently synthesized polybenzothiazoles (PBT; AA and AB type), representing a new class of high-performance polymers, were determined by molecular orbital calculations. In the case of the AAPBT chain, the most stable conformation was obtained at ϕ_1 (rotation angle about the bond joining the two bibenzothiazole moieties) = 20° and ϕ_2 (rotation angle about the bond joining the bibenzothiazole group and the *p*-phenylene group) = 10°. In the case of the ABPBT chain, the corresponding minimum energy rotational angle (ϕ') was found to be 20°. These conformations agree fairly well with both theoretical and experimental observations. The calculated axial band gaps were 1.94 and 2.08 eV for the AAPBT and ABPBT polymers, respectively, and these values are close to the corresponding value for polyacetylene, considered a prototype electrically-conducting polymer because of its novel electronic properties and manifold applications.

1. Introduction

There has been a growing interest to synthesize and characterize various types of aromatic heterocyclic polymers [1–3] because of their high thermal stability and resistance to most solvents. Their potential as high performance structural materials has been demonstrated in the fabrication of fibres, films and molecular composites of high mechanical strength and modulus [1–5]. Results of recent band structure calculations on similar polymers such as poly(*p*-phenylene benzobisoxazole) (PBO) and poly(*p*-phenylene benzobisthiazole (PBT) [6] and the structurally related polymers AAPBO and ABPBO [7, 8] have shown their promise as semiconducting materials. In fact, their calculated band gaps were very close to that found for polyacetylene, a polymer extensively studied because of its unique electrical properties [9, 10].

Standard extended Hückel calculations have been found to reproduce band structures of hydrocarbon polymers [6, 7, 11–14] fairly well. It was therefore decided to investigate the electronic properties of a new type of PBT polymers by means of band structure analysis using the extended Hückel technique within the tight binding approximation. The polymers of present interest are poly(6,6′-bibenzothiazole-2,2′-diyl-1,4-phenylene) (AAPBT) and poly(2,5-benzothiazole) (2,5-ABPBT) (Figs 1 and 2). In order to overcome some initial difficulties (such as nonalignment of a chemical repeat unit along a preferred direction and nonperiodicity), a specific periodic arrangement was chosen in which the second chemical unit was rotated 180° with respect to the first unit about the bond joining the two units. Similarly, in the case of ABPBT, four chemical repeat units were chosen in which the second two units were rotated 180° with respect to the first two units about the bond joining the pair. Further support for selecting such an arrangement was furnished by explicit molecular orbital (MO) calculations of the extended Hückel type on model compounds of AAPBO and ABPBO polymers.

2. Theory

The present investigation employs the extended Hückel theory within the tight-binding approximation which has been discussed in detail elsewhere [6, 7, 11–14]. The extended Hückel method is also known as the Mulliken–Wolfsberg–Helmholtz technique [15], which employs an empirical Hamiltonian representing one-electron energy. The energy expectation values were evaluated using a linear combination of atomic orbitals (LCAO). Briefly, the set of all energy bands associated from the solution of the secular equation

$$H(\boldsymbol{k})C_n(\boldsymbol{k}) = S(\boldsymbol{k})C_n(\boldsymbol{k})E_n(\boldsymbol{k}) \qquad (1)$$

descibes the band structure of the one-dimensional polymer chain, where $H(\boldsymbol{k})$ is the Hamiltonian operator, $S(\boldsymbol{k})$ is the overlap matrix, and $\mathrm{C}(\boldsymbol{k})$ is the expansion coefficient in LCAO. The Hamiltonian operator is modified according to this approximation as

$$H_{ij} = KS_{ij}(E_{ii} + E_{jj})/2 \qquad (2)$$

where K is a scaling parameter (usually 1.75) and E_{ii} denotes the one-electron eigenvalues of the basis levels. Owing to symmetry considerations the energy bands are determined within the first Brillouin zone, $-0.5\boldsymbol{K} \leqslant \boldsymbol{k} \leqslant 0.5\boldsymbol{K}$ (where $\boldsymbol{K} = 2\pi/\boldsymbol{a}$ is the

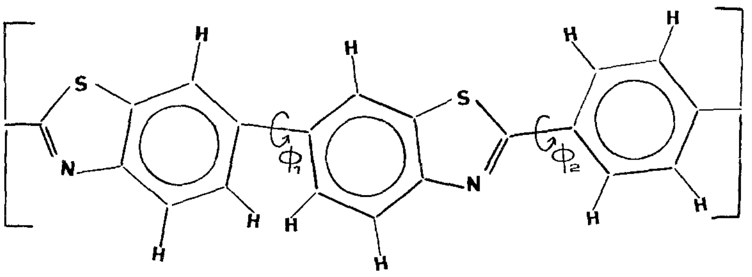

Figure 1 AAPBT chemical repeat unit in which ϕ_1 and ϕ_2 are the rotation angles about the two rotatable bonds.

reciprocal lattice vector and $\boldsymbol{a}$ is the basis vector of the translational symmetry which is parallel to the chain axis). The preferred conformation was determined from calculating the total energy per unit cell, as given by

$$\langle E_t \rangle = \frac{1}{\boldsymbol{K}} \int_{-\boldsymbol{K}/2}^{\boldsymbol{K}/2} E_t(\boldsymbol{k})\, d\boldsymbol{k} \qquad (3)$$

where $E_t(\boldsymbol{k})$ is the total energy at the wave vector $\boldsymbol{k}$ and, according to the extended Hückel method,

$$E_t(\boldsymbol{k}) = 2 \sum_{n}^{\text{occupied}} E_n(\boldsymbol{k}) \qquad (4)$$

The input values of the bond lengths and bond angles were obtained from the X-ray diffraction studies of PBT model compounds [16] and ABPBT itself [17]. The lattice sums were carried out only to first nearest neighbours because of the large size of the repeat unit. The extended Hückel parameters used for calculations were obtained from the literature [6, 12].

3. Results and discussion

A closed shell system has been adopted for the present calculations in which the repeat units of both AAPBT and ABPBT chains contain even numbers of valence electrons. Attempts have been made to determine the most stable conformation with respect to the rotations ϕ_1 and ϕ_2 by calculating the total energy of a unit cell as a function of $\boldsymbol{k}$ for different values of the dihedral angles ($0° \leqslant \phi_1 \leqslant 180°$; $0° \leqslant \phi_2 \leqslant 90°$) using increments of 10°. The results for AAPBT chain are shown in Figs 3 and 4. Owing to the variations of the lattice vectors for each rotation, the reciprocal lattice vector $\boldsymbol{k}$ is no longer a constant; the total energy per unit cell $\langle E_t \rangle$ was thus evaluated using a polynomial fit for $E_t(\boldsymbol{k})$ in Equation 3. From Fig. 5 it was observed that the minimum energy conformation was obtained for $\phi_1 = 20°$ (or its supplement 160°) and $\phi_2 = 10°$ with very small energy differences in the range of 0 to 20° and 160 to 180°. The value obtained for ϕ_1, which is the rotation between the two bibenzothiazole groups, is in good agreement with the corresponding conformation obtained for biphenyl [18]. The predicted value of 20° for ϕ_1 is also in excellent agreement with our previous studies [7] and the *ab initio* results of Almöf [19]. The preferred orientation of the other twist angle ϕ_2, which is the rotation of the lone phenylene ring with respect to the bibenzobisthiazole moiety, corresponds to $\phi_2 = 10°$ and the bond exhibits considerable rotational flexibility in the range of $\phi_2 = 0$ to 20°. The corresponding preferred angle in case of AAPBO is 0° (planar conformation). The nonplanar conformation predicted in the case of AAPBT is probably due to the presence of the relatively large sulphur atoms in place of the oxygen atoms found in the AAPBO chain. For the bibenzothiazole moiety, in the planar form ($\phi_1 = 0°$) the nonbonded distance between the closest orthohydrogens on adjacent phenyl rings is nearly 0.185 nm compared with the sum of van der Waals radii (0.24 nm). However, these repulsive interactions can be relieved by rotation to $\phi_1 = 20$ to 30°, at which the H–H distance would be about 0.21 nm. Such quasi-nonplanar structures could possibly result in interlocking the chains to form networks with improved chain packing.

Similar calculations were carried out for ABPBT; a typical plot of $E_t(\boldsymbol{k})$ against $\boldsymbol{k}$ is shown in Fig. 6. The conformational energy ΔE as a function of rotational angle ϕ' is shown in Fig. 7. It indicates the minimum energy conformation at $\phi' = 20/160°$. The preferred conformation of $\phi' = 20°$ (or its supplement 160°) is in good agreement with the results carried out on structurally similar model compounds of PBT [6]. In

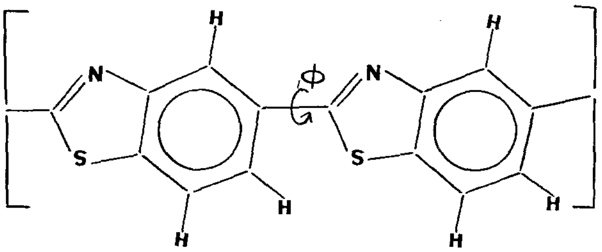

Figure 2 ABPBT with two chemical repeat units in which ϕ' is the rotation angle about the bond joining the two units.

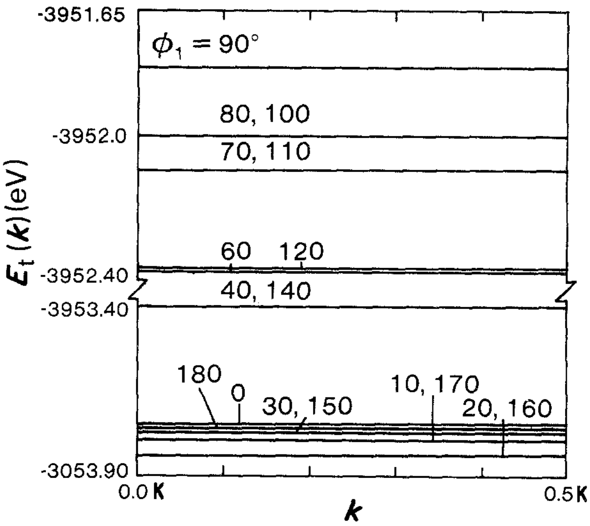

Figure 3 Dependence of $E_t(\boldsymbol{k})$ on $\boldsymbol{k}$ and ϕ_1 at $\phi_2 = 0°$ for AAPBT chain.

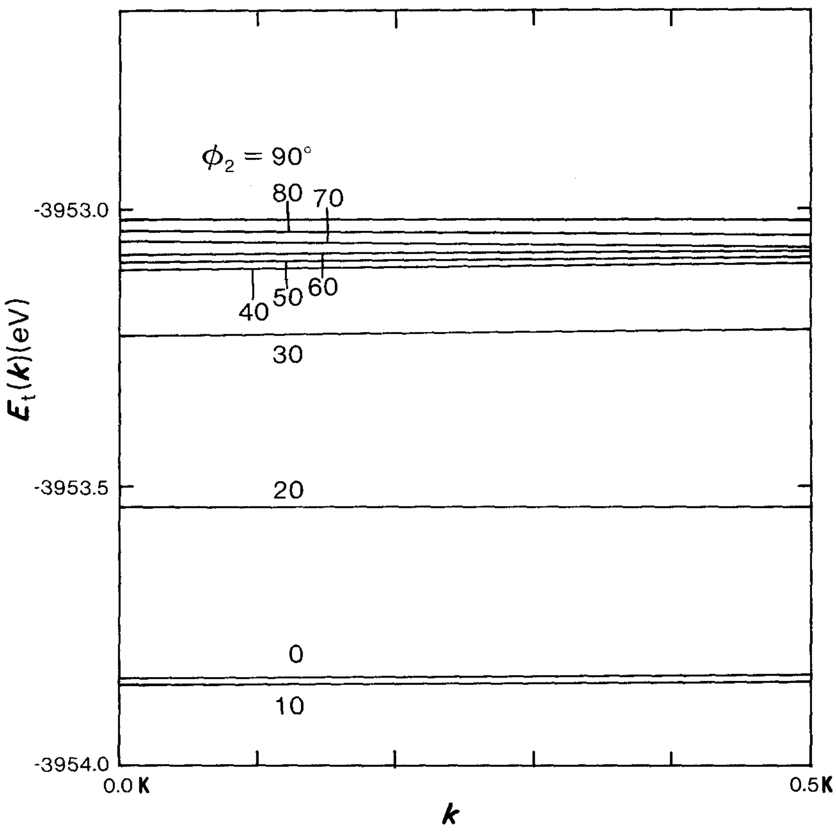

Figure 4 Dependence of $E_t(k)$ on k and $\phi_1 = 20°$ for AAPBT chain.

this case the nonplanarity could be ascribed to the repulsive interactions between the sulphur atom and the adjacent orthohydrogens on the neighbouring phenyl ring.

The axial band gaps (E_g) for the AAPBT and ABPBT chains in the preferred conformations were 1.94 and 2.98 eV, respectively. These values are consistent with that calculated previously for PBT [6] and are also close to the experimentally observed values (1.4 to 1.8 eV) for polyacetylene [9, 10], a polymer much studied because of it is promise as a conducting material upon doping with appropriate electron donors and electron acceptors. The present methodology has been successfully employed to predict enhanced conductivity upon doping polyacetylene [20], *cis*-poly(benzobisoxazole) (PBO) and *trans*-poly-(bensobisthiazole) (PBT) [21] with acceptor dopants such as iodine or bromine. Thus, investigations are underway to examine these new class of polymers in the doped state. A portion of the electronic band structures for each polymer is shown in Figs 8 and 9, respectively. To further elucidate the electronic behaviour such as charge transport and electron mobility, the dispersion (bandwidth) of the highest occupied valence band of both polymers was measured. The flatness (dispersion of the order of 0.1 eV) of these bands as compared to bandwidth of polyacetylene (theoretical estimate of the orders of 6.54 eV) [9] might be due to the nonbonding character of the corresponding crystalline orbitals. Another possibility is the non-planar conformations and the large size of the unit cells chosen for calculations which would

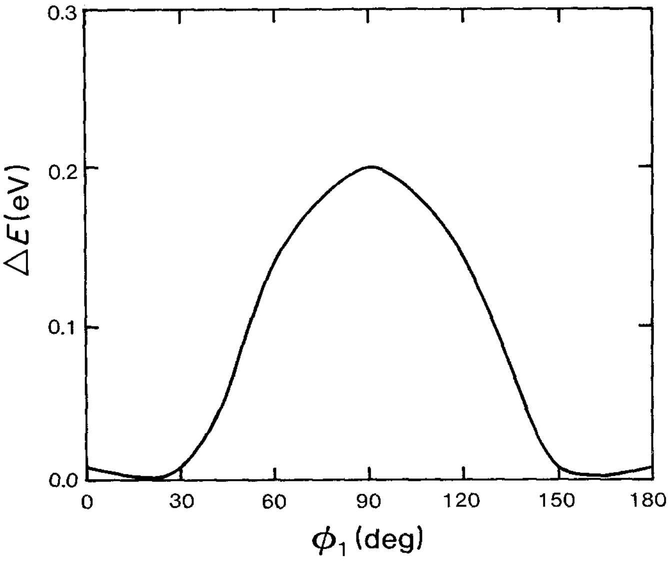

Figure 5 The conformational energy ΔE shown as a function of the rotational angle ϕ_1 for AAPBT, where ΔE is defined as the energy of a conformation relative to that of the preferred conformation.

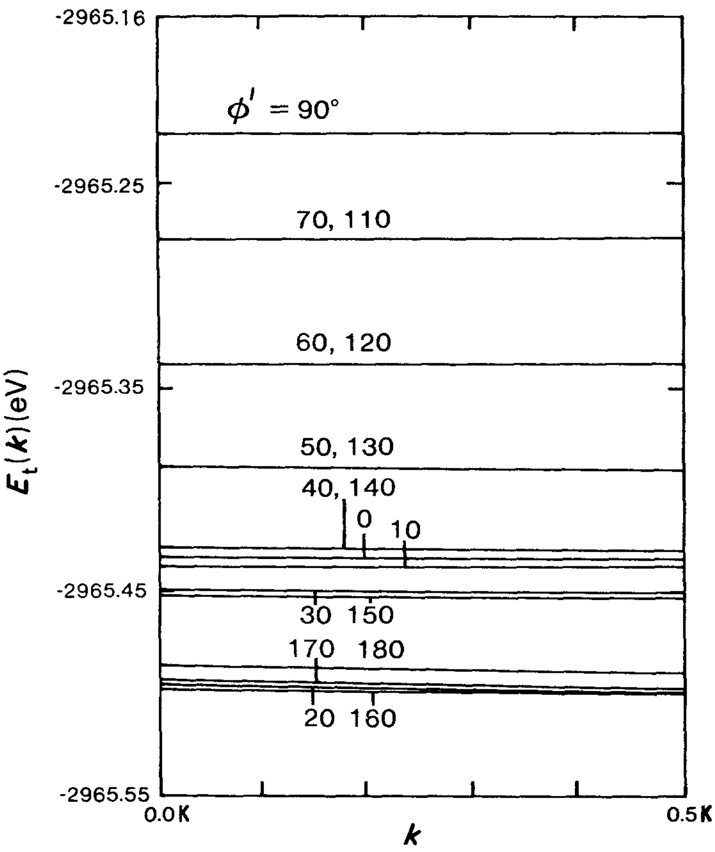

Figure 6 Dependence of $E_t(k)$ on k and ϕ' for the ABPBT chain.

eliminate the opportunity for significant electron delocalization. Moreover, the bandgap was found to increase in the chains deviated from the coplanar conformation and was a maximum at the perpendicular conformation. This prediction is in agreement with the previous calculations on similar model compounds [6, 7]. The dependence of E_g on rotational angle ϕ_1 for AAPBT is illustrated in Fig. 10. The ultraviolet–visible and Raman spectroscopic studies [5] have been made to examine the effect of protonation of a heterocyclic rigid-rod polymer poly(*p*-phenylene benzobisthiazole) and its model compounds, belonging to the same class of polymers. Unfortunately, at present, there are no experimental results available for comparison with these theoretical findings of band gaps and bandwidths of these high performance polymers.

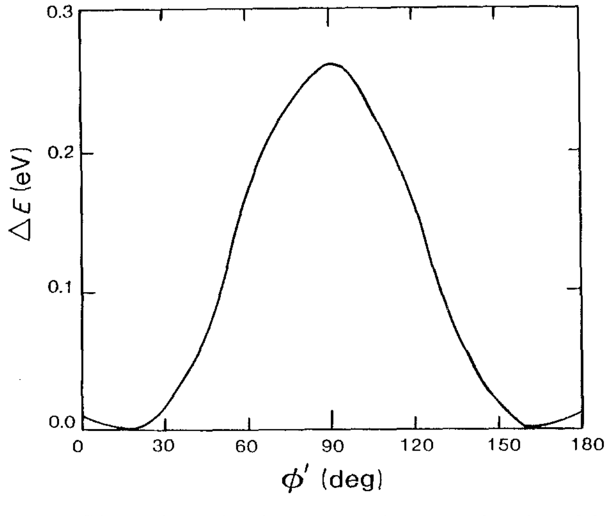

Figure 7 The conformational energy ΔE shown as a function of the rotational angle ϕ' for ABPBT chain.

The results borne out by these calculations indicate the potential of these high performance polymers as semi-conducting materials.

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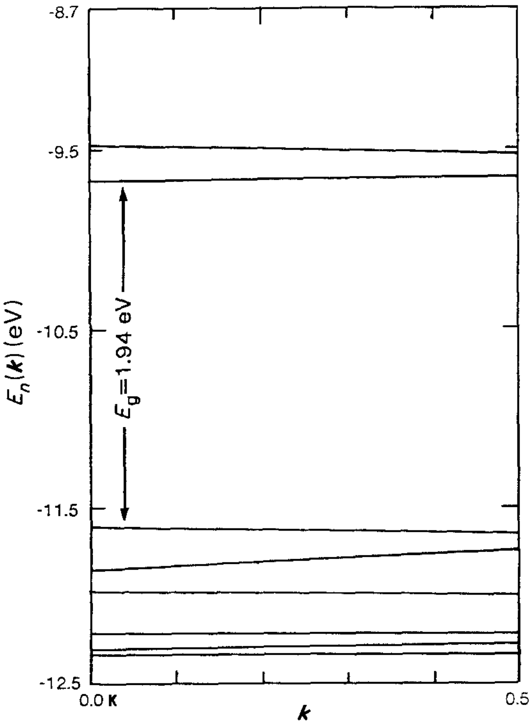

Figure 8 Electronic band structure of the AAPBT chain at the preferred (minimum energy) conformation ($\phi_1 = 20°$ and $\phi_2 = 10°$).

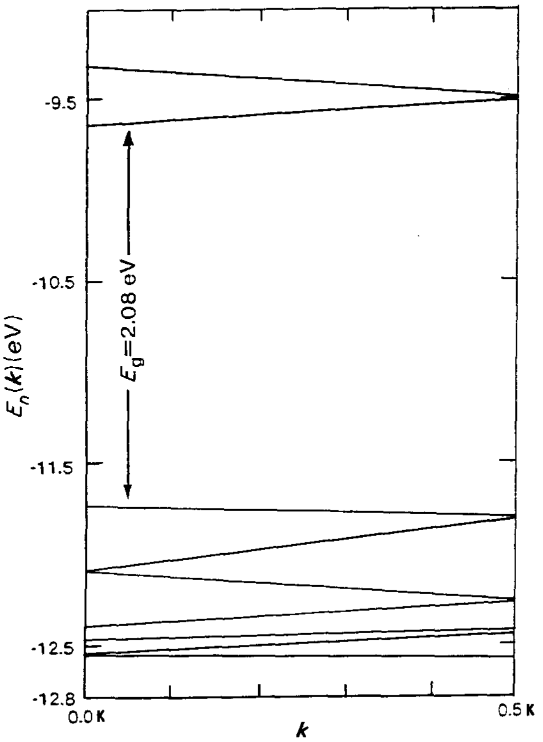

Figure 9 Electronic band structure of the ABPBT chain at the preferred conformation ($\phi' = 20°$).

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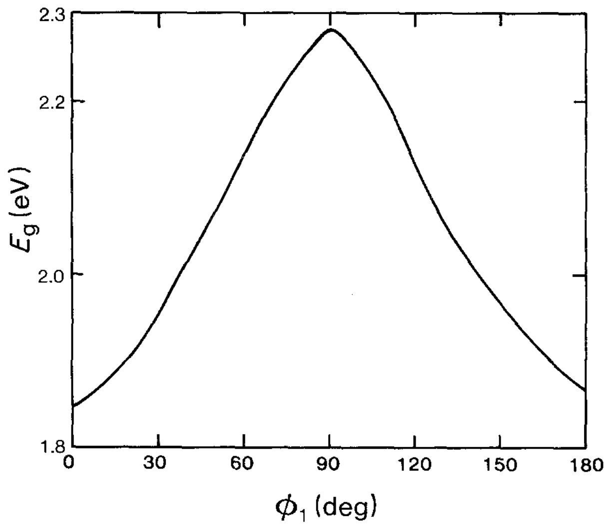

Figure 10 Dependence of the bandgap E_g on the rotational angle ϕ_1 at $\phi_2 = 0°$ for the AAPBT chain.

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