JOURNAL OF MATERIALS SCIENCE 18 (1983) 1119–1124

CNDO studies on nonplanar conformations in some *cis*- and *trans*-polybenzobisoxazoles and polybenzobisthiazoles

W. J. WELSH*, J. E. MARK‡
*Department of Chemistry and Polymer Research Center, University of Cincinnati, Cincinnati, Ohio 45221, USA and *Department of Chemistry, College of Mount St. Joseph, Mount St. Joseph, Ohio 45051, USA*

While essentially rigid in the axial direction, the rod-like polymers *cis*- and *trans*-polybenzobisoxazole (PBO) and polybenzobisthiazole (PBT) do exhibit conformational flexibility with respect to rotations about the bonds between alternating phenylenes and heterocyclic groups. Since preparation of high-strength materials from these polymers requires a high degree of alignment, this flexibility should be important in this regard. CNDO/2 molecular orbital calculations were therefore carried out to obtain the conformational-energy profiles of related model compounds. The *cis*- and *trans*-PBO models prefer the coplanar conformation while the barrier to the perpendicular conformation is about 8.4 kJ mol^{-1}. The *trans*-PBT model prefers $\phi = 20°$ with barriers to the coplanar and perpendicular conformations of about 2.1 and 25.0 kJ mol^{-1}, respectively. Model compounds of *cis*-PBT are bowed in the crystalline state. The bond-strain energies apparently responsible for bowing are estimated by comparing the CNDO/2 energy of the observed "bowed" molecule to that of a ficticious planar form. The "bowed" form is more stable by a large amount, indicating that in-plane bond-angle and bond-length distortions are not sufficient to relieve bond strain. Bowing hence appears to be a necessary alternative to these mechanisms for relieving the considerable strain within the planar form.

1. Introduction

The possible use of ordered polymer systems as self-reinforced polymer composites has been the focus of considerable interest and research recently [1–16]. Several rod-like polymers are especially promising since precipitated films and fibres of the materials exhibit high tensile strengths, good thermal and oxidative stabilities, and resistance to most common solvents. Hence these materials are of particular interest in applications where high-performance characteristics are required. Special interest has focused on the para-catenated polymers of the type shown in Fig. 1. The polybenzobisoxazole (PBO) shown here is designated the *cis* form on the basis of the relative locations of the two oxygen atoms in the repeat unit. Other, related polymers are the *trans*-PBO, and the *cis* and *trans* forms of the corresponding polybenzobisthiazole (PBT), in which the two oxygen atoms above are replaced by sulphur atoms. While essentially rigid in the axial direction, these polymers do possess some conformational flexibility in that rotations about the bonds connecting the phenylene ring and the aromatic-heterocyclic group should at least be possible. The preparation of high-strength materials consisting of rod-like polymers such as these requires a high degree of alignment of the rods. The extent of intramolecular rotational flexibility and thus deviations from planarity may be important in this regard, particu-

---

‡UC affiliation only.

0022–2461/83 $03.00 + .12

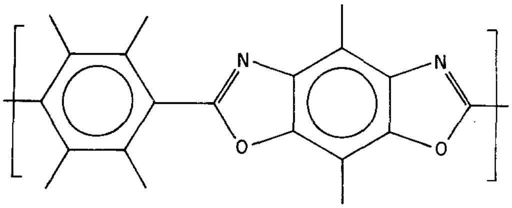

Figure 1 The PBO (polybenzobisozaxole) repeat unit shown in the *cis* form so designated because of the relative positions of the two oxygen atoms.

larly in terms of chain-packing effects and the solubility characteristics of the polymers.

Model compounds of the *cis*-PBT polymer chain, as illustrated in Fig. 2, have been shown to assume a slightly bowed configuration in the crystalline state [17]. The bowing is a result of the planar thiazole rings being inclined in the same direction from the best plane through the atoms of the fused benzene ring by an average of 2.6°. The bowing corresponds to an average inclination angle of 4.7° between the bonds connecting the end phenylenes to the benzobisthiazole and the best plane through the benzobisthiazole group. Such bowing is not present in the model compounds of *trans*-PBT or *cis*- or *trans*-PBO. If present in polymeric *cis*-PBT, this bowing would be expected to interfere with alignment of chains and hence have a deleterious effect on desirable properties. The present theoretical investigation was therefore undertaken in an attempt to characterize and elucidate both the conformational flexibility within the PBO and PBT polymers and the unusual bowing observed in model compounds of *cis*-PBT.

2. Theory and methodology

The basic technique employed consists of the Complete Neglect of Differential Overlap (CNDO/2) semi-empirical molecular orbital method [18] which for oxygen-containing species (like *cis*- and *trans*-PBO) is further nested in an iterative scheme for achieving direct geometry optimization [19]. In all cases, model compounds such as that illustrated in Fig. 2 for *cis*-PBT were considered.

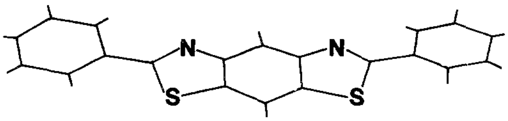

Figure 2 The *cis*-PBT model compound with the bowing illustrated in two dimensions.

Application of CNDO/2 with geometry optimization to such large species (36 atoms) is somewhat uncommon but was considered warranted in this case since it was desired to treat explicitly the influence of conjugation effects on the rotational flexibility of the species considered. The direct geometry optimization of the molecule is based upon the gradient of the potential energy function, the computation of which is made more efficient in terms of computer time by exploiting symmetry effects. Specifically, the number of coordinates defining the molecular geometry may be reduced by the use of symmetry coordinates, in which case non-totally symmetric coordinates may be ignored since the gradient, a totally symmetric function, vanishes for all such coordinates. The analytically-defined elements of the gradient of the potential energy function are obtained by differentiation of the CNDO/2 total molecular energy expression with respect to each of the totally symmetric coordinates. Convergence is achieved when the absolute value of each gradient element becomes less than a specified threshold value; a value of 1.0 eV/nm (9.65×10^{10} kJ mol^{-1} m^{-1}) has been found to be acceptable [19]. The CNDO/2 Self-Consistent Field (SCF) electronic energy is very sensitive to changes in the nuclear coordinates of the molecule. Hence, the convergence criterion for this portion of the iteration, taken as self-consistency between two successive calculations, was set to a value (10^{-9} eV) which is extremely small relative to that typically used (10^{-5} eV) in non-optimized CNDO/2 calculations [19].

The present calculations serve in part as a more extensive (particularly in terms of number of atoms considered) and less empirical complement to earlier molecular mechanics calculations carried out on some of these species [13]. These previous calculations considered small segments and represented the conformational energy as a sum of steric, torsional (including conjugational), and Coulombic contributions, each represented by a parameterized empirical equation.

In the calculations of the rotational flexibility of the species, the end-phenylene groups were both rotated in the same direction by an angle ϕ with respect to the plane of the heterocyclic group, as is illustrated in Fig. 3. An entire series of calculations was carried out for ϕ varied in increments of 20°. Preliminary calculations for cases in which the phenylenes were twisted in opposite

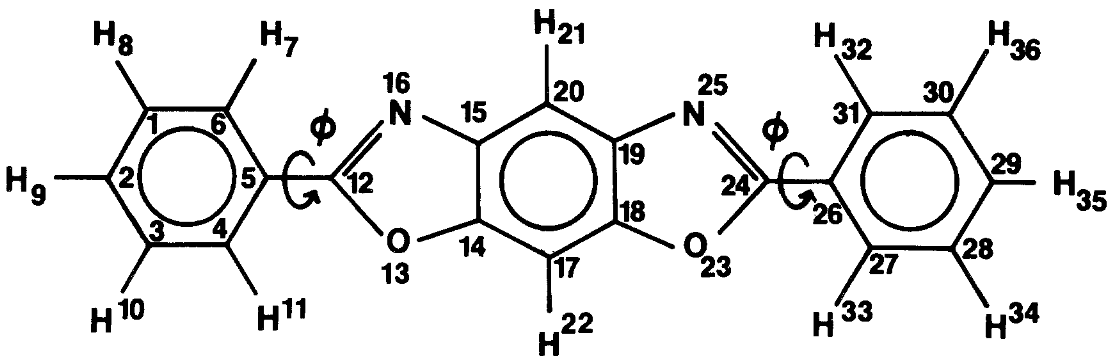

Figure 3 The *cis*-PBO model compound. The rotational angle ϕ represents the dihedral angle between the plane of the two end phenylenes and that of the heterocyclic ring system with $\phi = 0°$ corresponding to the coplanar form. The numbering scheme shown applies throughout the paper.

directions by the angle ϕ gave equivalent results, indicating that interactions between the terminal phenylene groups were negigible.

Considering the bowing in the *cis*-PBT model compound, it was of interest to obtain an estimate of the strain energy responsible for inducing this molecule to "bow" out of the planar conformation, as exists in the *trans*-PBT and *cis*- and *trans*-PBO model compounds. To this purpose, the CNDO/2 total energy of the *cis*-PBT model compound, shown in Fig. 2, was calculated and compared to that of a ficticious planar *cis*-PBT model molecule possessing essentially the same structural geometry (in terms of bond angles and bond lengths) as the actual "bowed" molecule. Values of equivalent bond angles and bond lengths in *trans*-PBT and *cis*-PBT model compounds are observed to be nearly identical in the crystalline state [17]. Also, it can be assumed that the *trans*-PBT model compound is not under considerable strain in its natural "unbowed" form. The planar *cis*-PBT studied here for comparison can therefore be considered the direct analogue of *trans*-PBT, apart from the fact that the "*cis*" form apparently does experience considerable strain. The present calculation provides a measure of the magnitude of this strain energy.

3. Structural information

The initial bond lengths and bond angles of the model compounds were those obtained in the X-ray studies of Wellman and co-workers on the PBO and PBT model compounds [17, 20]; the values are typical of aromatic-heterocyclic compounds. Except for one discrepancy to be noted later, the observed values of equivalent bond lengths and bond angles in the *cis* and *trans* isomers of both PBO and PBT are nearly the same. In that the *trans*-PBT is flat and the *cis*-PBT is bowed this agreement is not unusual since it is known that significant torsional distortions can occur within ring systems with little or no alteration in the values of the bond lengths and bond angles [21–23]. In addition, the uncertainty (standard deviation) in the observed bond lengths and bond angles for the orthorhombic *cis*-PBT, containing two independent molecules per unit cell, is about twice that for the monoclinic *trans*-PBT having only one molecule per unit cell. As expected, the phenylene groups had perfect two-fold symmetry. The only values of ϕ of relevance were therefore in the range 0 to 90°.

4. Results and discussion

4.1. Rotational flexibility in the model compounds

As described above, values of the geometry-optimized CNDO/2 total energy $E(\phi)$ were calculated as a function of the torsional angle ϕ. These are listed for selected values of ϕ in Table I for the

TABLE I Calculated values of the CNDO/2 total energy $E(\phi)^*$ as a function of the torsional angle ϕ

ϕ(degrees)	*cis*-PBO†	*trans*-PBO†	*trans*-PBT‡
0	−5821.926	−5821.973	−5394.538
20	−5821.917	−5821.960	−5394.564
40	−5821.909	−5821.949	−5394.433
60	−5821.883	−5821.904	−5394.292
80	−5821.861	−5821.884	−5394.207
90	−5821.857	−5821.878	−5394.202

*In units of electron-volts molecule^{-1} (= 0.010 363 kJ mol^{-1}).

†Geometry optimization used in calculation of energy.

‡Geometry optimization not currently available for sulphur-containing species.

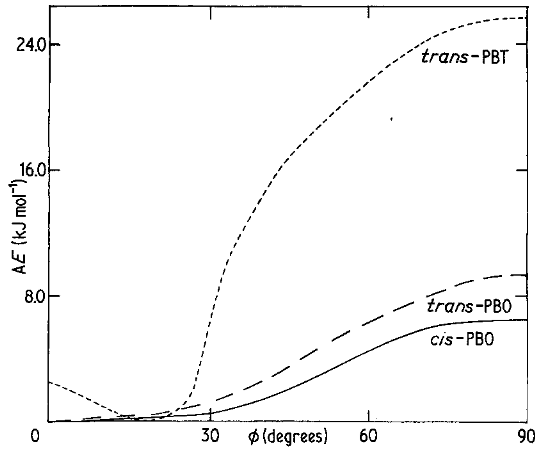

Figure 4 Plots of the rotational (conformational) energy ΔE (in kJ mol^{-1}) as a function of the torsional angle ϕ for the *cis*-PBO, *trans*-PBO and *trans*-PBT model compounds. For a given compound, values of ΔE were taken as the difference in total energy E between a given conformation ϕ and the conformation corresponding to the lowest calculated energy.

cis-PBO, *trans*-PBO, and *trans*-PBT model compounds. The conformational energy $\Delta E(\phi)$ corresponding to a given ϕ was taken as the difference in total energy between that conformation and the conformation associated with the lowest energy calculated. Values of $\Delta E(\phi)$ against ϕ are plotted in Fig. 4 for the *trans*-PBT and *cis*- and *trans*-PBO model compounds. In the case of *cis*- and *trans*-PBO, very similar conformational energy profiles were obtained. In both cases, the preferred conformation, corresponding to minimum total energy, corresponds to $\phi = 0°$ (coplanarity); this result is in excellent agreement with the planarity (*cis*-PBO) or near planarity (*trans*-PBO) observed for these model compounds in the crystalline state [20]. The barrier to rotation away from $\phi = 0°$ rises monotonically with increasing ϕ to maximum values of about 6.7 (*cis*) and 9.2 (*trans*) kJ mol^{-1}. The substantial barriers to rotation away from coplanarity imply that conjugation effects between the aromatic moieties (favouring coplanarity) dominate the steric repulsions (disfavouring coplanarity) between the orthohydrogen atoms on the phenylene group and nearby atoms within the heterocyclic group. As reported elsewhere [13], the bond connecting the phenylene ring to the heterocyclic group is shorter (0.146 nm) in these species than that found in analogous low molecular-weight molecules, suggesting that in the former case some double-bond character exists in these bonds as a result of long range conjugation effects. The present results corroborate results of earlier molecular mechanics calculations on the same compounds [13].

The conformational-energy profile of the *trans*-PBT model compound is quite different. The preferred angle is $\phi = 20°$ but the energy barrier to coplanarity is only about 2.1 kJ mol^{-1}. The value of ϕ observed in the crystalline state is about 23° [17], so the present results are in good agreement. Beyond $\phi = 20°$ the barrier rises sharply and monotonically, yielding a maximum barrier of about 25.0 kJ mol^{-1} at $\phi = 90°$. The barrier to rotation is relatively large and should be considered an upper estimate because for sulphur-containing molecules such as PBT geometry-optimization was not available. Hence, one would expect the structural geometry to become less "relaxed" and the energy increasingly overestimated as ϕ increases from 0°. Attempts to calculate the rotational flexibility within the *cis*-PBT model compound yielded an unusually high ($>$ 200 kJ mol^{-1}) maximum barrier to rotation. The unique structural features of *cis*-PBT and the unavailablity of geometry optimization in this case may contribute significantly to the magnitude of this calculated barrier, so further discussion of the conformational features of *cis*-PBT in this regard will be reported in a future communication.

4.2. Comparisons of the observed and calculated structural geometries of the PBO model compounds

As seen in Table I, the calculated total energies of the *cis* and *trans* isomers of the PBO model compound are virtually identical, differing by less than 0.05 eV molecule^{-1} (5.0 kJ mol^{-1}) at $\phi = 0°$. Likewise, their structural geometries and charge distributions are essentially the same. The calculated geometries are also in excellent overall agreement with those observed for each model compound in the crystalline state [17, 20]. Selected observed [20] and calculated values of the bond lengths and bond angles for the *cis*-PBO model compound (Fig. 3) are listed in Table II. For the bond lengths, the only major discrepancy is for the C12–O13 bond, where the calculated value is appreciably larger than the observed one. However, both observed [17] and calculated lengths of this bond in the *trans*

TABLE II Selected observed* and calculated† values of the bond lengths and bond angles for the *cis*-PBO model compound‡

	Observed	Calculated		
	($\phi = 0°$)	$\phi = 0°$	45°	90°
Bond lengths (nm)				
C5–C12	0.1456	0.1446	0.1446	0.1449
C12–O13	0.1325	0.1371	0.1370	0.1369
C12–N16	0.1325	0.1321	0.1320	0.1319
Bond angles (degrees)				
C5C6H7	119.75	118.6	119.0	119.8
C5C4H11	119.75	119.3	119.3	119.4
C4C5C12	121.2	118.0	118.2	120.9
C5C12O13	122.5	117.8	118.4	117.6

*X-ray values of Wellman *et al.* [20].
†CNDO/2 values.
‡See Fig. 3.

isomer are about 0.137 nm so the observed value of 0.132 nm in the *cis* isomer appears to be anomalous. Regarding bond angles, the calculated values are slightly smaller than those observed for the exocyclic angles C4C5C12 and C5C12O13. This discrepancy, which does not exist in the *trans* isomer, may be related to the anomaly noted for the C12–O13 bond length. Comparing the calculated values of the bond lengths as ϕ departs from 0°, a slight increase in the C5–C12 bond length and a corresponding decrease in the C12–O13 and C12–N16 bond lengths is noted. Since conjugation effects between the two ring systems should abate as coplanarity is reduced, it is expected that the C5–C12 bond joining the rings should weaken (and lengthen) while the bonds within the rings should strengthen (and shorten) as electron density shifts from *between* to *within* the rings as ϕ increases.

Since the present calculations refer to a single, isolated molecule, the good agreement between the calculated and observed geometries suggests that the geometry of these molecules in the crystalline state is not influenced significantly by intermolecular interactions operative in the crystal.

4.3. Charge distribution

Selected values of the atomic partial charges (in units of 10^{-3} of the electron's charge) are listed in Table III for the *cis*-PBO model compound in the coplanar ($\phi = 0°$) conformation. Corresponding values for the *trans* isomer are again virtually identical. In both cases the values calculated were very nearly invariant to changes in ϕ. However, there does appear to be a slight shift in electron density from C5 and C12 to N16 as ϕ departs from 0°, a result consistent with decreasing conjugation effects between the ring systems.

4.4. Bowing within the *cis*-PBT model compound

As mentioned earlier, the CNDO/2 total energy was calculated for both the actual "bowed" form of the *cis*-PBT model compound and the ficticious planar form. The results gave an energy of − 5368 and − 5308 eV, respectively, for the "bowed" and "flat" forms. This yields an energy difference of about 60 eV molecule^{-1} (about 5800 kJ mol^{-1}) in favour of the "bowed" form. These numbers should be taken as highly approximate upper limits since geometry optimization could not be implemented and CNDO/2 energies involving second-row atoms like sulphur are typically less reliable. Nevertheless, these results do indicate that rather large energies are involved in the bowing process. Bond-strain energies of this magnitude, induced within the planar form, would certainly be too large to be relieved by typical in-plane bond-length and bond-angle distortions. Bowing apparently occurs as the more energy-efficient alternative to these mechanisms. In a

TABLE III Calculated values of the partial charges* for selected atoms in the *cis*-PBO model compound

Atom	Partial charges		
	$\phi = 0°$	45°	90°
C5	− 16.1	− 10.8	− 4.15
C12	336.0	345.0	354.0
O13	− 293.0	− 291.0	− 290.0
N16	− 301.0	− 308.0	− 315.0

*In units of fraction of an electron's charge $\times 10^3$.

dynamic sense, one could picture the planar *cis*-PBT model compound undergoing in-plane bond-length and bond-angle deformations in order to relieve the strain. Failing to achieve this sufficiently, the molecule proceeds to "bow" as an alternative way of relieving the strain. Upon bowing, the molecule's bond angles and lengths "relax" to values experimentally indistinguishable from those of *trans*-PBT.

Acknowledgements

It is a pleasure to acknowledge the financial support provided by the Air Force Office of Scientific Research (Grant AFOSR 78-3683). We also gratefully acknowledge the helpful information and suggestions provided by Dr D. Bhaumik and Professor H. H. Jaffé of the University of Cincinnati.

References

1. G. C. BERRY, *Polym. Prep.* **18** (1977) 146.
2. C.-P. WONG, H. OHNUMA and G. C. BERRY, *ibid.* **18** (1977) 167.
3. J. R. MINTER, K. SHIMAMURA and E. L. THOMAS, *J. Mater. Sci.* **16** (1981) 3303.
4. G. C. BERRY, *J. Polym. Sci.* Part C, **65** (1978) 143.
5. C. -P. WONG, H. OHNUMA and G. C. BERRY, *ibid.* **65** (1978) 173.
6. T. E. HELMINIAK, *ACS Org. Coatings Plast. Prep.* **40** (1979) 475.
7. G. HUSSMAN, T. E. HELMINIAK and W. ADAMS, *ibid.* **40** (1979) 797.
8. J. A. ODELL, A. KELLER, E. D. T. ATKINS and M. J. MILES, *J. Mater. Sci.* **16** (1981) 3309.
9. J. F. WOLFE, B. H. LOO and F. E. ARNOLD, *Polym. Prep.* **20** (1979) 82.
10. C. ARNOLD, Jr, *J. Polym. Sci.* Part D **14** (1979) 265.
11. J. F. WOLFE and F. E. ARNOLD, *Macromol.* **14** (1981) 909.
12. J. F. WOLFE, B. H. LOO and F. E. ARNOLD, *ibid.* **14** (1981) 915.
13. W. J. WELSH, D. BHAUMIK and J. E. MARK, *ibid.* **14** (1981) 947.
14. D. BHAUMIK, H. H. JAFFÉ and J. E. MARK, *ibid.* **14** (1981) 1125.
15. W. J. WELSH, H. H. JAFFÉ, J. E. MARK and N. KONDO, *Makromol. Chem.* **183** (1982) 801.
16. W. J. WELSH, D. BHAUMIK and J. E. MARK, *J. Macromol. Sci. Phys.* **20** (1981) 59.
17. M. W. WELLMAN, W. W. ADAMS, R. A. WOLFF, D. S. DUDIS, D. R. WIFF and A. V. FRATINI, *Macromol.* **14** (1981) 935.
18. J. A. POPLE and D. L. BEVERIDGE, "Approximate Molecular Orbital Theory" (McGraw-Hill, New York, NY, 1970).
19. N. KONDO, PhD dissertation, University of Cincinnati (1978); H. H. JAFFÉ, CNDO/S and CNDO/2 (FORTRAN IV), QCPE 315 (1977).
20. M. W. WELLMAN, W. W. ADAMS, D. R. WIFF and A. V. FRATINI, Air Force Technical Report AFML-TR-79-4184 (University of Dayton), Part I; private communication.
21. D. J. CRAM and J. M. CRAM, *Acc. Chem. Res.* **4** (1971) 204.
22. H. J. LINDLER, *Tetrahedron* **32** (1976) 753.
23. A. V. FRATINI, private communication.

Received 12 July
and accepted 31 August 1982