Notes

AM1 Molecular Orbital Calculations of the Conformational Characteristics of the Rodlike Polymers Poly(*p*-phenylenebenzobisoxazole) (PBO) and Poly(*p*-phenylenebenzobisthiazole) (PBT)

YONG YANG AND WILLIAM J. WELSH*

Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121.
Received June 30, 1989;
Revised Manuscript Received November 10, 1989

Introduction

The aromatic heterocyclic rodlike polymers poly(*p*-phenylenebenzobisoxazole) (PBO) and poly(*p*-phenylenebenzobisthiazole) (PBT) are designated "high-performance" since films and fibers processed from them exhibit exceptional specific strength and modulus, thermooxidative stability, and environmental resistance.[1-4] Intense research activity has been directed toward the synthesis, characterization, and fabrication of these and related rodlike polymers for numerous applications.[1-9]

The optimization of many of the physical properties of these polymers is dependent on the degree of alignment of the rods composing the individual chains.[1-4,11] With respect to this alignment, the conformational properties of these polymers are important parameters at the molecular level.[1,8,11]

Previous theoretical studies,[12-15] using molecular mechanics (MM) and CNDO/2 molecular orbital[15] (MO) methods, have already investigated the structures and conformations of this family of polymers including PBO and PBT. The results have been compared with the crystal structures determined for PBT[16] and PBO[17] model compounds. However, this previous work entailed notable shortcomings. For example, the MM studies[14] excluded geometry optimization, assigned a torsional energy barrier height to the bridge bond which was admittedly an estimate, and economized by drastically limiting the size of the model compound. The CNDO/2 calculations[15] lacked geometry-optimization capabilities for the sulfur-containing PBT, which doubtless led to overestimation of rotational energy barriers.

In the present study, AM1[18] molecular orbital calculations with full geometry optimization were carried out on model compounds of the cis and trans forms of both PBO and PBT. The objective was to compute more conclusively and rigorously the conformational characteristics of the polymers without the shortcomings embodied in the previous theoretical studies cited above.[12-15]

Methodology

AM1[18] and MNDO[19] molecular orbital calculations were carried out using the AMPAC program.[20,21] MNDO is reported[18,19,22,23] to overestimate the effect of nuclear core–core repulsions. Consequently, it incorrectly and nearly invariably predicts a perpendicular conformation between ring systems connected by an essential single bond. AM1 was designed in part to remedy this shortcoming in MNDO.[18] Hence, the present study provides a good test case for side-by-side comparison of MNDO and AM1.

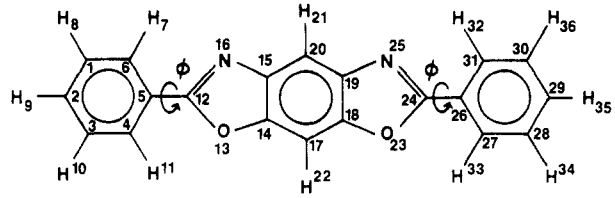

Figure 1. Illustration of the *cis*-PBO model compound considered in the present study, with numeration of atoms.

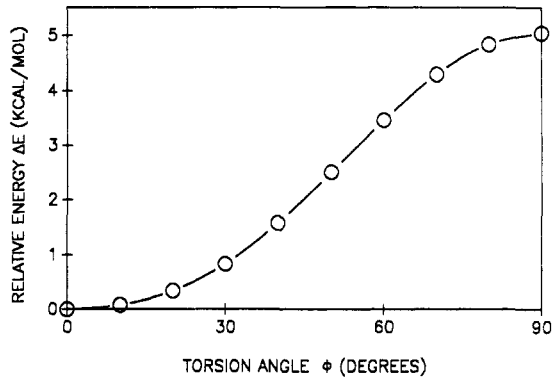

Figure 2. AM1-calculated conformational energy ΔE versus ϕ for the *cis*- and *trans*-PBO model compounds. The cis and trans forms gave nearly identical energy profiles; hence, a single curve is given.

The calculations implemented the default Davidon–Fletcher–Powell method[24] for energy minimization and the PRECISE option, as recommended,[23] for augmenting the convergence criteria. At present AM1 is parametrized only for H, O, C, and N atoms (i.e., not for S atoms) but is programmed to use available MNDO parameters for other atoms such as occurs for sulfur in PBT.[25] This amalgamation of AM1 and MNDO parameters appears to produce reasonable results.[23]

The AM1 or MNDO molecular energies E were calculated versus rotation angle ϕ (where $\phi = 0°$ and 180° correspond to the coplanar conformations) varied in increments of 10° over all unique conformations. Conformational energies, ΔE, were taken as differences in molecular energies normalized to the lowest calculated value of E.

An example of the model compounds considered in the present study is illustrated in Figure 1. A torsion angle ϕ was achieved by rotating the central heterocyclic ring while holding the end phenylenes in the same plane. Consequently, the calculated conformational energy ΔE is that associated with rotation about *two* equivalent bonds. The desired conformational energy ΔE *per rotatable bond* was thus taken as half the ΔE value calculated.

* To whom correspondence should be addressed.

0024-9297/90/2223-2410$02.50/0 © 1990 American Chemical Society

Table I
Conformational Comparisons[a] of AM1,[b] CNDO/2,[c] and MM[d] Calculations on Molecules under Study

	predicted ϕ, deg			relative energies[a] ϕ = 45°			ϕ = 90°		
model compd	AM1	CNDO/2	MM[e]	AM1	CNDO/2	MM[e]	AM1	CNDO/2	MM[e]
cis-PBO	0	0	0	1.0	0.25	1.6	2.5	0.80	3.5
trans-PBO	0	0	0	1.0	0.36	1.1	2.5	1.1	3.2
cis-PBT	27	*f*	57	0.13	*f*	0.20	0.85	*f*	0.38
trans-PBT	27	20	55	0.13	1.6[e]	0.14	0.85	3.9[e]	0.36

[a] All energy values are normalized as *per bond* energies in units of kilocalories per mole. [b] Present study. [c] Reference 15. [d] Reference 14. [e] Geometry optimization not employed. [f] Data not available.

Preliminary AM1 calculations and previous CNDO/2 studies[15] in which each of the two rotatable bonds was rotated separately indicated that the two rotations are virtually uncorrelated and thus additive energetically, a consequence of the fact that the two rotatable bonds are remote from each other.

The initial structural geometry for each model compound was taken from published X-ray crystallographic data,[16,17] and all C–H bond lengths were adjusted to reasonable initial values (~1.08 Å) using the molecular modeling program CHEM-X.[26]

It is perhaps necessary to stress that the authors regard the values of the AM1 molecular energies calculated in the present study with a healthy skepticism. First, the AM1 calculations were performed by and large in vacuo, i.e., without inclusion of any environmental effects such as solvent, neighboring chains, structural imperfections, and long-range interactions. Second, the AM1 method cannot be considered quantitative in the present application, and the results for the PBT model compounds may be influenced by the adoption of MNDO "sulfur" parameters required to remedy the absence of suitable AM1 values. Clearly, the fact that conformational energies are evaluated as *differences* in AM1 molecular energies mitigates the above concerns in that deficiencies in the molecular model or in the methodology employed will tend to cancel out. Still, the conformational energies themselves represent small differences between two large quantities (i.e., the molecular energies) so conformational energy differences on the order of 1 kcal mol^{-1} should be regarded as within the limits of accuracy of the methods employed. This caveat likely applies to many if not most of the theoretical studies of this type and does not suggest any shortcoming unique to AM1 or to the particular application at hand.

Results and Discussion

Conformational Energies. The AM1-calculated conformational energies ΔE versus ϕ for the *cis*- and *trans*-PBO model compounds are plotted in Figure 2. The energy profiles for both molecules are essentially identical; hence, only one curve appears on the graph. The energy is a minimum at ϕ = 0° (i.e., a coplanar conformation) and rises monotonically to a maximum at ϕ = 90° (the perpendicular conformation) some 5 kcal mol^{-1} (or 2.5 kcal mol^{-1} per rotatable bond) higher in energy. Hence, for both *cis*- and *trans*-PBO the predicted conformation is coplanar. The planarity predicted agrees with the planar conformations observed for these model compounds in the crystalline state.[17] The AM1 results also agree, at least qualitatively, with earlier MM[14] and CNDO/2[15] calculations. Specifically, AM1, CNDO/2, and MM calculations all find the conformational energy minimum for *cis*- and *trans*-PBO at the coplanar (ϕ = 0°) conformation, the energy maximum at ϕ = 90°, and nearly identical energy profiles for both the cis and trans forms.

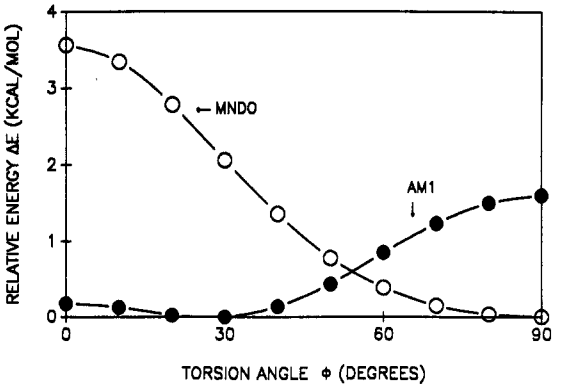

Figure 3. AM1-calculated conformational energy ΔE versus ϕ for the *cis*- and *trans*-PBT model compounds. Again, the cis and trans forms produced nearly identical energy profiles and so are represented by a single curve. Also included is the MNDO-calculated curve obtained for the *cis*-PBT model compound.

However, the three methods differ in the absolute magnitude of their ΔE values vs ϕ. For comparison, Table I lists the relative energies at ϕ = 45° and at ϕ = 90° as obtained by the AM1, CNDO/2, and MM calculations. While the AM1 and MM energies compare favorably, on average CNDO/2 gives values only 35% as large as those obtained by AM1. Taken together, the ratio of barrier heights for CNDO/2:AM1:MM is about 0.35:1.0:1.3 at ϕ = 45° and ϕ = 90°.

The consistently lower energy barriers found by CNDO/2 relative to AM1 may be traced to the tendency of CNDO/2 and other semiempirical methods to overestimate core–core repulsions and thus to underestimate barriers to all nonplanar conformations.[18,22,23] The relatively good agreement between AM1 and MM is somewhat surprising given that the MM calculations[14] excluded geometry optimization. However, only a slight reduction in the MM energies found would be expected had geometry optimization been included since steric congestion (giving rise to structural deformations) abates considerably as ϕ deviates from 0°.

The corresponding AM1 energy profiles for the *cis*- and *trans*-PBT model compounds (Figure 3) are again virtually identical and so are represented by a single curve. Also included in Figure 3 is the energy profile for *cis*-PBT as calculated by MNDO. It is apparent from the MNDO curve that it erroneously predicts an energy maximum at ϕ = 0° and minimum at ϕ = 90°. The MNDO method is thus shown again to be unacceptable for describing rotations about essential single bonds connecting aromatic rings.[18]

The AM1 energy profile for the PBT model compounds (Figure 3) predicts a minimum energy conformation at ϕ ~ 27°, in close agreement with the value ϕ = 23° observed in the crystalline state.[16] Nevertheless, the energy barrier to coplanarity (ϕ = 0°) is small at 0.25 kcal mol^{-1} (or 0.13 kcal mol^{-1} per rotatable bond). Beyond

$\phi = 27°$ the energy rises monotonically to a maximum of only 1.7 kcal mol^{-1} (0.85 kcal mol^{-1} per rotatable bond) at $\phi = 90°$.

In Table I, results of AM1, CNDO/2,[15] and MM[14] calculations are again compared for the PBT model compounds. All three methods predict nonplanar conformations ranging from 20–27° (AM1 and CNDO/2) to 55–57° (MM). While the range of ϕ values appears wide, the AM1 energy well is both shallow and wide in that the range $0° \leq \phi \leq 60°$ would be energetically accessible within 0.5 kcal mol^{-1}. Hence the rotatable bond in PBT would appear to exhibit a high degree of flexibility. Moreover, the MM values[14] were obtained without geometry optimization which, if included, would likely have reduced the value of ϕ from the 55–57° value obtained.

The AM1, CNDO/2, and MM energy profiles are again qualitatively similar for the PBT model compounds. However, quantitative differences are apparent from Table I. First, CNDO/2 barriers to $\phi = 90°$ are extremely high, no doubt primarily due to the absence of geometry optimization for PBT.[15] The AM1 and MM energy barriers are again reasonably consistent, although relative to AM1 the MM energy barrier at $\phi = 90°$ is about half as high.

AM1 yielded a virtually flat molecular structure for the *cis*-PBT model compound, in contrast to the bowing observed in the crystal structure.[16] AM1 also revealed an absence of any bowing in the *cis*- and *trans*-PBO and *trans*-PBT model compounds, in agreement with the crystal structure of each.[16,17] The absence of bowing in the AM1-calculated *cis*-PBT structure could suggest that the observed bowing[16] is intermolecular in origin. This possibility is currently under investigation.

Concluding Remarks

In light of the present analysis, the major conclusion is that rotational barriers are substantially lower for PBT compared with PBO. PBO is sterically less congested than PBT (because the oxygen atoms in PBO are smaller than the alternative sulfur atoms in PBT); hence, the conformation of PBO is dominated by conjugative effects favoring coplanarity (i.e., $\phi = 0°$). In PBT steric conflicts dominate conjugative effects at the coplanar conformation; hence, the preferred ϕ found, which is intermediate between 0° and 90°, represents a balance between conjugative effects (favoring coplanarity) and steric conflicts (favoring a more perpendicular conformation). This balance is more evident in PBT than in PBO and gives rise to a more moderate conformational energy profile.[12,13]

Acknowledgment. The authors acknowledge the Air Force Office of Science Research for providing funding for this line of research.

References and Notes

(1) A number of articles on PBO and PBT are in the July/August 1981 issue (Vol. 4) of *Macromolecules* and in the December 1980 and March 1981 special issues of *Br. Polym. J.*
(2) Allen, S. R.; Farris, R. J.; Thomas, E. L. *J. Mater. Sci.* **1985**, *20*, 4583 and pertinent references cited therein. Cohen, Y.; Thomas, E. L. *Macromolecules* **1988**, *21*, 433; *Ibid.*, 436.
(3) Allen, S. E.; Filippov, A. G.; Farris, R. J.; Thomas, E. L. *J. Appl. Polym. Sci.* **1981**, *26*, 291.
(4) Prevorsek, D. C. In *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic Press: New York, 1982; p 329.
(5) Ulrich, D. R. *Mol. Cryst. Liq. Cryst. Bull.* **1988**, *28*, 543.
(6) Teng, C. C.; Garito, A. F. *Phys. Rev. Lett.* **1983**, *50*, 350. *Ibid. Phys. Rev. B* **1983**, *28*, 6766.
(7) Dalton, L. R.; Thomson, J.; Nalwa, H. S. *Polymer* **1987**, *28*, 543.
(8) The Materials Science and Engineering of Rigid-Rod Polymers. *Abstracts of Symposium Proceedings*; Materials Research Symposium Series 134; Nov 28–Dec 2, 1988.
(9) Welsh, W. J.; Yang, Y.; Das, G. P.; Mark, J. E. In The Materials Science and Engineering of Rigid-Rod Polymers. *Abstracts of Symposium Proceedings*; Adams, W. W., Eby, R. K., McLemore, D. E., Eds.; Materials Research Series 134; 1989, and pertinent references cited therein, in press.
(10) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *234*, 73.
(11) Samulski, E. T.; DuPré, D. B. In *Advances in Liquid Crystals*; Academic Press: New York, 1979; Vol. 4, p 121.
(12) Welsh, W. J.; Bhaumik, D.; Jaffé, H. H.; Mark, J. E. *Polym. Eng. Sci.* **1984**, *24*, 218 and pertinent references cited therein.
(13) Welsh, W. J. In *Current Topics in Polymer Science*; Ottenbrite, R. M., Utracki, L. A., Inoue, S., Eds.; Macmillan: New York, 1987; Vol. I, p 217 and pertinent references cited therein.
(14) Welsh, W. J.; Bhaumik, D.; Mark, J. E. *Macromolecules* **1981**, *14*, 947. Bhaumik, D.; Welsh, W. J.; Jaffé, H. H.; Mark, J. E. *Ibid.*, 951.
(15) Welsh, W. J.; Mark, J. E. *J. Mater. Sci.* **1983**, *18*, 1119.
(16) Wellman, M. W.; Adams, W. W.; Wolff, R. A.; Dudis, D. S.; Wiff, D. R.; Fratini, A. V. *Macromolecules* **1981**, *14*, 935.
(17) Wellman, M. W.; Adams, W. W.; Wiff, D. R.; Fratini, A. V. Air Force Technical Report AFML-TR-79-4184; University of Dayton: Dayton, OH, 1979; Part 1.
(18) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(19) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(20) AMPAC, QCPE 506, Quantum Chemistry Program Exchange, Indiana University: Bloomington, IN.
(21) All calculations were carried out at the University of Missouri—St. Louis with computational resources provided by the University Office of Computing and Telecommunications.
(22) Fabian, W. M. F. *J. Comput. Chem.* **1988**, *9*, 369.
(23) Boyd, D. B.; Smith, D. W.; Stewart, J. J. P.; Wimmer, E. *J. Comput. Chem.* **1988**, *9*, 387.
(24) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163. Davidon, W. C. *Ibid.* **1968**, *10*, 406.
(25) Dewar, M. J. S.; Reynolds, C. H. *J. Comput. Chem.* **1986**, *7*, 140.
(26) CHEM-X, a product of Chemical Design, Ltd., Oxford, U.K.
(27) MM2 (1987) molecular mechanics force-field parameter set, courtesy of Prof. N. L. Allinger, University of Georgia, Athens.