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Barrier to phenyl rotation in poly(*p*-phenylene benzobisthiazole) from *ab initio* molecular orbital calculations

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Optimal molecular geometry and the barrier to internal phenyl rotation were obtained from *ab initio* molecular orbital calculations of model compounds of poly(*p*-phenylene benzobisthiazole). Bond lengths and angles are in good agreement with those found from a previous X-ray crystallographic study of a similar model compound. Based on the calculated torsional potential, the discrepancy between theoretical and experimental phenyl torsions is attributed to crystal packing forces. The calculated torsion barrier is three to five times greater than in previous semi-empirical AM1 molecular orbital calculations. Calculations were performed with the 6-31G* basis set and the rotation barrier was corrected for electron correlation employing second-order Møller–Plesset perturbation theory.

(Keywords: PBZT; rigid-rod polymers; torsional potential)

INTRODUCTION

It is well established that the rigid-rod polymer poly(*p*-phenylene benzobisthiazole)[1,2] (PBZT; *Figure 1*) forms films and fibres that exhibit exceptional specific strength, modulus, and thermo-oxidative and environmental resistance[3–5], although fibres display low compressive strength[3]. These properties, resulting from chain stiffness, molecular stability and extensive conjugation, are influenced by molecular packing. One mode of chain flexibility that affects packing efficiency is rotation of the phenylene moiety about the heterocycle-phenyl bonds. This flexibility has also been implicated as significant in fibre torsional moduli measurements[6].

Recent attention has focused on the potential for conducting and non-linear optical applications of PBZT[5,7,8]. Rotation of the phenylene moiety is also of interest for these applications because conjugation paths are shortened as a result of low barriers to rotation. It is known that the second hyperpolarizability, γ, of molecules can increase exponentially with conjugation length[9–11]. Rotational disorder could thus substantially decrease the non-linear optical response of PBZT. An accurate estimation of the rotational barrier is needed to assess the significance of this effect on electro-optic properties.

Phenyl rotation barriers were calculated previously for PBZT, as well as for the oxazole and imidazole analogues[12–14], with semi-empirical molecular orbital methods using model compounds similar to those used here. Geometry optimizations employing the AM1 Hamiltonian[12–14] resulted in structures very similar to crystal structures[15], while agreement between MNDO and experiment was unsatisfactory[12,13]. None of these methods employs polarization functions on heavy atoms, a deficiency which may be important particularly when comparing small conformational energy differences. Herein *ab initio* molecular orbital techniques incorporating such effects are used to calculate the barrier to phenyl rotation for the model compounds shown in *Figures 1* and *2*. Geometries of optimized structures are also compared to crystal structures and barrier heights compared to earlier molecular orbital calculations.

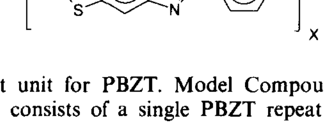

Figure 1 Repeat unit for PBZT. Model Compound 1, phenylenebenzobisthiazole, consists of a single PBZT repeat unit end-capped with hydrogen atoms

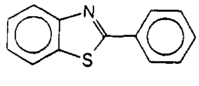

Figure 2 Model Compound 2: phenylbenzothiazole

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COMPUTATIONAL DETAILS

Ab initio molecular orbital geometry optimizations were performed at the Hartree-Fock self-consistent field (SCF) level using Gaussian 90[16] and GAMESS[17,18] programs. The 6-31G* double-zeta valence basis set with polarization functions on non-hydrogen atoms was employed. For all geometry optimizations, atoms comprising the heterocycle were constrained to lie in one plane and, similarly, atoms comprising the phenyl ring were constrained to a plane. For Compound 2, geometry optimizations were performed with the phenyl torsion allowed to optimize and with the torsion constrained to 30, 60 and 90°. The optimal torsion, 0°, corresponds to coplanarity between the heterocycle and phenyl moieties. The torsional potential, plotted as energies normalized to the energy of the fully optimized conformation, is shown in *Figure 3*. For Compound 1, the phenyl torsion also optimized to 0°. Only one additional optimization was performed in which the phenyl torsion was constrained to 90°. All optimizations were performed at the RHF/6-31G* level. Additionally, single-point calculations employing second-order Møller–Plesset perturbation theory[19], i.e. MP2/6-31G*//RHF/6-31G*, were performed on the conformations corresponding to the minima and maxima along the torsional potential in order to correct the rotational energy barriers for dynamic electron correlation. These were done using the Gaussian 92[20] suite of codes.

All frequencies for optimized Model Compounds 1 and 2, calculated analytically using Gaussian 90, were positive ensuring that these structures represented global minima along the torsional potential.

In addition to the *ab initio* optimizations, the AM1 Hamiltonian was used to optimize Compound 2, first with the phenyl torsion optimizing to 0° and again with the torsion constrained to 90°, so that comparison with the *ab initio* rotational barrier could be made with the same model compound. Ampac 4.5 was used for these calculations[21].

RESULTS AND DISCUSSION

Bond lengths and angles of the asymmetric unit of diphenylbenzobisthiazole found from an X-ray crystallographic study[15] are compared with those obtained from *ab initio* RHF/6-31G* geometry optimizations of Compounds 1 and 2 in *Table 1*. Overall, agreement for bond lengths and bond angles is good. Theoretical and experimental phenyl torsions are compared in *Table 2*. The optimal torsion angle found from *ab initio*, 0°, is in poor agreement with the X-ray value found for single crystals of 2,6-diphenylbenzobisthiazole[15] (23.2°). However, the torsional potential, presented in *Figure 3*, shows that the energy difference between the 0° and the 30° conformations is small (0.37 kcal mol^{-1}) so that the discrepancy can be attributed to crystal packing forces. The geometrical parameters for the 30° conformation are also included in *Table 1* to illustrate that this torsional rotation causes insignificant structural effects.

Figure 3 also shows that the barrier to phenyl rotation in Compound 1 calculated at the RHF/6-31G* level is 3.98 kcal mol^{-1}. Correction for post-SCF electron correlation at the MP2 level reduces the barrier to 3.89 kcal mol^{-1}. For Compound 2, the barrier calculated at the RHF/6-31G* level is 4.04 kcal mol^{-1}, while the MP2 correction lowers it to 3.90 kcal mol^{-1}. The added thiazole unit in Compound 1 therefore has only a minimal effect on the torsional barrier. The MP2 corrections observed here are similar in magnitude to correlation effects at the MP2 level observed in saturated systems[22] and to the ~0.5 kcal mol^{-1} correction in the biphenyl torsion barrier on going from the HF/6-31G* to the MP2/6-31G*//HF/6-31G* level. In these systems, however, inclusion of electron correlation increases the torsional barrier whereas the barriers are decreased in the present case. We know of no other similar rotational studies done at this level of sophistication for comparison of trends.

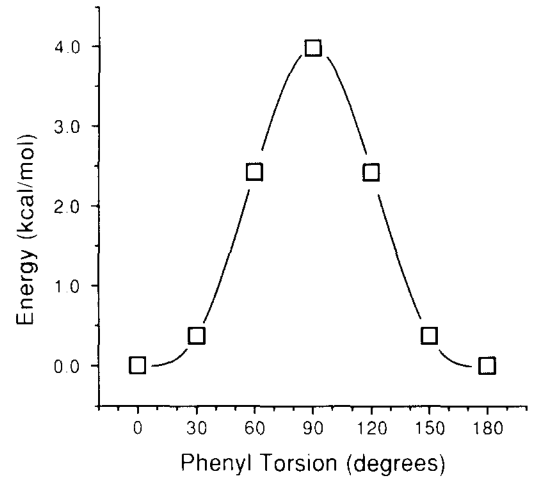
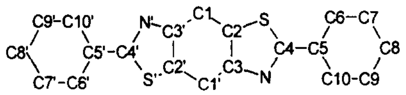


Figure 3 Torsional potential for Model Compound 2. A spline curve connects the data points

Two of the three previous semi-empirical studies[12,13] used the AM1 Hamiltonian together with MNDO parameters for sulfur, as AM1 parameters were then unavailable. Using Compound 1, Farmer *et al*[12] found an optimal torsion of 29° and a rotational barrier of 0.74 kcal mol^{-1} corresponding to a conformation with a 90° phenyl torsion. Yang and Welsh[13], utilizing a larger model compound, 2,6-diphenylbenzobisthiazole, found an optimal torsion of 27° and a barrier of 0.85 kcal mol^{-1} (for rotation of a single phenylene), again corresponding to a 90° phenyl torsion. Connolly and Dudis[14], utilizing the AM1 Hamiltonian with AM1 parameters for all atoms, recently reported an optimal phenyl torsion of 0° and a barrier height of 1.1 kcal mol^{-1} (for rotation about one bond) for *p*-dibenzothiazolebenzene. All semi-empirical studies, however, show a small energy difference between 0° and 30° conformations. These studies are summarized in *Table 2*.

The barrier to phenyl rotation found here is three to five times larger than those found from semi-empirical AM1 calculations. Similarly, *ab initio* rotational barriers for stilbene[23] and for thiophene and pyrrole oligomers[24] using a 3-21G basis set have been reported to be twice as large as the corresponding AM1 barriers. The overall shape of the torsional potential for Compound 2 is unchanged from the AM1 result of Connolly and Dudis[14], suggesting that predictions from AM1 are qualitatively correct. This is important when considering the effects of co-operativity on phenyl rotation in this class of molecules, requiring utilization of model compounds consisting of several repeat units[25].

Table 1 Experimental and theoretical bond lengths (Å) and angles (deg)



	Experimental[15]	Theoretical		
	Molecule shown	Compound 1	Compound 2	Compound 2; 30°
r(S-C2)	1.736(2)	1.744	1.744	1.744
r(S-C4)	1.758(2)	1.767	1.767	1.765
r(N-C3)	1.385(2)	1.383	1.383	1.385
r(N-C4)	1.292(2)	1.271	1.271	1.271
r(C1-C2)	1.376(2)	1.389	1.389	1.389
r(C1-C3′)	1.389(2)	1.387	1.379	1.379
r(C2-C3)	1.422(2)	1.392	1.392	1.392
r(C4-C5)	1.469(2)	1.479	1.479	1.479
r(C5-C6)	1.383(3)	1.390	1.390	1.390
r(C5-C10)	1.392(2)	1.394	1.394	1.393
r(C6-C7)	1.385(3)	1.385	1.385	1.385
r(C7-C8)	1.371(3)	1.384	1.384	1.385
r(C8-C9)	1.378(3)	1.388	1.388	1.387
r(C9-C10)	1.377(3)	1.381	1.381	1.382
∠(C2-S-C4)	88.9(1)	88.8	88.7	88.7
∠(C3-N-C4)	110.8(1)	112.2	112.1	111.8
∠(C2-C1-C3′)	117.3(1)	117.0	118.1	118.1
∠(S-C2-C1)	128.6(1)	129.0	129.6	129.6
∠(S-C2-C3)	109.0(1)	108.7	108.9	108.9
∠(C1-C2-C3)	122.4(1)	122.3	121.5	121.5
∠(N-C3-C1′)	124.6(1)	124.3	124.9	124.8
∠(N-C3-C2)	115.1(1)	115.2	115.2	115.3
∠(C1′-C3-C2)	120.4(1)	120.7	119.9	119.9
∠(S-C4-N)	116.3(1)	115.2	115.1	115.4
∠(S-C4-C5)	119.9(1)	121.5	121.7	121.1
∠(N-C4-C5)	123.8(1)	123.2	123.3	123.5
∠(C4-C5-C6)	121.6(1)	121.9	121.9	121.6
∠(C4-C5-C10)	119.3(2)	118.9	118.9	119.0
∠(C6-C5-C10)	119.1(2)	119.2	120.5	119.4
∠(C5-C6-C7)	120.5(2)	120.4	120.5	120.3
∠(C6-C7-C8)	120.0(2)	120.1	120.1	120.1
∠(C7-C8-C9)	120.0(2)	119.8	119.8	119.9
∠(C8-C9-C10)	120.5(2)	120.2	120.2	120.2
∠(C9-C10-C5)	120.0(2)	120.3	120.3	120.2

Values in column 2 are reproduced from a crystal study[15] for the compound shown and values in columns 3, 4 and 5, obtained from *ab initio* calculations as described in the text, correspond to optimized Compound 1, optimized Compound 2, and optimized Compound 2 with the phenyl torsion constrained to 30°. Numbers in parentheses are estimated standard deviations in the least significant digits

To illustrate the sensitivity of electronic properties to phenyl torsion, we have plotted in *Figure 4* the electronic band gap, calculated as the energy difference between the HOMO and the LUMO of Compound 2, and Koopman's ionization potential as functions of phenyl torsion angle. The band-gap increase seen with increasing torsion angle, from a minimum at 0° to a maximum at 90° lying 1.5 eV above the minimum, results from a decrease in π-electron delocalization.

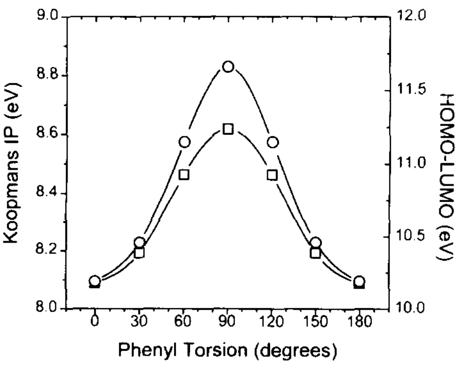
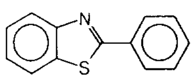
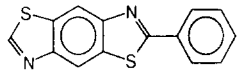
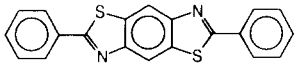
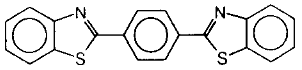


Figure 4 Band gap (○) and Koopmans ionization potential (□) as functions of phenyl torsion for Model Compound 2. Spline curves connect the data points

Table 2 Comparison of phenyl torsions and barriers to rotation

Compound	Method	Phenyl torsion (deg)	Rotational barrier[a] (kcal mol^{-1})	Reference
	RHF/6-31G*	0	4.00	This work
	MP2//6-31G*	–	3.90	This work
	AM1	0	0.86	This work
	RHF/6-31G*	0	4.04	This work
	MP2//6-31G*		3.89	This work
	AM1[b]	29	0.74	12
	AM1[b]	27	0.85	13
	Crystallography	23	–	15
	AM1	0	1.1[c]	14

[a] Values pertain to energy per rotatable bond
[b] MNDO parameters were used for sulfur atoms, AM1 parameters for all other atoms
[c] Heterocycles kept coplanar and the central phenyl group is 90° to the heterocycles

CONCLUSIONS

The single-bond torsional barrier in PBZT has been found to be three to five times larger than previous estimates. The quality of the basis set used and the invariance of results at the MP2 correlation level suggests that the results are quantitatively converged. Thus, the true molecular structures are planar and the crystallographically observed non-planar structures are attributable to crystal packing forces. The low rotation barrier is consistent with torsional disorder in polymeric systems, which can lead to substantial broadening of electronic absorptions of the order of 1–2 eV.

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