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RESEARCH LABORATORY**

**THEORETICAL STUDY OF TORSION
POTENTIALS IN 2,2'-DIHYDROXYBIPHENYL AND
2,2'-DIHYDROXY-5,5'-DIMETHYLBIPHENYL:
MODELING TORSIONS IN MULTI-PHENOLIC
SYSTEMS**

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14. ABSTRACT Using ab initio (6-31G*) and semiempirical (AM1, PM3) electronic structure calculations and force field (MM3) determinations, we have analyzed the molecular structure of 2,2'-dihydroxybiphenyl (BP), 2,2'-dihydroxy-5,5'-dimethylbiphenyl (MBP), and 2,5-di(2-hydroxyphenyl) phenol (TP). In both BP and MBP systems, there exist three predominant conformations for which the orientations of the hydroxyl groups are the distinguishing characteristic. Each method used determined that the optimized geometry of the cis structure was the overall lowest energy conformation. The phenyl groups in the systems show significant twist angles, ϕ (42-55 degrees), depending upon the hydroxyl group orientation. We have examined the energy of the BP and MBP systems as a function of torsion angle using each of the methods described above. Each of the methods of calculation predicts, for all three conformations, a 10-12-kcal/mol barrier to the coplanar torsion angle. The 6-31G* calculations predict a total of five energy minima for the three conformations, with no 90° barrier in the cis structure. The appearance and size of a 90° barrier, as well as the torsion angle for the minimum energy geometry, is dependent upon the theoretical method used. Examination of 2,5-di(2-hydroxyphenyl) phenol (TP) as a model for oligometric systems finds that pairwise interactions as demonstrated in BP and MBP dominate the relative energetics of their conformations.					
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I. INTRODUCTION

Synthesis and development of the thermochemiluminescent compound diazoluminomelanin (DALM) by Kiel et al.¹ has generated increasing interest in this polymer. Biosynthetically, the polymer is formed in both bacteria and mammalian cells in reaction to stress, or stimulation with nitrite, γ -interferon, and lipopolysaccharides²⁻⁵. It can also be synthesized via a copolymerization reaction of 3-amino-L-tyrosine and luminol initiated by nitrite^{1,6}. The optical activity of the DALM system is affected by electromagnetic radiation and temperature variations¹⁻³. The sensitivity of the DALM to microwave radiation³ and its ability to be formed within cells, suggests that when the mechanisms of its luminescence are better understood, it may potentially be useful as a cellular dosimeter in measuring microwave absorption and as a molecular temperature probe⁷.

Earlier structural studies by Wright using two-dimensional NMR techniques⁸ have proposed that the backbone of DALM is a poly(m-phenylene) structure, more specifically, a poly-tyrosine. Luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) can also be present in the polymer but it is not a requisite component for thermoluminescence. Physical characterization of DALM has suggested that the luminescence is due to an excitation of the backbone with subsequent energy transfer to the luminol.

To better understand the structural properties of the DALM system, we have selected several models for the DALM backbone; 2,2'-dihydroxybiphenyl (BP), 2,2'-dihydroxy-5,5'-dimethylbiphenyl (MBP), and 2,5-di(2-hydroxyphenyl)-phenol (TP), shown in Figure 1. In previous work using semiempirical methods⁹, we have noted that the electronic properties of poly-m-phenols can be used as representative models for the poly-tyrosine backbone. However, it was also noted that the structural parameters and energetic barriers for phenyl-phenyl rotation in BP were extremely sensitive to the selected computational method⁹.

The poly-phenol oligomers bear a close resemblance to the phenyl oligomeric units of poly(p-phenylene), PPP. The rotational barriers and the non-planarity between rings are a result of the competition between steric forces and electron delocalization, the latter of which is favored in coplanar conformations. In the PPP system the torsion angles vary

about 27° between neighboring rings in a single chain, an angle that is reduced by about 10° in the crystalline phase¹⁰. The torsion angle in the simplest oligomer of PPP, biphenyl, has been well studied¹¹⁻¹⁹ and ab initio methods have found a torsion angle for the minimum energy conformation ranging from 44° - 46° (depending upon basis set and correlation effects) with barriers to rotation at 0° and 90° ¹². The importance of the torsion angles to the electronic and conformational properties in PPP and PPV and other ring conjugated polymers has been well studied as relationships between this angle and band gaps^{20,21}, ionization potentials^{13,22}, and temperature dependent spectra²³⁻²⁷ have been reported.

Adjacent rings in oligomers of poly(p-phenylene vinylene) have also been found to be non-planar^{28,29} and torsion angles in trans-stilbene have been calculated to be from 15° to 30° depending on the computational method used³⁰. When the energy of the system is examined as a function of the torsion angle for the rotation of one ring, ab initio 3-21G and AM1 calculations predict a relatively flat energy surface between 30° and -30° with large barriers to rotation at 90° . MM-CHARMm methods also predict the 90° barrier with a smaller barrier at 0° ³⁰. When both rings in the trans-stilbene are rotated around the vinylene linkage, AM1 methods predict a minimum in energy at around 20° while MNDO methods predict a minimum at 90° ²⁸.

In previous work, we have found the optimal conformation of BP (Figure 1) is also non-planar⁹. The torsional potential for the adjacent phenyl rings is more complicated than the biphenyl case due to additional steric and hydrogen bonding interactions caused by the hydroxyl groups. The rotational barriers for the hydroxyl group for an individual phenol (about 2.7 kcal/mol) and phenol derivatives have shown that there can be significant conformational and electronic changes upon rotation³¹⁻³⁵. It is therefore likely that the orientations of the hydroxyl groups will be important when studying phenolic oligomers.

In the present paper we examine the relationship of the inter-ring torsion angles for BP and TP relative to their hydroxyl group orientations. The 2,2'-dihydroxy-5,5'-dimethylbiphenyl (MBP) has also been examined to further determine the effects of substituents at the 5-carbon positions (para to the hydroxyl groups). More generally, our

approach is to investigate the optimal conformations and torsion potentials for the model phenolic and derived systems using semi-empirical techniques (AM1, PM3), molecular mechanics methods (MM3), and ab initio Hartree-Fock (RHF) electronic structure calculations at the SCF and MBPT2 levels using the 6-31G* split valence basis set.

The remainder of this paper is structured as follows: in section 2, we present the quantum chemical methods used in the study; in Section 3 the results for the three molecules; and in Section 4 the conclusions for our work are given.

II. METHODS

As the future focus of this work will be more extended oligomeric systems, we have performed a comparative study of several methods to examine their dependability in modeling the phenolic systems. Geometry optimizations and torsion potential calculations have been carried out using molecular mechanics (MM3), semiempirical (AM1, PM3) and ab initio Hartree-Fock (6-31G* basis set) methods on each of the three molecules shown in Figure 1. All bond lengths and angles were optimized by force relaxation methods³⁶, with the exception of the phenyl-phenyl twist angle (ϕ) when mapping the torsional space of the phenolic oligomers. Force field determinations were performed using the Tinker program system³⁷ using the MM3 force field³⁸ with pi electron corrections³⁹. Semiempirical electronic structure computations were performed with the AM1 and PM3 Hamiltonians^{40,41}, which has been shown to give good geometries in similar systems^{30,31}, as implemented in the AMPAC 5.0 program⁴². Ab initio electronic structure calculations were carried out with the Gaussian 92 program system⁴³. Post-SCF electron correlation corrections were estimated at the second order Moller-Plesset level including only the valence electrons, at the SCF level determined geometry.

III. RESULTS AND DISCUSSION

A. 2,2'-Dihydroxybiphenyl (BP)

Our studies have indicated that the relative orientations of the hydroxyl hydrogens are a significant influence when examining the geometries of the BP system. There are three predominant conformations of the BP system, represented in Figure 2, for which the

orientation of the hydroxyl groups is the distinguishing trait. We have used several theoretical methods to study the dependence of the energy of the system upon the torsion angle between the rings. The optimized structural parameters for the lowest energy (a), (b), and (c) type conformations of BP are given in Table 1. While all theoretical methods used determined that the optimized geometry of the cis structure (2a) was the overall lowest energy conformation, there is only complete agreement on the predicted torsion angle for the head-to-tail conformation.

Notably, we have encountered five minima in our investigation of phenol rotation angle by the ab initio methods, as seen in Figure 3. The absolute minima is obtained for a cis conformation and the relative energies of the four other conformations are given in Table 2. These conformations were confirmed to be minima on the potential energy surface by frequency analysis which found no negative eigenvalues. The effects of electron correlation which have been investigated through the use of the MP2 level correction. The absolute energies of the all five minima decreased, and their relative energies also increased in magnitude with the exception of the first head-to-tail minima. The electron correlation correction for the difference between the cis global minimum and the minima for the other conformations is less than 0.7 kcal/mol. These influences of electron correlation are similar to those seen in previous work on biphenyl¹².

Table 2 also shows the energies of the minima found in the semi-empirical and molecular mechanics examinations of the torsion potential curves. Although all of the methods employed predicted the absolute minima to be the cis type conformation, the rotational energy curves determined by the ab initio method were not completely reproduced by the semi-empirical methods nor molecular mechanics, as can be seen by comparing Figures 3-5. The variances of the semi-empirical and molecular mechanics methods from the ab initio may possibly be due to the need for a better description of intramolecular hydrogen bonding, conjugation, and core repulsion effects.

The general inconsistencies amongst the simpler methods are also demonstrated in their torsion potentials. The ab initio 6-31G* results (Figure 3) show distinct different torsion potentials for each of the cis, trans, and head-to-tail conformers with small barriers to the coplanar conformations. Ring rotations for the trans and head-to-tail conformations encounter a small barrier, located at 90°, suggesting its source is the loss

of π conjugation. Each of the other three methods used showed some difficulties in reproducing the 6-31G* results.

The three torsional potential curves calculated using the PM3 Hamiltonian each showed only one rather flat minima at 90° (not shown here). Thus, the method failed to reproduce any of the 90° barriers seen in the ab initio calculations. Similar failures of the PM3 Hamiltonian to reproduce ab initio results have been noted by other authors working with similar systems¹⁴. Since the PM3 Hamiltonian fails to produce any structure in the torsion curves as compared to the 6-31G* results, and the results are inconsistent with the other methods, we have discontinued using this method for the BP system.

The MM3 method, which like the PM3 method tends to overestimate electrostatic interactions, had difficulty reproducing the peaks at 90° . Although the method did predict two minima in both the trans and head-to-tail curves, the second minima in both curves were negligibly small (Figure 4). The MM3 technique also predicted energy differences between the curves for the various conformations to be about half as large as the differences found in the other methods, as can be seen in Table 2. The AM1 calculations showed five minima but predicted a small 90° barrier for the cis conformation curve (Figure 5) while showing an asymmetry about 90° but no barrier for the trans conformation rotations. Both the AM1 and MM3 methods predicted the absolute minimum in the trans rotational curve to be near 140° whereas in the 6-31G* curve, the 140° minima is slightly higher in energy than the 65° minima.

The 90° energy barrier is asymmetric, and its value is dependent upon the computational method and hydroxyl group conformation. The 6-31G* studies predict a single minimum for the cis conformation, a 1.3 kcal/mol barrier from the conformational curve minimum for the head-to-tail orientation, and a 0.4 kcal/mol barrier for the trans orientation. The AM1 barriers are 0.7 kcal/mol for the cis conformation, 1.4 kcal/mol for the head-to-tail conformation and there is no barrier for the trans conformation. The MM3 barriers are the smallest; about 1.0 kcal/mol for both the head-to-tail and the trans conformations. The predicted barrier for the perpendicular conformation of biphenyl is slightly higher (1.5-1.6 kcal/mol^{12,19}) than BP, although the BP barriers are much lower than the 3.3 kcal/mol barrier seen in the perpendicular conformation of stilbene³⁰. However, the calculated energy barriers to coplanarity in the BP system (ranging from

10-12 kcal/mol), are much higher than the 3.2-3.8 kcal/mol barriers seen in the biphenyl system^{12,19} indicating that the hydroxyl groups have a strong steric influence on the system. Although more recent work using correlation consistent basis sets has raised the 90° rotational barrier to 2.1 kcal/mol and lowered the 0° barrier to 2.3 kcal/mol for biphenyl⁴⁴, the BP 0° barrier is sufficiently large to suggest that it is not likely to become coplanar at room temperature and oligomers will be strongly rotationally hindered.

Variations in the BP torsion angle also demonstrate a correlation between the inter-ring bond length and the torsion angle as shown in Table 3, the features of which are independent of the method used for the calculation. For each of the three conformations there are two minima in the bond length as a function of torsion angle. One minima occurs for a conformation with a torsion angle within several degrees of 45° and the other for a conformation with a torsion angle within several degrees of 135°. Thus, the shortest bond length occurs for a conformation having a torsion angle near, but not at, the angle for which the energy is a minimum. This is in contrast to the inter-ring bond lengths in bithiophene and biphenyl for which the shortest bond length occurs in the most stable conformation¹⁵. The bond length increases by 0.003 Å to 0.02 Å towards 0° and 180°, where the steric interactions are the greatest. Likewise, it increases by a smaller amount as the angle approaches 90°. The two local minima in the bond length appear even when the torsion potential curve produced only one minima in the energy, as in the case of the 6-31G* cis curve. There is also a correlation between the average C-C bond length within the rings and the torsion angle, the qualitative features of which are also independent of the theoretical method used. This bond length is a minimum, regardless of conformation, at around 90° and increases by 0.002 Å to 0.004 Å as the molecule approaches either of the co-planar configurations.

In comparing other structural features determined by the various methods, the MM3 technique yields relatively longer bond lengths for all three conformations (excepting C-O bonds). On the other hand, the AM1 calculations predict small inter-ring C-C bonds when compared to other methods. The AM1 method also predicts that the hydroxyl hydrogens will be 8°-10° out of the ring plane for each conformation. In the head-to-tail conformation, this displacement from the ring plane is the smallest among the compared methods. For this conformation, all of the other methods also predict at

least one of the hydrogens to be substantially out of the plane (by over 40° in the *ab initio* calculations). In all cases, regardless of the degree to which the hydrogen is out of the ring plane, the hydroxyl oxygen is at most only several degrees out of the plane.

B. 2,2'-Dihydroxy-5,5'-dimethylbiphenyl (MBP)

The 6-31G*, AM1 and MM3 optimized geometries for MBP are given in Table 4. The structural parameters are very similar to those seen in BP, especially those calculated using the MM3 technique. The torsion angle between the rings changes by no more than 0.2° except in the 6-31G* *cis* conformation and even in that situation there is only a 1.7° change. The inter-ring C-C bond changes by no more than 0.001 Å and the O-H bond length is completely unaffected by the methyl groups. In fact, none of the methods show any bond length to increase by more than 0.005 Å, indicating that the methyl substituent has little substantiative influence on the phenyl ring structures. The 6-31G*, AM1 and MM3 torsion curves are shown in Figures 6-8. The shapes of the curves and the angles of minimum energy are almost identical to those of BP. The relative energies of the minima are given in Table 5 and the ordering of these states is also the same as seen in BP.

Previous studies on biphenyls⁴⁵, thiophenes^{46,47}, cyano-substituted PPV²⁰ and *trans*-stilbenes³⁰ have shown that methyl attachments can cause significant departures from the optimal torsion angle found in the non-methylated compound, the degree of which is dependent upon the position of methyl attachment on the ring. However, the biphenyl work by Park et al.⁴⁵ indicates that methyl placements far from the inter-ring bond results in no change in the torsion angle. The strong similarities between the BP and MBP geometries and rotational energy surfaces suggests that this is also the case in the poly-phenol systems. The lack of influence of the methyl groups on the torsion potentials and geometries of the system, would suggest again, that the poly-phenol system is a good representation for the tyrosine backbone of DALM.

C. 2,5-Di(2-hydroxyphenyl)phenol (TP)

The purpose of this present work is to establish a fundamental basis for modeling the structure and dynamics of BP and longer oligomeric systems. While the previous two sections have elucidated the interactions leading to the three conformations, the overall

closeness of their energies and shallowness of the rotational barriers does not allow us to preclude any of the conformers. In fact, this situation becomes less clear when we consider the dynamics of conformation interconversions and models for larger oligomers.

In Figure 9, we illustrate four 2,5-di(2-hydroxyphenyl)phenol (TP) examples where the conformational questions appear more complex. Based upon the relative stabilization energies (Table 2) for the BP system, the lowest energy TP conformer would be expected to display a head-to-tail and a cis interaction (since a cis and a cis interaction would be impossible for the system to obtain). As can be seen in Table 6, which shows the relative energies of the TP conformations, the cis, head-to-tail is in fact the lowest energy conformer. It is interesting to note that in all the TP conformations, the torsion angles between the rings are within several degrees of the torsion angles found for the optimum geometries of the individual BP moieties with the same hydroxyl orientations. Through comparisons of Table 6 and Table 2 one can also see that the energy difference between any two TP's is similar to the energy differences between the component BP's. For example, the AM1 energy difference for the TP featuring the cis and trans interactions and the one featuring cis and head-to-tail interactions (the third and first entries in Table 6) is about 1.8 kcal/mol. This is close to the 2 kcal/mol difference there would be between systems of two BP's, one system having one cis and one trans BP, and the other system having one cis and one head-to-tail BP.

All of the TP configurations shown in Table 6 have torsion angles corresponding to the torsion angles that occurred for the absolute energy minima in the constituent BP's. However, one must also consider another minima in the energy of the TP system if the constituent BP's have torsion angles that correspond to local minima in the BP torsion curves. For example, the 6-31G* torsion curve for the head-to-tail BP conformation shows two minima, one occurring for a torsion angle of 55° and one for a torsion angle of 113°. The cis, head-to-tail TP in Table 6 shows the energy for the TP when the head-to-tail portion has a torsion angle of 55°. There is also a stable geometry, with an energy about 1.7 kcal/mol higher, for the cis, head-to-tail TP where the head-to-tail portion has a torsion angle of 115°. This 1.7 kcal/mol energy difference between the two TP's is close to the 1.2 kcal/mol difference between the two minima in the head-to-tail BP conformation (see Table 2). In other words, neighboring phenols in a TP behave very

much like their BP equivalents. Both this and the discussion above seem to indicate that neighboring phenols in TP are only slightly influenced by the third phenol and behave very much like a BP would which simplifies the study of the longer length oligomers. Investigations at correlated electron levels are needed to better distinguish these differences and are currently in progress.

D. Rotation of phenolic hydrogen

While previous investigations at SCF and correlated levels of the rotational barrier for the phenolic OH group have found it to be just 2.4-3.4 kcal/mol^{31,32-33} rotation of the interacting OH groups for the BP system is different in that a hydrogen bond needs to be broken to allow for OH group rotation. We have examined the barrier to the rotation of a hydroxyl group using ab initio computations (6-31G*). The two geometries corresponding to the two energy minima of the head-to-tail potential curve were used as starting points for a step-wise reaction coordinate. For both conformations, the hydrogen of the more planar hydroxyl group was rotated 180° from its starting torsion angle near 180° to a final torsion angle of 0° at which the conformation has been converted to a cis structure. While we would have preferred to use a partially frozen geometry to reduce the degrees of freedom and computational effort, the larger differences in the inter-ring torsion angles (ϕ) for the different conformations required a more relaxed geometry optimization. Figure 10 shows the energy of these two systems as a function of the OH torsion angle. The energy barrier at 90°, for both conformations, is asymmetric with a higher energy boundary in going from the cis to the head-to-tail conformation. There is a 1.2 kcal/mol barrier for the conversion of the minimum energy head-to-tail structure to cis but a 3.1 kcal/mol barrier for the reverse transformation. Similarly, there is a 2.2 kcal/mol barrier in converting the higher energy head-to-tail conformation to a cis structure but there is a 5.3 kcal/mol barrier for the reverse.

Figure 11 shows the torsion angle between the phenol rings as a function of the torsion angle of the hydroxyl group for the same two 6-31G* head-to-tail minimum energy conformations. The lowest energy conformation in the head-to-tail type structure has a ring torsion angle of 55° while the second minimum energy conformation has a ring torsion angle of 113°. As the hydroxyl group is being rotated the structure is changing to

a cis conformation for which the torsion angle at the minimum energy conformation is 106° . The ring torsion angle of the second energy minimum should then be expected to change only by a small amount as the hydroxyl group rotates, as Figure 11 confirms. The lowest energy conformation, however, upon the hydroxyl group rotation, evolves from a ring torsion angle of 55° to 105° . Interestingly, the ring torsion angle in this case does not significantly change until the hydroxyl group has rotated by 130° , well past the 90° barrier where the system has converted to the cis conformation indicating that the orientation of the hydroxyl group does not control the ring torsion angle, rather the ring torsion angle influences the hydroxyl group orientation.

IV. CONCLUSIONS

The BP system is similar to the biphenyl system in that the former also adopts a non-planar geometry. However, this molecule is more complicated due to the interactions of the hydroxyl groups. This is most readily seen in the torsion potential curves where there are three distinct forms, resulting from three different hydroxyl group orientations. The lowest energy conformation occurs when the hydroxyl groups pointed towards each other (cis), the highest when the hydroxyl groups point away from each other (trans), and the head-to-tail conformation is intermediate between these two.

The number of minima in the torsion curves and the height of the 90° barriers are dependent upon the method of calculation since the different methods deal very differently with the hydrogen bonding that occurs between the two hydroxyl groups. Neither the semi-empirical nor the molecular mechanics methods used were able to accurately reproduce the 6-31G* torsion curves. The 6-31G* calculations predict one minima in the cis torsion curve at 105° , two in the head-to-tail torsion curve at 55° and 113° , and two in the trans torsion curve at 68° and 122° . All methods predict that there will be a 10-12 kcal/mol barrier to the coplanar conformations and that the three individual torsion curves will begin to overlap in these regions. The torsion curves and conformations of the BP system show very little change when a methyl group is added para to the hydroxyl group.

Neighboring phenols in the TP system behave similarly to their BP counterparts. The torsion angles in TP are the same as those found in the minimum energy structures of

its constituent BP. There are also local minimum energy structures in the TP that correspond to the constituent BP being in local minima. This suggests that the constituent phenols in longer oligomers will act independently of phenols more than one unit away.

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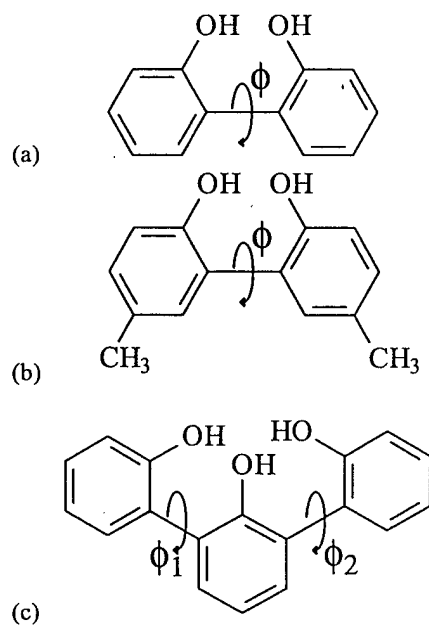


Figure 1 – Molecular structure of the three model compounds (a) 2,2' dihydroxybiphenyl (BP); (b) 2,2'-dihydroxy-5,5'-dimethylbiphenyl (MBP) and (c) 2,5-di(2-hydroxyphenyl)phenol (TP). ϕ represents the torsion angle between the adjacent phenyl rings.

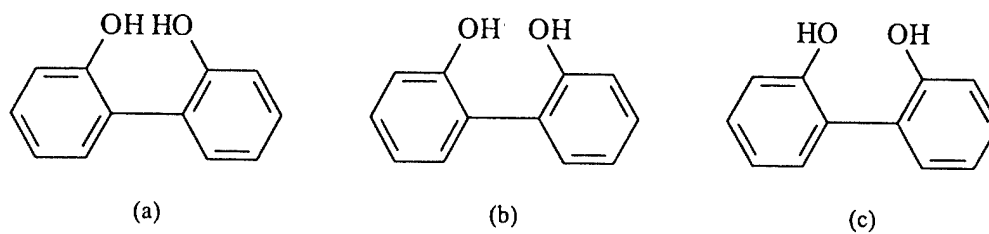


Figure 2 - Representations of the three hydroxyl orientations found in BP (a) cis (b) head-to-tail (c) trans.

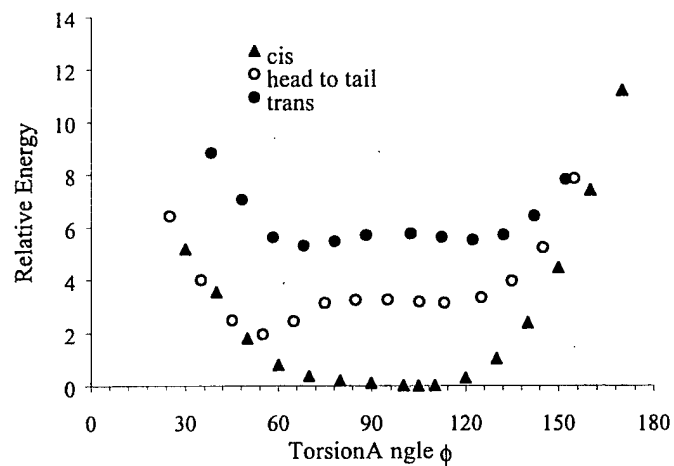


Figure 3 - Torsional potential curves (kcal/mol) for the three OH orientations of BP calculated at the SCF/6-31G* basis set level. Energies are relative to the low energy minimum of the cis conformation.

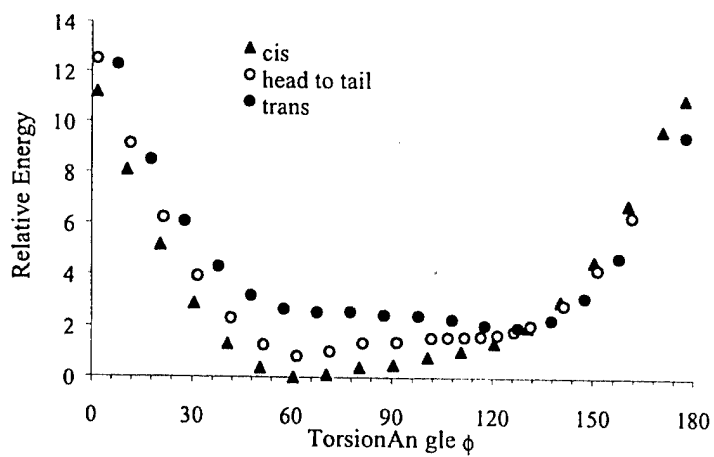


Figure 4 - Torsional potential curves (kcal/mol) for the three OH orientations of BP calculated with the MM3 force field including π electron corrections. Energies are relative to the low energy minimum of the cis conformation.

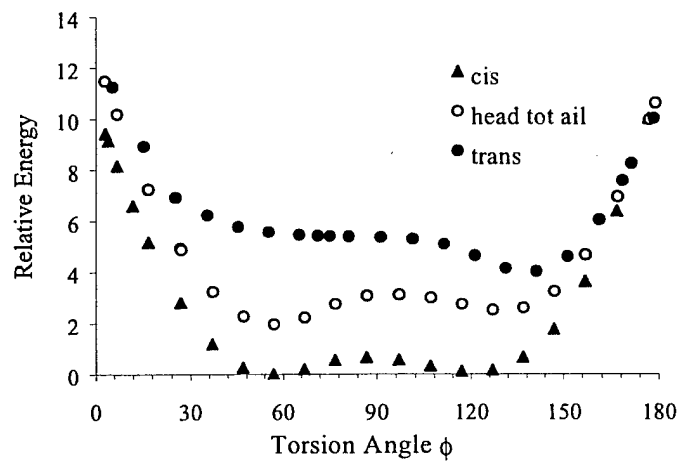


Figure 5 - Torsional potential curves (kcal/mol) for the three OH orientations of BP calculated with the AM1 Hamiltonian. Energies are relative to the low energy minimum of the cis conformation.

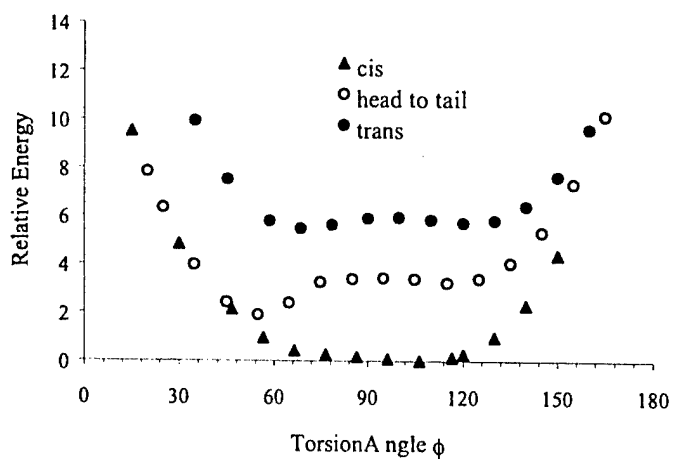


Figure 6 - Torsional potential curves (kcal/mol) for the three OH orientations of MBP calculated at the SCF/6-31G* basis set level. Energies are relative to the low energy minimum of the cis conformation.

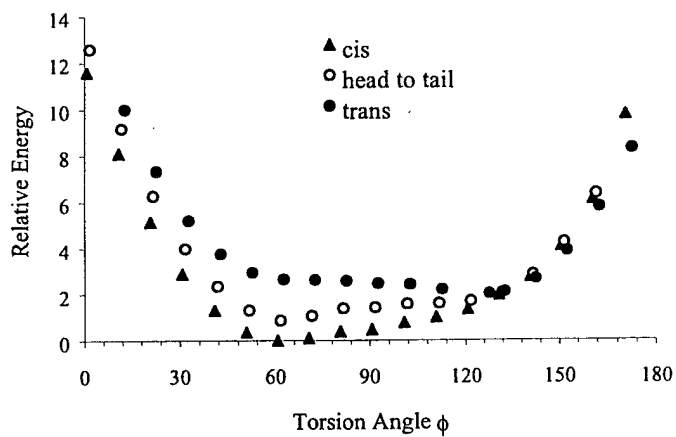


Figure 7 - Torsional potential curves (kcal/mol) for the three OH orientations of MBP calculated with the MM3 force field including π electron corrections. Energies are relative to the low energy minimum of the cis conformation.

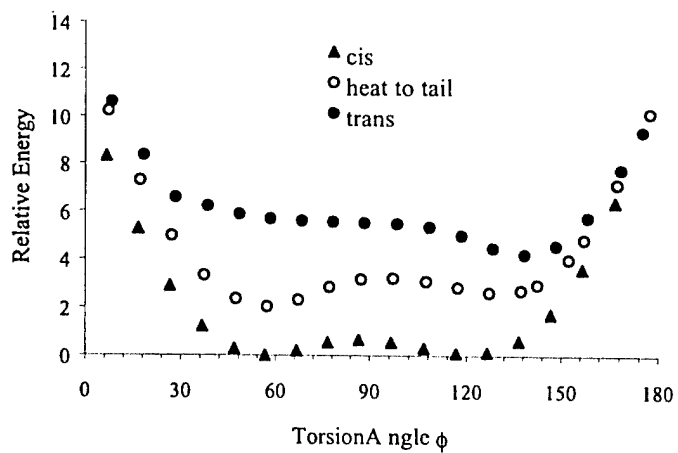


Figure 8 - Torsional potential curves (kcal/mol) for the three OH orientations of MBP calculated with the AM1 Hamiltonian. Energies are relative to the low energy minimum of the cis conformation.

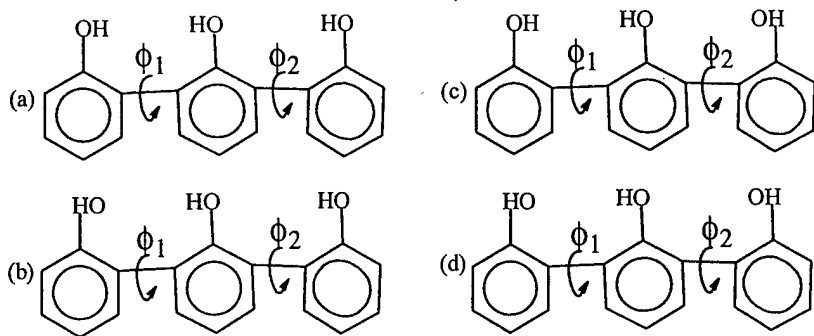


Figure 9 – Schematic illustrations of TP conformers with different hydroxyl group orientations, a) cis, head-to-tail, b) head-to-tail, head-to-tail, c) cis, trans, and d) head-to-tail, trans.

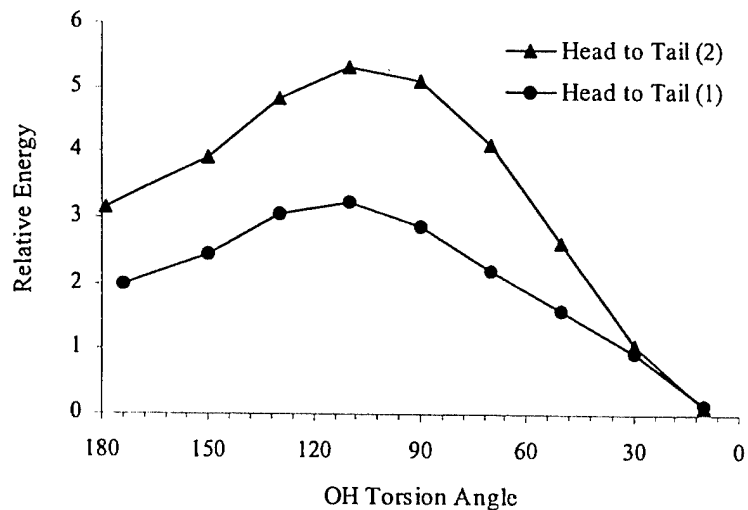


Figure 10 - Energy variation (kcal/mol) in changing from head-to-tail to cis BP conformation as determined by ab initio 6-31G* calculations. Curve (1) uses the geometry of the $<90^\circ$ minimum in the 6-31G* head-to-tail potential curve as the starting point. Curve (2) uses the geometry of the local minimum at 113° in the 6-31G* head-to-tail potential energy curve as the starting point. The more planar OH group is used as the reaction coordinate.

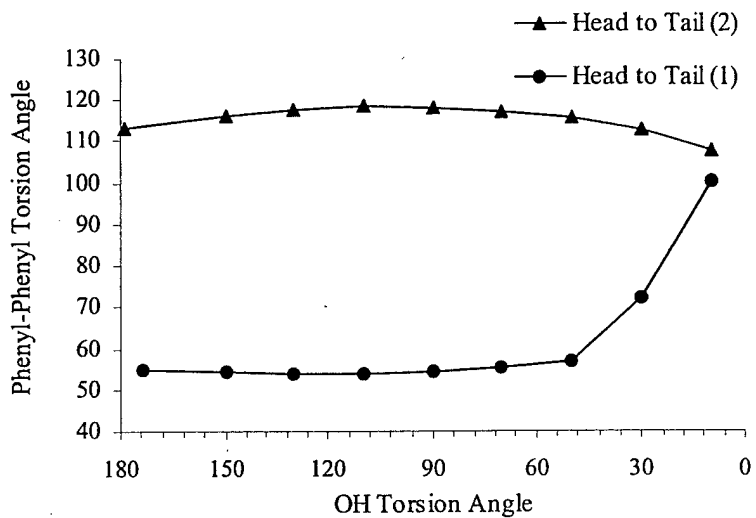


Figure 11 - Interdependence of OH group and phenyl torsion angles. Curve (1) uses the geometry of the $<90^\circ$ minimum in the 6-31G* head-to-tail potential curve as the starting point. Curve (2) uses the geometry of the local minimum at 113° in the 6-31G* head-to-tail potential energy curve as the starting point. The more planar OH group is used as the reaction coordinate.

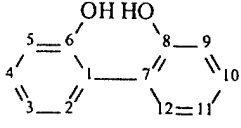
 Parameter	Cis			Trans			Head-to-tail		
	6-31G*	AM1	MM3	6-31G*	AM1	MM3	6-31G*	AM1	MM3
Avg r(C-C)	1.384	1.399	1.400	1.387	1.399	1.399	1.387	1.399	1.399
Avg r(C-H)	1.075	1.100	1.103	1.075	1.100	1.103	1.075	1.100	1.103
Avg r(C-O)	1.347	1.375	1.365	1.351	1.378	1.363	1.358	1.375	1.363
Avg r(O-H)	0.949	0.970	0.973	0.947	0.968	0.972	0.949	0.968	0.973
Inter-ring r(C-C)	1.499	1.461	1.509	1.494	1.460	1.498	1.496	1.462	1.506
Avg \angle (C-O-H)	110.5	108.6	113.8	110.4	107.8	112.7	110.3	108.2	112.1
\angle (C ₆ -C ₁ -C ₇ -C ₈)	104.8	56.9	60.6	68.3	138.6	127.8	55.0	57.1	61.7
\angle (C ₅ -C ₆ -O-H)	179.1	189.5	174.9	4.7	8.1	3.4	138.3	169.0	155.7
\angle (C ₉ -C ₈ -O-H)	179.1	189.2	174.9	4.7	8.0	3.4	353.3	351.9	358.3

Table 1- Structural parameters for BP: Average bond lengths (Å) and angles (°).

Conformation	6-31G*			AM1		MM3	
	Angle	Energy/SCF	Energy/MP2	Angle	Energy	Angle	Energy
Cis 1	104.8	0	0	56.9	0	60.6	0
Cis 2	-	-	-	120.7	0.097	-	-
Trans 1	68.3	5.320	5.924	-	-	68.0	2.550
Trans 2	122.4	5.544	6.167	138.6	4.018	127.8	1.965
Head-to-tail 1	55.0	1.976	1.572	57.1	1.969	61.7	0.832
Head-to-tail 2	113.1	3.149	3.489	130.6	2.514	110.6	1.590

Table 2 - Torsion angles ($^{\circ}$) and relative energies (kcal/mol) for the minima in the BP torsion curves. A dash indicates that a minimum did not occur in the given torsional potential curve.

Torsion Angle	Cis			Trans			Head-to-tail		
	6-31G*	AM1	MM3	6-31G*	AM1	MM3	6-31G*	AM1	MM3
15°	1.508	1.464	1.518	1.504	1.463	1.508	1.510	1.464	1.513
45°	1.497	1.461	1.509	1.493	1.459	1.498	1.497	1.462	1.505
ϕ_1	-	1.461 (56.9°)	1.509 (60.6°)	1.494 (68.3°)	-	1.502 (68.0°)	1.496 (55.0°)	1.462 (57.1°)	1.506 (61.7°)
90°	1.500	1.464	1.523	1.496	1.463	1.520	1.499	1.464	1.520
ϕ_2	1.499 (104.8°)	1.462 (120.7°)	-	1.494 (122.3°)	1.460 (138.6°)	1.498 (127.8°)	1.497 (113.0°)	1.461 (130.6°)	1.507 (110.6°)
135°	1.497	1.461	1.505	1.495	1.460	1.497	1.496	1.461	1.501
165°	1.506	1.464	1.510	1.505	1.464	1.506	1.505	1.463	1.508

Table 3 - Inter-ring carbon-carbon bond lengths (Å) and angles (°) for BP. ϕ_1 (<90°) and ϕ_2 (>90°) are the energetic minima in the torsion potential curve. Energetic minima angles (ϕ_1 and ϕ_2) are given in parentheses.

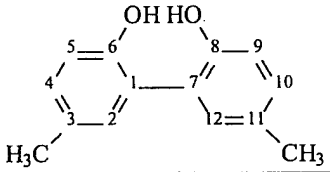
	Cis			Trans			Head-to-tail		
	6-31G*	AM1	MM3	6-31G*	AM1	MM3	6-31G*	AM1	MM3
Parameter									
Avg r(C-C)	1.389	1.400	1.401	1.388	1.400	1.400	1.388	1.400	1.400
Avg r(C-H)	1.076	1.101	1.103	1.077	1.101	1.103	1.076	1.100	1.103
Avg r(C-O)	1.349	1.375	1.365	1.352	1.378	1.363	1.360	1.376	1.364
Avg r(C-CH ₃)	1.511	1.481	1.520	1.512	1.481	1.520	1.512	1.481	1.520
Avg r(CH ₃ -H)	1.085	1.118	1.112	1.085	1.118	1.112	1.085	1.118	1.112
Avg r(O-H)	0.949	0.970	0.973	0.947	0.968	0.972	0.949	0.968	0.973
Inter-Ring r(C-C)	1.498	1.462	1.509	1.494	1.461	1.498	1.496	1.462	1.506
Avg ∠(C-O-H)	110.4	108.5	113.8	110.3	107.8	112.7	110.2	108.2	112.1
∠(C ₆ -C ₁ -C ₇ -C ₈)	106.5	56.7	60.7	68.5	138.4	127.8	54.7	57.3	61.7
∠(C ₅ -C ₆ -O-H)	178.6	189.6	174.9	5.2	8.4	3.5	137.2	168.7	155.8
∠(C ₉ -C ₈ -O-H)	178.6	189.6	174.9	5.3	8.4	3.5	353.1	351.7	358.3

Table 4 - Structural parameters for MBP: Average bond lengths (Å) and angles (°).

Conformation	6-31G*		AM1		MM3	
	Angle	Energy/SCF	Angle	Energy	Angle	Energy
Cis 1	106.5	0	56.7	0	60.7	0
Cis 2	-	-	116.7	0.090	-	-
Trans 1	68.5	5.470	-	-	72.8	2.610
Trans 2	122.1	5.705	138.4	4.208	127.8	2.027
Head-to-tail 1	54.7	1.904	57.3	2.041	61.7	0.865
Head-to-tail 2	113.6	3.235	127.3	2.620	110.5	1.591

Table 5 - Torsion angles ($^{\circ}$) and relative energies (kcal/mol) for the minima in the MBP torsion curves. A dash indicates that a minimum did not occur in the given torsional potential curve.

	6-31G*			AM1			MM3		
	ϕ_1	ϕ_2	Energy	ϕ_1	ϕ_2	Energy	ϕ_1	ϕ_2	Energy
Cis, Head-to-tail	103.3	55.0	0	58.9	57.5	0	61.6	63.2	0
Head-to-tail, Head-to-tail	54.9	54.5	0.824	59.1	58.7	1.614	63.4	62.8	0.955
Cis, Trans	104.7	68.3	3.185	57.4	137.8	1.806	60.3	125.8	1.357
Head-to-tail, Trans	56.6	68.6	5.675	58.3	137.4	4.070	62.8	124.8	2.510

Table 6 – Torsion angles ($^{\circ}$) and relative energies (kcal/mol) for TP conformations shown in Figure 9.