CNDO Calculations for Phenylene Rotations in Bisphenol A Polycarbonate

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ABSTRACT: Rotation barriers of phenylene rings in the backbone of Bisphenol A polycarbonate were estimated by means of quantum mechanical CNDO (complete neglect of differential overlap) calculations for model compounds. In good agreement with conclusions drawn from earlier solid-state nuclear magnetic resonance (NMR) studies, our results indicate that the hindrance to small-amplitude ring rotations is mild and that each phenylene ring may proceed with 180° flips of *distributed* barrier heights. The major contribution to the barrier of 180° flips comes from the repulsion between hydrogens ortho to the isopropylidene substituent in the neighboring phenylene rings. Synchronous motions of phenylene rings in the Bisphenol A unit minimize the repulsion. The barrier for large-amplitude synchronous ring rotations is estimated to be ca. 5 kcal/mol, which compares well with earlier solution-state NMR results.

Introduction

Molecular motions in glassy polycarbonates have received much attention. Illers and Breuer[1] studied the dynamic mechanical behavior of Bisphenol A polycarbonate (BPAPC) and proposed that the γ-relaxation observed near −100 °C at 1 Hz is related to the molecular origin for the toughness of BPAPAC. The assignment for the specific molecular motion involved in the γ-relaxation of BPAPC, however, has been a subject of controversy. Earlier proposals include (a) motion of the carbonate group,[2,3] (b) small molecular movement around the carbonate group,[4] (c) restricted rotational motion of the phenylene group,[5,6] and (d) movement of the two phenylene rings, the isopropylidene group, and the carbonate groups as a unit.[7-9] Some of these proposals are based on observations from indirect methods such as dynamic mechanical or dielectric analyses. In comparison, nuclear magnetic resonance spectroscopy (NMR) may be a more explicit technique in probing molecular motions. Recently, solid-state NMR results of Spiess[10] and Schaefer et al.[11] suggested that the dominant motion in BPAPC at ambient temperature is high (and distributed) frequency 180° flips of the phenylene ring about the C_2 axis. The flips are superimposed on slower small-amplitude ring oscillations about the C_2 axis and small-amplitude main-chain wiggles. More recent results of Roy et al.,[12] who studied the dynamics of ring rotation in BPAPC at various temperatures by means of ^{13}C NMR line-shape analysis, supported the conclusions of Spiess and Shaefer et al. Assuming inhomogeneous distribution of correlation times in the form of the Williams–Watts fractional exponential function, Roy et al. were able to simulate closely their NMR peak shapes as well as the γ-relaxation peak in the dynamic mechanical spectrum of BPAPC. An Arrhenius analysis of the central correlation time indicated an apparent activation energy of ca. 12 kcal/mol, which agrees well with values assigned for the γ-relaxation of BPAPC in dynamic mechanical[9] and dielectric[13] studies. In a separate NMR study[14] of *dissolved* polycarbonates, phenylene ring rotation was found to correlate well with the impact resistance at bulk state. All these evidences suggest that rotational motions of phenylene rings should be closely related to the molecular origin for the toughness as well as the γ-relaxation of BPAPC.

In supplement to experimental efforts, theoretical calculations of conformation energy maps for model compounds by means of molecular mechanics (which is adopted by Tonelli[15] in his pioneering conformational barrier calculations) or quantum mechanical methods may assist in the identification of possible motions within BPAPC. Among the quantum mechanical methods, semiempirical techniques such as CNDO (complete neglect of differential overlap) provide acceptable compromises between effort of computation and accuracy of the result, as compared to the ab initio calculations.[16] Reported here are results of our CNDO calculations for model compounds of BPAPC. Comparison among the present results, earlier experimental observations, and results of related quantum mechanical calculations by other workers is made wherever relevant.

Method of Calculation

The CNDO/2 program of Pople[16] was slightly modified to accommodate the relatively large model molecules here and used to construct conformation energy maps in this work. Structures of the adopted model compounds, which include phenyl bicarbonate (PB), diphenyl carbonate (DPC), 2-phenylpropane (PP), 2,2-diphenylpropane (DPP), and isopropylidenebis(phenyl bicarbonate) (PBPC), and corresponding definitions for the dihedral angles of phenyl or phenylene rotations are given in Figure 1. In our calculations, dihedral angles were varied progressively in 10° increments. Values of bond lengths and bond angles were those used by Erman et al.[17] and were assumed not to vary with the rotation of aromatic rings. These values agree well with more recent valence geometry information provided by Perez and Scaringe[18] in their X-ray diffraction analysis of 4,4′-isopropylidenediphenylbis(phenyl carbonate) (PDPPC) except that the latter gives a slightly shorter C=O bond distance. For further simplification of the molecular environment, the methyl groups in the isopropylidene unit were fixed at the staggered arrangement while only the most stable trans–trans conformation of the carbonate linkage was considered. The two methyl groups have been shown to prefer spatial arrangements close to the staggered conformation.[18,19] Results of earlier studies[18-20] indicated that the trans–trans conformation of the carbonate linkage is favored by ca. 1–3 kcal/mol over the cis–trans form while the cis–cis form is energetically highly unfavorable. Relative energies (in excess of the absolute minimum, which corresponds to the most stable angular position of the phenyl or phenylene rings) at various dihedral angles were used to construct the conformation energy map for each model compound.

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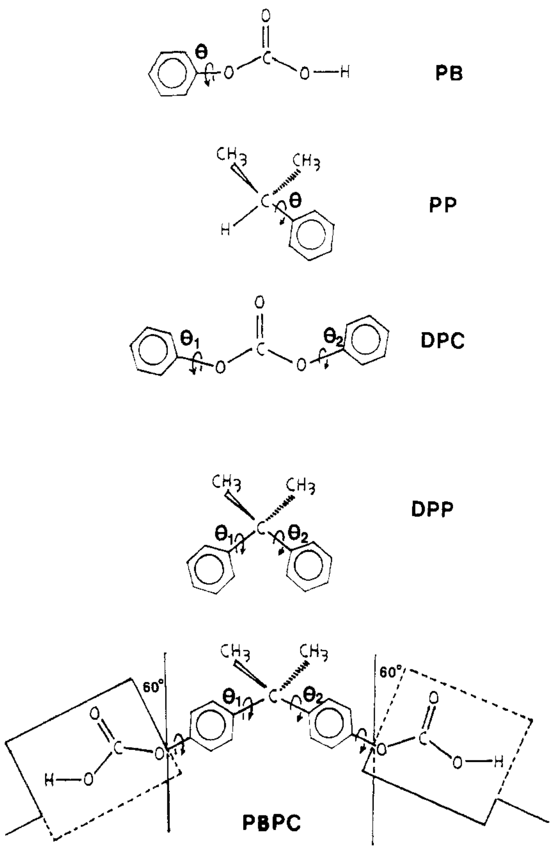

Figure 1. Structures of the model compounds. The dihedral angles are defined as the angle between the plane of the corresponding ring and the plane of paper in the direction indicated by the arrow.

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 \θ2
θ1\                   90°               180°              270°              360°
      4 4 3 2 2 2 2 2 2 2 2 2 2 2 3 4 4 5 4 4 3 2 2 2 2 2 2 2 2 2 2 2 3 4 4 5
      4 3 2 2 1 1 1 1 1 1 1 1 1 2 2 3 4 4 4 3 2 2 1 1 1 1 1 1 1 1 1 2 2 3 4 4
      3 2 2 1 1 1 0 0 0 0 0 1 1 1 2 2 3 3 3 2 2 1 1 1 0 0 0 0 0 1 1 1 2 2 3 3
      2 2 1 1 0 0 0 0 0 0 0 0 0 1 1 2 2 3 2 2 1 1 0 0 0 0 0 0 0 0 0 1 1 2 2 3
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      2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 1 2 3 2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 1 2 3
  90° 2 1 0 0 ● 0 0 0 0 0 0 0 ● 0 0 1 2 3 2 1 0 0 ● 0 0 0 0 0 0 0 ● 0 0 1 2 3
      2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 1 2 3 2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 1 2 3
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      2 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 2 3 2 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 2 3
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      2 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 2 3 2 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 2 3
      2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 1 2 3 2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 1 2 3
      2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 1 2 3 2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 1 2 3
 270° 2 1 0 0 ● 0 0 0 0 0 0 0 ● 0 0 1 2 3 2 1 0 0 ● 0 0 0 0 0 0 0 ● 0 0 1 2 3
      2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 1 2 3 2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 1 2 3
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 360° 5 4 3 3 3 3 3 3 3 3 3 3 3 3 3 4 5 5 5 4 3 3 3 3 3 3 3 3 3 3 3 3 3 4 5 5
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Figure 2. Relative conformation energies (in kcal/mol) for the rotational motion of phenyl groups in DPC. The filled circles (●) indicate absolute energy minima.

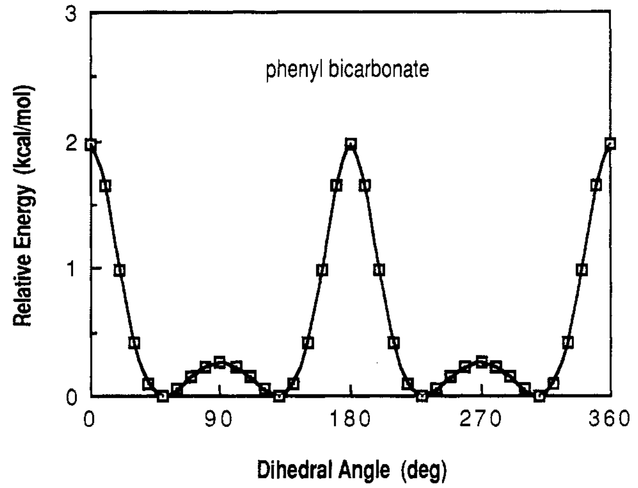

Figure 3. Relative conformation energies for the phenyl rotational motion in PB.

Due to the simplifying assumptions above, results of this work should be regarded as semiquantitative at most.

Results and Discussion

Diphenyl Carbonate (DPC). As shown in Figure 2, the conformation energy map of DPC is relatively featureless with maximum relative energies of only ca. 5 kcal/mol, in agreement with the value of 4.0 kcal/mol obtained by Bicerano and Clark[19] in their calculations using a combination of the AM1 (Austin Model 1) Hamiltonian in MOPAC (molecular orbital package) and the PRDDO (partial retentions of diatomoic differential overlap) technique. Rotational motions of the phenyl groups should thus be relatively easy, as also suggested by Laskowski et al.[20] in their ab initio calculations, although a lower value for the rotation barrier was implied in their work. For phenyl formate, Laskowski et al. obtained a phenyl rotation barrier of 0.7 kcal/mol where the energy maxima correspond to the arrangement that the phenyl group is coplanar with the carbonate group and the energy minima correspond to the arrangement that the phenyl ring is tilted by 64° from the coplanar conformation. As shown in Figure 3, our calculations on another structurally similar model compound, phenyl bicarbonate (PB), yielded a phenyl rotation barrier of 2.0 kcal/mol with the maxima at coplanar conformations and the minima located at a dihedral angle of 50° or the equivalent to the carbonate plane. The energy maxima also occur at coplanar conformations in DPC. While electron delocalization would favor the coplanar conformations, repulsion between the carbonyl oxygen and the ortho hydrogens would resist coplanarity. A relatively low maximum at the coplanar conformation indicates that the effect of core–core repulsion is only slightly stronger than that of electron delocalization. In addition, if one of the rings in DPC is fixed at an arbitrary position, the rotation barrier of the other may be in the range of 2–3 kcal/mol (depending on the actual position of the first ring), which is comparable to the value of 2.0 kcal/mol for phenyl rotation in PB. This suggests that the interaction between the two phenyl rings in DPC is relatively weak.

As for the locations of energy minima in DPC, our results indicate that they correspond to asymmetric arrangements: one of the rings would prefer to lie vertical to the carbonate plane and the other would favor a dihedral angle of 50° (or the equivalent). The dihedral angle between phenyl and carbonate groups was given as 45° in the crystal structure analysis[17] from which the present values of bond lengths and bond angles were obtained. In the crystallographic analysis of 4,4′-isopropylidene-

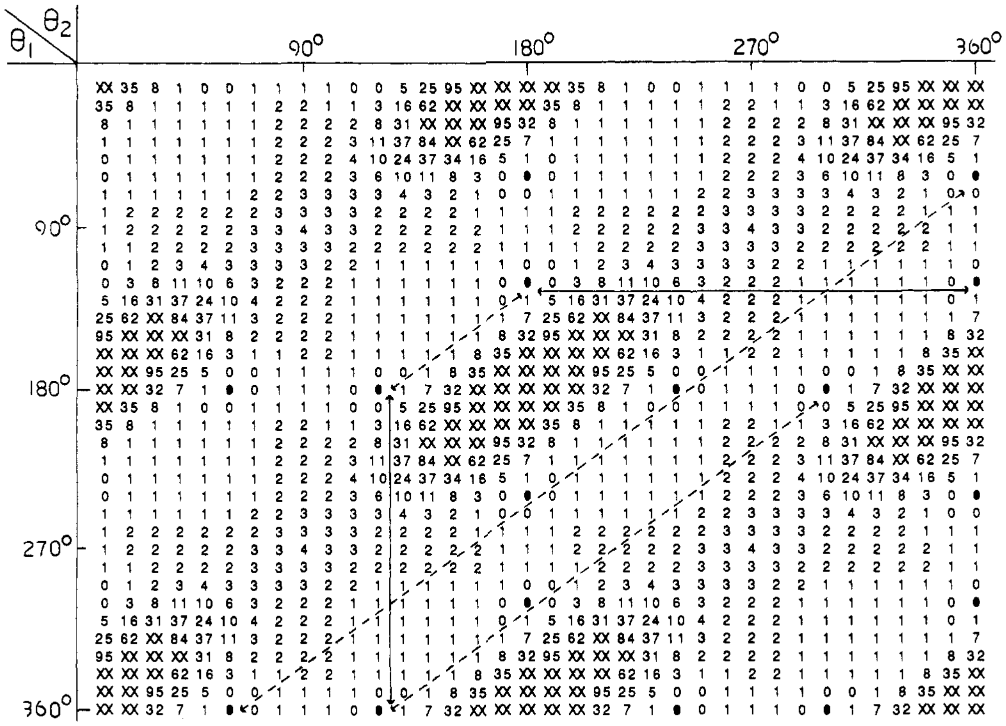

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Figure 4. Relative conformation energies (in kcal/mol) for the rotational motion of phenyl groups in DPP. The filled circles (●) indicate absolute energy minima. The XX's indicate relative energies in excess of 100 kcal/mol. The solid lines indicate examples of 180° flips. The dashed lines indicate examples of synchronous ring rotations.

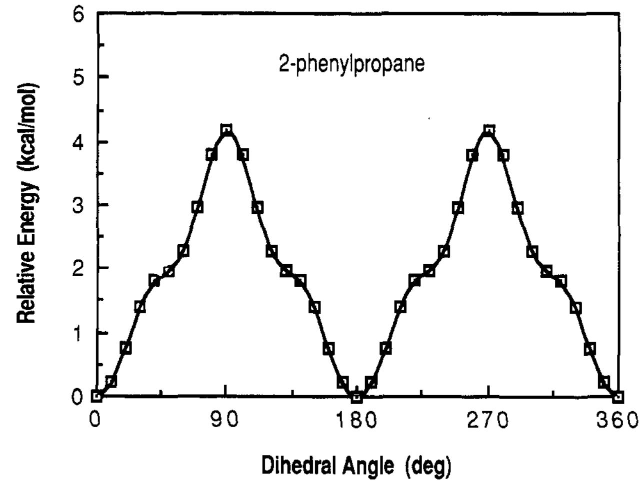
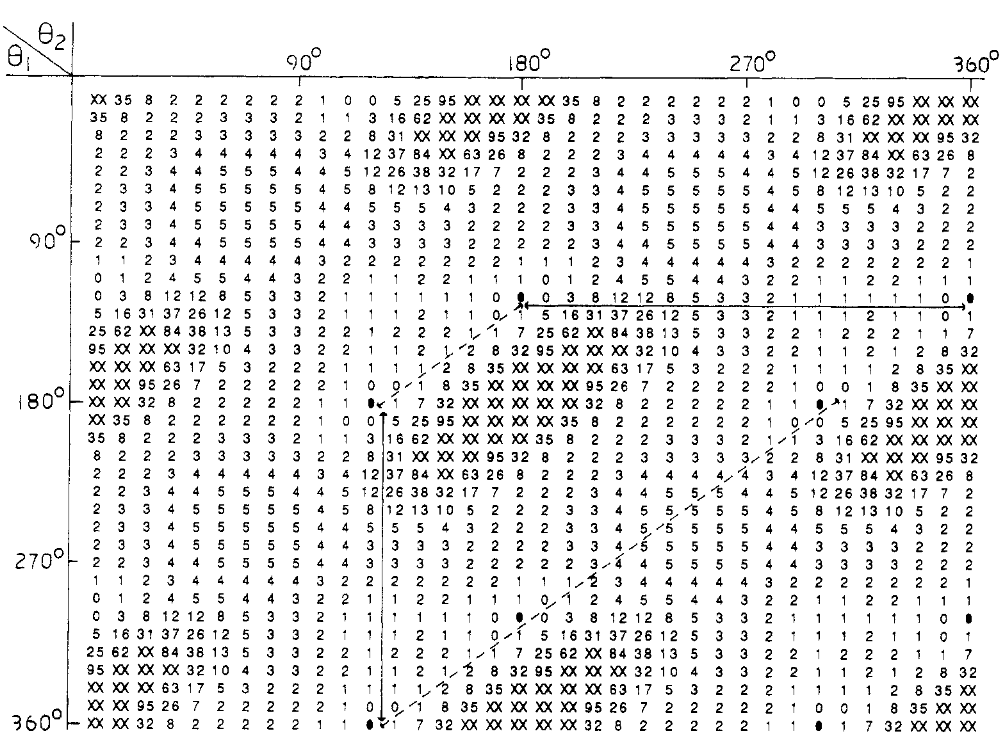


Figure 5. Relative conformation energies for the phenyl rotational motion in PP.

diphenylbis(phenyl carbonate) (PDPPC, in which bond angles and bond lengths are only slightly different from those estimated for DPC) by Perez and Scaringe,[18] three of the dihedral angles between the phenyl or phenylene rings and the neighboring carbonate group were found to be close to 90° while the remaining one is close to 50°. In the calculations of Bicerano and Clark,[19] the two phenyl rings were both at a dihedral angle of 44° to the plane of carbonate linkage in their optimized geometry of DPC. They noted that a nearly 90° rotation of one of the phenyl rings would bring about an arrangement very similar in energy with the optimized geometry. The relative energy we obtained for $(\theta_1, \theta_2) = (50°, 50°)$ is only 0.4 kcal/mol. It thus appears that the exact positions of minimum energy are subject to delicate variations in bond angles and bond lengths, which are not considered in this work. In spite of discrepancies in the positions of energy minima, the general picture of low-barrier phenyl rotations around the carbonate linkage is agreed upon by all the quoted and the present quantum mechanical studies.

2,2-Diphenylpropane (DPP). Given in Figure 4 are our results for DPP. High-energy barriers (exceeding 100 kcal/mol) are observed when the phenyl rings approach coplanarity. As may be observed from Figure 5, the energy barrier of phenyl rotation in 2-phenylpropane (PP) is comparatively low (i.e. 4.2 kcal/mol), indicating only moderate interaction between the phenyl and methyl groups. Therefore, the neglect of methyl rotations should not significantly affect general features of the results in this work. The repulsion between ortho hydrogens in the separate phenyl rings, then, must be the dominating factor for the rotational motion of phenyl rings in DPP. Locations of the absolute energy minima in the present calculation correspond to the situation that one ring (the "coplanar" ring) is in the plane defined by the C–C bonds connecting phenyl rings to the isopropylidene unit while the other phenyl ring (the "tilted" ring) is tilted by 60°. Local minima with relative energy of 0.9 kcal/mol are observed when both rings are tilted by 60°. In the optical anisotropy study by Erman et al.,[17] the dihedral angles of phenyl rings in DPP were estimated as 48° and 49°. Calculations of Bicerano and Clark[19] indicated that the favored dihedral angles for phenyl rings should be 48°. The corresponding dihedral angles in PDPPC were determined to be 61° and 36° by Perez and Scaringe[18] in their X-ray diffraction study. These results show clearly the tendency of the phenyl rings to avoid coplanar conformation as also revealed from a survey of bridged diphenyls,[21] confirming the importance of repulsion between ortho hydrogens in separate rings. The exact spatial arrangement at energy minima, however, seems to depend on slight variations in structural parameters.

Although hindered by humps in the conformation energy map, phenyl rings are still capable of large-amplitude rotational motions since approximately 60% of the total available space corresponds to conformation energies within 3 kcal/mol from the absolute minima. For example, the energy barrier for large-amplitude (in excess of ca. 120°)



θ_1 \ θ_2									90°									180°									270°									360°
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90°	2	2	3	4	4	5	5	5	5	4	4	3	3	3	3	2	2	2	2	2	3	4	4	5	5	5	5	4	4	3	3	3	3	2	2	2
	1	1	2	3	4	4	4	4	4	3	2	2	2	2	2	2	2	1	1	1	2	3	4	4	4	4	4	3	2	2	2	2	2	2	2	1
	0	1	2	4	5	5	4	4	3	2	2	1	1	2	2	1	1	1	0	1	2	4	5	5	4	4	3	2	2	1	1	2	2	1	1	1
	0	3	8	12	12	8	5	3	3	2	1	1	1	1	1	1	0	●	0	3	8	12	12	8	5	3	3	2	1	1	1	1	1	1	0	●
	5	16	31	37	26	12	5	3	3	2	1	1	1	2	1	1	0	1	5	16	31	37	26	12	5	3	3	2	1	1	1	2	1	1	0	1
	25	62	XX	84	38	13	5	3	3	2	2	1	2	2	2	1	1	7	25	62	XX	84	38	13	5	3	3	2	2	1	2	2	2	1	1	7
	95	XX	XX	XX	32	10	4	3	3	2	2	1	1	2	1	2	8	32	95	XX	XX	XX	32	10	4	3	3	2	2	1	1	2	1	2	8	32
	XX	XX	XX	63	17	5	3	2	2	2	1	1	1	1	2	8	35	XX	XX	XX	XX	63	17	5	3	2	2	2	1	1	1	1	2	8	35	XX
	XX	XX	95	26	7	2	2	2	2	2	1	0	0	1	8	35	XX	XX	XX	XX	95	26	7	2	2	2	2	2	1	0	0	1	8	35	XX	XX
180°	XX	XX	32	8	2	2	2	2	2	1	1	●	1	7	32	XX	XX	XX	XX	XX	32	8	2	2	2	2	2	1	1	●	1	7	32	XX	XX	XX
	XX	35	8	2	2	2	2	2	2	1	0	0	5	25	95	XX	XX	XX	XX	35	8	2	2	2	2	2	2	1	0	0	5	25	95	XX	XX	XX
	35	8	2	2	2	3	3	3	2	1	1	3	16	62	XX	XX	XX	XX	35	8	2	2	2	3	3	3	2	1	1	3	16	62	XX	XX	XX	XX
	8	2	2	2	3	3	3	3	3	2	2	8	31	XX	XX	XX	95	32	8	2	2	2	3	3	3	3	3	2	2	8	31	XX	XX	XX	95	32
	2	2	2	3	4	4	4	4	4	3	4	12	37	84	XX	63	26	8	2	2	2	3	4	4	4	4	4	3	4	12	37	84	XX	63	26	8
	2	2	3	4	4	5	5	5	4	4	5	12	26	38	32	17	7	2	2	2	3	4	4	5	5	5	4	4	5	12	26	38	32	17	7	2
	2	3	3	4	5	5	5	5	5	4	5	8	12	13	10	5	2	2	2	3	3	4	5	5	5	5	5	4	5	8	12	13	10	5	2	2
	2	3	3	4	5	5	5	5	5	4	4	5	5	5	4	3	2	2	2	3	3	4	5	5	5	5	5	4	4	5	5	5	4	3	2	2
	2	3	3	4	5	5	5	5	5	4	4	3	3	3	3	2	2	2	2	3	3	4	5	5	5	5	5	4	4	3	3	3	3	2	2	2
270°	2	2	3	4	4	5	5	5	5	4	4	3	3	3	3	2	2	2	2	2	3	4	4	5	5	5	5	4	4	3	3	3	3	2	2	2
	1	1	2	3	4	4	4	4	4	3	2	2	2	2	2	2	2	1	1	1	2	3	4	4	4	4	4	3	2	2	2	2	2	2	2	1
	0	1	2	4	5	5	4	4	3	2	2	1	1	2	2	1	1	1	0	1	2	4	5	5	4	4	3	2	2	1	1	2	2	1	1	1
	0	3	8	12	12	8	5	3	3	2	1	1	1	1	1	1	0	●	0	3	8	12	12	8	5	3	3	2	1	1	1	1	1	1	0	●
	5	16	31	37	26	12	5	3	3	2	1	1	1	2	1	1	0	1	5	16	31	37	26	12	5	3	3	2	1	1	1	2	1	1	0	1
	25	62	XX	84	38	13	5	3	3	2	2	1	2	2	2	1	1	7	25	62	XX	84	38	13	5	3	3	2	2	1	2	2	2	1	1	7
	95	XX	XX	XX	32	10	4	3	3	2	2	1	1	2	1	2	8	32	95	XX	XX	XX	32	10	4	3	3	2	2	1	1	2	1	2	8	32
	XX	XX	XX	63	17	5	3	2	2	2	1	1	1	1	2	8	35	XX	XX	XX	XX	63	17	5	3	2	2	2	1	1	1	1	2	8	35	XX
	XX	XX	95	26	7	2	2	2	2	2	1	0	0	1	8	35	XX	XX	XX	XX	95	26	7	2	2	2	2	2	1	0	0	1	8	35	XX	XX
360°	XX	XX	32	8	2	2	2	2	2	1	1	●	1	7	32	XX	XX	XX	XX	XX	32	8	2	2	2	2	2	1	1	●	1	7	32	XX	XX	XX

Figure 6. Relative conformation energies (in kcal/mol) for the rotational motion of phenylene groups in PBPC. The filled circles (●) indicate absolute energy minima. The XX's indicate relative energies in excess of 100 kcal/mol. The solid lines indicate examples of 180° flips. The dashed lines indicate examples of synchronous ring rotations.

synchronous ring rotations (i.e., θ_1 increasing while θ_2 is decreased, or vice versa) is only ca. 2 kcal/mol, and moderate-amplitude (ca. 60°) synchronous ring rotations from one energy minimum to another enjoy an even lower barrier of ca. 1 kcal/mol. The latter would allow the phenyl rings to rotate cooperatively from the "coplanar-tilted" combination at one minimum to the "tilted-coplanar" combination at another. Positions of the energy minima are such that, if the tilted phenyl ring is fixed, a 180° rotation of the coplanar ring corresponds to an equivalent energy minimum; the barrier of this 180° flip is ca. 11 kcal/mol, very close to the value of the apparent activation energy reported by Roy et al.[12] for the same type of motion in BPAPC. This type of motion was also noted by Bicerano and Clark[19] in their calculations for DPP, but the barrier was estimated to be 24 kcal/mol even when variations in bond parameters and the reorientation of methyl groups in the isopropylidene unit were allowed. The difference in the given values are not as serious as it appears if the flatness of the potential wells is considered. For example, if their positions of energy minima [i.e., $(\theta_1, \theta_2) = (50°, 50°)$ or the equivalent] were accepted, the 180° flip would have a barrier of ca. 36 kcal/mol from Figure 4. Alternatively, if the rings are viewed as moving rather freely within the potential wells, a 10° shift in the angular position of a tilted ring would increase the corresponding 180°-flip barrier to ca. 37 kcal/mol. The important feature here should be the highly distributed nature of the 180°-flip barrier. A significant disagreement, however, exists in the barrier for large-amplitude synchronous phenyl ring rotations, for which Bicerano and Clark obtained a value of 9.0 kcal/mol.

Isopropylidene Bis(phenyl bicarbonate) (PBPC). Shown in Figure 6 is the conformation energy map of PBPC, the largest model compound adopted in this study. The 60° tilt (from the all-in-plane conformation, see Figure 1) of carbonate groups was arbitrarily chosen. Further calculations indicated that major features of Figure 6 change only insignificantly with respect to the variation of tilt angles of the carbonate groups. Larger model compounds such as PDPPC would simulate more closely the structure of BPAPC but would require escalating computation efforts. Since the interaction between rings connected by the carbonate linkage has been found to be weak, the present choice of PBPC is considered adequate. As may be observed, the conformation energy map for rotations of phenylene groups in PBPC is similar to that for phenyl rotations in DPP except that the energy minima with θ_1 or θ_2 equal to 60° or 240° in DPP are not observed in Figure 6 due to the 60° tilt of carbonate groups. In addition, rotational freedom of phenylene rings is slightly more restricted than that of phenyl rings in DPP since only 45% of the available space in the conformation energy map is within 3 kcal/mol from the absolute minima. The barrier of large-amplitude synchronous ring rotations becomes ca. 5 kcal/mol in PBPC, as a result of the hindrance between the ortho hydrogen in the phenylene group and the carbonyl oxygen. However, the low barrier for moderate-amplitude synchronous ring rotations remains unchanged. The barrier of the 180° flips of phenylene rings from one energy minimum to another increases only slightly to ca. 12 kcal/mol, indicating that repulsion between ortho hydrogens in separate phenylene rings remains as the predominating factor. In comparison, the barrier of synchronous rotations of phenylene rings in PBPC was calculated as 9.9 kcal/mol by Bicerano and Clark.[19] Interestingly, before reoptimization using PRDDO, their first MNDO (modified neglect of differential overlap) estimate yielded a barrier of 4.4 kcal/mol. Using the Lennard-Jones potential function, force field calculations of Perez and Scaringe[18] on PDPPC yielded energy maps similar to those in Figure 6. The barrier for synchronous phenylene rotations may be estimated from their energy maps as ca. 2 kcal/mol when structural symmetry was assumed or as ca. 5 kcal/mol when structural asymmetry was allowed. The motion of phenylene groups in BPAPC has been identified in a previous solution-state NMR study by Connolly et al.[22] as stochastic diffusion with an apparent activation energy of ca. 5 kcal/mol.

Similar to the situation in DPP, the phenylene rings should be considered as distributed diffusely around the energy minima due to the shallow nature of the potential wells. The barrier to the 180° flip of a specific phenylene ring would thus depend on the position of the ring right before the flip. For example, if phenylene rings are considered to be distributed freely in regions where the relative energy is within the thermal energy kT (i.e., ca. 0.6 kcal/mol at room temperature), they would be able to oscillate with a total angular displacement of ca. 30° (see Figure 6) around the potential minima. The corresponding range of 180°-flip barriers would then be from 5 to 37 kcal/mol, which would correspond to a frequency range spanning 23 decades of time if the rate of successful flips follows the Arrhenius form as assumed by Bicerano and Clark.[19] These order of magnitude estimates are all in qualitative agreement with earlier NMR results for glassy BPAPC.[11,12]

Due to the comparatively lower barrier of ca. 5 kcal/mol, synchronous phenylene rotations would understandably be the preferred large-amplitude motion in the solution state, as supported by the solution NMR results of Connolly et al.[22] This type of motion, however, requires large free volume and thus would presumably be restricted in the glassy state. The small-amplitude (ca. 30°) oscillation requires very small free volume and thus should be present in the glassy state as well as in the solution state. In comparison, flipping of a single phenylene ring requires intermediate free volume and may thus still be present in the glassy state via the density (and thus free volume) fluctuation process and cooperative motion of the surroundings, as proposed by Schaefer et al.[23] and Perchak et al.[24] Results of Brownian dynamics computer simulations by Perchak et al.[24] on two-dimensional lattices of interacting benzene rings indicated that flipping of a single ring involves cooperative vibrational and rotational movements of surrounding rings. The simultaneous and synchronized rotation of the two phenylene rings in the Bisphenol A unit, if it exists in the glass state, would require much more extensive cooperative movements of the surrounding. It is thus felt that large-amplitude synchronous phenylene rotations may justifiably be considered as inhibited in the glassy state.

Conclusions

By means of quantum mechanical CNDO calculations, conformation energy maps for rotational motions of phenyl or phenylene rings in model compounds of BPAPC have been constructed and analyzed. It is observed that the hindrance from the carbonyl oxygen in the carbonate linkage or methyl groups in the isopropylidene unit to ring rotations is relatively weak. In comparison, the repulsion between hydrogens ortho to the isopropylidene linkage plays a predominant role in ring motions. Superimposed on small-amplitude oscillations, 180° flips of phenylene rings are subject to a different extent of repulsion (depending on actual angular positions of phenylene rings just before the flip) between the ortho hydrogens and thus distributed barrier heights. This would contribute at least partly to the frequency heterogeneity of 180°-flip ring motions observed in earlier NMR studies[10–12] of glassy BPAPC. Synchronous motions of the phenylene rings in the Bisphenol A unit minimize the repulsion effect and thus enjoy a low energy barrier of ca. 5 kcal/mol for full-range rotations. Due to the larger free volume required, this type of motion should be comparatively favored in the solution state.

Acknowledgment. Thanks are due to the CDC (Taiwan) and the Computer Center of NSYSU for their help during this work. Valuable suggestions from Prof. C. Chen of the Chung-Cheng Institute of Technology are greatly appreciated. This work is financially supported by a grant (Contract no. NSC-78-0208-M110-16) from the National Science Council, ROC.

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Registry No. PB, 13932-55-3; PP, 98-82-8; DPC, 102-09-0; DPP, 778-22-3; PBPC (copolymer), 25037-45-0; PBPC (SRU), 24936-68-3.