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CNDO Calculations for Phenylene Rotations in Polycarbonates

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ABSTRACT: Rotational motions of phenylene rings in tetramethyl-Bisphenol A polycarbonate (TMPC) were investigated by means of CNDO/2 (complete neglect of differential overlap) molecular orbital calculations on several model compounds. In drastic contrast to the unsubstituted counterpart (Bisphenol A polycarbonate, PC) studied previously, the mobility of phenylene rings in TMPC was found very much restricted. This is in good agreement with earlier solution NMR results. The repulsion between ortho hydrogens in neighboring phenylene rings connected to the same isopropylidene unit, previously identified as contributing most significantly to the hindrance of phenylene rotations in PC, remained important here; a more significant contribution, however, comes from the repulsion between the aromatic methyl and the carbonyl oxygen in the case of TMPC. This results in strong coupling of the carbonate linkage to the two neighboring rings. The model proposed earlier by Jones was adopted as an example to demonstrate differences in detailed molecular motions in PC and TMPC.

Introduction

Molecular motions in glassy Bisphenol A polycarbonate (PC; cf. Figure 1), which is known for its superior toughness, have received much attention in past years. A variety of techniques such as dynamic mechanical spectroscopy,[1-3] dielectric spectroscopy,[4-6] and solution[7-9] or solid-state[10-14] NMR have been used to explore the molecular motions in PC. In addition to experimental efforts, theoretical calculations by use of molecular mechanics[15-19] or quantum mechanical[20-23] methods have been made to assist in the identification of the possible modes of molecular motion.

In a previous quantum mechanical study[23] of phenylene rotations in PC, we have observed that the individual phenylene ring may undergo 180° flips with *distributed* energy barriers centered around 12 kcal/mol. The carbonate linkage provides only a minor hindrance to phenylene rotation; it is the repulsion between hydrogens ortho to the isopropylidene substituents in the neighboring rings that contributes most significantly to the 180° flip. This type of motion is in good agreement with earlier solid-state NMR observations.[10-12] In addition to the 180° flips, the two neighboring rings may also rotate synchronously to minimize the conflict between ortho hydrogens, resulting in a low barrier of ca. 5 kcal/mol. This agrees reasonably well with previous solution NMR results[7,8] although the experimentally determined activation energy varies from 3 to 5 kcal/mol depending on the solvent used.

In comparison to PC, which exhibits a low-temperature (ca. −100 °C at 1 Hz) relaxation with an apparent activation energy of ca. 11 ± 2 kcal/mol in dynamic mechanical or dielectric measurements,[1-6,24-26] tetramethyl-Bisphenol A polycarbonate (TMPC; cf. Figure 1) is a brittle polymer showing a relaxation peak near 50 °C at 1 Hz. The apparent activation energy in this case is approximately 19 kcal/mol.[2] It has been previously assumed that the secondary relaxation in TMPC is similar in molecular origin to that of PC and that the increased hindrance due to the presence of methyl substituents is responsible for the shift in the temperature range of the relaxation peak as well as the increase in the apparent activation energy.[2]

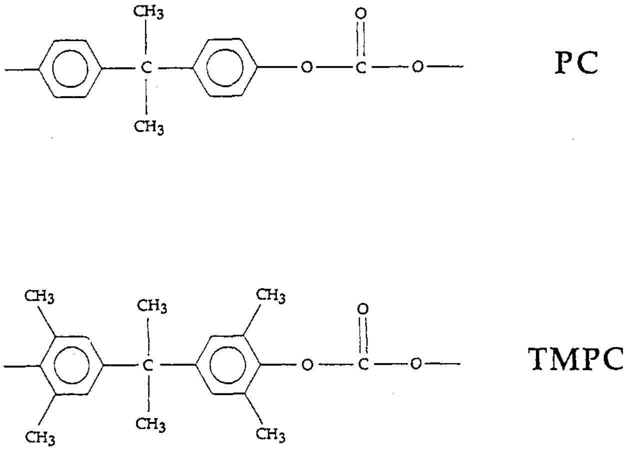

Figure 1. Structures of the monomer unit of Bisphenol A polycarbonate (PC) and tetramethyl-Bisphenol A polycarbonate (TMPC).

Reported here are results of our study for the rotation of phenylene in TMPC by use of the semiempirical CNDO/2 (complete neglect of differential overlap) method.[23] On the basis of the potential energy maps constructed, the mobility of the aromatic rings in TMPC is discussed and compared with that in PC. The present paper is therefore a supplement to the previous one, which is cited frequently throughout this report for the sake of conciseness.

Method of Calculation

The repeating units of PC and TMPC are shown in Figure 1. Selected model compounds for TMPC, including 2,2′,6,6′-tetramethyldiphenyl carbonate (M_4DPC), 3,3′,5,5′-tetramethyldiphenylpropane (M_4DPP), and 2,2′,6,6′-tetramethyl-4,4′-isopropylidenebis(phenyl bicarbonate) (M_4-PBPC), are given in Figure 2. The corresponding model compounds for PC have been analyzed in our previous work.[23] The CNDO/2 program of Pople[27] was used for the total energy calculation of model compounds. In these calculations, the dihedral angles were varied in 10° increments whereas values of bond lengths and bond angles (cf. ref 23 and literature cited therein) were assumed not to vary with the rotation of aromatic rings. For the sake of further simplifications, the neighboring aromatic rings were assumed to be in trans–trans geometry, and

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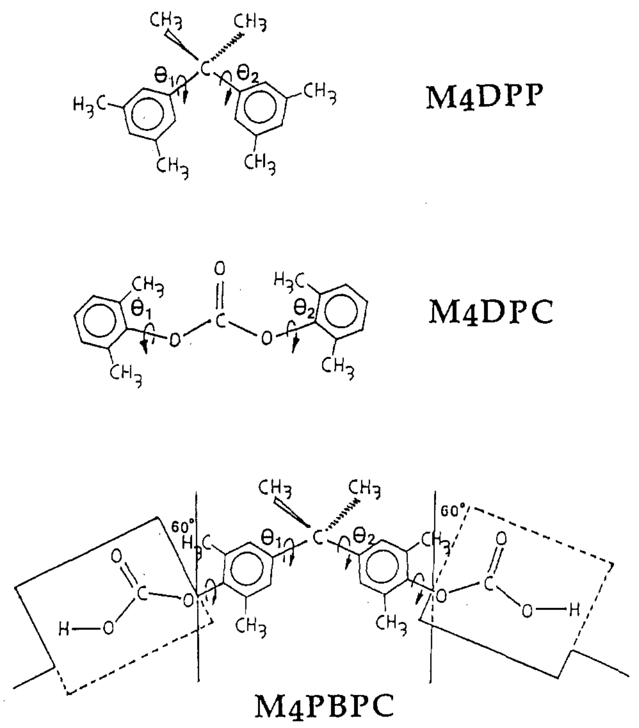


Figure 2. Structures of the model compounds of TMPC. The dihedral angles are defined as the angles between the plane of the corresponding ring and the plane of the paper (molecular plane) in the direction indicated by the arrow.

the two methyl groups in the isopropylidene unit were fixed at staggered arrangement, whereas the aromatic methyl groups were fixed in such a position that one of the hydrogen atoms laid coplanar with the aromatic ring and was pointing away from the carbonate linkage. Due to simplifying assumptions involved, the results here should be considered semiquantitative at most.

Results

Given in Figure 3 is the potential map of M$_4$DPP. It is essentially the same (cf. Figure 4 of ref 23) as that of the corresponding model compound (i.e., diphenylpropane, DPP) for PC. Both 180° flips and synchronous phenylene rotations are feasible here. The humps correspond to coplanar conformations with a strong interference between the ortho hydrogens of the phenylene rings. A closer look at the molecular geometry reveals that, although the calculations here are for the rotation of phenylene rings with the virtual bonds (i.e., the C_2-axes of the phenylenes) fixed, the map is equivalent to torsional motion of the virtual bonds with the phenylene rings fixed (i.e., "glued") to the virtual bonds.

Given in Figure 4 is the potential map of M$_4$DPC, which is drastically different (cf. Figure 2 of ref 23) from that of the corresponding model compound (i.e., diphenyl carbonate, DPC) for PC. In contrast to the case of nearly free rotation in DPC, the rotation of phenylene rings in M$_4$DPC is limited to moderate amplitudes (i.e., within 60° from the potential minima). The repulsion between the carbonyl and the ortho methyl is clearly responsible for the restricted phenylene rotations. The potential minima are located at $(\theta_1, \theta_2) = (65°, 65°)$ or the equivalent, indicating a moderate contribution from electron delocalization.

Given in Figure 5 is the potential map of M$_4$PBPC. The somewhat skewed appearance is a result of the 60° tilt of the carbonate groups. Different tilt angles may result in slightly different appearances of the potential map, but the general feature of the restricted phenylene rotations remains. In fact, the potential map is equivalent to a superposition of Figures 3 and 4 with proper consideration of the carbonate tilt. The repulsion between the phenylene rings through interference of ortho hydrogens is therefore still present. However, the major contribution to the restricted nature of the ring rotations clearly comes from the repulsion between the carbonate carbonyl and the ortho methyl groups. In good agreement with the present result, the phenylene rotational motion has been described as restricted in a previous solution NMR study[28] of TMPC.

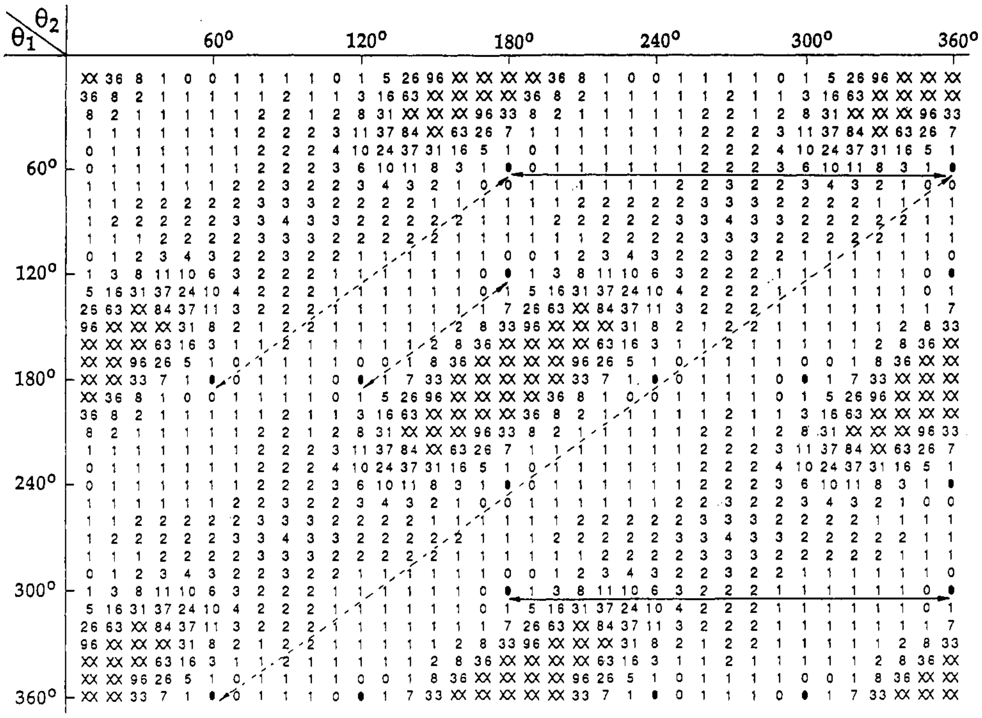
Discussion

Matrix Effect in the Glassy State. As has been stated in both the previous and the present occasions, the simplifying "structural rigidity" assumptions render the calculated potential maps somewhat qualitative. The failure to allow adjustments in bond angles and bond lengths in the transition state would result in an overestimation for the potential barrier of interest. On the other hand, a polymer chain in the glassy state is surrounded by relatively immobile neighboring entities. The force field (or the packing of molecular entities) around a specific chain segment (i.e., the "model compound") exerts resistance to the structural adjustment. This matrix effect brings more or less the specific segment back to structural rigidity.

In two separate molecular mechanics studies of poly(methyl methacrylate) (PMMA) and related polymers, Cowie and Ferguson[29] and Heijboer et al.[30] independently noted that the calculated barrier to rotation of the alkoxycarbonyl group (which they considered responsible for the β-relaxation of PMMA) was much too low if structural optimization was allowed. If, on the other hand, the movements of the main chain and neighboring groups were assumed constrained, the calculated barrier was brought near the experiment activation energy of the β-process. It was concluded that approximately half of the experimental barrier may be attributed to the matrix effect. This is in interesting agreement with an earlier analysis of Yannas and Luise,[31] who suggested that deformation of glassy polymers involves important contributions from the "intermolecular barrier". For polymers of short virtual bonds such as PMMA, they estimated that the intermolecular barrier may contribute equally as the intramolecular barrier. For polymers of long virtual bonds such as PC, they concluded that the intermolecular barrier dominates.

The frequently adopted methodology of structural optimization in quantum mechanical of force-field calculations corresponds to the case of a solitary molecule and therefore does not represent real situations in the glassy state. Our assumption of structural rigidity, however, fortuitously brought the model compounds closer to the situation of real-chain segments in the glassy state. The agreement between the calculated central activation energy of ca. 12 kcal/mol and that of 9–12 kcal/mol determined from solid-state NMR measurements[12,14] for 180° ring flips in PC may therefore be interpreted as a direct consequence of the strong matrix effect involved.

Matrix Effect in the Solution State. The matrix effect (or the intermolecular contribution) to the energy barrier of ring rotations in the solution state should understandably be weaker than that in the glassy state. Consequently, the potential maps we constructed for PC and TMPC (i.e., Figure 6 in ref 23 and Figure 5 here) should have overestimated the barriers of ring rotations. The calculated rotation barrier for full-range synchronous



$\theta_1 \backslash \theta_2$					60°						120°						180°						240°						300°						360°
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	36	8	2	1	1	1	1	1	2	1	1	3	16	63	XX	XX	XX	XX	36	8	2	1	1	1	1	1	2	1	1	3	16	63	XX	XX	XX	XX
	8	2	1	1	1	1	1	2	2	1	2	8	31	XX	XX	XX	96	33	8	2	1	1	1	1	1	2	2	1	2	8	31	XX	XX	XX	96	33
	1	1	1	1	1	1	1	2	2	2	3	11	37	84	XX	63	26	7	1	1	1	1	1	1	1	2	2	2	3	11	37	84	XX	63	26	7
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60°	0	1	1	1	1	1	1	2	2	2	3	6	10	11	8	3	1	●	0	1	1	1	1	1	1	2	2	2	3	6	10	11	8	3	1	●
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120°	1	3	8	11	10	6	3	2	2	2	1	1	1	1	1	1	0	●	1	3	8	11	10	6	3	2	2	2	1	1	1	1	1	1	0	●
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	26	63	XX	84	37	11	3	2	2	2	1	1	1	1	1	1	1	7	26	63	XX	84	37	11	3	2	2	2	1	1	1	1	1	1	1	7
	96	XX	XX	XX	31	8	2	1	2	2	1	1	1	1	1	2	8	33	96	XX	XX	XX	31	8	2	1	2	2	1	1	1	1	1	2	8	33
	XX	XX	XX	63	16	3	1	1	2	1	1	1	1	1	2	8	36	XX	XX	XX	XX	63	16	3	1	1	2	1	1	1	1	1	2	8	36	XX
	XX	XX	96	26	5	1	0	1	1	1	1	0	0	1	8	36	XX	XX	XX	XX	96	26	5	1	0	1	1	1	1	0	0	1	8	36	XX	XX
180°	XX	XX	33	7	1	●	0	1	1	1	0	●	1	7	33	XX	XX	XX	XX	XX	33	7	1	●	0	1	1	1	0	●	1	7	33	XX	XX	XX
	XX	36	8	1	0	0	1	1	1	1	0	1	5	26	96	XX	XX	XX	XX	36	8	1	0	0	1	1	1	1	0	1	5	26	96	XX	XX	XX
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240°	0	1	1	1	1	1	1	2	2	2	3	6	10	11	8	3	1	●	0	1	1	1	1	1	1	2	2	2	3	6	10	11	8	3	1	●
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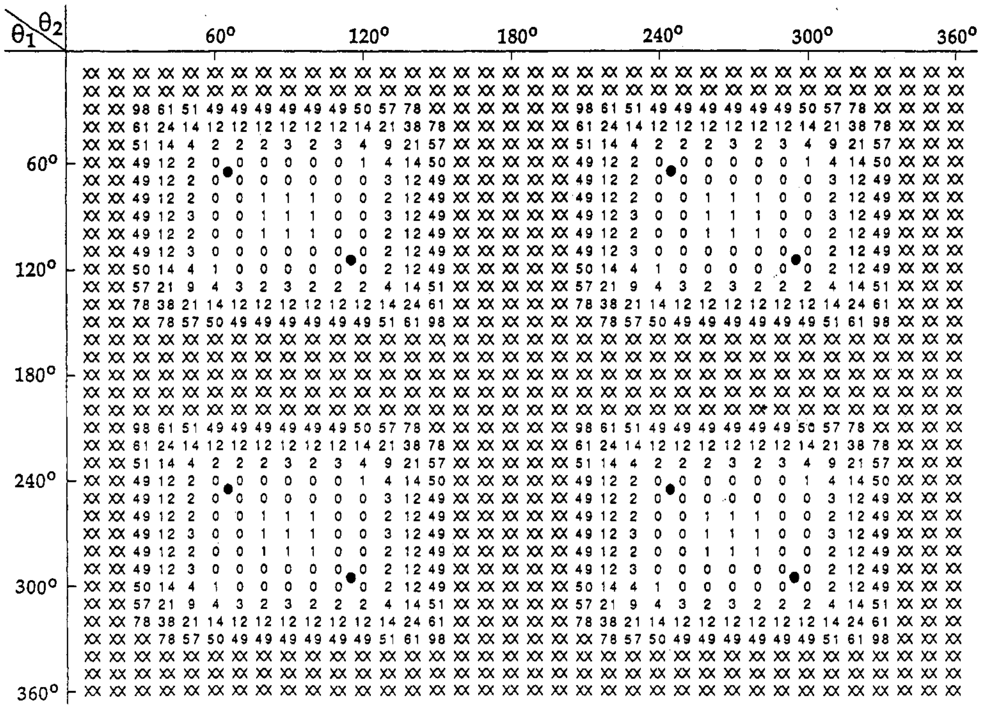
300°	1	3	8	11	10	6	3	2	2	2	1	1	1	1	1	1	0	●	1	3	8	11	10	6	3	2	2	2	1	1	1	1	1	1	0	●
	5	16	31	37	24	10	4	2	2	2	1	1	1	1	1	1	0	1	5	16	31	37	24	10	4	2	2	2	1	1	1	1	1	1	0	1
	26	63	XX	84	37	11	3	2	2	2	1	1	1	1	1	1	1	7	26	63	XX	84	37	11	3	2	2	2	1	1	1	1	1	1	1	7
	96	XX	XX	XX	31	8	2	1	2	2	1	1	1	1	1	2	8	33	96	XX	XX	XX	31	8	2	1	2	2	1	1	1	1	1	2	8	33
	XX	XX	XX	63	16	3	1	1	2	1	1	1	1	1	2	8	36	XX	XX	XX	XX	63	16	3	1	1	2	1	1	1	1	1	2	8	36	XX
	XX	XX	96	26	5	1	0	1	1	1	1	0	0	1	8	36	XX	XX	XX	XX	96	26	5	1	0	1	1	1	1	0	0	1	8	36	XX	XX
360°	XX	XX	33	7	1	●	0	1	1	1	0	●	1	7	33	XX	XX	XX	XX	XX	33	7	1	●	0	1	1	1	0	●	1	7	33	XX	XX	XX

Figure 3. Relative conformation energies (in kcal/mol) for the rotational motion of phenylene rings in M_4DPP. The filled circles (●) indicate absolute energy minima. The XX's indicate relative energies in excess of 100 kcal/mol.



$\theta_1 \backslash \theta_2$					60°						120°						180°						240°						300°						360°
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	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
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	XX	XX	61	24	14	12	12	12	12	12	12	14	21	38	78	XX	XX	XX	XX	XX	61	24	14	12	12	12	12	12	12	14	21	38	78	XX	XX	XX
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60°	XX	XX	49	12	2	0	0	0	0	0	0	1	4	14	50	XX	XX	XX	XX	XX	49	12	2	0	0	0	0	0	0	1	4	14	50	XX	XX	XX
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	XX	XX	49	12	3	0	0	0	0	0	0	0	2	12	49	XX	XX	XX	XX	XX	49	12	3	0	0	0	0	0	0	0	2	12	49	XX	XX	XX
120°	XX	XX	50	14	4	1	0	0	0	0	0 ●	0	2	12	49	XX	XX	XX	XX	XX	50	14	4	1	0	0	0	0	0 ●	0	2	12	49	XX	XX	XX
	XX	XX	57	21	9	4	3	2	3	2	2	2	4	14	51	XX	XX	XX	XX	XX	57	21	9	4	3	2	3	2	2	2	4	14	51	XX	XX	XX
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180°	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
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240°	XX	XX	49	12	2	0	0	0	0	0	0	1	4	14	50	XX	XX	XX	XX	XX	49	12	2	0	0	0	0	0	0	1	4	14	50	XX	XX	XX
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300°	XX	XX	50	14	4	1	0	0	0	0	0 ●	0	2	12	49	XX	XX	XX	XX	XX	50	14	4	1	0	0	0	0	0 ●	0	2	12	49	XX	XX	XX
	XX	XX	57	21	9	4	3	2	3	2	2	2	4	14	51	XX	XX	XX	XX	XX	57	21	9	4	3	2	3	2	2	2	4	14	51	XX	XX	XX
	XX	XX	78	38	21	14	12	12	12	12	12	12	14	24	61	XX	XX	XX	XX	XX	78	38	21	14	12	12	12	12	12	12	14	24	61	XX	XX	XX
	XX	XX	XX	78	57	50	49	49	49	49	49	49	51	61	98	XX	XX	XX	XX	XX	XX	78	57	50	49	49	49	49	49	49	51	61	98	XX	XX	XX
	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
360°	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX

Figure 4. Relative conformation energies (in kcal/mol) for the rotational motion of phenylene rings in M_4DPC. The filled circles (●) indicate absolute energy minima. The XX's indicate relative energies in excess of 100 kcal/mol.

ring rotations in PC was ca. 5 kcal/mol.[23] If the estimate of Yannas and Luise for glassy polymers of a weak matrix effect is accepted as a first approximation for dissolved PC, the apparent activation energy of synchronous rotation of phenylene rings would be ca. 2–3 kcal/mol. This is in good agreement with NMR results[7] of ca. 3 kcal/mol for a 10 wt % solution of PC in a low-viscosity solvent ($CDCl_3$). For the case of a more viscous solvent ($C_2D_2Cl_4$), the NMR analysis of Connolly et al.[8] indicated an increase in activation energy to ca. 5 kcal/mol in the concentration range of 5–10 wt %. These observations indicate that the matrix effect could be quite significant for PC even in the solution state.

Connection of Phenylene Rotation to Secondary Relaxation. Shortly after the 180° ring flipping has been identified as one of the major molecular motions in PC, Jones[32] proposed coupled carbonate bond torsion and ring flips involving cooperative movement of three consecutive rings (i.e., beyond one repeatig unit; cf. Figure 6) along the backbone of PC as the origin of the γ-relaxation. The proposed mechanism is consistent with the mechanical and dielectric sensitivity of the γ-relaxation while remaining reasonably local in nature to be considered as an elementary process. However, a closer look into his model indicates that ring flips are not a necessity; the repulsion between the carbonate carbonyl and the hydrogen ortho

θ_1 \ θ_2						60°						120°						180°						240°						300°						360°
	XX	50	59	XX	XX	XX	XX	XX	52	15	5	3	7	28	98	XX	XX	XX	XX	50	59	XX	XX	XX	XX	XX	52	15	5	3	7	28	98	XX	XX	XX
	50	32	62	XX	XX	XX	XX	XX	63	25	15	15	28	75	XX	XX	XX	XX	50	32	62	XX	XX	XX	XX	XX	63	25	15	15	28	75	XX	XX	XX	XX
	59	62	99	XX	XX	XX	XX	XX	XX	62	53	56	80	XX	XX	XX	XX	81	59	62	99	XX	XX	XX	XX	XX	XX	62	53	56	80	XX	XX	XX	XX	81
	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
60°	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
	52	63	XX	XX	XX	XX	XX	XX	XX	64	54	51	51	52	52	51	50	50	52	63	XX	XX	XX	XX	XX	XX	XX	64	54	51	51	52	52	51	50	50
	15	25	62	XX	XX	XX	XX	XX	64	27	16	14	14	14	14	14	13	13	15	25	62	XX	XX	XX	XX	XX	64	27	16	14	14	14	14	14	13	13
	5	15	53	XX	XX	XX	XX	XX	54	16	6	3	3	4	4	4	3	3	5	15	53	XX	XX	XX	XX	XX	54	16	6	3	3	4	4	4	3	3
120°	3	15	56	XX	XX	XX	XX	XX	51	14	3	1	1	2	2	1	0	●	3	15	56	XX	XX	XX	XX	XX	51	14	3	1	1	2	2	1	0	●
	7	28	80	XX	XX	XX	XX	XX	51	14	3	1	1	2	2	1	0	1	7	28	80	XX	XX	XX	XX	XX	51	14	3	1	1	2	2	1	0	1
	28	75	XX	XX	XX	XX	XX	XX	52	14	4	2	2	2	2	2	2	8	28	75	XX	XX	XX	XX	XX	XX	52	14	4	2	2	2	2	2	2	8
	98	XX	XX	XX	XX	XX	XX	XX	52	14	4	2	2	2	2	3	9	33	98	XX	XX	XX	XX	XX	XX	XX	52	14	4	2	2	2	2	3	9	33
	XX	XX	XX	XX	XX	XX	XX	XX	51	14	4	1	1	2	3	9	36	XX	XX	XX	XX	XX	XX	XX	XX	XX	51	14	4	1	1	2	3	9	36	XX
	XX	XX	XX	XX	XX	XX	XX	XX	50	13	3	0	0	2	9	36	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	50	13	3	0	0	2	9	36	XX	XX
180°	XX	XX	81	XX	XX	XX	XX	XX	50	13	3	●	1	8	33	XX	XX	XX	XX	XX	81	XX	XX	XX	XX	XX	50	13	3	●	1	8	33	XX	XX	XX
	XX	50	59	XX	XX	XX	XX	XX	52	15	5	3	7	28	98	XX	XX	XX	XX	50	59	XX	XX	XX	XX	XX	52	15	5	3	7	28	98	XX	XX	XX
	50	32	62	XX	XX	XX	XX	XX	63	25	15	15	28	75	XX	XX	XX	XX	50	32	62	XX	XX	XX	XX	XX	63	25	15	15	28	75	XX	XX	XX	XX
	59	62	99	XX	XX	XX	XX	XX	XX	62	53	56	80	XX	XX	XX	XX	81	59	62	99	XX	XX	XX	XX	XX	XX	62	53	56	80	XX	XX	XX	XX	81
	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
240°	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX
	52	63	XX	XX	XX	XX	XX	XX	XX	64	54	51	51	52	52	51	50	50	52	63	XX	XX	XX	XX	XX	XX	XX	64	54	51	51	52	52	51	50	50
	15	25	62	XX	XX	XX	XX	XX	64	27	16	14	14	14	14	14	13	13	15	25	62	XX	XX	XX	XX	XX	64	27	16	14	14	14	14	14	13	13
	5	15	53	XX	XX	XX	XX	XX	54	16	6	3	3	4	4	4	3	3	5	15	53	XX	XX	XX	XX	XX	54	16	6	3	3	4	4	4	3	3
300°	3	15	56	XX	XX	XX	XX	XX	51	14	3	1	1	2	2	1	0	●	3	15	56	XX	XX	XX	XX	XX	51	14	3	1	1	2	2	1	0	●
	7	28	80	XX	XX	XX	XX	XX	51	14	3	1	1	2	2	1	0	1	7	28	80	XX	XX	XX	XX	XX	51	14	3	1	1	2	2	1	0	1
	28	75	XX	XX	XX	XX	XX	XX	52	14	4	2	2	2	2	2	2	8	28	75	XX	XX	XX	XX	XX	XX	52	14	4	2	2	2	2	2	2	8
	98	XX	XX	XX	XX	XX	XX	XX	52	14	4	2	2	2	2	3	9	33	98	XX	XX	XX	XX	XX	XX	XX	52	14	4	2	2	2	2	3	9	33
	XX	XX	XX	XX	XX	XX	XX	XX	51	14	4	1	1	2	3	9	36	XX	XX	XX	XX	XX	XX	XX	XX	XX	51	14	4	1	1	2	3	9	36	XX
	XX	XX	XX	XX	XX	XX	XX	XX	50	13	3	0	0	2	9	36	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	50	13	3	0	0	2	9	36	XX	XX
360°	XX	XX	81	XX	XX	XX	XX	XX	50	13	3	●	1	8	33	XX	XX	XX	XX	XX	81	XX	XX	XX	XX	XX	50	13	3	●	1	8	33	XX	XX	XX

Figure 5. Relative conformation energies (in kcal/mol) for the rotational motion of phenylene rings in M_4DPC. The filled circles (●) indicate absolute energy minima. The XX's indicate relative energies in excess of 100 kcal/mol.

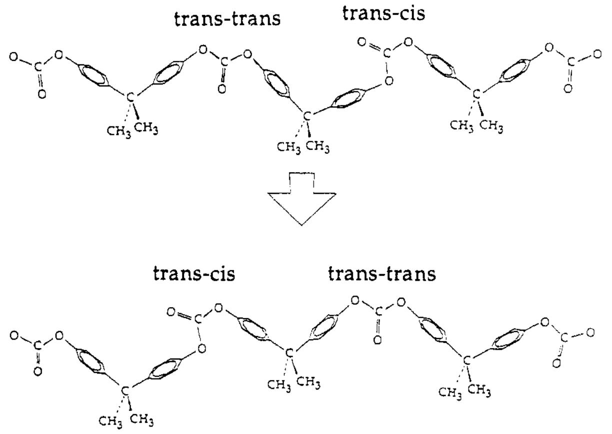

Figure 6. Molecular model proposed by Jones[32] for the γ-relaxation in PC.

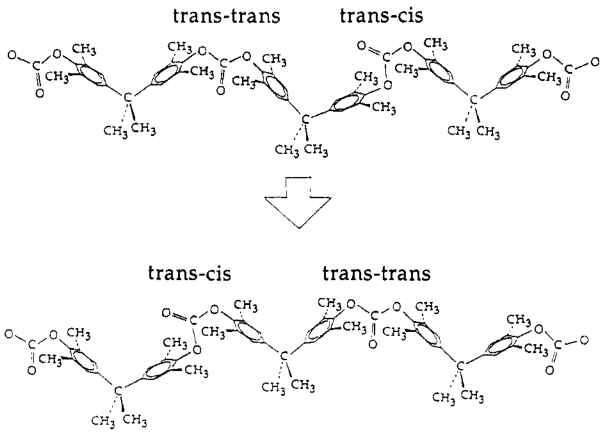

Figure 7. Corresponding model for TMPC as an extension of the model[32] proposed by Jones.

to the carbonate group is too low to induce the flips which must suffer stronger repulsion between ortho hydrogens in the neighboring phenylene rings connected to the same isopropylidene unit. If no flipping of phenylene rings is assumed, the hindrance of this type of motion would receive contributions from four passages of the carbonyl through the neighborhood of the hydrogens ortho to the carbonate group. Two of these passages correspond to carbonate rotation in the trans conformation; the barrier is ca. 2.5 kcal/mol according to our results.[23] The other two passages correspond to the transition between trans and cis conformations, which was not included in our calculations. Previous calculations in the literature indicated a broad range of estimates, from 2.4 to 7.7 kcal/mol,[22,33] for the barrier of trans–cis transition. If an intermediate value of ca. 5 kcal/mol is assigned to the trans–cis transition barrier, the potential barrier for the molecular motion proposed by Jones should be ca. 15 kcal/mol under the assumption that the four subbarriers are surmounted simultaneously so that the total barrier is the algebraic sum. Considering the rotational/torsional freedom of the carbonate linkage, it is highly unlikely that the latter assumption would be followed strictly. Relaxation of the simultaneity requirement should result in a lower value for the total effective barrier, and the value of ~15 kcal/mol should therefore represent an overestimation. Bearing this in mind, it may be said that the mechanism is at no apparent variance with the experimentally determined activation energy of 11 ± 2 kcal/mol for the γ-relaxation of PC.

In the case of TMPC, a methyl-substituted phenylene ring must flip with the carbonate unit to relieve the strong repulsion between the ortho methyl and the carbonate carbonyl (cf. Figure 7). The concurrent flips of four consecutive rings along the TMPC backbone correspond to two concurrent events of the single-ring flip in M_4DPP in terms of hindrance to the motion. Since the barrier to each ring flip is ca. 11 kcal/mol (cf. Figure 3), the simultaneous surmount of two of such barriers would result in an apparent activation energy of ~22 kcal/mol. This value again represents an overestimation due to the assumption of strict simultaneity and may therefore be considered as in reasonable agreement with the experimental value of 19 kcal/mol.

Conclusions

Motion of the carbonate linkage in PC is relatively free of hindrance from the phenylene rings. In comparison, phenylene rings connected to the central isopropylidene unit may experience stronger resistance to ring rotation or bond torsion due to the repulsion between ortho hydrogens. This repulsion, however, may be relieved if the two rings are allowed to rotate synchronously. These molecular characteristics result in the rotational flexibility of the long virtual bonds of PC.

The presence of methyl substituents in TMPC significantly decreases the rotational/rotsional freedom around the carbonate linkage; any large-amplitude torsional motion of the carbonate linkage has to be coupled to the rotation of phenylene rings. In this case, the isopropylidene linkage is comparatively the more flexible joint; the repulsion of phenylene ring rotation around this moiety becomes unavoidable for large-amplitude rotational or torsional motion of chain segments.

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Registry No. TMPC (copolymer), 52684-16-9; TMPC (SRU), 38797-88-5; M_4DPC, 36396-27-7; M_4DPP, 136089-40-2; M_4PBPC, 136089-41-3.