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Intrachain Rotations in Poly(ester carbonates). 1. Quantum Mechanical Calculations on the Model Molecules 2,2-Diphenylpropane, Diphenyl Carbonate, and Phenyl Benzoate

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ABSTRACT: This paper summarizes the first part of the results of a series of calculations intended to relate the properties of bisphenol A (BPA) polycarbonate and the poly(ester carbonates) (PEC) of BPA and terephthalic and/or isophthalic acids to their structure at the molecular level, by use of the techniques of applied theoretical chemistry. Quantum mechanical calculations utilizing the PRDDO technique were used to characterize the molecular motions associated with relaxations observed by dynamic mechanical spectroscopy (DMS). The intrachain rotations were studied by means of detailed calculations on 2,2-diphenylpropane, diphenyl carbonate, and phenyl benzoate, which are representative of short chain segments. The barrier to methyl group rotation was calculated to be ~6.6 kcal/mol. Oscillations of phenyl rings by ±30° only require ~3 kcal/mol. The barrier for the 180° flip of the phenyl rings attached to an isopropylidene group is estimated to be 9–10 kcal/mol. The ester phenyl ring is estimated to have a rotation barrier of ~13.4 kcal/mol in terephthalic PEC but a much higher barrier in isophthalic PEC. Cis–trans isomerization about C–O bonds should easily occur and provide a mechanism for crankshaft-type motion in the BPA fragments but not in the ester fragments. Large amplitude rocking motions of the carbonyl groups in the BPA fragments, over a range of ~70°, only require ~3 kcal/mol and can couple with any one of these motions. The results calculated for each type of motion were related to the role of that motion as a possible component of the relaxations observed by DMS.

Introduction

This paper summarizes the first part of the results of a series of calculations intended to relate the physical properties of bisphenol A (BPA) polycarbonate and the poly(ester carbonates) (PEC) of BPA and terephthalic and/or isophthalic acids to their structure at the molecular level by use of the techniques of applied theoretical chemistry.

The generic formula of BPA and of its PEC with terephthalic and/or isophthalic acid is schematically illustrated in Figure 1, where x denotes the amount of ester relative to the amount of the carbonate, C_1 denotes a carbon atom bonded to two phenyl rings and two methyl groups, C_m denotes a methyl carbon, C_e denotes an ester carbon, and C_c denotes a carbonate carbon. In addition, C_p will denote a phenyl ring carbon atom attached to either C_1, C_e, or C_c, instead of being attached to a hydrogen atom. In addition to x, another overall compositional variable is the relative percentage of terephthalic configurations with the two ester linkages para to one another, versus isophthalic configurations with the two ester linkages meta to one another.

As can be seen from Figure 1, there is only one carbonate linkage per carbonate monomer, while there are two ester linkages per ester monomer. There is, as a result, only one type of phenyl environment in the carbonate fragments, with the phenyl ring flanked by an isopropylidene group and a carbonate linkage para to each other. On the other hand, there are two general types of phenyl environments in the ester fragments. One of these environments has the phenyl ring flanked by an isopropylidene group and an ester linkage para to one another, while the other one has the phenyl ring flanked by two ester linkages either para or meta to one another. There are twice as many phenyl rings in the first type of environment than there are in the second type of environment, in the ester fragments.

A large amount of experimental work has been carried out on these materials.[1-20] The leading experimental techniques for understanding the transitions and relaxations which determine the molecular dynamics of BPA polycarbonate and PEC are dynamic mechanical spectroscopy (DMS)[2,3,8-10] and nuclear magnetic resonance (NMR) spectroscopy.[1,2,6,7,11-20] In this paper, the focus will be on characterizing the relaxations observed by DMS. To summarize, there are several relaxations in the polycarbonates. The α relaxation, or glass transition, occurs at the glass transition temperature (T_g) and is probably caused by large-scale segmental motions. The β relaxation, which occurs at lower temperatures, is believed to represent motions of short chain segments. Its activation energy has been estimated to be ~46 kcal/mol by Varadarajan and Boyer.[9] The γ and δ relaxations, which occur at still lower temperatures, are believed to represent motions of subunits of a monomer. The activation energy of the γ relaxation has been estimated to be 13–14 kcal/mol[8,10] and the activation energy of the δ relaxation has been estimated to be 7–8 kcal/mol.[10] There is substantial evidence that the γ relaxation is a composite relaxation dominated by intrachain motions. For example, the NMR experiments of O'Gara, Desjardins, and Jones[15] show that the dynamics of the γ transition in solution correlates well with its dynamics in the bulk polymer. The difference between the solution and the bulk polymer is that the chains are separated, and therefore the interchain interactions greatly reduced, in solution.

In spite of this very substantial experimental effort, the assignment of the specific molecular motions causing the relaxation peaks observed by DMS experiments is still controversial. This situation is caused in part by the subjective nature of the assignments of the peaks in the DMS spectra. For example, there are many ways in which subpeaks of different numbers and amplitudes, occurring at different temperatures, can be superimposed to give an observed DMS peak. The lack of systematic and detailed computational studies of the elemental motions possible in these materials, using reasonably accurate techniques of quantum chemistry, is one of the major reasons why such subjectivity of interpretation is possible. Such studies would greatly aid in characterizing the molecular motions associated with the DMS relaxation peaks.

At another level, such studies can be of great help in refining existing models for deformation in glassy polymers, or in creating better models. The currently most popular models for deformation are based on considerations of either free volume[21-23] or chain entanglement.[24,25] For example, free-volume theories use the change in volume, i.e., the densification, which usually accompanies physical aging, as their primary criterion. Chain entanglement arguments, which are rooted in the theory of

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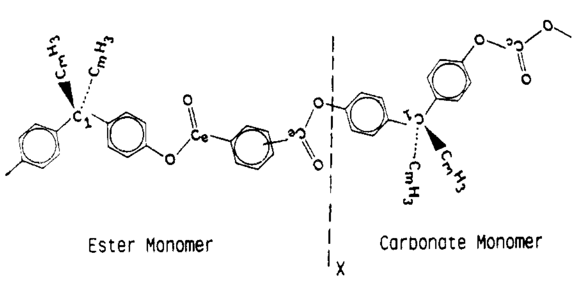


Figure 1. Schematic illustration of the generic formula of BPA and of its PEC with terephthalic and/or isophthalic acids, where x denotes the amount of ester relative to the amount of the carbonate, C_1 denotes a carbon atom bonded to two phenyl rings and two methyl groups, C_m denotes a methyl carbon, C_e denotes an ester carbon, and C_c denotes a carbonate carbon. The terephthalic and isophthalic configurations have the two ester groups para and meta to one another, respectively.

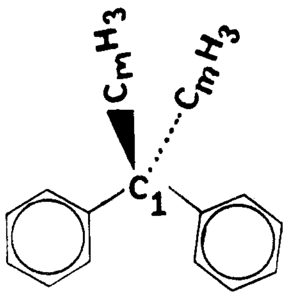


Figure 2. Schematic illustration of 2,2-diphenylpropane. C_1 denotes a carbon atom bonded to two phenyl rings and two methyl groups, and C_m denotes a methyl carbon.

rubber elasticity, suggest that improved physical aging resistance is due to lower entanglement molecular weight and hence a more dense chain-entanglement network. While both of these types of models are intuitively appealing, neither one can make quantitative predictions in a consistent manner.[3,21,23] It is, therefore, necessary to study the root cause of the observed behavior. This root cause lies in local structural features. A study of these features could start by first examining the rotational mobility of short chain segments. One could then proceed to study interchain (i.e., solid-state packing) versus intrachain effects, cooperative motions, the importance of persistence length and of chain entanglements, the amount of volume charge caused by specific types of segmental motions, and the effects of compositional substitutions. The computational techniques of quantum chemistry are ideal tools for such studies.

The Model Molecules

The simplest model molecules which can be used as a first step in studying the intrachain rotations in BPA and its PEC are 2,2-diphenylpropane (Figure 2), diphenyl carbonate (Figure 3), and phenyl benzoate (Figure 4).

2,2-Diphenylpropane represents a configuration of atoms common to both the carbonate and the ester monomers.

Diphenyl carbonate is the smallest model molecule that provides a realistic representation of the immediate environment of the carbonate linkage. Two different conformations have been depicted for diphenyl carbonate in Figure 3, namely, the trans,trans and the trans,cis conformations. This is also a cis,trans conformation which is equivalent to the trans,cis conformation. Williams and Flory[26] have suggested that these conformations can all occur in BPA, with the trans,trans conformation being the most stable by 1.3 kcal/mole and therefore being strongly preferred. The cis,cis conformation (not shown) was excluded by Williams and Flory[26] because of severe steric

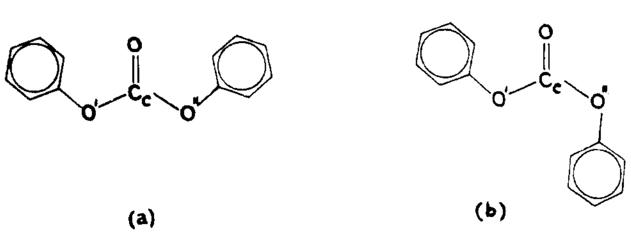


Figure 3. Schematic illustration of (a) *trans,trans*- and (b) *trans,cis*-diphenyl carbonate. C_c denotes a carbonate carbon. The two divalent oxygen atoms are labeled as O′ and O″.

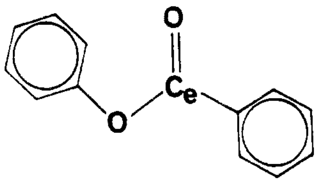


Figure 4. Schematic illustration of phenyl benzoate. C_e denotes an ester carbon.

overlaps between adjoining phenyl rings. Our initial calculations showed that the exclusion of the cis,cis conformation is indeed justified.

Phenyl benzoate is useful to determine (a) the intrinsic rotational properties of an individual diphenyl ester linkage, so that the differences between the terephthalic and isophthalic configurations can be better understood, and (b) the differences between carbonate and ester linkages.

Although many important conclusions can be reached by considering just these three small model molecules, it is desirable to perform additional calculations on larger molecules in which the phenyl rings are attached at both ends to the functional groups which provide for the chain continuation in the polymer, instead of being terminated by a hydrogen atom at one end. The results of these additional calculations are reported in the following paper.

Details of Calculations

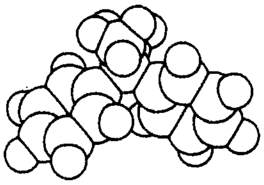
MNDO and AM1 Calculations. The ground-state structures of 2,2-diphenylpropane, diphenyl carbonate, and phenyl benzoate were first determined by using semiempirical quantum mechanical methods. Both the MNDO (modified neglect of differential overlap) and the AM1 (Austin model 1) hamiltonians available in MOPAC (molecular orbital package) were used to refine geometries of each of the three molecules, subject to symmetry constraints where appropriate. MNDO has been recognized as a good method for estimating bond lengths and angles and some, but not all, dihedral angles.[27] Examples of correct dihedrals are flat phenyl rings. MNDO incorrectly predicts that phenyl substituents in general do not conjugate with the ring. More recent versions of MOPAC[28] have included an extended parameter set in a new hamiltonian, AM1, in an attempt to deal with the glaring deficiencies in MNDO. As shown below for phenyl benzoate and diphenyl carbonate, AM1 is a definite improvement for conformational analysis.

2,2-Diphenylpropane. The structures were optimized subject to C_2 symmetry. The results are summarized in Table I, which lists the heat of formation, dipole moment, and ionization potential for each optimized structure and presents space-filling drawings to facilitate the visualization of the structures.

Both methods agree that the ground state will be a propeller-shaped structure. Indeed, only minor differences are evident between the conformations: the rings are predicted to twist about 50° from the C_p–C_1–C_p plane and the methyl groups swing 3° to 6° away from the normal

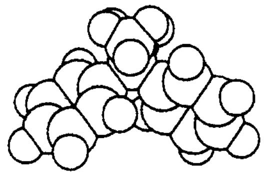
Table I
Summary of MNDO and AM1 Calculations for 2,2-Diphenylpropane

A. MNDO calculation



heat of formation = 53.4 kcal/mol
dipole moment = 0.024 D
ionization potential = 9.17 eV

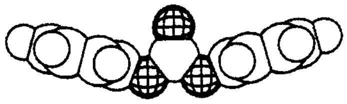
B. AM1 calculation



heat of formation = 40.3 kcal/mol
dipole moment = 0.233 D
ionization potential = 9.24 eV

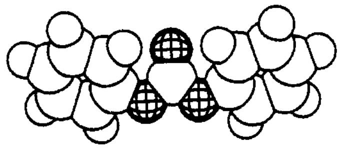
Table II
Summary of MNDO and AM1 Calculations for Diphenyl Carbonate

A. MNDO calculation



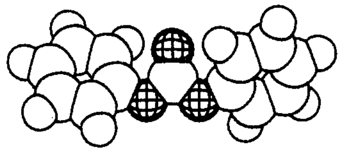
heat of formation = −63.8 kcal/mol
dipole moment = 0.218 D
ionization potential = 9.51 eV

B. AM1 calculation



heat of formation = −53.9 kcal/mol
dipole moment = 0.095 D
ionization potential = 9.59 eV

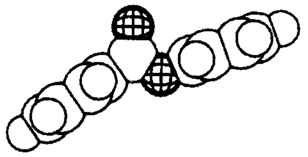
C. AM1 calculation



heat of formation = −53.4 kcal/mol
dipole moment = 0.115 D
ionization potential = 9.60 eV

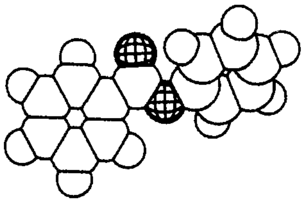
Table III
Summary of MNDO and AM1 Calculations for Phenyl Benzoate

A. MNDO calculation



heat of formation = −26.9 kcal/mol
dipole moment = 1.852 D
ionization potential = 9.32 eV

B. AM1 calculation



heat of formation = −19.7 kcal/mol
dipole moment = 2.149 D
ionization potential = 9.38 eV

to avoid the rings. Major differences are evident in the bond lengths, however. MNDO predicts substantially longer carbon–carbon single-bond lengths than AM1. For example, the C_1–C_m bond length predictions are 1.562 versus 1.528 Å, and the C_p–C_1 bond length predictions are 1.546 versus 1.511 Å. The aromatic C–C bond lengths predicted by AM1 are somewhat shorter as well. Despite the fact that the aromatic rings were given complete freedom, there is almost no deviation from planarity. The largest in-ring dihedral is a small fraction of a degree. Even the substituent dihedral is nearly planar, at 178.6°. The fact that MNDO and AM1 agree on the general conformation of this molecule is probably an accident: there is no other way to arrange the atoms without a large deformation.

Diphenyl Carbonate. Geometries with C_s symmetry were determined by MNDO and AM1. In addition, a geometry with C_2 symmetry was determined using AM1. Space-filling representations of these geometries are shown in Table II. In addition to the symmetry constraints, the six atoms comprising the carbonate functionality plus connecting phenyl atoms (denoted by C_p) were held coplanar. When MNDO is used, repulsions between atoms in the carbonate linkage and atoms in the phenyl rings are obviously overestimated. The phenyl rings are predicted to lie perpendicular to the carbonate plane, at a minimum of conjugation. AM1, however, predicts much flatter geometries, enabling the phenyl rings to conjugate with the oxygen lone pairs. Steric interaction of the ortho hydrogens on the phenyl rings with the carbonyl oxygen appears to preclude a completely planar conformation. The slightly more negative heat of formation for the C_s structure shown in Table IIB (−53.9 kcal/mol) compared to the C_2 structure shown in Table IIC (−53.4 kcal/mol) indicates that it may be the preferred conformation. The small difference in energy precludes a definitive statement that one conformation is preferred but rather indicates that both will be present.

Phenyl Benzoate. No symmetry elements are present in phenyl benzoate. The acid moiety and the C_p atoms were held coplanar, as above. The conformations predicted by MNDO and by AM1 are the most strikingly different of the three molecules studied. MNDO, as expected, predicts an orthogonal conformation for both rings. AM1 predicts the acid ring to be coplanar with the carbonyl group and the ester ring to have approximately the same conformation as in diphenyl carbonate.

PRDDO **Calculations.** The reoptimization of selected geometrical parameters, the performance of axial rotations to locate the angles at which the torsional barriers occur, and the reoptimization of selected geometrical parameters at fixed values of the axial rotations were all carried out by the partial retention of diatomic differential overlap (PRDDO) technique.[29]

PRDDO is an approximate ab initio technique which only uses slightly more computer time than the programs in the MOPAC package, while providing accuracy at the level of minimum basis set ab initio techniques such as STO-3G which require up to 20 times more computer time.[30,31] It differs in philosophy from semiempirical programs such as the MNDO and AM1 programs in the MOPAC package in its use of well-defined mathematical approximations to simplify the calculations, rather than relying on curve-fitting to available experimental data. Its results therefore do not depend on the availability and quality of experimental data on similar molecules or molecular processes.

In spite of these advantages of PRDDO, the MOPAC calculations described above were performed for the full geometry optimizations because the PRDDO program does not yet have analytical gradient procedures incorporated in it, making a full geometry optimization for a large molecule very cumbersome, as well as increasing the risk of "getting stuck" in a location other than the true minimum energy geometry on the potential surface. Geometries of rings in particular are difficult to optimize with PRDDO. The acyclic bond lengths and angles were modified to avoid spurious effects if PRDDO and MNDO disagreed strongly about these geometrical parameters.

In all of the PRDDO calculations, the following minimum basis set of orbital exponents, which are recommended by the program documentation, were used: 1s(H) = 1.24, 1s(C) = 5.67, 2s(C) = 2p(C) = 1.72, 1s(O) = 7.66, and 2s(O) = 2p(O) = 2.25.

For 2,2-diphenylpropane, the two geometrical parameters reoptimized by PRDDO in all the calculations were the C_p–C_1–C_p and C_m–C_1–C_m bond angles. In addition, since there is some steric repulsion between the methyl and the ortho phenyl hydrogens in the rotational transition states, the torsional angles of both of the phenyl rings about the C_1–C_p bonds were separately reoptimized in the final calculations of the barriers to methyl rotation, and the torsional angles of both of the methyl groups about the C_1–C_m bonds were separately reoptimized in the final calculations of the barriers to phenyl rotation. These torsional reoptimizations in the transition-state structures lower the rotation barriers by enabling the methyl and the ortho phenyl hydrogens to get out of each other's way.

All the bond lengths and bond angles which are not completely defined in terms of atoms within the same phenyl ring, including the torsional angles of the phenyl rings relative to the planar carbonate and ester linkages, were reoptimized by PRDDO in diphenyl carbonate and phenyl benzoate.

Whenever the molecule had a point group symmetry element such as a symmetry axis or a mirror plane, this symmetry element was utilized to simplify the calculations.

Relative Energies. The relative energy of a molecular conformation was defined as the difference between its total energy and the total energy of the most stable (lowest energy, base point) conformation for that molecule. Total energies are very large quantities, with magnitudes on the order of several hundred thousand kilocalories per mole for the molecules being considered here. The relative energies of low-lying conformations are small quantities, ranging from a fraction of a kilocalorie per mole to several kilocalories per mole, obtained by subtracting one very large total energy from another. Therefore, an approximate computational technique which can consistently be used to predict the general trends in conformational energies is of great practical value, even if it does not always predict relative energies correctly to within a small fraction of a kilocalorie per mole. While the most accurate ab initio computational techniques of applied theoretical chemistry can reliably compute such relative energies accurately to within a small fraction of a kilocalorie per mole, the use of these techniques to perform detailed computations on a series of large molecules is not yet practically feasible due to the speed and storage space limitations of available computers.

Molecular Volumes. Molecular volumes were calculated for structures of interest by using the SPACE program in the CHEMLAB-II software package.[32] This program, in effect, draws a sphere with a radius equal to its van der Waals radius around each atom and then performs a numerical integration over the resulting volume. Changes in volume are due to (a) changes in bond length, or the 1–2 overlap; (b) changes in bond angle, or the 1–3 overlap; and (c) steric overlap of two more distant atoms.

These volumes were calculated to prepare a database of the volume changes which occur during specific types of intrachain motions. This database can then be used in free-volume models to determine if the availability of more reliable input parameters can make the predictions of these models more quantitative and reliable. Unlike the other quantities discussed in this paper, however, the volume of a molecule is not rigorously defined in terms of the quantum mechanical interactions in the molecule. For example, the geometries and absolute and relative energies of various molecular conformations are among the rigorously defined quantitative results emerging from the solution of the quantum mechanical problem. Any inaccuracies in the calculated geometries or energies are solely due to the approximations used in the numerical solution of the Schrödinger equation, which completely describes the molecule. On the other hand, the molecular volume is not defined in terms of the Schrödinger equation but in terms of the van der Waals radii of the atoms. These radii are intuitively useful semiquantitative indicators of atomic size, a concept which itself has no precise physical meaning within the framework of quantum mechanics.

Hardware and Graphics. All the calculations were carried out on VAX 8600 and VAX 11/785 "superminicomputers". The continuing decrease in size and price, and increase in speed, available storage space, and reliability of computers, have made powerful computers more readily available. In particular, the development of new high-performance superminicomputers is very encouraging. As a result of these trends, it will become possible to address more and more complex problems in polymer science by increasingly more accurate computational techniques, making applied theoretical chemistry an increasingly more useful tool for studying polymers.

The MOGLI (molecular graphics library) program[33] was used on an Evans & Sutherland PS300 color graphics station, to visualize, manipulate, modify, and/or connect the structures of interest. The development of sophisticated three-dimensional color graphics stations and software is another encouraging step toward making applied theoretical chemistry more useful for studying complex macromolecules. Such "molecular graphics" has already contributed significantly to the design of new biologically active macromolecules. In the future, it can also be expected to play an increasingly important part in polymer science.

Results

The most important results of the rotational conformation and barrier calculations are summarized in Table IV for 2,2-diphenylpropane, Table V for diphenyl carbonate, and Table VI for phenyl benzoate. Other relevant results are also referred to at appropriate places in the text. In these tables, in addition to the notation defined above in the Introduction, O′ and O″ denote the two divalent oxygen atoms in diphenyl carbonate.

In Tables IV–VI, the customary convention of defining dihedral angles, namely, setting them equal to 0° when the

Table IV
Results for 2,2-Diphenylpropane[a]

rotation about axis, deg				rel energy, kcal/mol	bond angle, deg		molecular vol, Å^3
C_1–C_m	C_1–C_m'	C_1–C_p	C_1–C_p'		C_m–C_1–C_m	C_p–C_1–C_p	
-69.2	-69.2	131.9	131.9	0.0	107.1	109.8	195.21
110.8	-69.2	131.9	131.9	8.1	108.5	107.6	194.40
110.8	-69.2	132.2	146.6	6.6	109.5	109.5	194.70
110.8	110.8	131.9	131.9	16.1	110.4	106.2	193.48
110.8	110.8	144.9	137.3	14.7	110.8	108.5	193.83
-69.2	-69.2	161.9	131.9	2.3	108.0	112.6	195.10
-69.2	-69.2	101.9	131.9	3.0	107.1	108.9	194.62
-69.2	-69.2	-143.1	131.9	26.9	104.5	120.6	192.13
-54.1	-62.8	-143.1	131.9	24.0	105.9	122.7	192.33
-69.2	-69.2	-138.1	41.9	12.5	105.0	105.5	193.58
-52.5	-56.2	-138.1	41.9	9.0	105.9	107.3	194.04

[a] See the Introduction for the notation used.

Table V
Results for Diphenyl Carbonate[a]

rotation about axis, deg			rel energy, kcal/mol	molecular vol, Å^3
C_c–O″	O″–C_p	O″–O′		
0.0	-44.0	0.0	0.0	170.32
150.0	-44.0	0.0	0.6	170.08
-153.5	-44.0	0.0	4.0	169.93
0.0	176.4	0.0	1.6	169.87
0.0	-44.0	45.0	3.1	169.52
0.0	-44.0	-26.5	3.1	170.44

[a] See the Introduction for the notation used.

Table VI
Results for Phenyl Benzoate[a]

rotation about axis, deg			rel energy, kcal/mol	molecular vol, Å^3
O–C_p	C_e–C_p	C_e–O		
-46.4	0.2	180.0	0.0	163.22
176.5	0.2	180.0	2.9	163.15
-46.4	90.2	180.0	6.7	163.56
-74.4	90.2	67.5	18.0	163.77

[a] See the Introduction for the notation used.

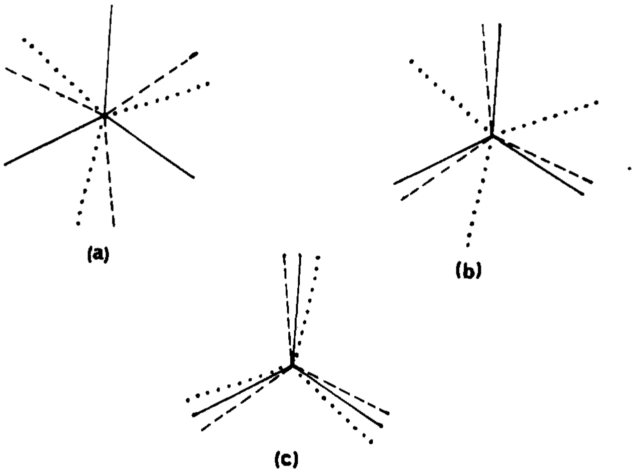


Figure 5. Schematic perspective illustration of the torsional orientations of the three bonds each of C_1 and the two C_m's in 2,2-diphenylpropane, when looking along each of the two C_1–C_m bonds in turn. The solid lines indicate the bonds of C_1, while the dashed and dotted lines indicate the bonds of the two C_m's. (a) Minimum-energy conformation. (b) Highest energy conformation for the rotation of one methyl group or the out-of-phase rotation of both methyl groups in the same direction. (c) Highest energy conformation for the simultaneous in-phase rotation in the same direction, or simultaneous rotation in opposite directions, of both methyl groups.

two planes defining them are coplanar, has been used. In discussing the results, however, it has often been found to be more convenient to refer to the value of a given torsional angle in terms of how much it differs from the same angle in the minimum-energy geometry for that molecule. The use of each one of these two different conventions where most appropriate should enable the reader to both be able to refer to the torsional angles in terms of a common frame of reference and at the same time be able to immediately evaluate how different an altered geometry is from the appropriate minimum-energy base-point geometry.

The convention is also adopted that for positive values of the angle of rotation, atoms are being rotated about an axis in a counterclockwise direction when looking down from the first atom defining the rotation axis toward the second atom defining the rotation axis. Finally, since a 360° rotation about any axis is a full rotation, a negative (clockwise) rotation by $-n$ degrees has the same effect as a positive (counterclockwise) rotation by $(360 - n)$ degrees.

Discussion

Geometry of 2,2-Diphenylpropane. The optimized geometry of 2,2-diphenylpropane has C_2 symmetry, with a twofold axis of rotational symmetry whose action rotates the methyl groups into one another and the phenyl groups into one another. For example, for each methyl hydrogen, there is a corresponding symmetry-equivalent hydrogen atom in the other methyl group. On the other hand, the three hydrogen atoms in the same methyl group are all slightly symmetry inequivalent with each other. They have slightly different C_m–H_m bond lengths, as well as slightly different C_1–C_m–H_m bond angles, where H_m denotes a methyl hydrogen, so that there is no local axis of threefold symmetry whose operation would result in interchanging the H_m's while keeping the methyl group in an orientation indistinguishable from its original orientation. Similarly, each atom in a given phenyl ring is in a different local bonding environment from all the other atoms in the same phenyl ring, but there is an atom symmetry equivalent to it in the other phenyl ring.

The phenyl rings are both tilted by 48.1° relative to the C_p–C_1–C_p plane, in a configuration similar to two blades of a propeller. This 48.1° value is in good agreement with the torsional angle of 46° calculated by Erman et al.[34] for the torsional minimum of a potential energy surface derived from force-field calculations. The three C_m–H bonds at each of the two C_m's is off by 9.25° from a conformation in which they would be exactly staggered relative to the three bonds at C_1. This result is also in good agreement with the 6° torsional angle calculated by Erman et al.[34] Since the two methyl group torsions are in opposite directions relative to one another, the three bonds on each C_m are at a torsional angle of 18.5° relative to the three bonds on the other C_m. The relative torsional orientations of the three bonds on each one of C_1 and the two C_m's are illustrated in the schematic perspective drawings in Figure 5. It is the presence and most favored propeller-blade orientation of the two phenyl rings that causes such a conformation for the methyl groups to be favored over one where both of the C_m's would be exactly staggered relative to C_1.

The C_p–C_1–C_p angle is 109.8°, while the C_m–C_1–C_m angle is 107.1°, showing that the phenyl rings form an angle larger than the tetrahedral angle (109.471°), thus taking up more space at the expense of the smaller methyl groups which form an angle smaller than the tetrahedral angle. The average C_1–C_m–H_m angle is 111.8°, consistent with the NMR prediction of ~111° by Bubeck, Smith, and Bales[2] in BPA, as well as being in agreement with the 111.4° and 111.8° values respectively calculated by PRDDO for the same angle in the staggered and eclipsed conformations of the ethane molecule.

Geometry of Diphenyl Carbonate. The optimized geometry of diphenyl carbonate is the trans,trans conformation of C_s symmetry, which has a mirror plane of symmetry perpendicular to the plane of the carbonate linkage. This mirror plane of symmetry contains C_c and the oxygen atom double-bonded to C_c and reflects the two phenyl rings into one another. The two phenyl rings are both at a torsional angle of 44° relative to the plane of the carbonate linkage, in agreement with the torsional angle of 45° determined by Yoon and Flory[35] in crystalline diphenyl carbonate. Since rotations of the phenyl rings about the O–C_p bonds are almost free rotations (see Table V), diphenyl carbonate does *not* have a strong preference for this geometry of C_s symmetry. For example, if one of the phenyl rings is rotated by approximately 88° about its O–C_p axis, an alternative trans,trans conformation of C_2 symmetry, with an axis of twofold symmetry instead of a mirror plane, is obtained. This alternative trans,trans conformation of C_2 symmetry is very similar in energy to the trans,trans conformation of C_s symmetry, as discussed above. (See ref 36 for another calculation recently reported on diphenyl carbonate.)

There are also a low-lying trans,cis and an equivalent cis,trans conformation, but no low-lying cis,cis conformation. The lack of a low-lying cis,cis conformation is due to the severe steric overlaps between adjoining phenyl rings, as pointed out by Williams and Flory.[26] The crystallographic value[35] of the O′–C_c–O″ bond angle is 108°. The present calculations give an optimized value of 105.8°. Either one of these two values is substantially smaller than the 120° angle in regular sp^2 hybridization. In a cis,cis conformation, therefore, the steric overlap is even more severe than it would have been if the bond angles around C_c had been 120°. The only way to substantially reduce this extreme steric repulsion is by opening the O′–C_c–O″ bond angle by a very large amount in the cis,cis conformation, which then in turn severely destabilizes the cis,cis conformation because of the magnitude of the geometrical distortion involved.

Geometry of Phenyl Benzoate. The symmetry point group of phenyl benzoate is C_1, i.e., there are no point group symmetry elements. The ester linkage and the phenyl ring directly attached to C_e are at an angle of 0.2° relative to one another; i.e., they are coplanar within the limits of numerical accuracy of the calculations. In crystalline phenyl benzoate, the phenyl ring attached to C_e is at an angle of 9.8° with the ester linkage.[37] This near coplanarity is caused by the stabilization resulting from resonance between the electrons in the phenyl ring and in the ester linkage when the planes of these two groups are coplanar with each other.

The other phenyl ring, which is attached to an oxygen atom and therefore has a bonding environment very similar to the bonding environments of the two phenyl rings in diphenyl carbonate, is calculated to have a torsional angle of 46.4° relative to the plane of the ester linkage. This angle is just a little larger than the 44° value calculated for the equivalent torsional angle in diphenyl carbonate, an effect which is not surprising since the second phenyl ring of phenyl benzoate lies on the same plane as the plane of the ester linkage and is therefore closer to the phenyl ring bonded to the oxygen atom than in diphenyl carbonate. Making the phenyl ring closer to being perpendicular to the ester linkage alleviates any small steric repulsions which may have resulted from this greater closeness of the two phenyl rings.

This torsional angle is 65.1° in crystalline phenyl benzoate,[37] substantially larger than either the angle calculated for phenyl benzoate or the angle observed in crystalline diphenyl carbonate.[35] There are two possible explanations for this 18.7° difference. First of all, the potential surface is very flat for this particular torsional motion, resulting in a very broad minimum. For example, if the phenyl ring is rotated by 18.7° to bring it to a torsional angle of 65.1°, the energy of the resulting conformation is only 0.6 kcal/mol above the energy of the base-point structure. Second, the geometry which allows for optimum packing in the crystalline state is not necessarily the same as the most stable geometry of the gas-phase (or "isolated") molecule, especially if it is possible to get a much more favorable crystalline packing environment by low-energy distortions from the gas-phase geometry. For example, gas-phase electron diffraction data indicate that the biphenyl molecule is nonplanar, with a torsional angle of 44.3° between the two phenyl rings in the minimum-energy conformation.[38] Calculations at the STO-3G level of approximation, which are of accuracy comparable to PRDDO, also predict a nonplanar minimum, with a torsional angle of 38.63° between the two phenyl rings.[39] Such a value of the torsional angle preserves some of the stabilization resulting from resonance between the electrons of the two phenyl rings, while reducing the steric repulsions between the ortho hydrogens. The coplanar conformation of biphenyl is calculated to be 2.05 kcal/mol above the twisted minimum-energy conformation.[39] On the other hand, the stabilization caused by the more efficient packing of planar biphenyl molecules is sufficient to overcome this energy difference and make the biphenyl molecule planar in crystalline biphenyl.[40]

Rotations of Methyl Groups. The local bonding environment of the methyl groups in BPA and in PEC with terephthalate- and isophthalate-derived ester linkages (Figure 1) is adequately represented in the 2,2-diphenylpropane molecule (Figure 2). There are three minima, at the base-point geometry and at methyl group rotations of 120° and 240° about the C_1–C_m axes relative to the base-point geometry. These three minima are slightly symmetry-inequivalent, since, as mentioned above, the three hydrogen atoms in the same methyl group have slightly different C_m–H_m bond lengths and C_1–C_m–H_m bond angles. There are three slightly symmetry-inequivalent maxima, at methyl group rotations of 60°, 180°, and 300° about the C_1–C_m axes relative to the base-point geometry. The highest maximum is at a 180° rotation. These maxima correspond to configurations in which the three C_m–H_m bonds are off by 9.25° from an orientation in which they would be exactly eclipsed relative to the bonds at C_m, when looking down the C_1–C_m bond.

The barrier to methyl group rotation will have its minimum value if one methyl group is at its most favored conformation while the other methyl group is going through its maximum-energy conformation. The two types of elementary motions under which this situation occurs are (a) the rotation of one methyl group while the second methyl group is stationary at its most favored conformation and (b) the simultaneous out-of-phase rotation of the two methyl groups in the same direction, so that when one of them is going through its transition state the other one is always at its minimum-energy conformation. These two types of elementary motions both have the same transition state geometry, which is illustrated in the schematic perspective drawing in Figure 5b.

The barrier to methyl group rotation will have its maximum value if both methyl groups are simultaneously going through their maximum-energy conformations. The two types of elementary motions under which this situation occurs are (a) the simultaneous in-phase rotation of the two methyl groups in the same direction and (b) the simultaneous rotation of the two methyl groups in opposite directions. These two types of elementary motions both have the same transition-state geometry, which is illustrated in the schematic perspective drawing in Figure 5c.

Any more complex motion of the two methyl groups can be described as a linear superposition of the four elementary motions described in the preceding two paragraphs, with a rotation barrier intermediate between the two extremes. The important quantities, therefore, are the rotation barriers for the two extreme cases schematically illustrated in Figure 5b,c.

It is useful to compare the methyl–methyl interactions in 2,2-diphenylpropane with those occurring in polyisobutylene (PIB),[41] where the chains are subject to large steric repulsions. Unlike BPA, where the small model molecule 2,2-diphenylpropane is adequate to study methyl group rotations, PIB chains are subject to large steric repulsions that computations on analogues of low molecular weight do not take into account since the steric strain is relieved at the chain ends. This observation points out the need to carefully consider the structures and energetics of each individual polymer when using calculations on model molecules to study polymeric properties.

The barrier heights were calculated under two different sets of conditions, namely, (a) with the torsional orientations of the phenyl rings kept fixed and (b) with the torsional orientations of the two phenyl rings allowed to separately reach their most favored configurations by reoptimization of the phenyl ring torsional orientations about the two C_1–C_p axes. Calculations of the second type give the lowest values of the rotation barriers. Comparison of the two sets of results makes it possible to assess the degree of cooperation, if any, required from the phenyl rings to rotate the methyl groups in the easiest manner possible.

The results of these calculations are summarized in Table IV. The C_m–C_1–C_m bond angle becomes slightly larger, and the C_p–C_1–C_p bond angle becomes slightly smaller, as first one and then the second methyl group are rotated into their transition-state conformations. This effect indicates that the methyl groups need more space in the nearly eclipsed transition-state structures than in the nearly staggered base-point structure. It is similar to the calculated increase of the C–C–H angle in ethane by 0.4° in going from the staggered to the eclipsed conformation, as mentioned in the subsection titled "Geometry of 2,2-Diphenylpropane". If the phenyl ring torsional orientations are allowed to relax, then the C_m–C_1–C_m bond angle opens a little more, and the C_p–C_1–C_p bond angle closes substantially less than if the phenyl ring torsional orientations are kept fixed.

The barrier to methyl group rotation is calculated to be 6.6 kcal/mol. If both methyl groups are forced to go through their highest energy conformations at the same time, the barrier is 14.7 kcal/mol, i.e., slightly more than twice the barrier for the case of only one methyl group being at its highest-energy conformation. These barriers are 8.1 and 16.1 kcal/mol, respectively, if the phenyl group torsional orientations are kept fixed. The amount of energy lowering obtained by the torsional relaxation of the phenyl groups is therefore almost exactly equal in both cases. This is because in both cases most of the energy lowering is caused by a small (~15°) reorientation of one of the two phenyl rings to remove a steric repulsion between a methyl hydrogen and a phenyl hydrogen in the ortho position. As will be seen in the following subsection, such small reorientations or "oscillations" of the phenyl rings from their orientations in the base-point geometry are extremely low-energy processes which can be expected to occur continuously. Therefore, the fact that the methyl group rotation barrier gets lowered from its already-low value of 8.1 kcal/mol to 6.6 kcal/mol by such small oscillations of the phenyl rings does not imply any special need for cooperation from the phenyl rings for the methyl rotations to occur.

The values calculated by PRDDO for these rotation barriers are expected to be quite reliable. For example, for ethane, the PRDDO barrier of 3.1 kcal/mol compares very favorably with the experimental barrier[42] of 2.9 kcal/mol. It is also of interest to compare the PRDDO barriers of 6.6 and 14.7 kcal/mol for one or both methyl groups in their transition state orientations, respectively, in 2,2-diphenylpropane with the CNDO/2 barriers[43] of 5.3 and 9.8 kcal/mol. The barriers calculated by PRDDO are higher than those calculated by CNDO/2. In addition, the barrier for the double methyl rotation transition state is less than twice the barrier for the single methyl rotation transition state with CNDO/2 but more than twice the barrier for the single methyl rotation transition state with PRDDO. In any case, the barrier to methyl group rotation as estimated by either technique is quite low, in the range of 5–7 kcal/mol.

Varadarajan and Boyer[9] have proposed that the DMS δ relaxation arises from methyl motions. A comparison of the computed methyl group rotation barriers with the activation energy of 7–8 kcal/mol estimated by Yee and Smith[10] for the DMS δ relaxation in polycarbonates where one or both methyl groups are replaced by ethyl groups strengthens the possibility that methyl motions are the cause of the DMS δ relaxation. If, as suggested by Yee and Smith,[10] an activation energy of 7–8 kcal/mole is indeed caused by the rotation of a pendant ethyl group, then the less hindered rotation of the smaller pendant methyl groups would be expected to occur with an activation energy of 5–7 kcal/mol and down to lower temperatures. The results of NMR experiments,[1] however, cast serious doubts on the identification of the methyl rotations as the cause of the DMS δ relaxation. These NMR experiments show that the methyl group rotational motions become slower than 10 KHz below a temperature of −120 °C, resulting in a "static" pattern for the spectrum. On the other hand, the DMS δ relaxation in BPA polycarbonate[9] occurs at about −220 °C. The most likely conclusion, therefore, is that the methyl group rotations are not the sole major contributors to the DMS δ relaxation, but that along with other, even lower energy motions such as oscillations of the methyl groups about their equilibrium positions in a potential well, ~30° oscillations of the phenyl rings (see below), and rocking motions of the carbonyl groups over a ~70° range (see below), they are among several types of contributing motions.

Rotations of Phenyl Rings Attached to Isopropylidene Groups. These types of phenyl rings are attached to an isopropylidene group at one end and to a carbonate group in the BPA fragments or an ester linkage in the ester fragments para to the isopropylidene group at the other end. Therefore, the best model molecules to use in studying these rotations have both phenyl rings attached at both ends to the functional groups which provide for chain continuation, instead of being terminated by a hydrogen atom at one end. The results of calculations on such very large model molecules are reported in the following paper. It is, however, useful to examine the rotations of the phenyl rings about the C_I–C_p bonds in 2,2-diphenylpropane and about the O–C_p bonds in diphenyl carbonate and phenyl benzoate. These much simpler calculations can also yield a wealth of useful information. In addition, their results can be compared with the results of calculations on the larger model molecules. Such a comparison can provide information about the degree of usefulness of calculations on smaller molecules when the best model molecule to study a particular problem is too large to be treated with the desired quantum mechanical techniques on available computers.

As mentioned above, the rotations of phenyl rings about the O–C_p bonds in diphenyl carbonate and phenyl benzoate are close to being free rotations. The higher one of the two slightly symmetry-inequivalent barriers (with one of them having the phenyl ring fully flipped compared to the other) encountered during this rotation in diphenyl carbonate (Table V) occurs at a torsional angle of 220° relative to the base-point conformation, and its height is only 1.6 kcal/mol. Similarly, the higher one of the two barriers encountered during this rotation in phenyl benzoate (Table VI) occurs at a torsional angle of 222.5° relative to the base-point conformation, and its height is only 2.9 kcal/mol. These small barriers are mainly caused by the bond angle openings required to reduce the steric repulsion between the doubly bonded oxygen atom and an ortho hydrogen atom in the rotating phenyl ring, as the phenyl ring is going through a configuration where it is nearly coplanar with the plane of the carbonyl group or the ester linkage.

The situation is much more complex for the rotations of the phenyl rings in 2,2-diphenylpropane (Table IV). First of all, torsional oscillations of up to ±30° of the phenyl rings only require ~3 kcal/mol of energy. Such oscillations will not be encountering any significant barriers, either intrachain or interchain, in the solid polymer. They should, therefore, occur down to very low temperatures and possibly contribute to the DMS δ relaxation. Up to ±30° oscillations of the phenyl rings have indeed been observed in NMR experiments.[12,17,19]

If one of the two phenyl rings in 2,2-diphenylpropane is held fixed at its equilibrium position while the other phenyl ring is rotated past it, two slightly symmetry-inequivalent minima are encountered, one being the base-point structure and the other one being the "fully flipped" structure at a torsional angle of 180° relative the base-point structure. There are two slightly inequivalent energy maxima, at rotations of 85° and 265° relative to the base-point structure, with the maximum at 85° having a slightly higher energy. (Because of the asymmetries in the geometry of 2,2-diphenylpropane, there is no reason for these two maxima to be exactly at rotations of 90° and 270°.) The barrier for this type of rotation is very high, i.e., 24 kcal/mol even after allowing for the torsional reorientation of the methyl groups to minimize methyl–phenyl interactions. This barrier is caused by a strong hard-sphere repulsion between ortho hydrogens on different phenyl rings. In spite of the opening of the C_p–C_I–C_p bond angle to 122.7°, which is itself a disfavored motion in the solid because it requires strong coupling from a symmetric vibrational "breathing" mode, causing bond angle distortions over a chain segment of considerable length, the contact distance between these two ortho hydrogens is still only 1.57 Å. Attempts to rotate one phenyl ring past the other, with the other phenyl ring being held fixed at any other torsional angle, also result in at least equally high rotation barriers. Therefore, the two phenyl rings will have to be moving synchronously in the lowest barrier pathways for phenyl ring rotation, to prevent the two phenyl rings from getting into each other's way.

The most effective synchronous phenyl ring pair motion in 2,2-diphenylpropane is the simultaneous rotation of the two phenyl rings by the same magnitude but in opposite directions (i.e., with opposite signs) about their respective C_I–C_p axes. Two barriers of almost identical energy are encountered during this type of motion, at rotations of 90° and 270° relative to the base-point structure. After allowing for the torsional reorientation of the methyl groups to minimize methyl–phenyl interactions, a barrier of 9 kcal/mol is obtained. The methyl groups torsional reorientation, which lower the barrier from 12.5 to 9 kcal/mol, is just a ~15° rotation of the methyl groups about their respective C_I–C_m axes, relative to their orientations in the base-point structure, to minimize steric repulsions between the methyl hydrogens and the phenyl hydrogens in the ortho position. The C_p–C_I–C_p and C_m–C_I–C_m bond angles in the transition state are both substantially smaller than the same angles in the base-point structure, with this effect being more pronounced in the higher energy transition state with unrelaxed methyl group orientations, showing that the most important effect is the minimization of methyl–phenyl interactions by the opening of C_p–C_I–C_m bond angles. The ~15° methyl group rotational reorientation is, however, a very small fluctuation from the base-point geometry, which can be expected to occur continuously. The significant reduction of the synchronous phenyl ring rotation barrier by allowing for this minor fluctuation does not, therefore, imply any special need for cooperation from the methyl groups in order for the synchronous phenyl ring rotation to occur. This conclusion is in agreement with the variable-temperature NMR data of Bubeck, Smith, and Bales.[2]

The 9 kcal/mol rotation barrier estimated here for synchronous phenyl ring rotations in 2,2-diphenylpropane is in agreement with the 10.1 kcal/mol barrier calculated[43] by using the CNDO/2 (complete neglect of differential overlap, version 2) technique. It is, however, in disagreement with Tonelli's conclusion,[44] based on simple van der Waals repulsion calculations, that the rotations in polycarbonate chains are nearly truly free rotations, as well as with the results of the MNDO calculations of Jones et al.[13] The MNDO technique has a tendency to miscalculate the relative energies of molecular conformations and especially to significantly underestimate rotation barriers.[27,31] Both Tonelli's calculations[44] and MNDO calculations (Table IIA) predict that the phenyl rings should be perpendicular to the carbonate linkages, in disagreement with crystallographic results.[35] PRDDO results are generally much more reliable for relative energies. However, more detailed optimization of the rotational transition-state geometry can be expected to also reduce the barrier estimated by PRDDO. The new, and thus far less extensively calibrated, AM1 technique apppears to be reliable in barrier ordering, if not in actual energies. Either method should be calibrated, where possible, by experiment.

Finally, the partially optimized 9 kcal/mol barrier also appears to disagree with the apparent activation energies deduced by O'Gara, Desjardins, and Jones[15] from their solution NMR data. Part of this apparent disagreement is caused by the incomplete optimization of the transition-state geometry in the present paper. On the other hand, future work along the lines recently reported by Roy, Jones, and Inglefield[11] can also help to remove this apparent discrepancy, by putting the interpretation of the results of the ^{13}C chemical shift anisotropy experiments on a firmer foundation. The NMR data can only be adequately interpreted if the fact that the phenyl ring flips are not restricted to occurring between two sharply defined energy minima but instead can occur from a considerable range of angles (±30°) traversed by the phenyl rings during their low-energy (<3 kcal/mol) large-amplitude oscillations is correctly accounted for. The observed frequency f of phenyl ring flips is related to the activation energy E_a, the Boltzmann factor kT, and the preexponential statistical weight w which is partially determined by the amount of phase-space available for the process, by the equation $f = w \exp(-E_a/kT)$. Therefore, for a given value of f, the value of E_a that satisfies this equation will be much smaller if the motion is assumed to occur between two sharp energy minima and hence to have a very small w.

The isopropylidene and the carbonate or the ester groups bonded to the phenyl rings are para to one another, with the C_1–C_p bonds lying almost on the same axis as the O–C_p bonds. Furthermore, the torsional angles which give the transition state relative to motion past the isopropylidene group are 45° to 50° out of phase with the torsional angles which give the transition state relative to motion past the carbonate group or the ester linkage. Therefore, the barriers in the BPA and PEC chains should occur at the same torsional angles as the barriers in 2,2-diphenylpropane. 90° rotations of the phenyl rings about O–C_p bonds in diphenyl carbonate and in phenyl benzoate give geometries with very low energies relative to the base-point structures used. Therefore, very little extra energy will be required to go over the rotation barrier when the diphenyl carbonate or phenyl benzoate fragment is linked to the 2,2-diphenylpropane fragment. It can, therefore, be estimated that the barriers for rotations of phenyl rings attached to isopropylidene groups will be 9–10 kcal/mol at the present level of approximation and probably slightly higher in the ester fragments than in the carbonate fragments. The facts that the rotations of the phenyl rings attached to isopropylidene groups require the motion of pairs of phenyl rings to occur synchronously and that even when considerably higher barriers have to be overcome than in methyl group rotations are in accordance with the observation by all the research groups whose NMR work has been referred to in this paper that the phenyl ring rotations will not be continuous but will rather be 180° flips.

The maximum 9–10 kcal/mol barrier estimated for these phenyl ring rotations based on intrachain interaction considerations and partially optimized transition-state geometries is smaller than the activation energy of 13–14 kcal/mol determined[8,10] for the DMS γ relaxation. The remaining part of the DMS γ-relaxation activation energy is probably due to interchain interactions, possibly including those of the types hypothesized in the models of Schaefer et al.[18] and of Mitchell and Windle,[45] where the existence of locally ordered packings of adjacent chain segments a few monomer units in length is assumed. A possibility raised by the present study, however, is that intrachain interactions might play a larger role in the description of the DMS γ relaxation than usually believed. Further experiments, and calculations involving more complete optimization of the transition-state geometry, are likely to shed some more light on these issues. The analysis of static correlation functions, as described by Fischer and Dettenmaier,[46] as well as the recent NMR data of Bubeck, Smith, and Bales,[2] is relevant in addressing the issue of whether lateral ordering is seen in amorphous polymers, supporting some kind of bundle or segmental ordering model. These results[2,46] seem to favor a random-coil type of model[47,48] over models which assume the existence of lateral ordering caused by the parallelization of chains.

The model of Yannas et al.,[49-51] which is based on force-field considerations and on motions of irreducible backbone segments, uses Tonelli's results[44] for the structural parameters of the model.[50] It would be useful to utilize the results of quantum mechanical computations, such as those described in the present paper, to define the values of the structural parameters in the model of Yannas et al.[49-51]

Rotations of Phenyl Rings Flanked by Two Ester Linkages. One-third of the phenyl rings in the ester fragments in PEC are flanked by two ester linkages instead of being attached to an isopropylidene group. NMR studies[1,2] indicate that the phenyl motions in the terephthalate units are somewhat more motionally restricted than the phenyl motions in BPA and that the phenyl motions in the isophthalate units are much more motionally restricted than the phenyl motions in the terephthalate units.

To understand the differences between the physical properties of BPA and PEC, it is crucial to understand the implications of the fact that one-third of the phenyl rings in PEC are in a completely different type of environment than in BPA. To understand the differences between terephthalic and isophthalic PEC, it is crucial to understand the differences in the motions of the phenyl rings in the isophthalate and terephthalate units. The techniques of applied theoretical chemistry are ideally suited to address these types of problems, both in the PEC and in other types of polymeric materials.

The results of rotation about the C_e–C_p bond in phenyl benzoate are relevant to this problem. When this type of rotation is carried out, the phenyl ring attached to C_e is gradually rotated away from its minimum-energy configuration coplanar with the ester linkage. There is a small and gradual increase in energy associated with the gradual elimination of the extended resonance between the phenyl ring and the ester linkage. The maxima for this rotation occur at the "perpendicular" conformations with rotation angles of 90° and 270°. The energy of the 90° conformation is 6.7 kcal/mol above the energy of the base-point geometry.

In the terephthalic and isophthalic PEC fragments, there are two such ester linkages coplanar with each ester phenyl ring. These two linkages are para to one another in terephthalate, and the two bonds connecting the phenyl ring to the two ester linkages are essentially coaxial with each other. Therefore, to a good approximation, it can be assumed that the barrier to rotation in the terephthalate will be almost entirely due to the loss of the extended resonance stabilization binding the phenyl ring to *both* of the ester linkages. Since the resonance stabilization in phenyl benzoate is 6.7 kcal/mol, the stabilization in the terephthalic ester fragment can then be estimated to be around $2 \times 6.7 = 13.4$ kcal/mol. A motion of one-third of the phenyl rings with an activation energy of ~13.4 kcal/mol would clearly be likely to contribute significantly to the DMS γ-relaxation.

The estimated barrier of ~13.4 kcal/mol for the rotation of terephthalic ester phenyl rings is distinctly higher than the estimated barrier of 9 to 10 kcal/mol for the rotation of phenyl rings attached to the isopropylidene groups, in agreement with the NMR studies[1,2] which indicate that the phenyl rings in the terephthalate units are more motionally restricted than the phenyl rings in BPA, with their motions ceasing on the NMR time scale at a higher temperature. It is, nevertheless, likely that the 3–4 kcal/mol difference estimated between the rotation barriers of the two types of phenyl rings overestimates the relative difficulty of the terephthalic ester phenyl ring motions. This is because the isopropylidene phenyl ring flips, which are more complex motions requiring pairs of phenyl rings to synchronize their motions to keep out of each other's way, will have lower preexponential statistical weights w than the terephthalic ester phenyl ring motions where a single phenyl ring can flip independently.

To more accurately pinpoint the energy barrier in the terephthalate fragments, to determine the types of motions which may be able to occur in the isophthalate fragments where the two ester linkages are meta to one another, and to more reliably compare the motions of the ester phenyls with the motions of the isopropylidene phenyls, it is necessary to carry out detailed calculations on larger clusters more accurately representing the different types of environments of the phenyl rings. The results of such calculations are reported in the following paper.

Trans,Trans versus Trans,Cis Isomerization about C–O Bonds. As mentioned above, Williams and Flory[26] estimated, on the basis of empirical force-field considerations, that in the polycarbonate of BPA trans,trans isomerization is preferred to trans,cis isomerization by 1.3 kcal/mol. As they also pointed out in their paper, such estimates are subject to a considerable latitude of uncertainty.

In the present calculations (Table V), the trans,trans conformation of the diphenyl carbonate molecule is preferred by 0.6 kcal/mol over the trans,cis conformation, with a barrier of 4 kcal/mol between these two conformations. The trans,cis local minimum is at a torsional angle of 150° about the C_c–O″ axis relative to the trans,trans geometry, while the rotation barrier is at a torsional angle of 206.5° relative to the trans,trans geometry.

To calibrate these results, the results obtained by using the PRDDO technique for a similar but simpler and much smaller molecule, dimethyl carbonate (Figure 6), can be compared with the results obtained by using the 3-21G technique which generally gives more accurate results but cannot be used for diphenyl carbonate because it requires an enormous amount of computer time. The 3-21G technique gives an improved description of the bonding by using a "split valence" basis set rather than a minimum basis set, thus allowing the valence electrons to relax into energetically more favored configurations. For dimethyl carbonate, 3-21G gives a relative energy of 1.7 kcal/mol for the trans,cis conformation and 8.6 kcal/mol for the energy barrier between the trans,trans and trans,cis conformations.[52] PRDDO gives 0.9 kcal/mol for the trans,cis conformation and 6.4 kcal/mol for the barrier. Both PRDDO and 3-21G predict that the trans,trans conformation will have C_{2v} point group symmetry (i.e., a twofold axis of rotational symmetry plus two mirror planes both containing the twofold axis but perpendicular to one another). Both methods also predict that the rotation barrier will occur at a torsional angle of 90° about the C_c–O″ axis and have C_1 symmetry, while the trans,cis conformation will occur at a torsional angle of 180° and have C_s symmetry.

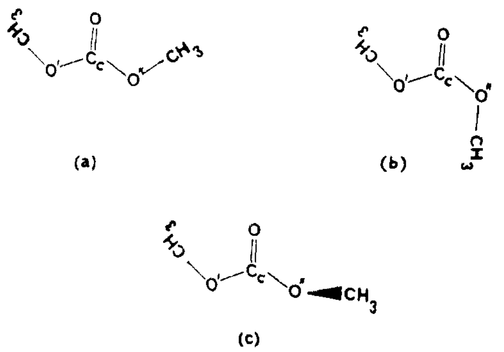


Figure 6. Schematic illustration of (a) *trans,trans*- and (b) *trans,cis*-dimethyl carbonate and (c) the transition state between them. C_c denotes a carbonate carbon. The two divalent oxygen atoms are labeled as O′ and O″.

The trends found for dimethyl carbonate in the PRDDO and 3-21G calculations are therefore the same, although the numerical values of the relative energies are different. Since dimethyl carbonate and diphenyl carbonate are similar molecules, a second and probably better estimate of the relative energies in diphenyl carbonate can be obtained by scaling each of the PRDDO relative energies in diphenyl carbonate with the 3-21G/PRDDO ratio for the same type of relative energy in dimethyl carbonate. This gives $0.6 \times 1.7/0.9 \cong 1.1$ kcal/mol for the relative energy of trans,cis diphenyl carbonate (very similar to the 1.3 kcal/mol value estimated by Williams and Flory[26]) and $4 \times 8.6/6.4 \cong 5.4$ kcal/mol for the rotation barrier.

Actually, for this type of rotation, the relative energy of the trans,cis conformation is a much more important quantity than the magnitude of the rotation barrier. This is because the existence of a low-lying trans,cis local minimum on the potential surface implies that a substantial amount of trans,cis configurations can become incorporated into the solid polymer as thermodynamic defects during manufacture, regardless of what the height of the rotation barrier separating the trans,trans and trans,cis conformations might be. The presence of two different types of local orientational environments around the carbonate linkages can then affect the winding of the chains and therefore properties such as persistence length and entanglement molecular weight, as well as enabling crankshaft-type cooperative intrachain motions to take place by simultaneous rotations of nearly parallel pairs of C_c–O bonds. An example of such a motion which becomes possible by the presence of both trans,trans and trans,cis configurations in the glassy polycarbonate, is the motion suggested by Jones[53] in his molecular level model for motion and relaxation.

At room temperature (25 °C), the Boltzmann factor kT is approximately 0.6 kcal/mol. Since there is a cis,trans conformation equivalent to the trans,cis conformation, conformations in which the bonding around one of the C_c–O bonds is cis rather than trans have a relative statistical weight of 2. Therefore, if the relative energy of the trans,cis conformation in the polycarbonate of BPA is assumed to be 1.1 kcal/mol, it can be estimated that the abundance of trans,cis and cis,trans conformations will be $[200 \exp(-1.1/0.6)]/[1 + 2 \exp(-1.1/0.6)] \cong 24\%$. Therefore, although the trans,trans conformation is strongly preferred, there are significant amounts of the trans,cis and cis,trans conformations, sufficient both to affect the winding patterns of the polymer chains and to enable crankshaft-type cooperative motions such as the one proposed by Jones[53] to take place.

The result of the present calculations, the estimate by Williams and Flory,[26] and the molecular level model proposed by Jones[53] for motion and relaxation in glassy polycarbonates all fit together very well both conceptually and in terms of the actual numerical values of the predictions made. Fourier transform infrared (FTIR) spectroscopy could be a valuable tool for examining these small relative energy differences and relating them to possible transitions from the higher energy trans,cis conformation to the lower energy trans,trans conformation during physical aging or to possible transitions from the trans,cis conformation to the more linear trans,trans conformation during tensile stress (as to be expected from considerations based on the theory of rubber elasticity). In this regard, it is interesting that Garcia[54] has reported the results of FTIR experiments on the trans–gauche energy difference and the trans/gauche abundance ratio for the glycol segment in polyethylene terephthalate, another system where two low-lying conformations exist. These experiments[54] show that there is no marked shift in the C–O stretching mode at 973 cm^{-1} during physical aging, and also suggest that the two low-lying conformations of the glycol segment in polyethylene terephthalate are <0.2 kcal/mol apart in energy. It would be valuable to perform similar experiments on BPA polycarbonate.

By contrast, there is no low-lying local minimum with cis bonding about the C_e–O bond in phenyl benzoate. This situation arises because of the relative proximity of the phenyl ring bonded directly to C_e. As the phenyl ring bonded to oxygen is rotated about the C_e–O bond into a cis orientation, severe steric repulsions arise between the two phenyl rings. As a result, it becomes necessary to get the two phenyl rings out of each other's way. This can best be accomplished by rotating the phenyl ring bonded to C_e by 90° to get it out of the way, a motion which, as was shown above, destabilizes the structure by making this phenyl ring perpendicular to the ester linkage and therefore destroying the extended resonance interaction. Still, no low-lying cis minimum is found, but only a complex motion (see Table VI) with an activation barrier of 18 kcal/mol which combines three rotational modes. In the solid polymers, these motions will be even more restricted than in the isolated phenyl benzoate molecule. For example, the ester phenyl ring will have to rotate into a conformation perpendicular to *two* ester linkages, with approximately twice the amount of resonance-breaking destabilization. It is clear, therefore, that the ester fragments of PEC will not have a low-lying configuration with cis bonding about the C_e–O bonds. This lack of low-lying local minima with cis bonding in the ester fragments is a very important difference between the carbonate and the ester fragments, whether the ester is terephthalic or isophthalic. It has important implications in terms of both the chain winding parameters of the ester fragments and the limitations it imposes on the cooperative intrachain motions which can occur.

Rocking Motions of Carbonyl Groups. The carbonyl group in diphenyl carbonate very adequately represents the local bonding environments of the carbonyl groups in the BPA fragments. As can be seen from Table V, large-amplitude rocking motions of the carbonyl groups, over a range of ~70°, only require ~3 kcal/mol and can couple with any one of the motions discussed above, as well as being among the contributors to the DMS δ relaxation. The results for positive and negative rocking angles are unequal because both of the phenyl rings are tilted by the same amount and in the same direction relative to the plane of the carbonate linkage, making the directions of positive and negative C=O rocking inequivalent. Since these C=O group rocking motions have been computed as rigid rotations without allowing for the resulting geometries to relax by reoptimization, it is clear that such rocking motions over the ~70° range will also be able to occur in the solid polymer without requiring much perturbation of the rest of the structure. On the other hand, when a C=O rocking motion of larger amplitude is performed so that the orientation of the C=O group goes outside of this ~70° range in either direction, the energy requirements rapidly go up. Such larger amplitude C=O rocking motions are similar to twisting someone's arm.

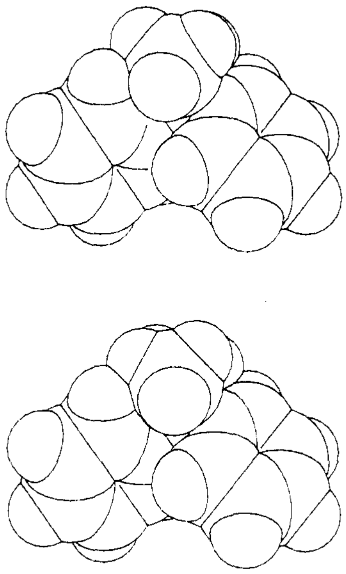


Figure 7. Space-filling representation of the structures defined in the last two lines of Table IV.

The ~70° range of low-energy rocking motions allowed by the present calculations is larger than the ~40° range found by Henrichs et al.[7] in a computer analysis of their variable-temperature ^{13}C NMR results. One reason for this difference might be the assumption made by Henrichs et al.[7] that the reorientation of the carbonyl group occurs as an activated process involving passage over an energy barrier. The present results relate to motion in a potential well, a more plausible event which the NMR results do *not* rule out.[7]

Molecular Volumes. The volume of 2,2-diphenylpropane (Table IV) has its maximum value for the minimum-energy base-point conformation. The volume decreases as the relative energy increases. This suggests that the methyl groups and the phenyl rings in the minimum-energy conformation are oriented in such a way as to minimize the steric repulsions between nonbonded hydrogen atoms on different methyl and phenyl subunits, resulting in the smallest amount of overlap between the atomic volumes of nonbonded atoms and therefore the largest amount of total volume occupied by the molecule. The phenyl ring hydrogens which are important in this respect are those in the ortho positions. This is illustrated in Figure 7, where the space-filling models corresponding to the last two lines of Table IV are shown. The apparently tiny bit of overlap between the phenyl and methyl hydrogens is responsible for the 3 kcal/mol energy difference. The rotation barriers are almost completely due to steric effects, with the magnitudes of the calculated rotation barriers following exactly the same order as the order of increasing overlap between the volumes of nonbonded atoms and hence the order of decreasing molecular volume. The magnitudes of the decreases in molecular volume in the rotational transition-state conformations are small, namely, 0.3% for the methyl group rotation transition state of 6.6 kcal/mol and 0.6% for the synchronous phenyl ring rotation transition state of 9 kcal/mol.

For diphenyl carbonate (Table V), there are deviations from the correlation of higher conformational energy with smaller molecular volume observed in 2,2-diphenylpropane. For example, the lowest energy, base-point trans,trans conformation only has the second highest molecular volume, and the trans,cis conformation only has the third highest molecular volume. The key factor here is the competition between resonance effects, which favor configurations where the plane of the carbonate linkage and the planes of the two phenyl rings are as coplanar as possible and steric repulsions between the doubly bonded oxygen atom and the hydrogen atoms in ortho positions on the phenyl rings, which favor configurations where the planes of these three planar subunits are as noncoplanar as possible. The tilted orientations of the two phenyl rings in the trans,trans and the trans,cis conformations are caused by a compromise being reached between maximizing resonance stabilization and minimizing nonbonded steric repulsions. On the other hand, a -26.5° rocking motion of the C=O group results in a maximally nonplanar conformation of very high molecular volume. Similarly, the relative energy of the transition state for the rotation about the C_c–O″ axis is higher than the relative energy of the transition state for the rotation about the O″–C_p axis; however, the transition state for the rotation about the O″–C_p axis is much more planar and therefore has a smaller molecular volume.

For phenyl benzoate (Table VI), the phenyl ring directly bonded to C_e is oriented at such an angle that it can be coplanar with the plane of the ester linkage and gain the full amount of resonance stabilization possible without causing steric repulsions. The transition-state structure for the rotation of the other phenyl ring about the O–C_p axis has the second phenyl ring also in a configuration which is almost lying on the same plane, with the increase in energy being mainly caused by the bond-angle distortions required to alleviate the resulting steric repulsions between one of its ortho hydrogen atoms and the doubly bonded oxygen atom. It is therefore closer to being planar than the lowest energy, base-point structure, resulting in a smaller molecular volume. On the other hand, the two transition states of higher energy have increasingly noncoplanar orientations for the planes of the ester linkage and the two phenyl rings, resulting in an increasingly larger molecular volume.

The changes in molecular volume for all the conformations listed in Tables II and III for diphenyl carbonate and phenyl benzoate are also small, being always less than 0.5% relative to the volume of the appropriate base-point structure.

Conclusions

Results were presented for the first part of a series of calculations intended to relate the properties of BPA polycarbonate and the PEC of BPA and terephthalic and/or isophthalic acids to their structure at the molecular level, by use of the techniques of applied theoretical chemistry. Quantum mechanical calculations utilizing the PRDDO technique were used to characterize the molecular motions associated with relaxations observed by DMS. The intrachain rotations were studied by means of detailed calculations on 2,2-diphenylpropane, diphenyl carbonate, and phenyl benzoate, which are representative of short chain segments.

The barrier to methyl group rotation was calculated to be ~6.6 kcal/mol. Oscillations of phenyl rings by ±30° only require ~3 kcal/mol. The barrier for the 180° flip of the phenyl rings attached to an isopropylidene group is estimated to be 9–10 kcal/mol. The barriers for the methyl group rotations and the flips of the phenyl rings attached to isopropylidene units are almost completely due to steric repulsions between nonbonded hydrogen atoms. The ester phenyl ring in terephthalic PEC is estimated to have a rotation barrier of ~13.4 kcal/mol, caused by the removal of an extended resonance stabilization effect. A much higher barrier and/or the need for a complex cooperative motion is expected for the ester phenyl ring rotation in isophthalic PEC. Cis–trans isomerization about C–O bonds should easily occur in the BPA fragments, with a resulting ~24% abundance of trans,cis and cis,trans conformations, providing a mechanism for crankshaft-type motion. This type of isomerization is not expected to occur in the ester fragments. Rocking motions of the carbonyl groups in the BPA fragments, over a range of ~70°, only require ~3 kcal/mol and can couple with and facilitate any one of these motions.

The results of detailed calculations on several larger clusters which more fully represent the different types of phenyl ring environments are reported in the following paper.[55] This paper also presents a summary of the most complete description of the relaxations observed by DMS that can be obtained by only considering isolated chain segments.

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Registry No. (BPA)(carbonic acid) (copolymer), 25037-45-0; BPA polycarbonate, 24936-68-3; (BPA)(carbonic acid)(terephthalic acid) (copolymer), 31133-78-5; (BPA)(carbonic acid)(isophthalic acid) (copolymer), 31133-79-6; (BPA)(carbonic acid)(isophthalic acid)(terephthalic acid) (copolymer), 31133-80-9; 2,2-diphenylpropane, 778-22-3; diphenyl carbonate, 102-09-0; phenyl benzoate, 93-99-2.

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Intrachain Rotations in the Poly(ester carbonates). 2. Quantum Mechanical Calculations on Large Model Molecules Fully Representing Each Type of Phenyl Ring Environment

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ABSTRACT: This paper continues the presentation of the results of a project to relate the properties of bisphenol A (BPA) polycarbonate and of its poly(ester carbonates) (PEC) with terephthalic and/or isophthalic acids to their structure at the molecular level, by use of the techniques of applied theoretical chemistry. Intrachain rotations and rocking motions of the phenyl rings were studied by means of detailed calculations utilizing the PRDDO and AM1 techniques on large molecules fully representing each type of phenyl ring environment. The major conclusions presented in the preceding paper, concerning the motions of the phenyl rings attached to isopropylidene groups and the motions of ester phenyl rings in terephthalic PEC, all remain valid, showing that the judicious use of calculations on smaller molecules is a valid procedure. There is no simple or cooperative low-barrier flipping motion for the ester phenyl ring in isophthalic PEC. In addition, the low-energy oscillation or rocking motion range for the isophthalic phenyl ring is only ±15°, while the range in terephthalic PEC is ±30°. The most complete description of the relaxations observed by dynamic mechanical spectroscopy, which can be obtained by only considering isolated chain segments, is also presented.

Introduction

This paper continues the presentation of the results of a project to relate the properties of poly(ester carbonates) (PEC) to their structure at the molecular level by use of the techniques of applied theoretical chemistry.

The work reported here consists of the continuation of the characterization of the molecular motions associated with relaxations observed by dynamic mechanical spectroscopy (DMS),[1-5] by use of quantum mechanical calculations utilizing the PRDDO[6] and AM1[7] techniques. Intrachain rotations and rocking motions of the phenyl rings were studied by means of detailed calculations on large molecules fully representing each type of phenyl ring environment. The reader is referred to the preceding paper[8] for a more detailed exposition of the problem, including a schematic illustration of the polymers being studied and most of the notation and acronyms being used.

Comparison of the present and the previous[8] results shows that the judicious use of calculations on smaller molecules is a valid procedure. The two sets of results are combined to provide the most complete description of the DMS γ and δ relaxations that can be obtained by considering isolated chain segments. This description is relevant both for the intrachain interactions in the solid

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