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Optical Anisotropies of Model Analogues of Polycarbonates

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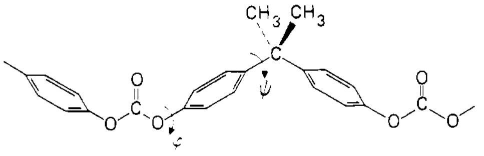
ABSTRACT: Depolarized light scattering and electric birefringence have been used to evaluate the optical anisotropy tensors for dimethyl carbonate, methyl phenyl carbonate, diphenyl carbonate, and 2,2-diphenylpropane. Rotational potentials about the phenyl axes in diphenyl carbonate and in diphenylpropane are estimated from force field calculations of interactions between nonbonded atoms. Rotations of the same sign ≈ |46°| of the phenyl groups in diphenylpropane and uncorrelated rotations ≈ |46°| about carbonate bonds are indicated. By combination of the information on structure, anisotropy, and conformation of these model compounds, the optical anisotropy tensors for carbonate and phenyl groups are estimated for these analogues of units occurring in the polycarbonate chain.

Introduction



The structure of the polycarbonate derived from 2,2-bis(4-hydroxyphenyl)propane presents a number of interesting features. The phenylene groups exhibit large anisotropies both in their electric (optical) polarizability[1,2] and in their magnetizability.[3] The carbonate group, like phenylene, is essentially rigid and coplanar; its configuration appears to be trans,trans to the virtual exclusion of other forms.[4] The optical anisotropy of the carbonate group is smaller than that of phenylene, but it possesses an appreciable dipole moment. Torsional rotations may occur about both of the bonds pendant to the phenylene group. Potentials affecting rotations ϕ about C^{ph}–O bonds are twofold symmetric. Examination of models assures that rotation about the pair of these bonds adjoining a given carbonate group should be independent. Rotations ψ about the pair of C^{ph}–C bonds at the isopropylidene group are dominated by severe steric interactions between ortho hydrogen atoms of the respective phenylene groups. The rotations for the bond pair at a given isopropylidene group, consequently, are strongly interdependent, rotations of the same sign being overwhelmingly preferred.

The investigations reported in this paper and in its sequel[5] were undertaken for the express purpose of examining the tenability of treating the anisotropy of the optical polarizability as a constitutive property. The question specifically addressed is the following: Can molecular polarizability tensors be formulated realistically as sums of contributions from constituent groups? Since addition of tensor contributions is required, the structural geometry must be accurately represented, and proper averaging over various conformations is essential. Being the tensor sum of constitutive contributions, the optical anisotropy may be an especially sensitive index of molecular conformation.[2,6]

In the work reported in this paper, we have examined the optical anisotropies of model compounds that embody the structural components comprising the polycarbonate chain. The four compounds chosen for this purpose are dimethyl carbonate (DMC), methyl phenyl carbonate (MPC), diphenyl carbonate (DPC), and 2,2-diphenylpropane (DPP). The intensities of depolarized Rayleigh scattering (DRS) by solutions of each compound in carbon tetrachloride have been measured over ranges of concentration. By extrapolation to infinite dilution, the results yield the (squared) molecular anisotropy defined by

$$\gamma^2 = (3/2)\ \mathrm{tr}\ \langle\hat{\alpha}\hat{\alpha}\rangle \qquad (1)$$

where tr denotes the trace and $\hat{\alpha}$ is the traceless, or anisotropic, part of the molecular polarizability tensor α; i.e.

$$\hat{\alpha} = \alpha - (1/3)(\mathrm{tr}\ \alpha)\mathbf{E} \qquad (2)$$

E being the identity matrix. The angle brackets in eq 1 and elsewhere below denote the configurational average.

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Table I
Summary of Experimental Results

compound	$\langle\gamma^2\rangle$, A^6	${}_{\mathrm{m}}K \times 10^{12}$, cm^5 statvolt^{-2} mol^{-1}	$\langle\mu^{\mathrm{T}}\hat{\alpha}\mu\rangle$, A^3 D^2	μ, D
DMC	3.86 ± 0.3	36.4 ± 3.6	0.130 ± 0.015	0.87 ± 0.05
MPC	31.6 ± 1.6			
DPC	72.0 ± 4.0	169.2 ± 18	−1.04 ± 0.12	0.87 ± 0.05
DPP	40.0 ± 2.0			

Molar Kerr constants ${}_{\mathrm{m}}K$ have been determined from measurements of electric birefringence of two of the compounds, DMC and DPC, dissolved in carbon tetrachloride. The molar Kerr constant is related to molecular parameters according to

$$ {}_{\mathrm{m}}K = \left(\frac{2\pi N}{15}\right)\left[\frac{\langle\mu^{\mathrm{T}}\hat{\alpha}\mu\rangle}{(kT)^2} + \left(\frac{\epsilon - 1}{n^2 - 1}\right)\frac{\mathrm{tr}\,\langle\hat{\alpha}\hat{\alpha}\rangle}{kT}\right] \qquad (3) $$

where N is the Avogadro number, μ is the permanent dipole moment, μ^{T} is its transpose, ϵ is the static dielectric constant of the medium, n is the refractive index, k is the Boltzmann constant, and T is the absolute temperature. The second term in eq 3 can be evaluated from γ^2 obtained through the DRS measurements. The first term, which is dominant for compounds such as the carbonates having substantial dipole moments, furnishes the quantity of interest, $\mu^{\mathrm{T}}\hat{\alpha}\mu$, this being the product of the square of the magnitude of the dipole moment and the component of $\hat{\alpha}$ parallel to the dipole moment.

Since the principal axes of $\hat{\alpha}_{\mathrm{DMC}}$ must coincide with the principal axes of the DMC molecule and hence are known, two parameters suffice to define $\hat{\alpha}_{\mathrm{DMC}}$. They may be determined from γ^2 and ${}_{\mathrm{m}}K$. As an arbitrary device, or convention, we identify $\hat{\alpha}_{\mathrm{DMC}}$ with the tensor contribution of the carbonate group. Differences between $\hat{\alpha}_{\mathrm{MPC}}$ and $\hat{\alpha}_{\mathrm{DMC}}$ are attributed to the phenyl group, according to this convention. Inasmuch as the principal axes of phenyl are likewise implicit in its structure, two parameters serve to define the effective tensor of this group as it occurs in these compounds. Hindrances to torsional rotation about the $\mathrm{C^{ph}}$–O bond are ill-defined; estimates of the conformational energy are not sufficiently accurate for the purpose. From the determinations of γ^2 for MPC and DPC, and of ${}_{\mathrm{m}}K$ for DPC, both $\hat{\alpha}_{\mathrm{ph}}$ for the phenyl group and the mean torsion angle ϕ can be determined. Independent support for the mean value thus obtained is provided by comparison with values of ϕ for analogous esters[7] and with the conformation of DPC in the crystalline state as determined by X-ray crystallography.[8]

Torsional angles specifying rotations of phenyl and methyl groups in DPP can be determined reliably and within narrow limits from calculations of conformational energies. Hence, the trigonometric averages required for evaluation of the conformational averages $\langle\gamma^2\rangle = (3/2)\langle\mathrm{tr}\,(\hat{\alpha}\hat{\alpha})\rangle$ and $\langle\mu^{\mathrm{T}}\hat{\alpha}\mu\rangle$ are susceptible to estimation within acceptable limits of uncertainty. The measured value of $\langle\gamma^2\rangle$ for DPP serves to fix one of the two parameters required to evaluate $\hat{\alpha}_{\mathrm{ph}}$ in DPP. The other parameter can be estimated satisfactorily from results for other aromatic compounds.

The polarizability tensors for the carbonate and phenyl groups in situations simulating their counterparts in the polycarbonate chain are thus determined. Compounding the inductive influences of the carbonate linkage with that of the isopropylidene residue, one may estimate the tensor applicable to the phenylene group in the polycarbonate chain. This tensor is applied in the following paper[5] to the analysis of the optical anisotropy of the polycarbonate molecule.

Experimental Section

Materials. Dimethyl carbonate (DMC) and diphenyl carbonate (DPC), stated to be of 99% purity, were obtained from Aldrich Chemical Co. The melting point of DPC was 80 °C (lit. mp 80 °C). The DMC contained solid foreign material and was therefore distilled before use. Methyl phenyl carbonate (MPC) was synthesized in good purity from phenyl chloroformate and methanol, using pyridine to suppress phenol formation. The sample had a refractive index of 1.4965 and a density of 1.145 g/mL. It identity was confirmed by proton NMR, which gave resonances at δ 3.9 and 7.1 with intensities in the ratio 3:5. Purity was checked by GPC and was found to be at least 99.9%. 2,2-Diphenylpropane (DPP) was obtained from Pfaltz and Bauer. Its melting point was 28–28.5 °C (lit. mp 29 °C).

Depolarized Rayleigh Scattering. The DRS measurements were carried out with an improved version[9] of the apparatus previously described.[10,11] It consists of a 15-mW He–Ne laser with vertical polarization exceeding 1000:1, a lens for partial focusing, a quartz sample cell of square cross section, 1 × 1 cm i.d., a Glan-Thompson analyzer prism with an extinction ratio better than 5×10^{-6}, a chopper operating at 1 kHz, an EMI 9558 (S-20) photomultiplier detector operated at 1 kV, and a PAR 186 lock-in amplifier phased to the chopper. Full details of the instrument, its calibration against samples of known scattering power, and the procedure for the analysis of data will be presented elsewhere.[9]

Measurements were carried out on carbon tetrachloride solutions at 25 °C. Intensities I_{HV} were converted to Rayleigh ratios R_{HV} by comparison with the previously determined intensity $I_{\mathrm{HV}} = 0.074\ (\pm 0.001) \times 10^{-6}\ \mathrm{cm}^{-1}$ for carbon tetrachloride.[10] The apparent optical anisotropy $\gamma_{\mathrm{app}}{}^2$ of the solute molecule at the given concentration was calculated according to

$$ \gamma_{\mathrm{app}}{}^2 = \Delta R_{\mathrm{HV,mol}}(\lambda/2\pi)^4[3/(n^2 + 2)]^2 15/\rho \qquad (4) $$

where $\Delta R_{\mathrm{HV,mol}}$ is the portion of the Rayleigh ratio attributed to the solute (see eq 24 of ref 11), λ is the wavelength of the light in vacuo, n is the refractive index of the solution, and ρ is the number density of molecules of solute. Measurements were repeated at several volume fractions of the solute. The molecular anisotropy γ^2 was obtained by extrapolation of $\gamma_{\mathrm{app}}{}^2$ to infinite dilution.

DRS measurements on DPC, MPC, DMC, and DPP are shown in Figure 1. Values of γ^2 obtained by extrapolation to infinite dilution are given in the second column of Table I.

Electric Birefringence. Measurements were carried out with a sample cell designed by Suter[12] which is completely rigid with brass electrodes separated by ceramic spacers. The dimensions of the cell are 0.35 × 1.0 × 14.5 cm. The quartz windows are secured between Teflon elastomer O-rings and metal plates held fast by four screws. The tension on each of the screws was adjusted until the background birefringence, due to distortion of the windows, was minimized. The remainder of the apparatus is similar to that used previously.[13,14] It consists of a He–Ne laser, polarizing and analyzing prisms, and a photomultiplier detector. A Tropel Model 100 single-frequency He–Ne laser was used to ensure that I_0 did not vary during the measurement. (The long-term stability after passing through the polarizer was 0.3%.) The power supply furnished a steady dc voltage (0–15 kV) across the electrodes of the cell. Birefringence introduced by application of the voltage was measured with a Babinet compensator (Karl Lambrecht, D/B/A Crystal Optics series no. 170). The compensating technique previously described[1,13,14] was employed in the determination of birefringences.

Values of the Kerr constants, $B = \delta/2\pi l E^2$, where δ is the retardation, l is the length of the cell, and E is the electric field strength, were determined for solutions of the several compounds

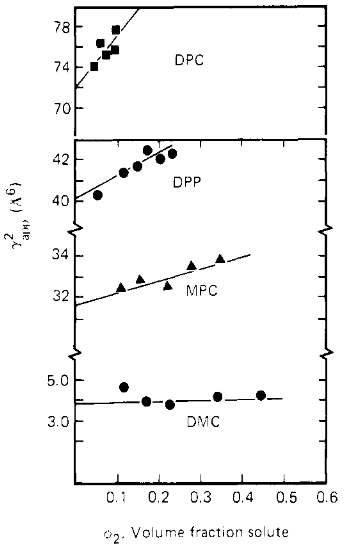

Figure 1. Apparent molecular optical anisotropies obtained from depolarized Rayleigh scattering intensities on solutions of diphenyl carbonate (DPC), diphenylpropane (DPP), methyl phenyl carbonate (MPC), and dimethyl carbonate (DMC) in CCl_4 at 25 °C at the volume fractions plotted on the abscissa.

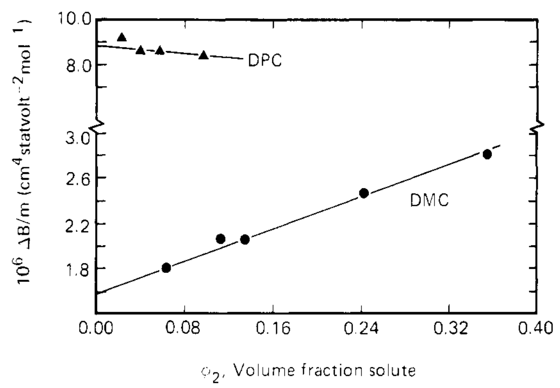

Figure 2. Ratios of excess Kerr constants ΔB to the molarity m (in mol cm^{-3}) for solutions of DPC and DMC in CCl_4 at 25 °C plotted against their volume fractions.

in carbon tetrachloride at concentrations ranging from 0.03 to 0.4 in volume fraction. The retardations were proportional to E^2 up to 4 × 10^4 V cm^{-1}. The molar Kerr constant ${}_{\mathrm{m}}K$ at infinite dilution was evaluated according to the relationship[13]

$$ {}_{\mathrm{m}}K = 54\lambda n(n^2 + 2)^{-2}(\epsilon + 2)^{-2}[\lim_{m\to 0} (\Delta B/m) \times 10^3 + V_s B_0] \quad (5)$$

where n and ϵ are the refractive index and dielectric constant, respectively, both of which differ little from the values for the solvent at the lowest concentrations used; $\Delta B = \Delta B_{\mathrm{soln}} - B_0$, where B_0 is the solvent birefringence, m is the concentration in moles/cm^3, and V_s is the solute molar volume in cm^3.[15] Values of $\Delta B/m$ for DPC and DMC are plotted against concentration in Figure 2. Molar Kerr constants for these substances obtained from the intercepts of the least-squares lines by use of eq 5 are presented in the third column of Table I.

Dipole Moments. The dipole moment of the carbonate group of DPC in CCl_4 was determined with a WTW dipole meter Model DM-01 at a fixed frequency of 2.0 MHz at 25 °C. Calculations were carried out as described in ref 16. Results are given in the last column of Table I.

Optical Anisotropies of Dimethyl Carbonate, Methyl Phenyl Carbonate, and Diphenyl Carbonate

Structure and Conformation. A recent X-ray crystallographic[8] analysis of DPC yields the information included in Figure 3. The bond lengths are close to those occurring in aromatic esters.[7,17] The bond angles differ slightly from values for the esters. Both ∠OC*O and ∠C*OC$^{\mathrm{Ph}}$ (where atoms of the carbonyl group are identified by asterisks) are about 2° greater than the corresponding angles in aromatic esters; compare Hummel and Flory.[7] They differ substantially from the earlier estimates of Williams and Flory.[4] The angle τ (see Figure 3) required for the analysis that follows is 67°. The same angle is assumed for DMC and MPC. The adoption of identical bond angles for aliphatic and aromatic carbonates is inconsequential, as will be apparent below. The torsion angles ϕ are 45° in the crystal.[8]

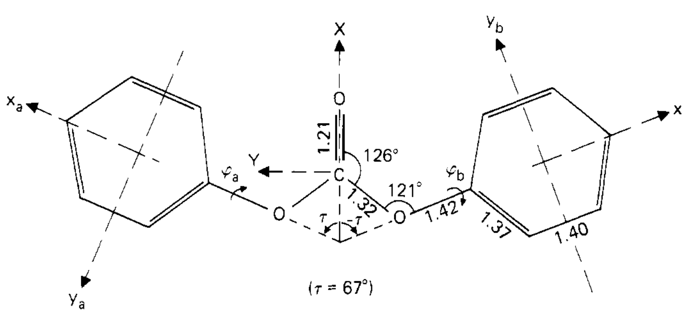

Figure 3. Molecular geometry of diphenyl carbonate (DPC). Bond lengths in Å and bond angles in degrees are from X-ray crystallographic analysis.[8] Coordinate systems $(xyz)_a$ and $(xyz)_b$ are embedded in the respective phenyl groups as indicated; the z axes normal to the phenyl rings assume the complementary directions as required for right-handed Cartesian systems. The molecular reference frame XYZ, likewise right-handed, is centered in the carbonate group. In the crystal[8] $\phi_a = \phi_b = 45°$.

The carbonate group, like the ester group, is planar; it may be presumed to be predominantly trans,trans.[4] Structural symmetry requires the torsional potential affecting rotations about the C$^{\mathrm{Ph}}$–O bond to be twofold symmetric about the planar ($\phi = 0, \pi$) and perpendicular ($\phi = \pm\pi/2$) conformations. The potential is dominated by two opposing effects: (i) steric interactions between the carbonyl oxygen O* and an ortho CH group of phenyl, which oppose coplanarity ($\phi = 0$) of the phenyl and carbonate groups, and (ii) electron delocalization favoring the planar configuration. Nonbonded interactions may be estimated by force field calculations. The delocalization energy may be represented by

$$E_{\mathrm{deloc}} = -B_\phi \cos^2 \phi \quad (6)$$

where B_ϕ is a constant. In crystalline phenyl benzoate ϕ = 65°.[17] The same angle occurs in the diphenyl ester of p-phenylenediacrylic acid.[18] A value of B_ϕ of 2–3 kcal/mol is required to reproduce this result.[7] The slightly larger bond angles in the carbonates (see above) ease the steric repulsions appreciably. Hence, the favored value of ϕ may be expected to occur at a smaller angle, as found in the crystalline state[8] (see above). Force field calculations using Hill's[19] modification of the 6-exp function for nonbonded interactions with parameters given elsewhere[7] are shown in Figure 4. A value of B_ϕ = 2 kcal/mol places the minimum at ϕ = 45°, the crystallographic value. Energies at the maxima at ϕ = 0° and 90° are 0.76 and 0.79 kcal/mol relative to the minimum. The crystallographic value of ϕ may, of course, be affected by intermolecular interactions peculiar to the crystal. Inasmuch as ϕ cannot be accurately estimated independently, we treat this angle as an adjustable parameter.

Polarizability Tensors for the Carbonates. The anisotropic part of the polarizability tensor $\hat{\alpha}_{\mathrm{C}}$ of the carbonate group, which we identify with that of DMC, is conveniently expressed in the molecular reference frame XYZ in Figure 3. With phenyl replaced by methyl, whose polarizability is cylindrically symmetric about the O–C

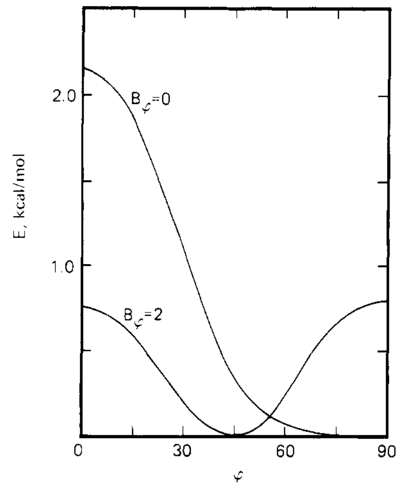

Figure 4. Conformational energy of DPC calculated as a function of torsion angle ϕ measured from coplanarity of the phenyl and carbonate groups. The parameter for the delocalization energy (see eq 6) was assigned the value $B_\phi = 2$ kcal/mol in order to locate the minimum at $\phi = 45°$, the value found in the crystalline state.[8]

axis, these are the symmetry axes of $\hat{\alpha}_C$, which therefore can be expressed by

$$\hat{\alpha}_C = \mathrm{diag}\ (\hat{\alpha}_{C,X}, \hat{\alpha}_{C,Y}, \hat{\alpha}_{C,Z}) \tag{7}$$

with

$$\hat{\alpha}_{C,X} + \hat{\alpha}_{C,Y} + \hat{\alpha}_{C,Z} = 0 \tag{8}$$

The tensors $\hat{\alpha}$ for MPC and DPC may be formulated by considering the hypothetical process

$$\text{-O-CH}_3 + \text{H-C}_6\text{H}_5 \rightarrow \text{-O-C}_6\text{H}_5 + \text{CH}_4$$

in which an O–C bond is replaced by an O–C^{ph} bond and H–C^{ph} is replaced by an aliphatic H–C bond. If differences between the polarizabilities of the two bonds of each pair are deemed to be negligible and if the major effects of substitution on the benzene ring could be ignored, then $\hat{\alpha}$ for MPC would be, simply,

$$\hat{\alpha}_{MPC} = \hat{\alpha}_C + \hat{\alpha}_{ph} \tag{9}$$

the tensors being expressed in the same reference frame and mutually oriented in accordance with structure and conformation of the MPC molecule. (The group tensor $\hat{\alpha}_{ph}$ actually includes $\hat{\alpha}_{C-H}$; in more literal notation it should be expressed as $\hat{\alpha}_{ph-H}$.) In recognition of the fact that the effects noted above cannot be ignored, we let them be subsumed in the effective tensor, $\hat{\alpha}_{ph}$, for the phenyl group as combined in the given molecule.[2,13] Thus, $\hat{\alpha}_{ph}$ may depend markedly on the substituents attached to the ring.[2,13]

Let the tensor(s) $\hat{\alpha}_{ph}$ be expressed in the xyz coordinate system(s) shown in Figure 3. The x axis is identified with the bond joining the substituent (O, in this case) to the ring, the y axis is parallel to the plane of the ring, and the z axis is perpendicular thereto. Obviously, x, y, and z are principal axes for the phenyl groups in the compounds considered. The present choice of coordinate system differs from that used previously[2,13] through interchange of the axes y and z.

We let $\Delta\alpha$ denote the excess polarizability parallel to the x axis relative to the mean transverse polarizability, and $\Delta\alpha^\dagger$ the anisotropy about the x axis; i.e.

$$\Delta\alpha = \alpha_x - (\alpha_y + \alpha_z)/2 \tag{10}$$

$$\Delta\alpha^\dagger = \alpha_y - \alpha_z \tag{11}$$

(In consequence of the interchange of y and z axes, the sign of $\Delta\alpha^\dagger$ is reversed from previous usage.[2,13]) Then

$$(\hat{\alpha}_{ph})_{xyz} = \Delta\alpha\ \mathrm{diag}\ (2/3, -1/3, -1/3) + \Delta\alpha^\dagger\ \mathrm{diag}\ (0, 1/2, -1/2) \tag{12}$$

Transformation of $\hat{\alpha}_{ph,a}$ for the first phenyl group in Figure 3 from coordinate system $(xyz)_a$ into the molecular reference frame XYZ is accomplished according to

$$(\hat{\alpha}_{ph,a})_{XYZ} = \mathbf{R}_Z(\tau)\mathbf{R}_x(\phi)(\hat{\alpha}_{ph})_{xyz}\mathbf{R}_x^{-1}(\phi)\mathbf{R}_Z^{-1}(\tau) \tag{13}$$

where $\mathbf{R}_x(\phi)$ is the transformation for a rotation ϕ of the phenyl group about the x axis, and $\mathbf{R}_Z(\tau)$ is the transformation for rotation about the Z axis through the angle τ measured from the XYZ system for the DPC molecule. Thus

$$\mathbf{R}_x(\phi) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \kappa & -\sigma \\ 0 & \sigma & \kappa \end{bmatrix} \tag{14}$$

where $\sigma = \sin\phi$ and $\kappa = \cos\phi$, and

$$\mathbf{R}_Z(\tau) = \begin{bmatrix} c & -s & 0 \\ s & c & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{15}$$

where $s = \sin\tau$ and $c = \cos\tau$. The angles τ and ϕ are defined in Figure 3; they are measured from the planar conformation in the rotation senses consistent with the directions of the Z and x_a axes, respectively.

Effecting the transformation of $(\hat{\alpha}_{ph})_{xyz}$ according to eq 13 and substituting the result in eq 9, together with substitution of eq 7 therein, one obtains the (symmetric) tensor $\hat{\alpha}_{MPC}$, with elements in the XYZ system given by

$$\begin{aligned}
\hat{\alpha}_{MPC,11} &= \hat{\alpha}_{C,X} + (c^2 - 1/3)\Delta\alpha + s^2(\kappa^2 - 1/2)\Delta\alpha^\dagger \\
\hat{\alpha}_{MPC,12} &= sc\Delta\alpha - sc(\kappa^2 - 1/2)\Delta\alpha^\dagger \\
\hat{\alpha}_{MPC,13} &= -s\sigma\kappa\Delta\alpha^\dagger \\
\hat{\alpha}_{MPC,22} &= \hat{\alpha}_{C,Y} + (s^2 - 1/3)\Delta\alpha + c^2(\kappa^2 - 1/2)\Delta\alpha^\dagger \\
\hat{\alpha}_{MPC,23} &= c\sigma\kappa\Delta\alpha^\dagger \\
\hat{\alpha}_{MPC,33} &= \hat{\alpha}_{C,Z} - 1/3\Delta\alpha - (\kappa^2 - 1/2)\Delta\alpha^\dagger
\end{aligned} \tag{16}$$

The tensor so defined is representative of the molecule shown in Figure 3 with the second phenyl group replaced by methyl. Subscripts a identifying the phenyl group are omitted in the equations 16.

Introduction of the second phenyl group in the b position in Figure 3 yields DPC. The required transformations of $(\hat{\alpha}_{ph,b})_{xyz}$ are $\mathbf{R}_x(\phi)$ and $\mathbf{R}_Z(-\tau)$. The result is

$$\begin{aligned}
\hat{\alpha}_{DPC,11} &= \hat{\alpha}_{C,X} + 2(c^2 - 1/3)\Delta\alpha + s^2(\kappa_a^2 + \kappa_b^2 - 1)\Delta\alpha^\dagger \\
\hat{\alpha}_{DPC,12} &= sc(\kappa_b^2 - \kappa_a^2)\Delta\alpha^\dagger \\
\hat{\alpha}_{DPC,13} &= s(\sigma_b\kappa_b - \sigma_a\kappa_a)\Delta\alpha^\dagger \\
\hat{\alpha}_{DPC,22} &= \hat{\alpha}_{C,Y} + 2(s^2 - 1/3)\Delta\alpha + c^2(\kappa_a^2 + \kappa_b^2 - 1)\Delta\alpha^\dagger \\
\hat{\alpha}_{DPC,23} &= c(\sigma_a\kappa_a + \sigma_b\kappa_b)\Delta\alpha^\dagger \\
\hat{\alpha}_{DPC,33} &= \hat{\alpha}_{C,Z} - 2/3\Delta\alpha - (\kappa_a^2 + \kappa_b^2 - 1)\Delta\alpha^\dagger
\end{aligned} \tag{17}$$

Analysis of Experimental Results. The two independent components of $\hat{\alpha}_C$ for the carbonate group may be deduced from the experimentally measured values of γ^2 and $\mu^T\hat{\alpha}\mu$ for DMC and from the dipole moment μ. Thus, according to eq 1, 7, and 8,

$$\gamma_{DMC}^2 = 3(\hat{\alpha}_{C,X}^2 + \hat{\alpha}_{C,Y}^2 + \hat{\alpha}_{C,X}\hat{\alpha}_{C,Y}) \tag{18}$$

and, since the dipole moment is directed along the X axis,

$$(\mu^{\mathrm{T}}\hat{\alpha}\mu)_{\mathrm{DMC}} = \mu^2\hat{\alpha}_{\mathrm{C},X} \tag{19}$$

From the experimentally determined values of $\gamma_{\mathrm{DMC}}{}^2$ and $(\mu^{\mathrm{T}}\hat{\alpha}\mu)_{\mathrm{DMC}}$ given in Table I, we thus obtain

$$\hat{\alpha}_{\mathrm{C}} = \mathrm{diag}\ (0.17, 1.04, -1.21)\ \text{Å}^3 \tag{20}$$

The mean-squared optical anisotropies $\langle\gamma^2\rangle$ for MPC and DPC are conveniently evaluated from sums of the averages of the squares of the elements of $\hat{\alpha}$ given by eq 16 and 17, respectively; i.e.

$$\langle\gamma^2\rangle = 3/2 \sum_{t,t'=1,2,3} \langle\hat{\alpha}_{tt'}{}^2\rangle \tag{21}$$

as follows from eq 1. With simplifications arising from the independence of ϕ_{a} and ϕ_{b}, evaluation of the mean squares of the elements requires $\langle\kappa^2\rangle \equiv \langle\cos^2\phi\rangle$, $\langle\kappa^4\rangle \equiv \langle\cos^4\phi\rangle$, and $\langle\sigma^2\kappa^2\rangle = \langle\kappa^2\rangle - \langle\kappa^4\rangle$.

The quantities $\langle\mu^{\mathrm{T}}\hat{\alpha}\mu\rangle$ for these compounds are related to the primary optical parameters according to

$$\langle\mu^{\mathrm{T}}\hat{\alpha}\mu\rangle_{\mathrm{MPC}} = \mu^2[\hat{\alpha}_{\mathrm{C},X} + (c^2 - 1/3)\Delta\alpha + s^2(\langle\kappa^2\rangle - 1/2)\Delta\alpha^{\dagger}] \tag{22}$$

and, since ϕ_{a} and ϕ_{b} are independent,

$$\langle\mu^{\mathrm{T}}\hat{\alpha}\mu\rangle_{\mathrm{DPC}} = \mu^2[\hat{\alpha}_{\mathrm{C},X} + 2(c^2 - 1/3)\Delta\alpha + s^2(2\langle\kappa^2\rangle - 1)\Delta\alpha^{\dagger}] \tag{23}$$

As a tentative approximation, we assign the torsion angle ϕ a discrete value ϕ^* and ignore fluctuations therefrom. This angle is treated as one of the parameters, together with $\Delta\alpha$ and $\Delta\alpha^{\dagger}$ that characterize the phenyl groups in MPC and DPC. Analysis of the experimental results for $\langle\gamma_{\mathrm{MPC}}{}^2\rangle$, $\langle\gamma_{\mathrm{DPC}}{}^2\rangle$, and $\langle\mu^{\mathrm{T}}\hat{\alpha}\mu\rangle_{\mathrm{DPC}}$ according to the relations above yields

$$\Delta\alpha = 4.0 \pm 0.15\ \text{Å}^3$$
$$\Delta\alpha^{\dagger} = 3.0 \pm 0.5\ \text{Å}^3$$
$$\phi^* = 46 \pm 1.0°$$

Calculated values of quantities determined experimentally are insensitive to $\Delta\alpha^{\dagger}$ but depend critically on ϕ^*. A change of ϕ^* by 1° effects changes of 6–10% in the values of $\langle\gamma^2\rangle$ and $\langle\mu^{\mathrm{T}}\hat{\alpha}\mu\rangle_{\mathrm{DPC}}$. The optical measurements therefore afford an independent and sensitive method for determining the effective value of ϕ. The result is in good agreement with both the crystallographic value and rough estimates based on conformational interactions.

Effects of fluctuations of ϕ and ϕ_{min} may be ascertained from the approximate potential function shown in Figure 4. According to this curve, calculated for $B_\phi = 2.0$ kcal/mol, $\langle\kappa^2\rangle \equiv \langle\cos^2\phi\rangle = 0.482$ and $\langle\kappa^4\rangle \equiv \langle\cos^4\phi\rangle = 0.315$, which may be compared with $\cos^2\phi^* = 0.483$ and $\cos^4\phi^* = 0.233$, respectively, for $\phi^* = 46°$. These averages give $\langle\gamma_{\mathrm{DPC}}{}^2\rangle = 77.2$ Å^6 compared with 72 Å^6 according to experiment (Table I). (The discrepancy for $\langle\gamma_{\mathrm{MPC}}{}^2\rangle$ is smaller; $\langle\mu^{\mathrm{T}}\hat{\alpha}\mu\rangle_{\mathrm{DPC}}$ is accurately reproduced.)

The value observed for $\langle\gamma_{\mathrm{DPC}}{}^2\rangle$ is reproduced exactly by averaging over the torsional potential calculated for $B_\phi = 1.4$ kcal/mol, which gives $\langle\kappa^2\rangle = 0.400$ and $\langle\kappa^4\rangle = 0.234$. The minimum in the function is shifted from ca. 45° to ca. 50°. Thus, the effect of assigning a discrete value to ϕ^* is reflected in a displacement of ϕ in the vicinity of $\phi = \phi_{\mathrm{min}}$ by ca. 5°, which is of no significance in reference to other evidence bearing on the torsional potential. Adoption of a fixed value of ϕ for present purposes is therefore justified.

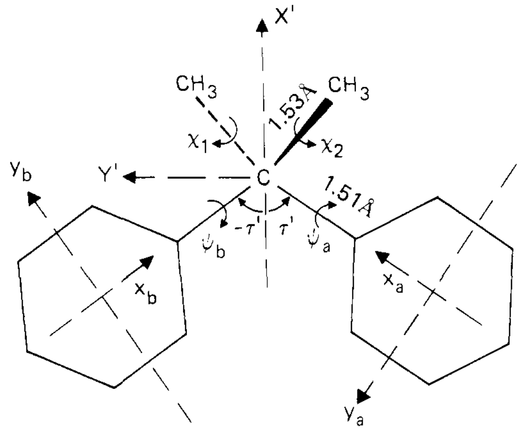

Figure 5. Molecular geometry of 2,2-diphenylpropane (DPP). Bond angles at the quaternary carbon are assumed to be tetrahedral. The *xyz* axes embedded in the phenyl groups correspond to those in Figure 3. The molecular reference frame $X'Y'Z'$ is affixed to the isopropylidene group.

The value found for $\Delta\alpha^{\dagger}$ is close to those for other aromatic compounds;[2,13] e.g., $\Delta\alpha^{\dagger}$ for benzene is 3.63 Å^3, for toluene it is 3.0 Å^3, and for $C_6H_5CH(CH_3)_2$ and the *p*-chloro derivatives of these compounds it is 3.0 ± 0.3 Å^3.[2,13] A somewhat larger value of 3.8 Å^3 was indicated for the bromo analogues.[13]

Optical Anisotropy of Diphenylpropane (DPP)

The structure of DPP is shown in Figure 5. Interactions between the ortho protons of the phenyl groups and the methyl groups introduce strong steric interdependences between the two main rotation angles, ψ_{a} and ψ_{b}. Conformational energies associated with rotations ψ_{a}, ψ_{b}, χ_1, and χ_2 about the bonds pendant to the quaternary carbon in DPP (Figure 5) were calculated using the Lennard-Jones 6–12 potential for each proximate pair of atoms. Parameters were chosen in the manner described previously.[20,21] An inherent threefold potential with a barrier of 2.8 kcal/mol was assigned to the C–CH$_3$ bonds.[20] Calculations for *n*-alkanes carried out in this manner are in close agreement with results obtained with the Hill potential employed above. Rotations about the C–C$^{\mathrm{Ph}}$ bonds were considered to be unaffected by an inherent potential in light of the negligible barrier in toluene.[22]

All bond angles in the isopropylidene group were assigned the symmetrical tetrahedral value. The effects of bond-angle strain should be negligible inasmuch as steric repulsions are small within the preferred range of the configuration space. Bond angles were therefore fixed in these calculations.

The calculated conformational energy surface displays minima at $\psi_{\mathrm{a}} = \psi_{\mathrm{b}} = \pm 46°$ and at $\chi_1 = \chi_2 = \pm 6°$. (Coincidence of ψ_{min} with ϕ^* is fortuitous.) The energy surface over ψ_{a} and ψ_{b} with $\chi_1 = \chi_2 = 6°$ is portrayed by the contour diagram shown in Figure 6a. Contours for χ_1 and χ_2 for $\psi_{\mathrm{a}} = \psi_{\mathrm{b}} = 46°$ are shown in Figure 6b. As is evident from these diagrams, the potential well is fairly broad, covering a range of about ±15° in both ψ and χ. Beyond these regions, severe steric interferences occur. Further energy calculations made by varying ψ_{a} and ψ_{b} for values of χ_1 and χ_2 differing from 6° yielded approximately the same shapes for the potential energy contours for the former pair. It suffices therefore to fix χ_1 and χ_2 at 6° and to confine averaging to ψ_{a} and ψ_{b} using the energy surface in Figure 6a for this purpose.

The DPP molecule can be considered to be formed from neopentane and two molecules of benzene according to the hypothetical process

$$C_6H_5\text{–}H + C(CH_3)_4 + H\text{–}C_6H_5 \rightarrow (C_6H_5)_2C(CH_3)_2 + 2CH_4$$

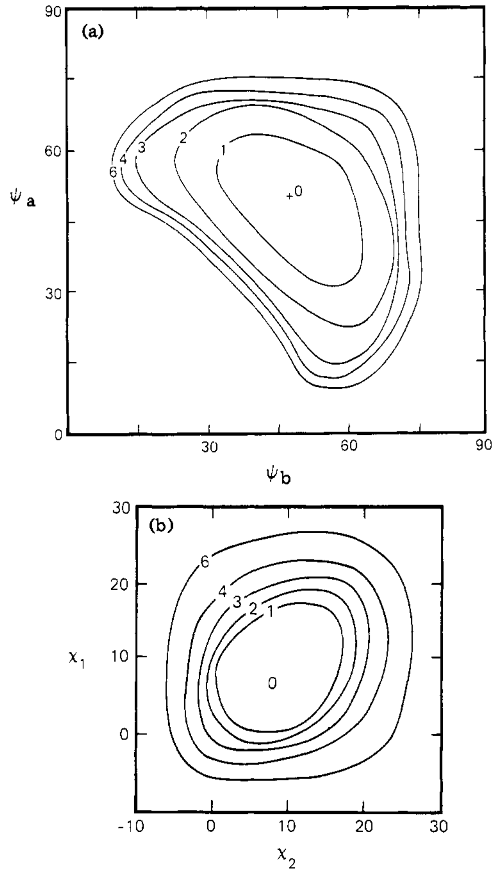

Figure 6. Energy surfaces calculated for DPP shown by contours at energies given in kcal/mol: (a) surface over ψ_a and ψ_b for $\chi_1 = \chi_2 = 6°$. (b) surface over χ_1 and χ_2 for $\psi_a = \psi_b = 46°$.

which involves no net changes in the numbers of C–C and C–H bonds. The neopentane molecule is symmetric. Hence, following the argument employed for the formulation of the anisotropy tensors for phenyl carbonates, we let

$$\hat{\alpha}_{DPP} = \hat{\alpha}_{ph,a} + \hat{\alpha}_{ph,b} \tag{24}$$

where the two phenyl tensors are presented in the same coordination system. It is to be understood that $\hat{\alpha}_{ph}$ must represent the phenyl group subject to the effects of the isopropylidene substituent to which it is attached in DPP. It may be expected to differ from $\hat{\alpha}_{ph}$ for the phenyl groups in DPC.

The polarizability tensor $\hat{\alpha}_{DPP}$ for diphenylpropane may be formulated in the reference frame $X'Y'Z'$ by analogy to the procedure employed for formulating $\hat{\alpha}_{DPC}$. Terms corresponding to those from $\hat{\alpha}_C$ are absent. The contribution of phenyl group b appearing on the left-hand side of Figure 5 is

$$(\hat{\alpha}_{ph,b})_{X'Y'Z'} = \mathbf{R}_Z(-\tau')\mathbf{R}_x(\psi)(\hat{\alpha}_{ph})_{xyz}\mathbf{R}_x^{-1}(\psi)\mathbf{R}_Z^{-1}(-\tau') \tag{25}$$

where $\mathbf{R}_x(\psi)$ is given by eq 14 with $\sigma = \sin \psi$ and $\kappa = \cos \psi$, and $\mathbf{R}_Z(-\tau')$ is defined by eq 15 with $c = \cos \tau'$ and $s = -\sin \tau'$. For phenyl group a, the corresponding transformation applies with $-\tau'$ replaced by τ'. With alterations following from these assignments, eq 17 and 21 are applicable to DPP.

Averages of the trigonometric functions of ψ_a and ψ_b were evaluated numerically from the potential energy surface of Figure 6a. Values thus obtained are $\langle \kappa^2 \rangle = \langle \cos^2 \psi \rangle = 0.432$ and $\langle \kappa^4 \rangle = \langle \cos^4 \psi \rangle = 0.209$. The corresponding effective angles are 48.9° and 47.5°, which are only slightly greater than $\psi_{min} = 46°$.

Use of the quoted configurational averages and adoption of 3.0 Å^3 for $\Delta\alpha^\dagger$ on the grounds that this parameter is little affected by substitution enable one to evaluate $\Delta\alpha$ from the observed value of $\langle \gamma_{DPP}^2 \rangle$ using eq 17 modified as described. The result thus obtained is $\Delta\alpha = 5.2$ Å^3. It exceeds $\Delta\alpha$ for the phenyl group in DPC owing, presumably, to the stronger effect of substitution with a benzylic group that allows greater electron delocalization than is offered by the oxygen of the carbonate group.

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