SHORT COMMUNICATIONS

MOLECULAR POLARIZABILITY ANISOTROPY OF CYCLOPROPANE*

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Specification of the optical polarizability ellipsoid of the cyclopropane system is an essential prerequisite for the investigation by the Kerr effect technique of conformational isomerism in molecules containing the cyclopropyl grouping. The principal electron polarizabilities of the cyclopropane ellipsoid can be obtained directly from the molar Kerr constant and the electron polarization (using equations 22, 27, and 30 of ref.1) since, from symmetry, \( b_1 = b_2 \neq b_3 \), where \( b_1 \) and \( b_2 \) are the in-plane polarizabilities and \( b_3 \) is directed perpendicularly to the plane of the three carbon atoms. The appropriate solution-state measurements from which the molar Kerr constant \( mK(C_3H_6) \) can be derived are summarized in Tables 1 and 2.

Experimental

Cyclopropane gas (\( > 99\% \) purity) from the Matheson Co., U.S.A., was dried over KOH pellets before being passed into weighed amounts of solvent.

Apparatus, techniques, symbols used, and methods of calculation have been described before.2-4 The quantities \( \Delta \epsilon, \Delta d, \Delta n, \) and \( \Delta B \) are the differences found between the dielectric constants, densities, refractive indices, and Kerr constants respectively, of the solutions containing weight fractions \( \omega_z \) of solute and of the appropriate solvent. The following data apply at 25°C for the solvents used:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \epsilon_1 )</th>
<th>( d_1 )</th>
<th>( (n_1) )D</th>
<th>( 10^7B_1 )</th>
<th>( 10^{12}sK_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>2.0199</td>
<td>0.77389</td>
<td>1.4235</td>
<td>0.059</td>
<td>0.0147</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.2725</td>
<td>0.87378</td>
<td>1.4973</td>
<td>0.410</td>
<td>0.0756</td>
</tr>
</tbody>
</table>

Discussion

Ramaswamy5 has recorded the electron polarization of cyclopropane as 13.93 c.e. from which the sum \( b_1 + b_2 + b_3 \) is calculable as 16.56.§ Substitution of the quantities \( mK = 1.0 \times 10^{-12}, \Delta P = \Delta P_2 = 14.5, \) and \( \Delta P = 13.93 \) in equations 27 and 30 of ref.1 leads to a polarizability anisotropy \( (b_1 - b_3) \) of \( \pm 1.45 \). Thus two possible sets of molecular polarizability semi-axes emerge for cyclopropane:

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§ The polarizability semi-axes of bonds or groups \( b_u, b_v, \) or \( b_\nu \) or of molecules \( b_1, b_2, \) or \( b_3 \) are quoted throughout in \( \text{Å}^3 \) units.
3 Le Fèvre, R. J. W., "Dipole Moments." 3rd Edn. (Methuen: London 1953.)

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$b_1 = b_2 = 6.00$ and $b_3 = 4.55$ or alternatively $b_1 = b_2 = 5.04$ and $b_3 = 6.49$. The error in the experimental molar Kerr constant results in an uncertainty of $\pm 0.02$ in $b_1$ and $b_2$ and $\pm 0.05$ in $b_3$ for each set of axes. The magnitude of our optical polarizability anisotropy for cyclopropane as a solute is larger than the value of $\pm 0.80$, obtained by Bridge and Buckingham from measurements of the depolarization ratio of Rayleigh scattering from cyclopropane gas (using light of wavelength $6328 \text{ Å}$).

### Table 1

**INCREMENTAL DIELECTRIC CONSTANTS, DENSITIES, REFRACTIVE INDICES, AND KERR CONSTANTS FOR SOLUTIONS AT 25°**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\varepsilon_1$</th>
<th>$\varepsilon_2$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
<th>$\alpha P_2$ (c.c.)</th>
<th>$R_D$ (c.c.)</th>
<th>$\mu$ (D)</th>
<th>$10^4 \alpha (mK_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_3\text{H}_6$</td>
<td>$-0.28$</td>
<td>$-0.257$</td>
<td>$-0.075$</td>
<td>$0.1$</td>
<td>$14.5$</td>
<td>$14.3$</td>
<td>$0$</td>
<td>$1.0 \pm 0.1$</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_6$</td>
<td>$-0.63$</td>
<td>$-0.346$</td>
<td>$-0.125$</td>
<td>$-0.90$</td>
<td>$14.3$</td>
<td>$14.5$</td>
<td>$0$</td>
<td>$2.8 \pm 0.3$</td>
</tr>
</tbody>
</table>

6328 Å. The $\text{C}_3\text{H}_6$ gas anisotropy together with $\beta P(\text{C}_3\text{H}_6) = 13.93$ c.c. leads to $b_1 = b_2 = 5.79$ and $b_3 = 4.98$ or $b_1 = b_2 = 5.25$ and $b_3 = 6.06$. The differences between the polarizabilities from the Kerr effect and those derived from the scattered light data may be attributed to a state-dependence of the molecular anisotropy and/or to our neglect of possible hyperpolarizability contributions to the Kerr effect. Buckingham, Prichard, and Whiffen have recently measured the molar Cotton--

Mouton constant of gaseous cyclopropane from which they evaluate the anisotropy of magnetic susceptibility \( k_3 - k_1 \) as \(-32 \times 10^{-30}\) e.m.u., i.e.

\[
\Delta K = K_3 - K_1 = -19.3 \times 10^{-6} \text{ c.c./mole},
\]
on the basis that \( k_3 - k_1 \) is negative. Their assignment of the sign of the magnetic anisotropy is qualitatively consistent with evidence from p.m.r. studies\(^9\)\(^-\)\(^12\) of cyclopropane derivatives which have clearly established the existence of a region of high shielding above the plane of the three carbon atoms. If \( b_1 > b_3 \), the negative sign of \( \Delta K \) is also consistent with the predictions of an approximate quantum mechanical relationship (see equation 41 of ref.\(^13\)) connecting anisotropies of diamagnetic susceptibility and electric polarizability. Thus we conclude that for cyclopropane (as a solute in cyclohexane) \( b_1 = 6.0 \) and \( b_3 = 4.5 \).

The electron polarizabilities of the three-carbon nucleus \( b_{1(n)} \) may be extracted from the molecular \( b \) values by deducting six C–H contributions [using \( b_{L(C-H)} = b_{T(C-H)} = b_{V(C-H)} = 0.65\)^\(^11\)] to give \( b_{1(n)} = b_{T(n)} = 2.1 \) and \( b_{V(n)} = 0.65 \). If each C–C bond is assumed to be axially symmetric about the intercentre line then the C–C bond parameters follow as \( b_L = 1.8 \), and \( b_T = b_V = 0.22 \) [cf. the semi-axes found\(^1\(^4\) for C(sp\(^3\))-C(sp\(^3\)) for which \( b_L = 0.97 \), and \( b_T = b_V = 0.26 \)]. Alternatively if the saturated C–C aliphatic bond ellipsoids are regarded as applicable to the cyclopropane system then by additivity the polarizability parameters of the carbon nucleus are calculated as \( b_{L(n)} = b_{T(n)} = 1.85 \), and \( b_{V(n)} = 0.78 \). The differences \( \Delta b_1 = b_1(\text{obs.}) - b_1(\text{calc}) \) are \( \Delta b_{L(n)} = \Delta b_{T(n)} = +0.25 \) and \( \Delta b_{V(n)} = -0.13 \), i.e. the polarizability and hence the electron mobility in the plane of the carbon nuclei is greater than that predicted for a system composed of saturated carbon–carbon sigma bonds alone.

Finally we note that \( \sigma_2(\Delta K) \) and hence the apparent molecular anisotropy of cyclopropane is greater in benzene than in cyclohexane. We attribute this\(^1\(^5\) to the formation of a very weak cyclopropane : benzene collision complex, stabilized by normal van der Waals interactions, in which there is a tendency for the \( C_3 \) axis of the cyclopropane to be coincident with the \( C_6 \) axes of neighbouring benzene molecules. The degree of such association would be small since the upfield shift of the cyclopropane protons in benzene relative to cyclohexane is less than 0.1 p.p.m. (using tetramethylsilane as internal reference).

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