POLARITY, POLARIZABILITY, AND STRUCTURE OF ESTERS.

1. ELECTROOPTIC PARAMETERS OF ESTER GROUPS

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Esters (RCOOR') make up a widely encountered and important class of organic compounds. Their spatial structure has been investigated repeatedly [1]. The literature offers very complete data on the rotation around the C(O)-O bond. It has been established that the ground-state conformation for the overwhelming majority of esters is the planar s-cis conformation shown in Fig. 1. The second energy minimum of the potential function for rotation around this axis corresponds to the planar s-trans conformation; this minimum lies significantly above the ground-state minimum ($\Delta H^\circ \approx 1-5$ kcal/mole). The rotation around the R-C(O) bond has also been investigated in sufficient detail. The internal rotation around the O-R' bond has been studied least thoroughly, and we do not know of any information on the predominant conformations appearing as a result of rotation around this bond for esters in solutions.

The absence of stereospecific proton spin–spin coupling constants prevents the solution of this problem by NMR; the general complexity of the spectrum in the vicinity of 1000 cm$^{-1}$

Fig. 1. Ground-state conformation and geometric parameters of esters.
Fig. 2. Determination of τ_E in (I) and (III); an explanation is given in the text.

Fig. 3. System of coordinates adopted for the determination of the polarizability ellipsoid of an ester group.

TABLE I. Experimental Values of the Dipole Moments (DM) and Molar Kerr Constants (mK) of the Esters RCOOMe.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>DM, D</th>
<th>mK · 10^{-12}, esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>Me</td>
<td>1.77±0.02</td>
<td>18±5</td>
</tr>
<tr>
<td>(II)</td>
<td>H</td>
<td>1.73±0.03</td>
<td>38±10</td>
</tr>
<tr>
<td>(III)</td>
<td>CCI₃</td>
<td>2.32±0.02</td>
<td>51±4</td>
</tr>
<tr>
<td>(IV)</td>
<td>Ph</td>
<td>1.81±0.08</td>
<td>96±6</td>
</tr>
</tbody>
</table>

hinders the use of vibrational spectroscopy for this purpose. On the other hand, the investigation of such rotation by measuring the Kerr effect [2] seems promising.

The quality of a conformational analysis performed by measuring the Kerr effect is largely determined by the quality of the parametrization of the theoretical calculations, viz., by the selection of the magnitude and direction of the dipole moment (DM) and the polarizability axes of the bonds and groups in the molecule. The electrooptic parameters previously used to investigate the spatial structure of esters led to incorrect results. For example, a conformation with an OCOR' dihedral angle equal to ~30° was assigned to a series of different esters in [3]. The correction of the electrooptic parameters from [3] which was subsequently undertaken in [4] did not improve the agreement between the experimental and theoretical Kerr constants even for the simplest esters. Apparently, the electronic interactions in the esteric fragment render the direct transfer of the polarity and polarizability parameters determined for other classes of organic compounds incorrect. The most acceptable procedure is to determine group characteristics, i.e., the magnitudes and directions of the dipole moments and the polarizability axes, for the esteric group as a whole. For this purpose we studied the esters RCOOMe, where R = Me (I), H (II), CCI₃ (III), and Ph (IV).

EXPERIMENTAL

The samples of the esters investigated were distilled in an inert atmosphere before the measurements. The purity of the products was monitored chromatographically.

The dipole moments and Kerr constants were measured in dilute solutions in CCl₄ at 25°C. The experimental values are presented in Table 1.

The molecular anisotropy (γ²) for compound I was determined from the degree of depolarization of the Rayleigh scattering of dilute solutions in CCl₄. It was equal to 1.80 Å⁸ (compare 1.65 Å⁸ in [5]).