CONFORMATION OF COMPOUNDS WITH TWO
GEMINAL HALOMETHYL GROUPS

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In the presence of two irregular groups at one atom, a large number of rotational isomers is possible, which hinders the investigation of the three-dimensional structure of such molecules. Compounds in which rotation occurs around the carbon-heteroatom bonds has been considered. In contrast to them, for 1,3-dihalopropanes and their derivatives, an equilibrium of more than two forms is possible [1, 2]. The use of additive methods — dipole moments (DM) and the Kerr effect — does not permit a determination of the position of equilibrium for 1,3-dihaloderivatives as a result of the equal polarity and close anisotropy of the polarizability of sterically unhindered conformers [2, 3]. Therefore polar substituents must be introduced adjacent to the central atoms of the system X—C—C—C—X.

The two-substituted 1,3-dihalopropanes (I)-(V) were investigated by the methods of DM, Kerr effect, Rayleigh light scattering, and IR spectroscopy:

\[ \begin{align*}
R^1 & \quad XCH_2CH_2X \\
R_2 & \\
X=R^1=R^2=Cl & ; X=Cl, R^1 \neq R^2=CH_3-O-CH_3 & ; \\
X=Cl, R^1 \neq R^2=0 & ; X=R^1=Cl, R^2=H & ; \\
X=R^1=Br, R^2=H & .
\end{align*} \]

Calculations of the DM, Kerr constants (KC), and molecular anisotropies were performed on the assumption of tetrahedral valence angles of the Csp3 atoms and a C1—C2—C3 angle in (III) of 120°. The values of the DM and axes of the ellipsoids of polarizability of the bonds and groups were used considering their surroundings and interactions. For the CH2—Cl bonds in (I), (II), and (IV), as well as C2—Cl in (IV), the DM 1.74 D was determined according to the relationship between the moments of the C—Cl bonds and the $^{35}$Cl NQR frequency [4] of compound (IV) [5], considering the experimental conditions (20° K); a comparison was made with $\nu(C1)$ in CH3Cl, measured at the same temperature. This moment considers the inductive interaction of the dipoles to a definite degree.

### TABLE 1. Polarity and Polarizability of 1,3-Dichloropropanes, Symmetrically Substituted at the C2 Atom

<table>
<thead>
<tr>
<th>Compound</th>
<th>Parameter</th>
<th>$\eta$</th>
<th>$\nu$</th>
<th>$\nu^*$</th>
<th>$\nu^g$</th>
<th>$\nu^s$</th>
<th>$\nu^g^g$</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>$\mu$, D</td>
<td>3.55</td>
<td>2.33</td>
<td>0.35</td>
<td>2.81</td>
<td>0.94</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>$10^{11} K$</td>
<td>-86</td>
<td>54</td>
<td>1.0</td>
<td>-64</td>
<td>-3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(II)</td>
<td>$\mu$, D</td>
<td>3.81</td>
<td>2.52</td>
<td>0.09</td>
<td>2.38</td>
<td>1.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$10^{11} K$</td>
<td>38</td>
<td>33</td>
<td>0.7</td>
<td>97</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(III)</td>
<td>$\mu$, D</td>
<td>4.73</td>
<td>3.30</td>
<td>0.50</td>
<td>3.05</td>
<td>2.33</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>$10^{11} K$</td>
<td>405</td>
<td>60</td>
<td>3.9</td>
<td>-123</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$10^{11} K$</td>
<td>13</td>
<td>6</td>
<td>3</td>
<td>16</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the CH$_2$Cl bonds in (I)-(IV), $b_L = 3.60$ Å$^3$ and $b_T = 2.00$ Å$^3$, as in ethyl chloride [6]; for C$_2$-Cl in (IV) $b_L = 3.83$ Å$^3$ and $b_T = 1.87$ Å$^3$, as in isopropyl chloride [7]. The dichloromethylene group has the following parameters: $m = 1.60$ D (experimental moment of CH$_2$Cl)$_2$, $b_1 = 4.64$ Å$^3$, $b_2 = 6.95$ Å$^3$ and $b_3 = 3.55$ Å$^3$ [8]. The polarity of the C-Br bonds as a function of their mutual orientation and the polarizability are cited in [9]; the polarity of the 3,3-dimethyloxethane fragment and the polarizability of the C-O bond are cited in [10]. For various conformations of (III) we consider the inductive interaction of the dipoles of C = O and C-Cl according to [11]: in the case of a trans-orientation of the C-Cl and C$_{sp^2}$-C$_{sp^3}$ bonds, $m(C=O) = 2.67$ D, $m(C-Cl) = 1.70$ D; in the case of a gauche-orientation 2.60 and 1.84 D, respectively. The polarizabilities of the C = O, C-C, and C-H bonds were used according to [12].

According to the nature of the substitution at the C$_2$ atom, the investigated compounds break down into two groups. For (I)-(III), substitution is symmetrical, so that four conformations of the C$_1$-C-C-C-C$_1$ chain are possible: trans-trans (tt), trans-gauche (tg), gauche-gauche with arrangement of the chlorine atoms on different (gg') or on the same (gg) side of the C-C-C plane.

The last form is considered impossible as a result of "parallel 1:3-interaction" [1]. The DM, molar Kerr constants $m_K$ and molecular anisotropies of compounds (I)-(III), calculated for these conformers, are cited in Table 1, together with the values determined experimentally in CCl$_4$ at 20°.

It should be noted that for polysubstituted propanes, as a rule, the number of conformers realized is less than the number of sterically permitted conformers (tt, tg, gg) [1]. Thus, for (I) an equilibrium of two forms was established in the liquid. Their identification and the determination of the position of the equilibrium were performed on the basis of a graphical comparison of the calculated and experimental DM, $m_K$, and molecular anisotropies [13] (Fig. 1).

The experimental data correspond to the equilibrium of two conformers, tg and gg', in a 1:9 ratio, although the negative $m_K$ (see Table 1) is evidence of the possible presence of a negligible fraction of the tt form. The predominance of the gg' conformation is quite understandable: each C-Cl bond in it is in the trans-position with respect to one of the bonds of the dichloromethylene group and in the gauche-position with respect to the other, as in the more stable conformer of 1,2,2-trichloropropane, a model compound possessing one irregular group in the corresponding surroundings [2]. In the tg form, the trans-C-Cl bond has a gauche-orientation with respect to the C$_2$-Cl bonds, which, on the basis of the data for 1,2,2-trichloropropane [2], corresponds to the participation in the equilibrium of no less than 90% of the gg' conformation according to the experimental results. Let us note also that the latter conformation in CCl$_4$ may be relatively profitable on account of electrostatic interactions, since it is practically nonpolar.

The sterically hindered gg form is not realized, in accord with the hypothesis of [1, 2, 14]. 3,3-Bis-(chloromethyl)oxethane (II) is an analog of 1,3-dichloro-2,2-dimethylpropane, containing a polar group without additional possibilities for internal rotation. The chloromethyl groups are bonded to a quaternary carbon atom, so that in the consideration only of the closest interactions, the enthalpies of all three permitted steric forms should be almost equal (deviation on account of a change in the angles when the four-membered ring is closed), and considering the statistical weights, the ratio tt:tg:gg' should be closed to 1:2:2.

There are no spectral data for (II). We obtained the IR spectra in the liquid and crystalline state, as well as of solutions in CS$_2$ and acetonitrile (Fig. 2). A comparison of them permits us to conclude that in the pure liquid and in solutions there is an equilibrium of at least two conformers: during crystallization part of the bands disappear (noted by an asterisk in Fig. 2). In the spectra of the liquid and solutions, these bands have low intensity, which is associated with the predominance of the form in which the substance