# POLARITY, POLARIZABILITY ANISOTROPY, AND CONFORMATIONS OF 1,2,2,2-TETRACHLOROETHYL ALKYL ETHERS

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In order to elucidate the three-dimensional and electronic structure of  $\alpha$ -chloro ethers, we studied chloromethyl, dichloromethyl, and 1-chloroethyl alkyl ethers [1]. In the present work, the electrooptical parameters obtained for the  $\alpha$ -chloro ethers, presented in our previous work [1], were used to determine the structure of 1,2,2,2-tetrachloroethyl alkyl ethers CCl<sub>3</sub>CHClOR, where R = CH<sub>3</sub> (I), C<sub>2</sub>H<sub>5</sub> (II), CH(CH<sub>3</sub>)<sub>2</sub> (III), and C(CH<sub>3</sub>)<sub>3</sub> (IV). In order to obtain a more accurate assessment of the effect of the alkoxy substituent, we also studied symmetrical ethers ROR, where R = CH<sub>3</sub> (V), C<sub>2</sub>H<sub>5</sub> (VI), CH(CH<sub>3</sub>)<sub>2</sub> (VII), and C(CH<sub>3</sub>)<sub>3</sub> (VIII). Independent structural information was also obtained by molecular mechanics calculations.

#### EXPERIMENTAL

Ethers (I)-(IV) were obtained by the treatment of chloral hemiacetals by  $SOCl_2$ . These hemiacetals were prepared from chloral and the corresponding alcohol according to McElvain and Curry [2]. After distillation in vacuum in an inert atmosphere, the samples had the following physical constants: 1,2,2,2-tetrachloroethyl methyl ether (I), bp 79-80°C (30 mm),  $nD^{25}$  1.4823; 1,2,2,2-tetrachloroethyl ethyl ether (II), bp 62-63°C (12 mm),  $nD^{25}$  1.4741; 1,2,2,2-tetrachloroethyl isopropyl ether (III), bp 74-76°C (10 mm),  $nD^{25}$  1.4666; 1,2,2,2tetrachloroethyl tert-butyl ether (IV), bp 57-58°C (1 mm),  $nD^{25}$  1.4733. Commercial samples of diethyl (VI) and diisopropyl ethers (VII) were fractionated over Na prior to the measurements. A sample of di-tert-butyl ether (VIII) was obtained in 30% yield from  $(CH_3)_3COI$ ,  $(CH_3)_3COH$ , and  $Ag_2CO_3$  according to Masada and Sakajiri [3], bp 106°C,  $nD^{25}$  1.3940,  $d_4^{25}$ 0.7574.

The dipole moments (DM) and molecular Kerr constants (KC) of all the compounds studied were found in dilute solution in  $CCl_4$  at 25°C (Table 1).

The molecular mechanics calculations were carried out using the method of Kabachnik et al. [6]. These calculations and those for the determination of the theoretical values of the DM and KC were carried out on ES-1010 and ES-1033 computers.

### RESULTS AND DISCUSSION

<u>Symmetrical Ethers.</u> The dipole moments of ethers (V)-(VIII) measured under identical conditions (see Table 1) do not form a monotonic series, apparently as a consequence of the concurrent change of both the polarity of the alkoxy group, which is given by the m(Alk-O) group DM, and the COC bond angle. Data have been given on the geometries of (V) and (VI) [7], but no information is available for (VII) and (VIII). The molecular mechanics method, assuming rigid bonds, was used to calculate the optimum angular conditions for ethers (V)-(VIII). The COC bond angle was found to be 113, 113, 116, and 136°, respectively. The first two values are in good accord with the values 111.7-112.6° found by various methods for (V) and (VI) [7]. The value of 116° for (VII) may be correlated with the value of 116.1° (COC bond angle in dipropyl ether [8]). We may conclude that molecular mechanics satisfactorily conveys the trend for change in the COC bond angle in symmetrical ethers.

Using the calculated value for the COC bond angle, m(Alk-0) is found to be 1.20 D for  $CH_3$  and  $C_2H_5$ , 1.34 D for  $CH(CH_3)_2$ , and 1.62 D for  $C(CH_3)_3$ . These values for the group DM were also used in our subsequent calculations.

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Fig. 1. Configuration and angle designations in the Newman projection along the (C1)C-O bond for (I)-(IV).

TABLE 1. Experimental Parameters for (I)-(VIII)

Compound	$\frac{\Delta \varepsilon}{\Delta \omega_2}$	$\frac{\Delta n_D^2}{\Delta \omega_2}$	$\frac{\Delta n_D}{n_1  \Delta \omega_2}$	$\frac{\Delta d}{d_1 \Delta \omega_2}$	$\frac{\Delta B}{B_1 \Delta \omega_2}$	Dipole moment,	$\begin{vmatrix} m^{K \cdot 10^{12}}, \\ e.s.u \end{vmatrix}$
(I) (II) (III) (IV) (V) (VI) (VI) (VII) (VIII)	6,079 6,494 7,480 7,779  4,016 3,223 1,751	$\begin{array}{c} 0,060\\ 0,063\\ 0,026\\ 0,052\\ -\\ -0,610\\ -0,536\\ -0,386\end{array}$	$\begin{array}{c} 0,014\\ 0,015\\ 0,006\\ 0,012\\ -\\ -0,144\\ -0,126\\ -0,089\\ \end{array}$	$\begin{array}{c} -0,043 \\ -0,108 \\ -0,163 \\ -0,147 \\ -0.554 \\ -0.546 \\ -0.522 \end{array}$	$\begin{array}{r} -58,\!48\\ -30,\!22\\ -28,\!69\\ -37,\!23\\ -\\ -14,\!28\\ -21,\!33\\ -8,\!56\end{array}$	2,49 2,66 2,95 3,10 1,32 * 1,34 1,42 1,21	$ \begin{vmatrix} -89,4\\-51,1\\-52,6\\-71,5\\-3,9 \\+\\-8.0\\-16,2\\-7,5 \end{vmatrix} $

\*CC1<sub>4</sub>, 25°C [4, p. 65]. +CC1<sub>4</sub>, 25°C [5, p. 50].

The Kerr constant for (V) calculated using the standard polarizability ellipsoid (PE) of the C-O bond ( $b_L = 0.89$ ,  $b_T = b_V = 0.46$  [9]) is 3.4 (here and subsequently, the polarizability is given in Å<sup>3</sup> and the Kerr constants are given in esu·10<sup>12</sup>). This value is in virtual accord with the experimental value. On the other hand, the theoretical Kerr constant for conformationally homogeneous (VIII) is 2.8, which differs even in sign from the experimental value. Ether (VIII) has a symmetry axis oriented in the direction of the DM. The molecular PE may be determined for this compound (see the work of Vereshchagin [9], p. 44) and  $C(CH_3)_3$ -O and C-O bond polarizability ellipsoids may then be calculated using an additive scheme. The required values for  $_{m}K$ ,  $\mu$ , and MRD = 41.14 Å<sup>3</sup> were determined in the present work. The molecular anisotropy measured in cyclohexane  $\gamma^2 = 4.18$  Å<sup>6</sup> was given by Vereshchagin [5, p. 172]. The molecular PE for (VIII) found using these data has semiaxes b, = 15.13, b, = 16.42,  $b_3 = 14.88$ ; the  $b_1$  axis is oriented in the direction of the molecular dipole moment. One axis lies in the plane of the COC bond angle, while the other is perpendicular to the former two axes. The selection between  $b_2$  and  $b_3$  remains arbitrary, which leads to two sets of roots for PE (C(CH<sub>3</sub>)<sub>3</sub>-O-):  $b_1 = \overline{7.31}$ ,  $b_2 = 7.70$ ,  $b_3 = 8.21$  (1) and  $b_1 = 8.24$ ,  $b_2 = 7.70$ 7.54,  $b_3 = 7.44$  (2); and for the PE of the C-O bond in di-tert-butyl ether:  $b_L = 0.70$ , bT = 0.37, bV = 0.88 (1a) and bL = 1.64, bT = 0.21, bV = 0.11 (2a) ( $b_2$  and bT lie in the COC plane). It is difficult to select between roots (1) and (2) and between (1a) and (2a) on the basis of the available data, but we note that the semiaxes for the first set have less deviation from the standard values.

The PE for ethers (VI) and (VII) cannot be tested due to the conformational nonhomogeneity of these compounds. Thus, two variants were tested in subsequent calculations.

<u>Tetrachloroethyl Alkyl Ethers.</u> The conformational scheme adopted for ethers (I)-(IV) is shown in Fig. 1. The zero values for dihedral angles  $\tau = (Cl_3)CCOC$  and  $\varphi = (Cl)COCR^1$  are found for the eclipsed conformation. Figure 1 shows  $\tau = 180^\circ$  and  $\varphi = 60^\circ$ .

Compound	Confor- mation	CICO	coc	τ	Φ	E <sub>rel</sub> , kcal/mole
(I) (H) (III)	A B C A C	114,2 114,1 114,1 114,4 114,0 114,4	$115,0 \\ 115,0 \\ 117,2 \\ 117,4 \\ 116,9 \\ 117,4 \\ 116,9 \\ 117,4 \\ 116,9 \\ 117,4 \\ 117,4 \\ 110,9 \\ 110,1 \\ 100,100,10 \\ 100,100,10 \\ 100,10 \\ 100,10 \\ 100,10 \\ 100,100,10 \\ 100,100,10 \\ 100,100,10 \\ 100$	170 168 140 168 139	$ \begin{array}{c} (60)\\ 181\\ 282\\ 68\\ 161\\ 69\\ \end{array} $	$ \begin{array}{c c} - \\ 0,00 \\ 1,33 \\ 1,81 \\ 0,00 \\ 0,56 \\ \end{array} $
(IV)	B —	114,4 117,0	121,8 126,2	144 191	(60)	2,29

TABLE 2. Bond Angles (deg) and Relative Conformer Energies from Molecular Mechanics Data

Prior to undertaking the conformational analysis of (I)-(IV) by molecular mechanics, we must convince ourselves that this method is capable of transmitting the structural features of  $\alpha$ -halo ethers. For this purpose, we calculated the potential curve for rotation about the (C1)C-O bond in methyl chloromethyl ether using the rigid bond approximation. The global minimum on this curve corresponded to a gauche conformation with optimized COC bond angle (115°) and CLCOC torsion angle (67°) in good accord with the experimental values 114.2° and 70.5°, respectively [10].

The analogously calculated potential curves for (I) and (IV) display a single, deep but rather sloping minimum at  $\tau = 120-240^{\circ}$ . In the case of the ethyl and isopropyl derivatives, the potential curves feature local minima related to change in  $\varphi$ . Table 2 gives the characteristics for the conformers corresponding to these minima.

Correlation of the calculated data indicates that the major conformations of tetrachloroethyl alkyl ethers have transoid arrangement of the  $Cl_3C-C$  and O-C bonds. Ethers (I) and (IV) should be conformationally uniform, while a conformational equilibrium related to rotation of the alkyl residue is possible for (II) and (III). The IR spectrum of (I) from 500 to 1700 cm<sup>-1</sup> is invariant in the range from -80 to +30°C, which indicates conformational homogeneity of the tetrachloroethyl alkyl ethers with regular substituents. In the IR spectra of (II) and (III), many bands in the range from 900 to 1500 cm<sup>-1</sup> have complex structures, indicating the existence of several conformers.

Additional information on the structures of (I)-(IV) was obtained from the DM and Kerr constant data. The same parameters were used in the calculation of the theoretical parameters as for other  $\alpha$ -chloro ethers [1]. In addition, the m(C-CCl<sub>3</sub>) group DM was derived from the polarity for CH<sub>3</sub>-CCl<sub>3</sub> (1.73 D [4, p. 52]) and the PE for the C-CCl<sub>3</sub> bond was estimated from the data for hexachloroethane (b<sub>1</sub> = 7.30, b<sub>2</sub> = b<sub>3</sub> = 8.50 [9, p. 95]). The parameters for the alkoxy groups were given above. When necessary, we used the bond angles derived from molecular mechanics calculations.

Analysis of the theoretical curves for DM as a function of angle  $\tau$  (the dipole moment is independent of  $\varphi$  in the first approximation) shows that agreement with the experimental values for (II)-(IV) is found for  $\tau = 180 \pm 10^{\circ}$ . According to the DM data, the value of  $\tau$  for (I) is 200°, which is somewhat out of the range of that common for the other compounds and may be related to imperfect parametrization for (I). The DM data unequivocally indicate predominantly transoid conformation of the Cl<sub>3</sub>C-C-O-C chain in these compounds. Conformations with markedly lower values of  $\tau$  (type C in Table 2) cannot exist in the mixture in amounts greater than 10-20%. On the whole, the conclusions derived from the DM and molecular mechanics data are in quantitative accord within experimental error.

The calculation of the theoretical dependence of the molar Kerr constant of (I) was carried out using the standard PE for the C-O bond for the methoxy group. Agreement with experiment was achieved for  $\tau = 170 \pm 10^{\circ}$ . In the calculation for the KC of (IV), variants (1) and (2) obtained above were taken as the PE of the tert-butoxy group. When using PE (1), the theoretical and experimental KC values coincide at  $\tau = 135 \pm 10^{\circ}$ , while in the case of PE (2), they agree for  $\tau = 170 \pm 10^{\circ}$ . The latter value of  $\tau$  is in good accord with all the available estimates for this parameter and, thus, ellipsoids (2) and (2a) correctly describe the contribution of the alkoxy group for (IV). Apparently PE (2a) better describes the anisotropy of the polarizability of the alkoxy group in the case of alkyl groups other than CH<sub>3</sub> in comparison with the standard PE of the C-O bond, although the reasons for this finding are not yet clear. Thus, the theoretical Kerr constants for all the permissible conformations of (II) and (III) calculated using the standard PE of the C-O bond are highly underestimated. The use of PE (la) in the additive calculation leads to the same results. On the other hand, the use of PE (2a) in the case of (II), for example, leads to theoretical Kerr constants of -63, -8, and +80 for conformations A, B, and C, respectively. The conformation populations in the equilibrium mixture may be estimated using their relative energies (see Table 2). If we neglect the entropy change, the conformation populations at the experimental temperature are 0.87, 0.09, and 0.04. Then, the theoretical Kerr constant of (II) may be estimated to be -52. The analogously calculated Kerr constant of (III) is -20. Taking account of the approximate nature of the calculation, the agreement of the experimental and theoretical KC is also satisfactory for this compound.

Thus, the structural data for tetrachloroalkyl ethers obtained by three methods are in good agreement and permit consideration of the conformations of these compounds in solution.

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#### CONCLUSIONS

l. The 1,2,2,2-tetrachloroethyl group in ethers is found with the  $CCl_3$  group trans to the O-C bond.

2. The polarizability ellipsoid of the C-O bond in the tert-butoxy group has major semiaxes  $b_L = 1.64$ ,  $b_T = 0.21$ , and  $b_V = 0.11$  Å<sup>3</sup>.

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