

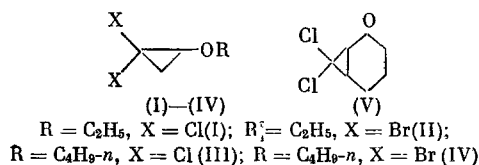
THE POLARITY AND STERIC STRUCTURE
OF CERTAIN CYCLOPROPYLALKYL ETHERS

B. A. Arbuzov, S. G. Vul'fson,
L. A. Monetina, and A. N. Vereshchagin

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Conformational investigations in the series of cyclopropane derivatives have been conducted rather widely for compounds in which internal rotation occurs around the C-C_{cycl} bond, especially for aromatic, unsaturated, and carbonyl derivatives. Here the main attention has been directed toward the investigation of the steric conditions of conjugation with the participation of the three-membered ring. In principle such an interaction is also possible for heteroatomic derivatives of cyclopropane. However, very few data on the steric structure have been obtained. For cyclopropylamine [1] and cyclopropylphosphine [2], checkerboard conformations are realized, and both heteroatom-hydrogen bonds have a gauche-orientation relative to the C¹-H bond. In such a conformation, conjugation of the unshared electron pair of the heteroatom with the orbitals of the atoms of the three-membered ring is possible [2]. We were interested in investigating the steric structure of cyclopropane derivatives, containing other heteroatoms, in particular, cyclopropylalkyl ethers.

We determined the dipole moments (DM) of a number of 1,1-dihalo-2-alkoxy-cyclopropanes (I)-(IV), formed in the addition of dichloro- and dibromocarbenes to alkylvinyl ethers



Under the condition of a "checkerboard" orientation of the bonds, three conformations with trans- and gauche-arrangement of the alkoxy group and the geminal C-H bonds are possible for them (Fig. 1). The polar halogen substituents disrupt the symmetry of the molecule, making the energy of the two gauche-conformations different, but at the same time permitting an investigation of the rotation of the alkoxy groups by the method of dipole moments. In the calculation of the moments of various steric structures according to a vector additive scheme, a significant role is played by the correct selection of the moments of the bonds and groups used. It is known that a change in the hybridization of the carbon atoms changes the polarity of the bonds formed by them; in particular, a definite set of additive values was obtained by cyclopropane derivatives [3]. Since it does not include C_{ring}-O bonds, their polarity must be determined.

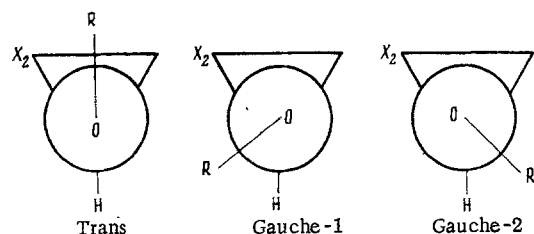


Fig. 1. Possible conformations of cyclopropylalkyl ethers.

A simultaneous determination of it and the unknown conformation of the molecules is possible on the basis of the data of two methods - DM and the Kerr effect. However, the Kerr constants (KC) of compounds (I)-(IV) depend on the internal rotation around the C-C bonds in alkyl radicals, without influencing the moment, but changing the anisotropy of the polarizability of the molecules. Therefore, we conducted a joint consideration of the data of the two methods for the bicyclic ether 7,7-dichloro-2-oxabicyclo[4,1,0]heptane (V), in which the closing of the ring limits the number of possible rotational isomers.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Branch of the Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 2, pp. 331-334, February, 1975. Original article submitted May 28, 1974.

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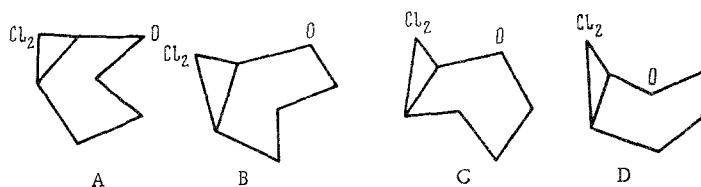


Fig. 2. Possible conformations of 7,7-dichloro-2-oxabicycloheptane: A, B) half-chair; C) anti-boat; D) syn-boat.

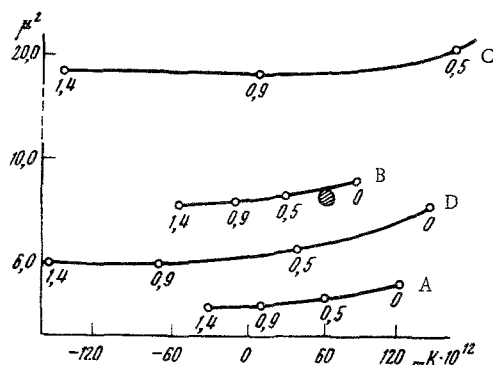


Fig. 3

Fig. 3. Dependence of the squares of the dipole moments on the Kerr constants of the conformers A-1 of 7,7-dichloro-2-oxabicycloheptane in the case of variation of the moment of the C-O bond from 0 to 1.40 D (notations of the conformers the same as in Fig. 2).

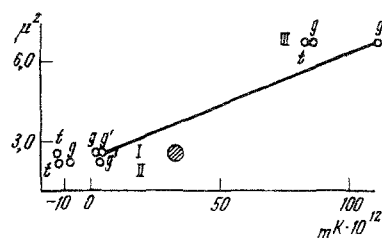


Fig. 4

Fig. 4. Relationship between the squares of the dipole moments and Kerr constants of cyclopropylalkylethers (II). I) Trans, II) gauche-1, III) gauche-2 conformations relative to the C(ring)-O bond; t, g, g') conformations relative to the O-Csp³ bond.

The conformations of the six-membered rings, condensed with three-membered rings, are of great interest, since stability of the boat form has been detected for them [4]. No such investigations were conducted for heterocycles.

Four possible conformations of the molecule of (V) were considered (Fig. 2). Their DM and KC were calculated using the parameters of cyclopropane derivatives, cited in [3, 5]. The DM of the C-O bonds were assumed equal to 1.40 D (from the experimental value of the moment of tetrahydropyran [6]); the polarizability of the C-H, C-C, and C-O bonds is cited in [7]. The DM and KC of possible conformers of (V) calculated with the indicated value of (C-O) are cited in Table 1, together with the experimental values. As can be seen, the DM is close to that calculated for a half-chair, B, but all the calculated KC differ from the experimental value even in sign. For an analysis of the polarity and polarizability of (V) we used the assumption indicated above of a change in the moment of the C-O bond when a carbon atom is inserted into the cyclopropane ring. The change in the squares of the DM and KC of the conformers A-1 in the case of variation of the moment of this bond in (V) from 0 to 1.40 D is given in Fig. 3. The molecular DM are practically independent of the value of $m(\text{C-O})$, while it influences their KC greatly. A comparison of the calculated data with the experimental data permits us unambiguously to assign the half-chair conformation B to (V) and simultaneously to determine the moment of the C_{ring}-O bond; it is equal to 0.2 D.

Calculations were performed for (I)-(IV) with this value. For the ethyl ethers (I) and (II) it is possible to calculate the KC. Rotation around the O-CH₂CH₃ bond, while not influencing the DM, leads to three KC for the trans (t) and two gauche (g, g') orientations of the C_{ring}-O and CH₂CH₃ bonds. The relationship between the squares of the DM and KC [8] for (II) is cited in Fig. 4. It is evident that this compound in CCl₄ is represented by a mixture of conformers with a 0.2 content of gauche-2. The selection of the second form on the basis of the experimental data is impossible, but the obvious steric hindrance of the trans-conformer forces us to give preference to gauche-1. It should be noted that the best agreement of the

TABLE 1. Polarity and Polarizability of Dichlorooxabicyclo[4,1,0]heptane

Conformation	μ, D	$m^{K \cdot 10^{12}}$	Conformation	μ, D	$m^{K \cdot 10^{12}}$
A	2,13	-32	C	4,32	-143
B	2,88	-54	D	2,52	-155

TABLE 2. Dipole Moments and Kerr Constants of the Investigated Compounds

Compound	$\Delta\epsilon/\Delta\omega$	$\Delta d/\Delta\omega$	$\Delta n_D/\Delta\omega$	$\Delta n_D^2/\Delta\omega$	$\Delta B/\Delta\omega$	μ, D	$m^{K \cdot 10^{12}}$
(I)	4,160	-0,243	-0,024	-0,109	76,741	1,86	90
(II)	2,134	-0,064	0,026	0,116	18,510	1,59	34
(III)	3,611	—	—	-0,058	—	1,84	—
(IV)	1,706	—	—	-0,194	—	1,62	—
(V)	11,109	-0,115	0,041	0,172	52,920	3,04	62

calculated and experimental data is achieved in the case of a gauche-conformation of the chain $C_{ring}-O-CH_2CH_3$. Analogous results were obtained for (I). The DM corresponds to a 0.4 content of the gauche-2 form (μ_{trans} 1.31, $\mu_{gauche-1}$ 1.22, $\mu_{gauche-2}$ 2.47, μ_{exp} 1.86 D). The butyl ethers (III) and (IV) have DM that practically coincide with those found for the ethyl analogs (Table 2), which is an indication of identity of the conformations relative to the $C_{ring}-O$ bond.

EXPERIMENTAL METHOD

The compounds (I) and (III) were produced according to the methods of [9, 10].

1,1-Dibromo-2-ethoxycyclopropane (II). (II) was produced by the addition of dibromocarbene (from $CHBr_3$ and $t-BuK$) in pentane to ethylvinyl ether at -10 to 0° . The isolation and purification by the usual methods for adducts of carbenes were conducted as rapidly as possible and without access to light, since the product is unstable, yield 25%; bp $62-63^\circ$ (8 mm); n_D^{20} 1.5060; d_4^{20} 1.8003. Found: C 24.30; H 3.29; Br 65.85%; MR 40.26. $C_5H_8OBr_2$. Calculated: C 24.60; H 3.20; Br 65.60%; MR 40.97.

1,1-Dibromo-2-butoxycyclopropane (IV). Analogously to (II), from vinylbutyl ether we obtained (IV) with a yield of 20%, bp $28-30^\circ$ (0.15 mm); $n_D^{25.5}$ 1.4172. In the IR spectra of (II) and (IV) the bands of the double bond were absent; tests with $KMnO_4$ are negative. Found: C 30.85; H 4.40; Br 58.76%. $C_7H_{12}OBr_2$. Calculated: C 30.88; H 4.41; Br 58.2%.

The adduct (V) was produced analogously, yield 68%, bp 87° (13 mm); $n_D^{22.5}$ 1.4955; cf. [11].

The dipole moments and Kerr constants were determined in CCl_4 at 20° analogously to [5]. The experimental data are cited in Table 2.

CONCLUSIONS

1. The dipole moment of the $C-O$ bond, containing a cyclopropane carbon atom, was determined.
2. 1,1-Dihalo-2-alkoxycyclopropanes in CCl_4 are represented by two conformers with a gauche-orientation of the system $H-C_{ring}-O-R$.
3. 7,7-Dichloro-2-oxabicyclo[4,1,0]heptane exists in a half-chair conformation.

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