ELECTRONIC AND SPATIAL STRUCTURE OF DICHLOROMETHYL ARYL ETHERS

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α-Haloalkyl aryl ethers are examples of compounds whose properties are determined by competitive orbital interactions with participation of the lone pairs of an O atom [1, 2]. In the present work we used ^{35}Cl NQR, IR spectroscopy, and measurements of dipole moments (DM) and birefringence in an electrical field to study the dichloromethyl aryl ethers (DCME's) p-$RC_6H_4OCHCl_2$ with R = H(I), Me (II), t-Bu (III), F (IV), Cl (V), CH_2Cl (VI), NO_2 (VII), and OCH_3 (VIII).

EXPERIMENTAL

Compounds I-V, VII, and VIII were obtained by chlorination of the corresponding aryl formates by PCl_5 as in [3]. The aryl formates were obtained by esterification of the phenols by formic–acetic anhydride in the presence of pyridine according to [4].

4-Chloromethylphenyl Dichloromethyl Ether (VI). A 19.1-g portion (0.1 mole) of II and 1 g of PCl_5 were placed in a two-necked flask equipped with a reflux condenser and a tube reaching the bottom for the supply of gases. A moderate stream of dry Cl_2 was passed through the mixture for 12 h at 195°C. Distillation gave 4.3 g of II with bp 103-106°C (15 mm) and 9.4 g (53%) of VI with bp 150-160°C (15 mm). PMR spectrum (CCl_4, δ, ppm): 4.45 s (2H, $C\underline{H}_2Cl$), 7.30 s (1H, $C\underline{H}Cl_2$), 6.9-7.4 m (4H, $C_6\underline{H}_4$).

The physical constants of the compounds obtained are presented in Table 1. The IR spectra were recorded on a UR-20 spectrophotometer; the intensities of the bands for dilute solutions in CS_2 were determined by direct integration over the contour followed by extrapolation to infinite dilution. The ^{35}Cl NQR spectra were recorded at 77°K on an IS-3 pulse spectrometer. The dipole moments and the molar Kerr constants were determined for dilute solutions in CCl_4 at 25°C.

RESULTS AND DISCUSSION

The properties of unsaturated chlorinated ethers are determined to a considerable extent by the orbital interactions involving the lone pairs of the O atoms and, in the case of DCME's, by the interactions with the orbitals of the aromatic ring and the C–Cl bond.

The constants σ_R^0 can serve as quantitative characteristics of n, π interactions. The relationship of these characteristics to the intensities of bands in the vibrational spectra of aromatic molecules was pointed out in [6]. Table 2 presents the values of the integrated intensities of the ν_8 band (or bands) for I-VI and the values of $\sigma_R^0(OCHCl_2)$ calculated on their basis (values of σ_R^0 from [6] were used in the calculations). The mean value of $\sigma_R^0(OCHCl_2)$ was −0.25, which is in good agreement with the values −0.230 and 0.255 (an absolute value) from [5]. It should be noted that the absolute value of $\sigma_R^0(OCHCl_2)$ found in this manner is smaller than the analogous constants in anisoles (−0.43) and in monochloromethyl ethers (−0.34). One of the reasons for the weakening of the n, π conjugation reflected by this tendency may be the competition of the n, σ interaction. The ^{35}Cl NQR frequencies are highly sensitive to it [7].

Table 3 presents data from the NQR spectra of the compounds studied (no NQR signal was detected in glassy samples of III and VIII). In all cases the number of signals corresponds to the number of Cl atoms in the molecules. In the case of VI, the signal at 33.480 MHz is assigned to the Cl atom of the CH_2Cl group. In V the Cl atom in the aromatic ring produces one of the low-frequency signals (apparently, the one with ν = 34,790 MHz).

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TABLE 1. Physical Characteristics of the Dichloromethyl Aryl Ethers p-RC_6H_4-$OCHCl_2$

Compound	R	bp, deg C (p, mm Hg)	n_D^{25} (lit. n_D^{20})	d_4^{25}	DM, D	$m^K \cdot 10^{12}$, esu
(I)	H	97–98(15) (compare [3])	1,5330 (compare [3])	1,2889	1,97±0,09	90±9
(II)	Me	109–110(14) (compare [3])	1,5285 (compare [3])	1,2398	2,22±0,06	189±20
(III)	*t*-Bu *	142–143(15)	1,5170	1,1428	2,43±0,06	249±31
(IV)	F	95–96(17)	1,5100 (cf. [5])	1,3809	1,33±0,16	9±32
(V)	Cl	119–120(15) (compare [3])	1,5497 (cf. [3])	1,4118	1,19±0,09	10±7
(VI)	CH_2Cl †	156–157(15)	1.5570	1,3916	–	–
(VII)	NO_2	mp 33-35 (compare [3])	–	–	–	–
(VIII)	OMe ‡	135–137(15)	1,5325	–	–	–

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*Found: C, 55.43; H, 6.24%. Calculated for $C_{11}H_{14}Cl_2O$: C, 56.66; H, 6.07%.

†Found: C, 42.21; H, 3.14%. Calculated for $C_8H_7Cl_3O$: C, 42.61; H, 3.13%.

‡Found: C, 47.20; H, 3.70%. Calculated for $C_8H_8Cl_2O$: C, 46.40; H, 3.90%.

TABLE 2. Integrated Intensities of the ν_8 Band (A) in the Dichloromethyl Aryl Ethers p-$ROC_6H_4OCHCl_2$ and Values of $\sigma_R{}^0$ ($OCHCl_2$) Calculated from Them

Compound	A, liter/mole·cm	σ_R^0 ($OCHCl_2$)
(I)	1334	−0,26
(II)	431	−0,23
(III)	432	−0,26
(IV)	232	−0,27
(V)	242	−0,23
(VI)	931	−0,26

TABLE 3. Frequencies and Signal-to-Noise Ratios in the ^{35}Cl NQR Spectra of the Dichloromethyl Aryl Ethers p-$RC_6H_4OCHCl_2$

Compound	ν ^{35}Cl, MHz	Signal/noise
(I)	35,324, 37,821	40, 40
(II)	35,481, 37,640	40, 25
(IV)	34,140, 36,990	50, 25
(V)	34,790, 34,903, 37,812	5, 5, 15
(VI)	33,480, 34,904, 37,528	8, 18, 12
(VII)	35,610, 35,880	10,10

In all the compounds studied except VII the signals of the two Cl atoms of the $CHCl_2$ group differ strongly from one another: $\Delta\nu \approx 2.6$ MHz. Such differences between geminal Cl atoms were previously observed only in cyclic molecules [8]. There is no doubt that the reason for this in I-VI is the different orientations of the Cl atoms relative to the lone pairs of the O atom. The frequency of one of the signals of Cl in DCME's is ~0.8 MHz lower, and the frequency of the other signal is ~1.6 MHz higher than $\nu(CH_2Cl_2) = 35.991$ MHz. The increase in frequency is attributed to the inductive influence of the alkoxy group. The decrease in the frequency under the influence of the geminal OR substitute is typical of α-chloro ethers and can serve as a quantitative characteristic of the n, σ interaction. This decrease amounts to ~3 MHz in aliphatic mono-α-chloro ethers, ~1.7 MHz in dichloromethyl alkyl ethers, and ~1 MHz in monochloromethyl aryl ethers [1, 9]. On the basis of this characteristic, the n, σ interaction of the lone pairs of the O atom and the C—Cl bonds is less pronounced in DCME's than in the previously studied α-chloro ethers.

The weakening of the orbital interactions detected for DCME's cannot have an effect on their spatial structure. The conformations of these molecules may be characterized by two angles of internal rotation, viz., ClCOC = τ and COCC = ϕ. In the conformations with τ ~ 60° (gg) the two Cl atoms have identical orientations with respect to the lone pairs of the O atom, and the angle between C—Cl bonds and the lone pair of the π type is equal to ∿30°. In the conformations with τ ∿ 180° (gt) the Cl atom found in the trans position is orthogonal to this lone pair and is, consequently, not subject to a specific geminal interaction. The Cl atoms in the gt conformation of DCME's are analogous to the axial and equatorial Cl atoms in cyclic α-chloro ethers, where Δν is also equal to ∿2.5 MHz [8]. Thus, the NQR data allow us to state that I-VI crystallize in the gt conformation with respect to C_{sp^3}—O bond.

In aliphatic dichloromethyl ethers the gt conformer is a minor component in the equilibrium with the gg conformer [10]. The gt and gg conformers also coexist in melts and solutions of DCME's, as follows from the IR-spectroscopic data. Thus, the spectra of liquid samples of I, II, and IV have bands of moderate intensity with wave numbers equal to 587, 582, and 583 cm^{-1}, respectively [δ(CCCl) of the gg conformer], which are absent in the spectra of crystals. An investigation of the temperature dependence of the intensities of this band and the ν(CCl) band of the gt conformer (802, 805, and 802 cm^{-1} for the same compounds) made it possible to determine the difference between the enthalpies of the gg and gt conformers, which amounted to —0.12, +0.14, and —0.36 kcal/mole for I, II, and IV (the accuracy of the determination of ΔH was <0.2 kcal/mole). In the case of dichloromethyl alkyl ethers, this quantity amounts to ∿1.2 kcal/mole [10]. The gt conformers have a doubled statistical weight in comparison to the gg conformers; since the values of ΔH are small, the entropic factor predominantly makes the gt conformers predominant in melts and solutions of DCME's. An investigation of their polarity leads to the same conclusion.

The experimental dipole moments of I-V are presented in Table 1. The values $m(C_{sp^3}—O) = 0.95$ D and $m(C_{sp^2}—O) = 0.98$ D were taken from [2] for the calculation of the theoretical values of the dipole moments. The decrease in the strength of the n, σ interaction in the molecules studied renders the use of the value of the dipole moment of CH_2Cl_2, which equals 1.62 D, for $m(CHCl_2)$ correct.

The theoretical values of the dipole moments of the gg and gt conformers for I-V were equal to 0.84 and 2.54, 1.13 and 2.68, 1.17 and 2.95, 1.14 and 1.42, and 1.22 and 1.38 D, respectively. On the basis of these data we estimated the mole fractions of the gg conformers in solutions of I-III as 0.45 ± 0.07, 0.38 ± 0.05, and 0.38 ± 0.04. Since the dipole moments of IV and V are scarcely dependent on the conformation, the composition of the mixtures was not determined for them by such a method.

The dihedral angle ϕ can be evaluated on the basis of the polarizability of the DCME's. The experimental values of the molar Kerr constants are presented in Table 1. The theoretical values were calculated with the use of the molecular ellipsoid of CH_2Cl_2 ($b_1 = 5.85$, $b_2 = 6.92$, $b_3 = 5.72$ Å^3) as the polarizability ellipsoid of the $CHCl_2$ group, while the polarizability ellipsoids of the other bonds and groups were taken from [2].

The steric interactions in the gg conformers of DCME's are practically analogous to those in 2,6-dichloroanisoles, and it may be assumed that an orthogonal orientation of the aromatic ring and the COC fragment is also realized for them [11]. We note that the overall range of variation of the Kerr constants in the gg conformers is $<20 \cdot 10^{-12}$ esu.

The theoretical values of the Kerr constants calculated with the use of the mole fractions presented above vary monotonically as the angle ϕ in the gt conformer is varied from 33 to 73, from 128 to 170, and from 98 to $141 \cdot 109^{-12}$ esu in I-III, respectively, reaching the extreme values when ϕ = 0 and 90°. Analyzing the calculated values of the Kerr constants, we may note that in all cases, they approximate the experimental values when ϕ = 90°. This tendency is clearly expressed, and it may be assumed that the orientation of the plane of the aromatic ring and the COC fragment in the molecules studied is nearly orthogonal.

CONCLUSIONS

1. In dichloromethyl aryl ethers the n, π and n, σ interactions with the participation of the lone pairs of the O atoms are weakened in comparison to unsaturated ethers and the previously studied α-chloro ethers.

2. In solutions and liquid samples of dichloromethyl aryl ethers gauche, gauche and gauche, trans conformers with respect to the C_{sp^3}—O bond coexist, and in crystals only gauche, trans conformers are realized.

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Among the α-halo ethers, the derivatives with trihalomethyl groups have been inadequately studied [1]. In this communication we shall present data obtained with the aid of ^{35}Cl NQR, vibrational spectroscopy, and measurements of the dipole moments and the Kerr effect for the compounds $ROCCl_3$, where R = Me (I), Et (II), Ph (III), p-$CH_3C_5H_4$ (IV), p-ClC_6H_4 (V), and p-FC_6H_4 (VI).

EXPERIMENTAL

Compounds I and II were obtained by chlorinating the corresponding bis(alkoxythiocarbonyl) disulfides $[ROC(S)S]_2$ according to the method in [2]. Compounds III and IV were obtained by chlorinating the corresponding chlorothioformates ROC(S)Cl according to the method in [3]. Compounds V and VI were obtained by chlorinating the dichloromethyl aryl ethers $ROCHCl_2$ in the presence of PCl_5 according to the method in [4]. The physical characteristics of the compounds investigated are presented in Table 1.

The ^{35}Cl NQR spectra were recorded at 77°K on an IS-3 pulsed spectrometer, the Raman spectra were recorded on a DFS-24 spectrometer with excitation by an He—Ne laser, and the IR spectra were recorded on a UR-20 spectrophotometer. The experimental values of the dipole moments and the molar Kerr constants determined for dilute solutions in CCl_4 at 25°C are presented in Table 1.

RESULTS AND DISCUSSION

The specific properties of α-chloro ethers are determined by the n—σ orbital interactions with the participation of the lone pairs of the O atom and the orbitals of the C—Cl bonds [5]. The ^{35}Cl NQR frequencies are very sensitive to such interactions and decrease under the influence of the O-containing substituent in α-chloro ethers in comparison to $\nu(^{35}Cl)$

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