Ab initio calculations of atomic interaction in the $ClCH_2OCH_3$ molecule

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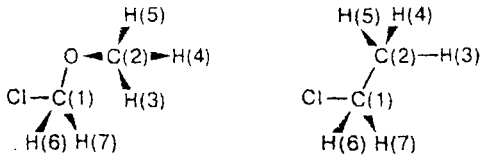
Ab initio calculations of both $ClCH_2OCH_3$ and $ClCH_2CH_3$ molecules and various $ClCH_2OCH_3$ structures with fixed angles of rotation of the methoxy group about the C—O bond were performed by the restricted Hartree—Fock method in the valence-split 6-31G* basis set with full optimization of the geometry. The populations of the valent p-orbitals of the chlorine atoms in these molecules have been analyzed. The ^{35}Cl NQR frequencies and the asymmetry parameters of the electric field gradient (EFG) at the ^{35}Cl nuclei have been calculated. Good agreement with experimental NQR frequencies was obtained for the calculations where only the populations of the less diffuse 3p-components of these orbitals were used. The ^{35}Cl NQR frequency in $ClCH_2OCH_3$ is lower than that in $ClCH_2CH_3$ due to the higher population of the less diffuse component of the p_σ-orbital of the Cl atom in the former molecule.

Key words: *ab initio* calculations, methyl chloromethyl ether, ethyl chloride, p-orbital populations, ^{35}Cl NQR frequencies, asymmetry parameters.

In molecules containing a nonlinear triatomic group Y—C—M the effect of the heteroatom M on the indicator atom Y does not usually correspond to the inductive effect of the M atom or of the substituent containing this atom. M atoms more electronegative than carbon increase the electron population of atom Y while less electronegative M atoms decrease the electron population of atom Y.[1—4] This noninductive effect of M on Y is explained by different conjugation effects that depend on the nature of the heteroatom M. However, a systematic analysis of the results of investigations of such compounds and, in particular, of their NQR frequencies (ν) and the asymmetry parameters (η) of the electric field gradient (EFG) at the nuclei of halogen Y, allowed one to conclude that this noninductive effect is mainly due to the same factor for all M: the direct through-the-field polarization of the C—Y bond caused by the charge of the M atom (see, for instance, Refs. 1—4). This effect was not considered when estimating the inductive effect of the M atom or that of the substituent containing the M atom.[5]

Recently, it has been shown (see Refs. 6—9) that, in contrast to the commonly accepted belief (see Refs. 10—12), the ν and η in NQR characterize the electron distribution not of the whole valent p-shell of the halogen atom, as follows from the Townes—Dailey theory, but only its less diffuse part. In this connection, a further study of the spatial distribution of the electron density on the chlorine atom in compounds containing a Cl—C—M group and analysis of the origin of the anomalous ratio of their ^{35}Cl NQR frequencies is of interest. Therefore, we performed *ab initio* calculations of these molecules using the restricted Hartree—Fock method in the valence-split 6-31G* basis set, in which each valent orbital is represented by a combination of two components of different size (for instance, it consists of 3p- and 4p-functions for the chlorine atom). In this work we report on the results obtained for the molecule $ClCH_2OCH_3$ (**1**), which has become a classical object in studying the noninductive effect of the M atom with the unshared electron pairs on the Y atom in the Y—C—M group. A calculation for the molecule $ClCH_2CH_3$ (**2**) was carried out for comparison.



1 **2**

The calculations of compounds **1** and **2** were carried out using the "Gaussian 92 for Windows program".[13] Molecule **1** was first calculated with full geometry optimization, and then at different values of the angle of rotation (φ) of the methoxy group about the C(1)—O bond. For molecules **1** and **2** the nucleus of the Cl atom was chosen as the origin, with the z axis directed along the Cl—C bond, and the x axis lying in the plane of the figure.

The geometry of molecule **1** has been studied by various methods.[14—18] The results of these studies differ somewhat. Thus, the length of the Cl—C bond determined by gas electronography is 1.87 Å,[15] while that determined by microwave spectroscopy is 1.822 Å [18] or 1.813 Å.[17] In the first case the angle φ is equal to 76 ± 5°, in the second case it is 70°37′ or 69°40′. The optimized geometric parameters of molecule **1** (Table 1) are close to the corresponding experimental values.

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Table 1. Bond length (d), interbond angles (α), and rotation angles (β) in molecules **1** and **2**

Molecule	Bond	d/Å	Angle	α/deg	Angle	β/deg
1	Cl—C(1)	1.815	ClC(1)O	112.3 (112.8)*	ClC(1)OC(2)	−73.2
	C(1)—O	1.356 (1.362)*	C(1)OC(2)	116.3 (114)*	C(1)OC(2)H(3)	−55.1
	O—C(2)	1.404 (1.421)*	OC(2)H(3)	110.8	C(1)OC(2)H(4)	66.7
	C(2)—H(3)	1.087	OC(2)H(4)	111.1	C(1)OC(2)H(5)	186.0
	C(2)—H(4)	1.083	OC(2)H(5)	106.7	C(2)OC(1)H(6)	46.0
	C(2)—H(5)	1.079	OC(1)H(6)	112.9	C(2)OC(1)H(7)	169.8
	C(1)—H(6)	1.081	OC(1)H(7)	108.4		
	C(1)—H(7)	1.075				
2	Cl—C(1)	1.799	ClC(1)C(2)	111.5	ClC(1)C(2)H(3)	180.2
	C(1)—C(2)	1.517	C(1)C(2)H(3)	109.2	C(1)C(2)H(3)H(4)	121.2
	C(2)—H(3)	1.086	C(2)C(1)H(4)	11.9	C(1)C(2)H(3)H(5)	238.9
	C(2)—H(4)	1.083	ClC(1)H(5)	106.3	H(3)C(2)C(1)H(6)	−61.0
	C(2)—H(5)	1.083	ClC(1)H(6)	106.2	H(3)C(2)C(1)H(7)	61.5
	C(1)—H(6)	1.079	C(2)C(1)H(7)	111.8		
	C(1)—H(7)	1.079				

* Experimental values.[18]

The optimized geometry of molecule **2** (Table 1) satisfactorily reproduces that found experimentally. For instance, according to microwave spectra, the lengths of the C—Cl and C—C bonds in molecule **2** are 1.788(2) and 1.522(6) Å, respectively.[14]

Previously, molecule **1** has been calculated in the CNDO/2 and CNDO/BW approximations with varied rotation angles φ.[19] It has also been calculated by the CNDO/SW method at different values of φ with allowance for the overlap of the AOs of the unshared electron pairs of the oxygen atom with other AOs as well as at zero overlap integrals.[3]

Using the populations of the valent p-AOs of the chlorine atom obtained from the above calculations, the quadrupole coupling constants e^2Qq_{mol} or ^{35}Cl NQR frequencies were estimated by the Townes—Dailey[10–12] method and compared with experimental data. However, the authors of Refs. 3,19 succeeded in elucidating the mechanism of the noninductive interaction of the geminal Cl and O atoms in molecule **1** resulting in an anomalous decrease in the ^{35}Cl NQR frequency of compound **1**. As has been clarified, one of the reasons for this behavior is the inadequacy of the Townes—Dailey theory. Calculating the e^2Qq_{mol} and ν (or η) value from the populations of the valent p-AOs of chlorine one should use only the contributions of their less diffuse components. In this case the consistency between the calculated and experimental ν and η values is quite satisfactory (see Refs. 6—9).

The ^{35}Cl NQR frequencies of the most energetically favorable structures **1** and **2** calculated using Eq. (1) and the populations of the 3p-components of the valent p-orbitals of chlorine atoms (Table 2)

$$\nu = (e^2Qq_{atom}/2h)[(Np_x + Np_y)/2 - Np_z](1 + \eta^{2/3})^{1/2}, \quad (1)$$

$$\eta = |3(Np_x - Np_y)/(2Np_z - Np_x - Np_y)|, \quad (2)$$

are close to the experimental values (ν = 29.814 MHz[20] and ν_{av} = 32.702 MHz[12] at 77 K). The same frequencies estimated from the total populations of the p-orbitals or from the "more diffuse" 4p-contributions are, as was expected, essentially different (Table 2). Hence, to elucidate the reasons for the anomalous fact that the ^{35}Cl NQR frequency of compound **1** is lower than those of alkyl chlorides one should analyze the populations of the less diffuse 3p-components of the valent p-orbitals of their Cl atoms. At the same time, an analysis of the total populations of these orbitals is required to study the character of the interaction of these atoms with other atoms of the molecule.

The dependences of the populations of the valent p_z-orbitals of the chlorine and C(1) atoms of molecule **1** as well as those of their components on the angle of rotation (φ) of the methoxy group about the C(1)—O bond are shown in Fig. 1. These dependences are nearly the same for both components of the p_z-orbital of the

Table 2. Calculated populations (ΣNp) of the valent p-orbitals and their components (2p, 3p, 4p) for the Cl and C(1) atoms in molecules **1** and **2**, ^{35}Cl NQR frequencies (ν), and the EFG asymmetry parameters (η) at the ^{35}Cl nuclei

Molecule	Contribution	Cl					C(1)
		Np_x	Np_y	Np_z	ν/MHz	η (%)	Np_z
1	2p	—	—	—	—	—	0.502
	3p	1.293	1.302	0.975	30.004	4.28	0.240
	4p	0.677	0.681	0.261	55.736	1.19	—
	ΣNp	1.970	1.983	1.236	40.581	2.63	0.742
2	2p	—	—	—	—	—	0.499
	3p	1.302	1.303	0.958	32.095	0.11	0.274
	4p	0.676	0.678	0.249	57.044	0.56	—
	ΣNp	1.978	1.981	1.207	42.330	0.58	0.773

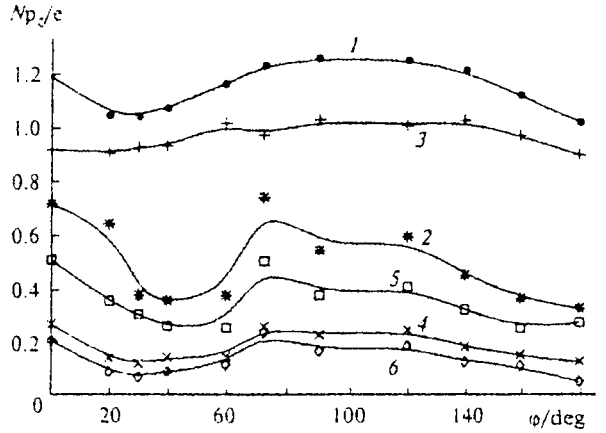

Fig. 1. Dependences of populations of the p_z-orbitals of the Cl (*1*) and C(1) (*2*) atoms in molecule **1** and those of their components on the angle φ: Cl, $3p_z$ (*3*), $4p_z$ (*4*); C(1), $2p_z$ (*5*), $3p_z$ (*6*).

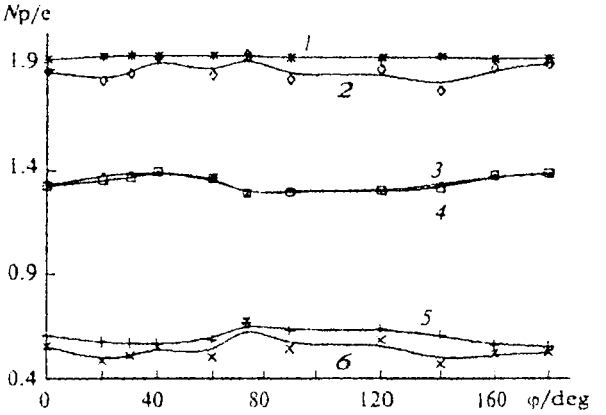

Fig. 2. Dependences of populations of the p_x- (*1*) and p_y-orbitals (*2*) of the Cl atom in molecule **1** and those of their $3p_x$ (*3*), $3p_y$ (*4*), $4p_x$ (*5*) and $4p_y$ (*6*) components on the angle φ.

C(1) atom. The change in the population of the less diffuse 2p-component as the angle φ varies ($\Delta N2p_z$(C) = 0.508 − 0.256 = 0.252 e) is larger than that of the more diffuse 3p-component ($\Delta N3p_z$(C) = 0.240 − 0.051 = 0.189 e). The population of the latter is somewhat lower than that of the 4p-component of the valent p_z-orbital of the chlorine atom. Their dependences on the angle φ are exactly the same. This is consistent with the effect of the methoxy group on the Cl atom along the C(1)—Cl bond.

The dependences of the populations of the $3p_z$- and $4p_z$-components of the p_z-orbital of the chlorine atom on the angle φ are essentially different. In both cases the interval of the change in the populations as the angle φ varies is comparatively small ($\Delta N3p_z$(Cl) = 1.033 − 0.900 = 0.133 e and $\Delta N4p_z$(Cl) = 0.272 − 0.121 = 0.151 e). In the range of φ from ≈ 20° to 140° one of the components increases (Fig. 1) when the other decreases. This is likely caused by redistribution of the electron density between the components of the p_z-orbital of the chlorine atom due to the effect of the methoxy group, including its effect through the bonds.

The dependences of the populations of the $3p_x$- and $4p_x$-components of the valent p_x-orbital of the Cl atom on the angle φ in molecule **1** are mirror images of each other. As a consequence, the total population of the orbital in question remains nearly unchanged (Fig. 2), *i.e.*, redistribution of the electron density between these components (within the limits of ~0.1 e) occurs as the angle φ changes. The dependence of the population of the $3p_y$-component of the valent p_y-orbital of the Cl atom on the angle φ is nearly the same as that for the $3p_x$-component. The character and the limits in the change of the population of the $4p_y$-component as φ varies differ from those for the $4p_x$-component. The populations of these components are nearly the same only at φ = 40° and 73°. The $4p_y$-component has a lower population than the $4p_x$-component at other values of φ, due to the transfer of its electron density to other AOs. The dependences for the $4p_y$- and $3p_z$-components are directly opposite when φ is in the range from ≈ 40° to 180°.

Thus, in the case of rotation of the methoxy group about the C(1)—O bond, a change in the "polarization" of the p_x-orbital of the Cl atom occurs with nearly complete retention of its total population. In the case of the p_y-orbital of the Cl atom, the analogous redistribution is subjected to an additional effect resulting in a decrease in the electron density of its less diffuse $4p_y$-component (excluding φ = 40° and 73°). The effect of the methoxy group on the electron population of the $p_\sigma(p_z)$-orbital of the Cl atom occurs by polarization of this orbital and through the bonds involving the p_z-orbital of the C(1) atom.

To explain the abnormally high electron density on the Cl atom in molecule **1** as compared with that of alkyl chlorides and, in particular, the anomalous ratios of the ^{35}Cl NQR frequencies of these compounds, the concept of conjugation between the AOs of the unshared electron pairs of the oxygen atom and the bonding or antibonding orbital of the C—Cl bond is often used.[11,12,19] However, overlap of the pertinent orbitals in structure **1** can hardly be assumed since there are no conditions for its realization. Nevertheless, the orientation of the methoxy group relative to the Cl atom affects the ^{35}Cl NQR frequency of compound **1**. Since the ^{35}Cl NQR parameters are mostly determined by the populations of the less diffuse components of the valent p-orbitals of the Cl atom, it follows from Eq. (1) that the decrease in the ^{35}Cl NQR frequency of this molecule can be due to the increase in the corresponding contribution of the $3p_z$-component and the decreased influence of the $3p_x$- and $3p_y$-components. According to the *ab initio* calculations, this $3p_z$-component has its highest population when φ is in the range from ≈ 50° to 160°, while the sum of the populations of the $3p_x$- and $3p_y$-components has its lowest value when φ is in the range from ≈ 70° to 120°. The conditions favorable for a decrease in the ^{35}Cl NQR frequency of molecule **1** and the most energetically favorable shape of this molecule correspond to the interval of φ values from ≈ 60° to 150° (Fig. 3).

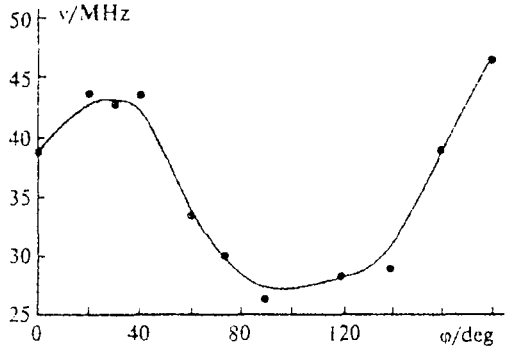

Fig. 3. Dependence of the ^{35}Cl NQR frequency (ν) calculated from the populations of the 3p-components of the valent p-orbitals of the Cl atom in molecule **1** on the angle φ.

The populations of both the p_x- and the p_y-orbitals of the Cl atoms in compounds **1** and **2** as well as those of the corresponding components differ insignificantly. At the same time, the population of the p_z-orbital of the Cl atom and those of its components in molecule **1** are much higher than those in molecule **2**. This is due to the specific character of the polarization of the C—Cl bonds in the structures in question caused by the direct through-the-field effect of the adjacent O or C atoms (according to the *ab initio* calculations, their charges are −0.560 e and −0.482 e, respectively). The fact that the excess in the electron density on the p_z-orbitals of the Cl atoms in molecules **1** and **2** is close to its deficiency on the p_z-orbitals of the C(1) atoms bonded to the Cl atoms is in agreement with such polarization. The fact that the population of the less diffuse $3p_z$-component of the p_z-orbital of the Cl atom in molecule **1** is higher than that in molecule **2** is the main reason for the lower ^{35}Cl NQR frequency in the first molecule.

The EFG asymmetry parameters at the ^{35}Cl nuclei in compounds **1** and **2** were not measured experimentally. Their values, calculated from Eq. (2) using the total populations of the valent p-orbitals of the Cl atoms and those of the 3p- and 4p-components, are close to zero. This is in agreement with experimental data for other compounds of the $ClCH_2X$ series. For instance, for $ClCH_2OC_3H_7$ $\eta = 0.0 \pm 0.8\%$, for $ClCH_2Si(CH_3)_3$ $\eta = 0.5 \pm 0.4\%$, *etc.*[22] However, one should keep in mind that the asymmetry parameters calculated from the populations of the valent p-orbitals of the Cl atoms or their outer 4p-components are usually close to zero even for molecules whose experimental η values substantially differ from zero, and agreement is reached when only the contributions from the inner 3p-components are used.[6–9]

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