CHARACTERISTIC FEATURES OF INTERACTION BETWEEN ATOMS
IN CHLORO-SUBSTITUTED 1,4-DIOXANE FROM *ab initio* CALCULATIONS

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Ab initio calculations in a split-valence shell 6-31G(d) basis for the 2-chloro-1,4-dioxane (with axial and equatorial Cl atom) and 2,3-cis-dichloro-1,4-dioxane molecules with full optimization of their geometry were performed. The major contribution to the lowering of the NQR frequencies of the axial Cl atoms compared with the equatorial Cl atoms comes from the higher pσ-electron population of the former in these molecules. The populations of the orbitals for the unshared electron pairs of the axial and equatorial Cl atoms are identical in these molecules. But these orbitals are polarized differently, which also has some effect on the ratio of the NQR frequencies of these atoms. The differences in the electron populations of the axial and equatorial Cl atoms for the studied molecules are due to the asymmetry of the electron distribution in the Cl atoms geminal to them, which is responsible for the different polarization of the valence p-orbitals of the axial and equatorial Cl atoms.

.In cyclic α-chloroethers, the ^{35}Cl NQR frequencies for axial Cl atoms are about 2.5 MHz lower than for equatorial Cl atoms. This is explained by hyperconjugation between the unshared electron pair of the O atom and the C–Cl bond or its anti-bonding orbital (see, for example, [1-3]). The "anomeric effect", the longer length of C–X axial bonds compared with equatorial C–X bonds, etc. are explained in this way [1, 4, 5]. The same interaction is assumed, for example, for fluorochloromethanes, chloromethylalkyl ethers [1-3, 5], whose ^{35}Cl NQR frequencies are significantly lower than we would expect based on the electronegativities of the F and O atoms or the inductive effect of these atoms or the substituents including them.

Analysis of the NQR spectra for a large number of compounds with a nonlinear triatomic group Y–Z–M (Z = C, Si, Ge, P etc. M = H, C, F, O, Si, Ge, Sn etc.) or Y–Z = M (Z = C, P; M = C, N, O, S etc.) led to the conclusion that the effect of M on Y in these groups does not correspond to the electronegativity and the inductive effect of the M atom or the substituent including it. This noninductive effect is mainly due to participation of the Y atom $p\sigma$-electrons in the interaction with the M atom. The change in the $p\sigma$-electron population of the Y atom as M is varied obeys a common rule for any M and a given Z: as the electronegativity of M (the electron density on the M atom) increases, the indicated population increases and vice versa. This rule is obeyed by compounds containing an M atom with unshared electron pairs (M = O, N, F etc.), presumably with active unoccupied d orbitals (M = Si, Ge, Sn, P etc.), or without either (M = H, C). This excludes the possibility of explaining the unusual properties of such compounds by p,σ- or $p,\sigma*$-conjugation.
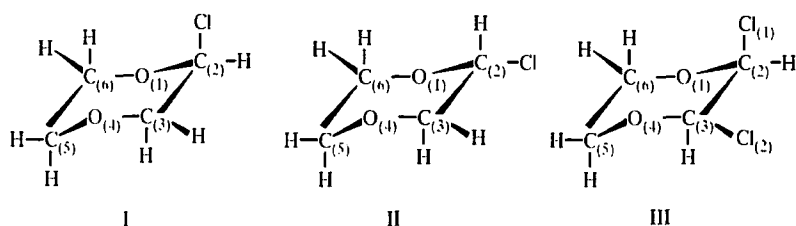
Let us assume that this noninductive effect of M on Y is reduced mainly to the same effect for any Y, Z, and M: to polarization of the Z–Y bond under the action of the charge of the M atom directly through the field (see, for example, [5-7]). Such an effect is not taken into account when estimating the induction constants of substituents [5,8]. Its contribution Δv to the ^{35}Cl NQR frequency may be estimated from the equation [9,10]:

$$\Delta v = q\cos\alpha(\delta v/\delta Ez)\, 4\pi\epsilon\epsilon_0 r^2 \tag{1}$$

where α is the angle between the axis of the Z–Cl bond and the electric field vector E for the field created by the charge q of the M atom, $\delta v/\delta E_z$ is the Stark shift of t he NQR frequency (v), ϵ is the dielectric constant, ϵ_0 is the

vacuum permittivity, r is the distance between the charge q and the center of the electron cloud for the Z–Cl bond. Starting from this common mechanism for the effect of M on Y and Eq. (1), the different effect of the M = O atom on the Cl atoms located in axial and equatorial positions of cyclic α-chloroethers can be explained by several factors. First of all, the charge on the M atom is not a point charge but is rather a space charge; it does not have spherical symmetry. So the effect on a geminal Y (or Cl) atom depends not only on the overall charge on the M atom but also on the relative orientation of M and the Z–Y (C–Cl) bond. Secondly, the bond lengths and the angle of the Cl–C–M moieties with an axial and an equatorial Cl atom are different in the α-chloroether molecule. So the $\Delta\nu$ values for these moieties should be different.

I II III

For further study of the reason for the different effect of the M = O atom on axial and equatorial Cl atoms located in a position geminal to the O atom, we performed *ab initio* calculations for 2-chloro-1,4-dioxane with an axial (I) and an equatorial (II) Cl atom, and also for 2,3-*cis*-dichloro-1,4-dioxane (III) by the restricted Hartree–Fock method in a split-valence shell 6-31G(d) basis with full optimization of the geometry for the molecules. We used the program Gaussian 94W [11]. The origin of the coordinate system was chosen as the point where the nucleus of the Cl atom was located, and the z axis was directed along the C–Cl bond while the x axis was located in the ClCO plane.

Similar calculations were performed for the $ClCH_2OCH_3$ molecule for different rotation angles of the methoxy group about the C–O bond, and also for the $ClCH_2CH_3$ derivative (for comparison) [12]. We have shown that a change in orientation of the methoxy group relative to the Cl atom affects the ^{35}Cl NQR frequency. The p_x- and p_y-orbital populations of the Cl atom in these molecules and also the corresponding components of these orbitals are insignificantly different. At the same time, the populations of the $p_z(p\sigma)$-orbitals of the Cl atom and its components in the first compound are appreciably higher than in the second compound, which also is responsible for the lower ^{35}Cl NQR frequency in the first case. In both molecules, the excess electron density in the p_z-orbital of the Cl atom is close to the electron density deficit in the p_z-orbital of the adjacent C atom, which is consistent with the concepts of polarization of the $\overset{\frown}{C}$–Cl bond in these molecules under the action of the charge on the geminal O or C atom (respectively -0.48 and 0.56) [12].

According to our calculations, the total energy for structure I is 0.55 eV lower than for II, and the axial C–Cl bond in I is appreciably longer than the equatorial bond in II (Table 1). In going from compound I to II, the $O_{(1)}$–$C_{(2)}$ bond is slightly elongated and the bond angles $O_{(4)}$–$C_{(3)}$–$C_{(2)}$ and $C_{(6)}$–$O_{(1)}$–$C_{(2)}$ as well as the dihedral angles formed with participation of $C_{(2)}$ are decreased. The other geometric parameters for these two conformations are very close.

In derivative III, the axial C–Cl bond is somewhat longer than the equatorial bond, and they both are shorter than the corresponding bonds in compounds I and II and also the real bonds in 2,3-*cis*-dichloro-1,4-dioxane III. From the experimental data, the $O_{(1)}$–$C_{(2)}$ bond in molecule III adjacent to the axial C–Cl bond is somewhat shorter than the $C_{(3)}$–$O_{(4)}$ bond adjacent to the equatorial C–Cl bond. However, this cannot be considered as a proof for participation of the $O_{(1)}$ atom in p,σ-conjugation with the $C_{(2)}$–$Cl_{(1)}$ bond or its antibonding orbital, since this is excluded due to their spatial arrangement. The optimized lengths of the $O_{(1)}$–$C_{(2)}$ and $C_{(3)}$–$C_{(4)}$ bonds adjacent respectively to the axial and equatorial C–Cl bonds are practically the same in molecule III, and somewhat shorter than the experimental values; and the maximum discrepancy between the optimized and experimental values is 0.06 Å. Considering that the experimental lengths are measured for crystalline material [13] while the optimized lengths are calculated for an individual molecule, this discrepancy can be considered quite acceptable.

TABLE 1. Bond Lengths (d), Bond Angles (α), and Torsional Angles (β) in Molecules I-III, Calculated by the RHF/6-31G* Method, and the Experimental Values

Bond	d, Å			
	I	I	III	III$_e$ [13]
C–Cl$_{ax}$	1.821	—	1.799	1.819
C–Cl$_{eq}$	—	1.782	1.767	1.781
O$_{(1)}$–C$_{(2)}$	1.368	1.384	1.373	1.394
C$_{(2)}$–C$_{(3)}$	1.522	1.519	1.529	1.528
C$_{(3)}$–O$_{(4)}$	1.392	1.400	1.377	1.425
O$_{(4)}$–C$_{(5)}$	1.402	1.403	1.411	1.473
C$_{(5)}$–C$_{(6)}$	1.515	1.516	1.516	1.513
C$_{(6)}$–O$_{(1)}$	1.415	1.411	1.415	1.466

Angle	α, degrees		
	I	II	III
Cl$_{ax}$–C$_{(2)}$–O$_{(1)}$	111.2	—	111.5
Cl$_{eq}$–C–C	—	110.4	113.6
O$_{(1)}$–C$_{(2)}$–C$_{(3)}$	111.6	110.4	108.2
O$_{(4)}$–C$_{(3)}$–C$_{(2)}$	111.4	108.7	111.0
C$_{(5)}$–O$_{(4)}$–C$_{(3)}$	112.3	112.5	111.7
C$_{(6)}$–C$_{(5)}$–O$_{(4)}$	109.7	109.5	109.6
C$_{(6)}$–O$_{(1)}$–C$_{(2)}$	115.4	112.1	115.5

Angle	β, degrees		
	I	II	III
C$_{ax}$–C$_{(2)}$–O$_{(1)}$–C$_{(6)}$	73.5	—	69.7
Cl$_{eq}$–C–C–O	—	-178.8	-180.4
O$_{(1)}$–C$_{(2)}$–C$_{(3)}$–O$_{(4)}$	50.3	57.2	56.2

We have shown that the *ab initio* calculations of the ^{35}Cl NQR frequencies (ν) and asymmetry parameters η for the electric field gradient (EFG) at the ^{35}Cl atom mainly are determined not by the populations (N) of the entire valence p shell of the Cl atom, but rather by the population of its less diffuse part, belonging to the $3p$-components in the split-valence shell 6-31G(d) basis [5, 12, 14-16], since the ^{35}Cl NQR parameters estimated from these populations and the equations given below are usually close to the experimental values:

$$\eta = (e^2 Qq_{at})/2h[(Np_x + Np_y)/2–Np_z]](1 + \eta^{2/3})^{1/2}, \tag{2}$$

$$\nu = |[3(Np_x + Np_y)/(2Np_z–Np_x–Np_y)]| \tag{3}$$

Consistent with this, the ^{35}Cl NQR frequencies of molecules I and II, calculated in this way (Table 2), reproduce the experimental values reasonably well (ν_{77}= 29.908 and 32.176 and 34.986 MHz respectively [1]), while the values determined using the total populations ($N(3p)$ + N(4p)) of the valence p-orbitals of the Cl atoms or their 4p-components differ significantly from the experimental values.

The satisfactory agreement achieved between the calculated and experimental ^{35}Cl NQR frequencies of the studied molecules allows us to conclude that the quantum chemically calculated electron distributions in these molecules are correct. Unfortunately, the values of η for the compounds under discussion were not experimentally measured, and likewise for the ^{35}Cl NQR frequency for compound II. However, considering the satisfactory agreement between the η values estimated from the populations of the $3p$-components of the valence p-orbitals for the Cl atoms and Eq. (3) and the experimentally determined values for a whole series of chlorine-containing compounds [5,15], we may assume that the η values calculated in this way for the studied molecules (Table 2) will be close to the experimental values.

TABLE 2. RHF/6-31G* Populations of Valence p-Orbitals for Cl Atoms (ΣNp) and Their $3p$- and $4p$-Components, and also the ^{35}Cl NQR Frequencies (v_c) and EFG Asymmetry Parameters (η_c) at the ^{35}Cl Nuclei Calculated From the Populations in Molecules I-III

Molecule	Orbital	Npx, e	Npy, e	Npz, e	v_c, MHz	η, %
I	$3p$	1.295	1.303	0.972	30.429	3.98
	$4p$	0.669	0.672	0.261	54.573	0.87
	ΣNp	1.964	1.975	1.233	40.360	2.25
II	$3p$	1.306	1.309	0.957	32.584	1.20
	$4p$	0.659	0.662	0.218	58.946	1.15
	ΣNp	1.965	1.971	1.175	43.429	1.17
III Cl$_{ax}$	$3p$	1.309	1.309	0.954	32.912	1.31
	$4p$	0.650	0.660	0.236	56.097	1.86
	ΣNp	1.959	1.969	1.190	42.450	1.61
III Cl$_{eq}$	$3p$	1.306	1.320	0.940	34.842	4.26
	$4p$	0.655	0.649	0.197	60.244	0.26
	ΣNp	1.961	1.969	1.137	45.288	1.79

Analysis of the p-orbitals valence populations and their $3p$-components in the Cl atoms allows us to draw conclusions concerning the nature of their interaction with other atoms of the molecule and about the reason for the lowering of the ^{35}Cl NQR frequency in the case of the axial Cl atoms compared with the equatorial atoms. The populations of the corresponding orbitals of the unshared electron pairs (ΣNp_x and ΣNp_y) for axial and equatorial Cl atoms respectively in molecules I, II, and also in molecule III are practically identical (Table 2). At the same time, these orbitals are polarized differently: the less diffuse $3p$-components of the valence p_x- and p_y- orbitals of the axial Cl atoms (in molecule I) are less populated than for the equatorial atoms (in molecule II). Such polarization, according to Eq. (2), makes some contribution to the lowering of the ^{35}Cl NQR frequency for the axial Cl atoms compared with the equatorial atoms. The ratio for the populations of the more diffuse $4p$-components of the p_x- and p_y- orbitals of the axial and equatorial Cl atoms is inverted (Table 2).

In molecules I, II, and III, the populations of the $3p$-components of the p_z ($p\sigma$)-orbitals in the axial Cl atoms, in contrast, are substantially higher than in the equatorial atoms. This also makes a major contribution to the lowering of the NQR frequency. The higher populations of the $p\sigma$-orbitals for the axial Cl atoms compared with the equatorial atoms is also responsible for the fact that the negative charge on the axial Cl atom in compound I is twice as high as on the equatorial atom in II. In molecule III, this difference is even more appreciable (Table 3).

The negative charges on the $O_{(1)}$ atom in structures I and II are practically identical and somewhat less than on the $O_{(4)}$ atom. In derivative III, the negative charge on the $O_{(1)}$ atom geminal to the axial Cl atom is somewhat higher than on the $O_{(4)}$ atom geminal to the equatorial Cl atom.

Knowing the geometry of the molecule (Table 1) and the charges on its atoms (Table 3), using Eq. (1) we can estimate the contribution to its ^{35}Cl NQR frequency from polarization of the C-Cl bond under the action of the charges of the geminal atoms $O_{(1)}$, $C_{(3)}$, and H, assuming these charges to be point charges. In structures I and II, the charges on the $O_{(1)}$ and $C_{(3)}$ atoms are negative, while the charges on the H atom bonded to $C_{(2)}$ are positive.

TABLE 3. Charges on Atoms (q, e) in Molecules I-III, Calculated by the RHF/6-31G* Method

Molecule	Cl$_{ax}$	Cl$_{eq}$	$O_{(1)}$	$C_{(2)}$	$C_{(3)}$	$O_{(4)}$	$C_{(5)}$	$C_{(6)}$
I	-0.120	—	-0.596	0.053	-0.010	-0.608	-0.029	-0.027
II	—	-0.060	-0.599	0.043	-0.002	-0.625	-0.023	-0.031
III	-0.071	-0.014	-0.601	0.062	0.044	-0.585	-0.040	-0.031

According to ideas about such polarization, the $O_{(1)}$ and $C_{(3)}$ atoms should lower the ^{35}Cl NQR frequency of the geminal Cl atom, while the H atom should increase it. Calculations using Eq. (1) show that polarization of the axial C–Cl bond under the action of the charges on the $O_{(1)}$, $C_{(3)}$, and H atoms directly through the field is responsible for the lowering of the ^{35}Cl NQR frequency in conformation I by 5.16 MHz, and by 5.87 MHz for the equatorial bond in structure II.

Consequently, polarization of the C–Cl bonds in substituted 1,4-dioxanes I and II under the action of the charges on the geminal atoms $O_{(1)}$, $C_{(3)}$, and H cannot be the reason for the lower NQR frequencies of axial Cl atoms compared with equatorial Cl atoms, if these charges are assumed to be point charges. As already noted, in reality the atomic charges are not point charges. So in analysis of the effect of geminal atoms on the indicated parameters, in addition to the atomic charges we must take into account the characteristic features of their spatial distribution.

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