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Geminal Interaction and Effect of "Positive Charge"

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Abstract—Quantum-chemical calculations of the molecules containing Cl–C–M group (M=C, N, O, F) were carried out using RHF/6-31G(d) and MP2/6-31+G(d) methods. The calculations are aimed at verifying concept on "positive charge" effect of the central atom of the group suggested as understanding of non-inductive effect of heteroatom M on the Cl (Y) atom in Y–Z–M moieties (geminal interaction). It is shown that C atom in such systems bears negative or small positive charge, and hence "positive charge" effect is excluded. The non-inductive effect originates from the polarization of Cl–C (Y–Z) bonds due to the influence of the charge on any M atom directly through space on any Y and Z.

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We believe (e.g., see [1-6]) that non-inductive effect of heteroatom M on reference atom Y in a non-linear triatomic molecule Y–Z–M or Y–Z=M (geminal interaction) originates from the polarization of Y–Z bond under the action of the charge on the M atom directly through field at any Y, Z and M. Recently a suggestion was revived which had been advanced 30–35 years ago when only fragmentary data, the results of studying separate compounds or of narrow series had been obtained, that this interaction differed by its nature for the M atoms bearing either lone electron pairs or vacant *d* orbitals. It was suggested [7–11] that non-inductive interaction of geminal atoms Y and M in the sets Y–C–M and Y–Z–M was due to a certain effect of the "positive charge" on the central atom when its electronegativity was lower than those of the atoms Y and M. For the case of the M atom bearing vacant *d* orbitals (α effect [12]), it is suggested that non-inductive effect of the M atom on the Y atom is caused by the interaction between the lone electron pair on the atom Y and vacant *d* orbitals of the atom M, as has been accepted formerly (e.g., see [1, 3, 7]). The groundlessness of this understanding of the α-effect follows from experimental data on ^{35}Cl NQR spectra of compounds from $ClCH_2MXX'X''$ series. According to these data, increase in ^{35}Cl NQR frequency of organoelemental compounds of this series with M = Si, Ge and Sn as compared with organic analogs (M = C) can result only from decrease in population of the Cl atom $p_\sigma(p_z)$ orbital in the organoelemental molecules [1–6]. This was indicated also by the results of nonempirical quantum-chemical calculations of $ClCH_2M(CH_3)_3$ molecules (M = C, Si) by the RHF/6-31G(d) method which revealed the fact that increase in ^{35}Cl NQR frequency of (chloromethyl) trimethylsilane as compared with its organic analog was caused basically by the decrease in population of 3*p* component of valence p_σ-orbital on its Cl atom, that is, by polarization of C–Cl bond [13, 14]. According to equation (1) [15] the decrease in population of lone electron pairs of Cl atoms (p_x and p_y orbitals) due to the electron transfer on the vacant *d* orbital of M atom should, on the contrary, lead to a decrease in ^{35}Cl NQR frequency of organoelemental compounds as compared with organic ones, that does not match experimental observations [13, 14].

$$\nu = (e^2Qq_{at}/2h)[-N_z + (N_x + N_y)/2](1 + \eta^2/3)^{1/2}. \qquad (1)$$

Here e^2Qq_{at} is the atomic constant of quadrupole interaction, *h* is Plank constant. According to Towns–Daily theory, this equation connects NQR frequency (ν) with populations of N_x, N_y and N_z valence p_x-, p_y- and p_z-orbitals of Cl atoms. This theory does not assume linear dependence of the frequency on "charges on Cl atoms and total populations of their p_z-orbitals involved into formarion of σ bond," as unfortunately is claimed in [10, 11] with reference to

[1] where this statement is lacking. This equation allows to consider the involvement of certain orbitals of Cl atoms in the interaction with other atoms of the molecule affecting their population.

The essence of the assumed effect of "positive charge" is as follows [7–11]. If electronegativity of the atoms Y and M in the Y–Z–M moiety is higher than that of positively charged central atom Z, then the increase in the electronegativity of M atom leads to the increase in negative charge on Y despite the inductive effect of M. Positive effective charge at the nucleus of Z atom grows leading to compression of its atomic (basic) orbitals. Due to the compression, the energy of electron interaction with the nucleus of Z atom (V_{ne}) decreases, kinetic energy (T) of electrons grows (in compliance with the indeterminacy principle) and electrostatic interaction of electrons (V_{ee}) increases. Delocalization of electrons from atom Z over the positively charged atoms Y and M leads to a change in the situation. The virial relation $V/T = 2 : 1$ distorted at the compression of orbitals of Z atom gets restored. Further changes in kinetic and potential energies due to delocalization of electrons of the positively charged Z atom are considered. Its vacant orbitals in the case of large positive charge on Z atom are suggested to be "capable of being real," etc. [7–9]. This "descriptive imaging by means of virtual process of selecting by variation principle the possible wave functions" [7, 8] led B.A. Suvorov [7–9] to an unexpected conclusion that the reason for "anomalous" effect of electronegative heteroatom M on the atom Y in the Y–Z–M was the effect of "positive charge" of the central atom Z.

We noted [2] that calculation by RHF/6-31G(d) method of the classical object $ClCH_2OCH_3$ for the study of non-inductive influence of M atom on Y in Y–C–M moiety showed that the charge on C atom of methylene group, namely, on the central atom of Y–C–M set, was negative (–0.065 *e*) rather than large positive. Hence, there is no reason to apply the "positive charge" effect of partially negatively chaged C atom for explaining "anomalous" high electron density on Cl atom in this molecule and "anomalously" low ^{35}Cl NQR frequency in this compound.

Prior to introducing the concept of the effect of "positive charge" for explanation of "anomalous," that is, not corresponding to inductive effect of heteroatom M on the atom Y in Y–Z–M groups of organic and organoelemental molecules one should make sure that the central atom Z in such objects always possesses a substantial positive charge. For testing this situation we performed quantum-chemical calculations of a series of simple molecules containing Cl–C–M group displaying distinct "anomalous" effect of the heteroatom M on the atom Cl (e.g., see [1]): $ClCH_2OCH_3$ (**I**), $ClCH_2OC_2H_5$ (**II**), $CH_3CHClOC_2H_5$ (**III**), $ClCH_2F$ (**IV**) and $ClCH_2\overline{NC(O)CH_2CH_2CH_2}$ (**V**). For comparison, we also calculated the molecule $ClCH_2CH_3$ (**VI**). In all the calculations we applied restricted Hartree–Fock method (RHF) with split and polarized 6-31G(d) basis, and also performed calculations of higher level: Hartree–Fock with accounting for electronic correlation by the second order Møller–Plesset method (MP2) with split and polarized basis and diffuse functions for heavy atoms 6-31+G(d) [16]. The calculations were carried out using GAUSSIAN 03W program [17]. Coordinate system origin was located at the Cl atom, Z axis was directed along Cl–C bond. The results of RHF/6-31G(d) calculations of electron distribution in the molecules were tested using experimental ^{35}Cl NQR data. For this purpose the NQR frequencies were calculated by Eq. (1) and from populations of 3*p* components of valence *p* orbital of Cl atoms in the studied molecules (Table 1) and the calculated values were compared with experimental data. The e^2Qq_{at} value in (1) is found from experimental NQR frequency of Cl_2 molecule and populations of 3*p* components of valence *p* orbitals of Cl atoms in this molecule are obtained by calculation with the same method. This procedure for estimation of NQR frequency has been proposed earlier. It was tested on a large number of organic and organoelemental compounds (e.g., [1, 18, 19]), and this also confirms the validity of Eq. (1) which was used for judging on interaction of certain orbitals of Cl or Br atoms with other atoms in the molecule.

The results of estimation of ^{35}Cl NQR frequencies of the studied molecules are in satisfactory agreement with the experimental data obtained at 77 K confirming the validity of the calculations performed of electron distribution over Cl atoms in these molecules. Noticeably differs from the experimental value only the NQR frequency of $ClCH_2F$ (Table 1). As might be expected, the M atom in Cl–C–M moieties, including the case of $ClCH_2CH_3$, bears significant partial negative charge which is much less on Cl atoms while the central atom C can be charged both positively and negatively, in the majority of the studied molecules it is just negative. A small positive charge it bears only in the $CH_3CHClOC_2H_5$ molecule (Table 2). As known, the atomic charges in a molecule can differ

significantly at the calculation with different basic sets. Nevertheless, qualitatively the results of calculations using methods of different level, RHF/6-31G(d) and MP2/6-31+G(d), mostly coincide. The negative charges on C atoms of these molecules calculated by MP2/6-31+G(d) method accounting for electronic correlation are considerably higher than obtained by RHF/6-31G(d) calculation. The charge on C atom in $ClCH_2F$ molecule calculated by RHF/6-31G(d) method is small positive, and calculated by MP2/6-31+G(d) method, is large negative.

Thus, in the studied molecules with "anolmalous" effect of M heteroatom on Cl atom the principal assumption of the effect of "positive charge" is not fulfilled: there is no large positive charge on the atom C separating them. Mostly in the studied molecules the C atom bears negative charge, and in the molecules where its charge is positive its value is small. Therefore it is wrong to introduce the effect of "positive charge" explaining the inductive influence of M heteroatom on the reference atom in organoelemental molecules. Moreover, it is impossible to claim that this explanation is preferable over the concept of "through space" interaction used in [7] in the comparison of chemical shifts in ^{19}F NMR spectra of certain compounds. These spectra hardly allow to advance the mechanism of non-inductive geminal interaction of atoms and even about both their inductive and non-inductive interaction because even no correlation is found between the chemical shifts in ^{19}F NMR spectra and induction constants of substituents for a wide series of compounds. For example, in the series of compounds F_2CXX' only a weak tendency is observed in the change of ^{19}F NMR chemical shifts for narrow series of compounds at varying sum of Taft's induction constants of substituents X and X' [1]. Proceeding from this tendency it is hardly possible to judge about the character of interaction of atoms in the molecules. Analysis of possibility of applying the data of ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR spectroscopy to the study of electronic effects in organic and organoelemental molecules leads to a conclusion (e.g., see [1, 2, 20]) that there is no base for suggesting that NMR data give reliable indication of substituents effects on the electron distribution at a reference atom.

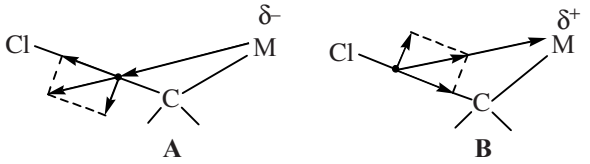
The suggestion on the non-inductive influence of heteroatom M on the atom Y in the groups Y–Z–M and Y–Z=M in organic and organoelemental molecules as a result of polarization of Y–Z bond under the action of the charge on the M atom directly through field appeared not as a result of "figural description by means of "virtual" process…" [7], but from the analysis of a huge number of experimental data and calculations of organic and organoelemental compounds. These data attest (e.g., see [1–6]) that: (1) Into the non-induction interaction with atom M basically are involved the p_σ-electrons of the atom Y at any Y, Z and M; (2) At any Y, Z and M (M is an atom with or

Table 1. Population of valence *p* orbitals of Cl atoms (ΣNp) and their 3*p* components in the molecules **I–VI** calculated by RHF/6-31G(d) method, the ^{35}Cl NQR frequencies (ν_{calc}) calculated from these components, and experimental ^{35}Cl NQR frequencies at 77 K (ν_{exp}^{77})

Molecule	Orbital	Np_x, *e*	Np_y, *e*	Np_z, *e*	ν_{calc}, MHz	ν_{exp}^{77}, MHz
I	3*p*	1.293	1.302	0.975	30.013	29.814 [18]
	ΣNp	1.970	1.983	1.236		
II	3*p*	1.293	1.301	0.976	29.883	29.917 [19]
	ΣNp	1.971	1.982	1.239		
III	3*p*	1.292	1.295	0.982	29.051	29.668 [20]
	ΣNp	1.969	1.976	1.257		
IV	3*p*	1.303	1.315	0.960	32.554	33.799[a] [21]
	ΣNp	1.965	1.981	1.182		
V	3*p*	1.297	1.304	0.962	31.487	32.082 [22]
	ΣNp	1.974	1.980	1.216		
VI	3*p*	1.302	1.303	0.958	32.095	32.646 [21]
	ΣNp	1.979	1.980	1.207		32.759

[a] At 20 K.

without lone electron pairs and/or vacant *d* orbitals) the observed dependence between charge or electronegativity of atom M on p_σ-electron density at the atom Y in organic and organoelemental molecules does not correspond to induction effect. Therefore it is reaso-nable to suggest that the mechanism of this noninductive influence is the same at any Y, Z and M. Such common mechanism could be the polarization of Z–Y bond at the action of the charge on the atom M directly through field. Therewith, the partially negatively charged atom M shifts electron cloud of Z–Y bond toward atom Y (**A**), while positively charged makes the same toward atom Z (**B**). Such interaction of equally and oppositely charged objects is known from the physical grounds.



A **B**

Its contribution to the frequency of ^{35}Cl NMR for a series of molecules has been estimated qualitatively. The results of estimation fit satisfactorily to the experimental observations [1, 21, 22]. This effect of heteroatom M on the atom Cl (Y) directly through field is expectable [1, 23] taking into account the features of determination of induction constants of substituents used for estimating inductive and noninductive interaction of atoms in molecules by comparing particular properties of compounds with these constants. Such effect is excluded at the estimation of induction constants of heteroatoms M or substituents including such heteroatoms because these constants are commonly determined from the series of compounds always containing C atom in geminal position to the reference atom or reaction center Y [1, 2, 23].

As noted above the unique mechanism of the noninductive effect of heteroatom M on the atom Y in the group Y–Z–M or Y–Z=M in organic or organoelemental compound, which is absolutely acceptable from the physical viewpoint is confirmed by a great number of experimental data and calculations. Therefore there is no reasons to propose specific, never confirmed explanations for non-inductive interaction of geminal atoms for a narrow series of compounds.

Table 2. Charges (*q*) on the atoms Cl, C and M in the groups Cl–C–M of molecules **I–VI** calculated by RHF/6-31G(d) and MP2/6-31+G(d) methods

Molecule	RHF			MP2		
	Cl	C	M	Cl	C	M
	q, *e*					
I	–0.142	–0.065	–0.560	–0.071	–0.232	–0.412
II	–0.145	–0.063	–0.573	–0.066	–0.201	–0.410
III	–0.151	0.098	–0.590	–0.091	0.011	–0.398
IV	–0.084	0.025	–0.354	–0.013	–0.107	–0.342
V	–0.122	–0.191	–0.660	–0.048	–0.397	–0.187
VI	–0.119	–0.375	–0.482	–0.064	–0.425	–0.597

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