

***Ab initio* and MNDO Calculations of the ^{35}Cl NQR Parameters of Some Organic and Inorganic Molecules ***

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The results of *ab initio* and MNDO calculations of the $\text{Cl}_2\text{C}=\text{CHOCH}_3$, XCOCi ($\text{X}=\text{CH}_3$, OCH_3 and COCl), $4\text{-ClC}_6\text{H}_4\text{CH}_2\text{Cl}$, $(\text{CNCl})_3$ and PCl_5 with total optimization of their geometry are presented. The *ab initio* calculations were executed using Hartree-Fock theory and the split valence basis set 6-31G* (RHF/6-31G*/RHF/6-31G*). Using the calculated *p*-orbital populations of the Cl atoms in these molecules the ^{35}Cl NQR frequencies and asymmetry parameters of the EFG at the ^{35}Cl nuclei have been determined. When the populations of the less diffuse components of orbitals in the split valence basis set are used the calculated and experimental ν and η values are in good agreement. Linear correlations between these calculated and corresponding experimental ν and η values are obtained. The causes of the nonconformity of the earlier calculated ν and η values and their experimental ones are analysed.

Key words: *Ab initio* calculations, *p*-orbital populations, ^{35}Cl NQR frequency, asymmetry parameter.

Introduction

Reliable quantitative correlations between experimental ^{35}Cl NQR frequencies (ν) and asymmetry parameters (η) of the electric field gradient (EFG) at the ^{35}Cl nuclei of various compounds and corresponding results of quantum mechanical calculations are of principal importance for chemical structure theory and NQR methods. However, at present reliable correlations between these experimental and calculated data are lacking. Whereas the calculated and experimental ^{35}Cl NQR frequencies of some series of compounds correlate the calculated η values are always considerably lower than the experimental ones and do not correlate (see e.g. [1–6]).

The ν and η values of halogen-containing molecules are usually calculated from the valence *p*-orbital populations of halogen atoms, which are determined by semiempirical quantum mechanical calculations (see e.g. [1–6]). Corresponding *ab initio* calculations, however, are scarce, presently. Only in some works they were used for the calculation of quadrupole coupling constants or the EFG at the indicator nucleus (see e.g. [7–9]).

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Results and Discussion

We have carried out *ab initio* and MNDO calculations on some chlorine-containing molecules (Table 1) with total optimization of their geometry using the “Gaussian 92 for Windows” program [10]. MNDO calculations have been executed using the valence sp-basis. *Ab initio* calculations and geometry optimization have been carried out using Hartree-Fock theory and the split valence basis set 6-31G* (RHF/6-31G*/RHF/6-31G*), in which any valence orbital is represented by the combination of two orbitals of different size. This basis set is polarized. It enables to take into account the change of shape of heavy atom orbitals under the action of different factors.

According to the optimization results, the molecules $\text{Cl}_2\text{C}=\text{CHOCH}_3$, XCOCi ($\text{X}=\text{CH}_3$, OCH_3 and COCl), $4\text{-ClC}_6\text{H}_4\text{CH}_2\text{Cl}$ and $(\text{CNCl})_3$ are practically planar. The methyl group in the $\text{Cl}_2\text{C}=\text{CHOCH}_3$ molecule deviates from its plane by $\sim 17^\circ$. The carbon atom and one of the hydrogen atoms of the methyl group in CH_3OCOCi lie in the molecular plane. The carbon atom of this group and the Cl atom are in cis-positions to each other. Both parts of the ClOCCOCi molecule lie in the same plane. Its Cl and O atoms are in cis-positions to each other as well. The C-Cl bond of the chloromethyl group in $4\text{-ClC}_6\text{H}_4\text{CH}_2\text{Cl}$ lies in a plane which is perpendicular to the molecules plane. Phosphorus pentachloride



Table 1. Populations of the Cl atom valence p -orbitals (Np) and their sum ($\sum Np$) obtained from *ab initio* (I) and MNDO calculations (II) of some molecules, calculated (v_c , η_c) and experimental (v_e , η_e) [16–18] ^{35}Cl NQR frequencies (v) and asymmetry parameters (η) of the EFG at the ^{35}Cl nuclei in them.

Molecule	Method	Orbit.	Np_x, e	Np_y, e	Np_z, e	v_c, MHz	v_e, MHz	$\eta_c, \%$	$\eta_e, \%$
$\text{Cl}_2\text{C}=\text{CHOMe}$ cis-Cl	I	$3p$	1.311	1.329	0.917	37.544	36.904	6.70	7.3 ± 1.5
		$4p$	0.645	0.626	0.172	61.884	—	6.15	—
		$\sum Np$	1.956	1.955	1.089	47.481	—	0.17	—
trans-Cl	II	$3p$	1.984	1.976	1.107	47.832	—	1.374	—
		$4p$	1.318	1.320	0.920	37.136	37.188	0.75	0.0 ± 0.5
		$4p$	0.647	0.636	0.177	61.884	—	3.55	—
		$\sum Np$	1.965	1.956	1.097	47.318	—	1.56	—
		$3p$	1.987	1.979	1.130	46.737	—	1.406	—
MeCOCl	I	$3p$	1.275	1.318	0.986	29.125	28.962	20.77	20.0 ± 2.0
		$4p$	0.656	0.630	0.230	55.093	—	9.44	—
		$\sum Np$	1.943	1.961	1.196	41.435	—	3.57	—
		$3p$	1.969	1.991	1.214	41.982	—	4.31	—
MeOCOC	II	$3p$	1.287	1.331	0.966	32.072	34.224	19.24	14.3
		$4p$	0.656	0.630	0.230	38.504	—	9.44	—
		$\sum Np$	1.943	1.961	1.196	41.435	—	3.57	—
		$3p$	1.969	1.991	1.214	41.982	—	4.31	—
ClOCCOCl	I	$3p$	1.284	1.342	0.945	34.576	33.621	23.64	33.5 ± 1.0
		$4p$	0.634	0.612	0.183	58.663	—	7.5	—
		$\sum Np$	1.918	1.954	1.128	44.308	—	6.68	—
		$3p$	1.958	1.991	1.197	42.628	—	6.37	—
$(\text{CNCl})_3$	II	$3p$	1.296	1.348	0.925	37.149	36.755	19.65	22.0 ± 1.0
		$4p$	0.625	0.605	0.142	63.046	—	6.34	—
		$\sum Np$	1.921	1.953	1.067	47.697	—	5.52	—
		$3p$	1.958	1.990	1.044	50.976	—	5.16	—
4-ClC ₆ H ₄ CH ₂ Cl 4-Cl	I	$3p$	1.304	1.318	0.943	34.261	34.567	5.81	6.3 ± 0.7
		$4p$	0.653	0.647	0.185	61.942	—	1.94	—
		$\sum Np$	1.957	1.965	1.128	45.647	—	1.44	—
		$3p$	1.304	1.306	0.945	33.545	33.754	0.90	1.2 ± 0.7
-CH ₂ Cl	I	$4p$	0.674	0.672	0.242	57.410	—	0.70	—
		$\sum Np$	1.978	1.978	1.187	43.343	—	0.00	—
		$3p$	1.355	1.284	0.939	35.915	33.751	28.09	—
		$4p$	0.613	0.594	0.288	42.082	—	9.03	—
PCl_5 Cl_{eq}	II	$\sum Np$	1.968	1.878	1.227	38.376	—	19.40	—
		$3p$	1.967	1.957	1.352	33.400	—	2.54	—
		$4p$	1.302	1.302	0.974	30.489	29.258	0.05	—
		$\sum Np$	0.670	0.670	0.361	41.159	—	0.00	—
Cl_{ax}	I	$3p$	1.972	1.972	1.335	34.905	—	0.00	—
		$4p$	0.670	0.670	0.361	41.159	—	0.00	—
		$\sum Np$	1.972	1.972	1.335	34.905	—	0.00	—
		$3p$	2.000	2.000	1.011	54.186	—	0.00	—

is trigonal-bipyramidal. In this molecule the axial P-Cl bonds are considerably longer (2.145 Å) than the equatorial ones (2.027 Å). These results, as well as the considerably greater partial negative charges at the axial Cl atoms ($-0.259 e$), than those at the equatorial ones ($-0.045 e$), conform with the considerably lower ^{35}Cl NQR frequency of the former [11]. The results of geometry optimization of the PCl_5 , CH_3COCl and CH_3OCOC agree with their experimental geometry [12–14].

In the calculations of plane molecules, the coordinate origin is chosen to be at the Cl nucleus, the Z axis coincides with the Cl-C bond direction and the X axis is directed perpendicularly to the molecule-plane. In the calculation of PCl_5 the coordinate origin is chosen

to be at the equatorial Cl nucleus, the Z axis is directed along the Cl-P bond, and the X axis – perpendicularly to the equatorial plane of the molecule.

The populations of valence p -orbitals of the Cl atoms in the molecules studied, which are obtained from *ab initio* and MNDO calculations of these molecules, are used for the estimation of their ^{35}Cl NQR frequencies and asymmetry parameters of the EFG at the ^{35}Cl nuclei (Table 1) using the Townes and Dailey equations (see e.g. [5, 15])

$$v = (e^2 Q q_{\text{at}} / 2 h) [(N p_x + N p_y) / 2 - N p_z] \cdot (1 + \eta^2 / 3)^{1/2},$$

$$\eta = |3(N p_x - N p_y) / (2 N p_z - N p_x - N p_y)|.$$

The ν values, which are estimated using the total populations of the Cl atom valence p -orbitals ($N 3p + N 4p$), obtained from *ab initio* calculations of the molecules studied, are considerably higher than the corresponding experimental ones and the η values, estimated using these populations, are considerably lower (Table 1) [16–18]. The ν and η values obtained from MNDO calculations are close to those obtained from *ab initio* calculations. For other molecules the ^{35}Cl NQR frequencies and asymmetry parameters of the EFG at the ^{35}Cl nuclei, which are estimated using the population of the Cl atom valence p -orbitals obtained from semiempirical calculations of these molecules, differ considerably from the corresponding experimental values (see e.g. [1–6]). Introduction of various corrections to these calculated NQR frequencies somewhat improves the conformity of the experimental and calculated ν values [6]. However the disagreement still remains. The use of total populations of the Cl atom p -orbitals obtained by us from *ab initio* calculations does not improve this conformity either. This applies equally to the η values. The essential difference between the experimental and calculated ν and η values is, evidently, due to the fact that at such calculations the p -orbital diffusiveness and strong dependence of the EFG on the distance to the charges which create this EFG are insufficiently taken into account. The EFG varies inversely to the cube of this distance (see e.g. [6, 19]). This dependence shows that the correctness of the calculations of ν and η depends on the correct estimation not of the total populations of the valence p -orbitals of Cl, but of those parts of these diffuse orbitals which mostly determine the EFG at the Cl nucleus. Therefore we supposed that the analysis of the populations of separate components of the Cl p -orbitals in the split valence basis set which is used in *ab initio* calculations, is a better way for the correct estimation of the ν and η values. Taking into account that the electrons nearest to the ^{35}Cl nucleus contribute most to the EFG at this nucleus, we have calculated the ν and η values of the molecules studied using the populations of the least diffuse components of the Cl atom p -orbitals (3 p -orbitals) in the split valence basis set 6-31G*. The ν and η values calculated this way turned out to fall near the experimental ones (Table 1). The η value for ClOCCOCl is an exception, being considerably lower than the experimental one [17]. However the ν value of this molecule, calculated using the same populations of the Cl atom p -orbitals, is close to the experimental one. Taking this into ac-

count, as well as the fact that our calculated η value for ClOCCOCl is close to the experimental values for the majority of compounds of the XCOCl series, which are considerably smaller than the experimental η value for ClOCCOCl, we arrive at the conclusion the η value of ClOCCOCl should be remeasured.

Linear correlations are observed between the experimental and calculated (using the 3 p -components of the Cl atom p -orbital populations) ν and η values (Figs. 1 and 2)

$$\nu_c = 2.179 + 0.946 \nu_e, \quad r = 0.986, \quad n = 8,$$

$$\eta_c = 0.413 + 0.998 \eta_e, \quad r = 0.968, \quad n = 7.$$

The η values for ClOCCOCl are left out in Fig. 2. Nevertheless, such good conformity between calculated and experimental η values has not been obtained before. The coefficient at ν_e in the above equation is also close to unity and the free term (2.179) is considerably nearer to 0 than in an analogous equation in which the population of the Cl atom p -orbitals, obtained from MNDO calculations, and correction factors which somewhat take into account the diffusibility and inequivalence of the Cl atom p -orbitals are used [6]. The points in Fig. 1 corresponding to MeOCOCl and to the equatorial Cl atoms in PCl_5 deviate from this correlation.

The populations of the more diffuse 4 p -components of the Cl atom p -orbitals in the split valence basis set 6-31G* are considerably smaller than the less diffuse ones (3 p -). Taking this and the strong dependence of the EFG at the ^{35}Cl nucleus upon the distance to charges which create this EFG into account, one may suppose that the electrons in the more diffuse and less populated 4 p -orbitals of the Cl atom produce only a negligible contribution to the EFG and, consequently, to the ^{35}Cl NQR frequency and asymmetry parameter of the EFG at the ^{35}Cl nucleus.

One of the unshared electron pairs of the Cl atom in plane chlorine-containing molecules, in which this atom is bonded to the sp^2 -hybridized carbon atom, does probably take part in the p, π -conjugation with the π -electron system of a molecule. The other unshared electron pair of the Cl atom, the symmetry axis of which lies in the molecule-plane, does probably not take part (see e.g. [5, 20]). Therefore the electron density distribution of such Cl atoms can not be axially symmetric. According to this, in the majority of such compounds the experimental asymmetry parameters of the EFG at the ^{35}Cl nuclei differ noticeably from

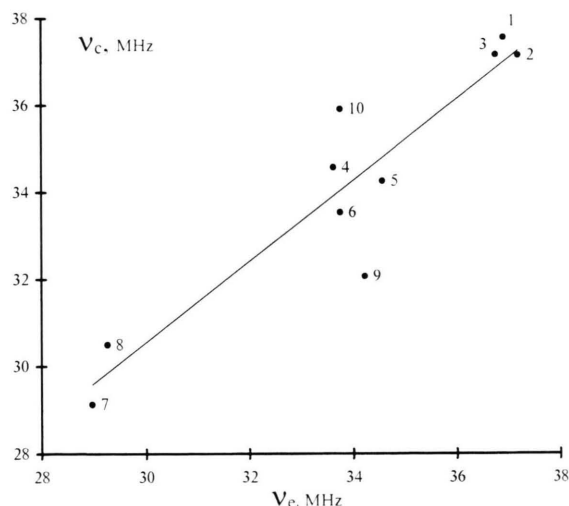


Fig. 1. Correlation between experimental (v_e) and obtained from *ab initio* calculations (v_c) ^{35}Cl NQR frequencies for the molecules: $\text{Cl}_2\text{C}=\text{CHOMe}$, cis-Cl (1) and trans-Cl (2); $(\text{CNCl})_3$ (3); ClOCCOCl (4); 4- $\text{ClC}_6\text{H}_4\text{CH}_2\text{Cl}$, 4-Cl (5) and CH_2Cl (6); MeOCOCl (7); PCl_5 , Cl_{ax} (8) and Cl_{eq} (9) and MeOCOCl (10)

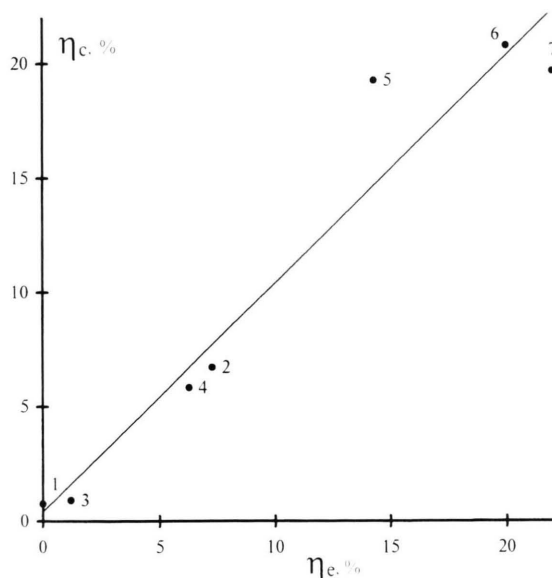


Fig. 2. Correlation between experimental (η_e) and obtained from *ab initio* calculations (η_c) asymmetry parameters of the EFG at the ^{35}Cl nuclei in the molecules: $\text{Cl}_2\text{C}=\text{CHOMe}$, trans-Cl (1) and cis-Cl (2); 4- $\text{ClC}_6\text{H}_4\text{CH}_2\text{Cl}$, CH_2Cl (3) and 4-Cl (4); MeOCOCl (5); MeOCOCl (6); $(\text{CNCl})_3$ (7).

zero. However, the analysis of the results of *ab initio* calculations of some planar molecules (Table 1) shows that the total populations of both valence p_x - and p_y -orbitals of the Cl atoms are appreciable smaller than $2e$. Consequently, both unshared electron pairs of these Cl atoms take part in the interaction with other AOs. In this case the η value can not serve as a direct characteristic of the participation of the Cl atoms unshared electron pair in the p,π -interaction (or in some other interaction).

The total populations of the cis-Cl atom p_x - and p_y -orbitals in $\text{Cl}_2\text{C}=\text{CHOMe}$ are practically the same. According to the existing representations, this leads to a conclusion about axial symmetry of this Cl atom electron distribution. However, the experimental value of the asymmetry parameter of the EFG at this nucleus differs appreciable from zero (Table 1). The total populations of the trans-Cl atom p_x - and p_y -orbitals in this molecule on the contrary, somewhat differ between themselves. However, the experimental η value for this Cl atom is practically zero. The ratio of the populations of less diffuse components of valence p -orbitals for cis- and trans-Cl atoms corresponds to the experimental η values in this and the other compounds studied (Table 1).

We arrive at the conclusion that the asymmetry parameter of the EFG at the ^{35}Cl nucleus characterizes only part of the asymmetry of the Cl atom electron distribution, i.e. in a certain region around the Cl atom nucleus. This region corresponds to the size of the $3p$ -component orbitals in the split valence basis set 6-31G*. Therefore, the estimation of η and v values using total populations of the Cl atom p -orbitals will lead to incorrect results. And conclusions concerning the participation of unshared electron pairs of the Cl atom or its p_σ -electrons in interaction with the other AO in a molecule, which are made on the basis of experimental ^{35}Cl NQR frequencies or asymmetry parameters of the EFG at the ^{35}Cl nuclei, may prove to be incorrect too. This does not diminish the importance of NQR for the study of electron and spatial structure of chemical compounds, especially since in molecules, in which the Cl atom is bonded with an atom of the second period of the periodic table, the electron density in this space region around the Cl atom nucleus is larger. It feels the changes stipulated by the mutual interaction of atoms in a molecule to a greater extent.

Conclusions

1. The essential difference between the experimental and calculated ν and η values of chlorine-containing molecules is due to the fact that in the calculations the diffusiveness of the Cl atom p -orbitals and the strong dependence of the EFG at the ^{35}Cl nuclei on the distance of the charges, is not sufficiently taken into account.

2. The correctness of the ν and η value calculations depends on the correct estimation not of the total populations of the Cl atom valence p -orbitals, but of those parts of these diffuse orbitals which mostly determine the EFG at this nucleus.

3. The ν and η values, estimated using the populations of the less diffuse components of the Cl atom

valence p -orbitals, which are obtained from *ab initio* calculations of the $\text{Cl}_2\text{C}=\text{CHOCH}_3$, XCOCI ($\text{X}=\text{CH}_3$, OCH_3 and COCl), $4\text{-ClC}_6\text{H}_4\text{CH}_2\text{Cl}$, $(\text{CNCl})_3$ and PCl_5 using Hartree-Fock theory and the split valence basis set 6-31G*, conform best to the corresponding experimental values.

4. A satisfactory linear correlation between the experimental and this way calculated ν and η values is observed.

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