Correlation between the ^{35}Cl NQR Parameters of Chloro-containing Organic and Organometallic Compounds and the Results of *ab initio* Calculations*

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The results of comparison of experimental ^{35}Cl NQR parameters for a great number of organic and organometallic compounds and estimated ones using *ab initio* calculations at the RHF/6-31G(d) level were systematized. The NQR frequency changes on going from one compound to another depend, in general, on the changes of populations of the Cl atom p_σ-orbitals in these compounds and, first of all, of populations of their less diffuse parts.

Key words: ab initio Calculations; p-orbital Populations; ^{35}Cl NQR Frequency; Asymmetry Parameter; Chloro-containing Organic and Organometallic Compounds.

Introduction

According to NQR theory the ^{35}Cl NQR frequencies and asymmetry parameters of the EFG at the ^{35}Cl nuclei in chloro-containing molecules characterize the spatial electron distribution of the Cl atom. These NQR parameters are bounded up with the populations (N) of the halogen atom valence p-orbitals by the simple equations (see, e.g., [1, 2]):

$$\nu = (e^2 Q q_{\text{at}})/2h \cdot [Np_x + Np_y)/2 - Np_z]\,(1+\eta^2/3)^{1/2}, \qquad (1)$$

$$\eta = \left| 3\,(Np_x - Np_y)/(2\,Np_z - Np_x - Np_y) \right| . \qquad (2)$$

However, the ν and η values, calculated using these equations and total populations of the Cl atom valence p-orbitals, obtained from semi-empirical or *ab initio* calculations of corresponding molecules, considerably differ usually from the experimental ones (see, e.g., [3]). This difference is due (see, e.g., [3]) to the strong dependence of the EFG at the atomic nucleus on the distance r between the latter and the charges, which create this EFG (see, e.g., [1, 2]).

$$e\,q_{zz} = -e \int \varphi^* \,[(3\cos^2\theta - 1)/r^3]\,\varphi\,\mathrm{d}\tau . \qquad (3)$$

This dependence is not taken into account at the estimation of the ν and η values using the equations (1) and (2) and total populations of the indicator atom valence p-orbitals. We believe that this EFG and therefore the NQR parameters depend, in general, on the electron distribution of not the whole valence p-shell of the indicator atom, but on the less diffuse part of this shell. It is shown that the fine conformity between the experimental and calculated ν values, as well as between the η ones is observed at the using for the estimation of these NQR parameters not the total populations of the Cl atom valence p-orbitals but the populations of their less diffuse $3p$-components, obtained from RHF/6-31G(d) calculations. Such calculations were performed for some organic and organometallic molecules (see, e.g., [3]).

Results and Discussion

In the present communication the results of *ab initio* calculations of a great number of chloro-containing organic and organometallic molecules with total optimization of their geometry were presented and the results of study of connection between the latters and the ^{35}Cl NQR parameters for these compounds were systematized. The calculations of all compounds studied were carried out using the restricted Hartree-Fock method in the valence-split 6-31G(d) basis set and the Gaussian 94W program [4]. The calculated populations of the less diffuse $3p$-components of the Cl atom valence p-orbitals in this basis set and equations (1) and (2) were used to estimate the ν and η values of the compounds studied. The $e^2 Q q_{\text{at}}/2h$ val-

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Table 1. Experimental (ν_e) [3, 6–8] and calculated (ν_c) [3, 9–14] ^{35}Cl NQR frequencies and asymmetry parameters of the EFG at the ^{35}Cl nuclei (η_e and η_c accordingly) [3, 7] as well the populations of the Cl atom p_z-orbitals (Np_z) and their $3p_z$-components ($N3p_z$) in some organic and organometallic molecules.

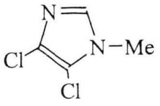
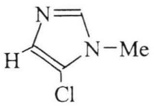
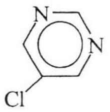
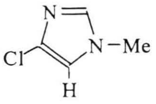
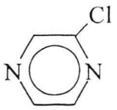
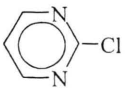
No.	Molecule	ν_e, MHz	η_e, %	Ref.	ν_c, MHz	η_c, %	$N3p_z$, e	Np_z, e	Ref.
1 1′	$Cl_2C=CHOCOCH_3$	38.220 36.876	1.2±0.6 7.3±1.8	[3]	37.857 37.811	2.28 7.16	0.915 0.915	1.083 1.082	[a]
2 2′	$ClCH_2COCl$	37.517 30.437	1.2±1.0 17.6±1.0	[3]	37.338 30.292	3.138 23.48	0.918 0.978	1.127 1.206	[a]
3 3′	$Cl_2C=CHOCH_3$ cis-Cl trans-Cl	36.904 37.188	7.3±1.5 0.0±0.5	[3]	37.544 37.136	6.70 0.75	0.917 0.920	1.089 1.097	[3, 9]
4 4′		37.699[b] 35.840		[6]	36.805 35.921	2.37 5.49	0.924 0.932	1.083 1.100	[a]
5	$(CNCl)_3$	36.760[b]	22.0±1.0	[3]	37.149	19.65	0.925	1.067	[3, 9]
6	$Cl_2C=CH_2$	36.552[b]		[6]	36.888	6.17	0.923	1.095	[10]
7	2-chlorotiophen	36.961		[3]	36.477	2.49	0.925	1.097	[11]
8		36.822[b]		[6]	35.557	1.06	0.934	1.104	[a]
9		36.123			35.624	2.86	0.932	1.104	[a]
10	$1,2\text{-}Cl_2C_6H_4$	35.728[b]		[3, 6]	35.633	8.50	0.933	1.109	[3]
11	$3\text{-}ClC_5H_4N$	35.238		[3, 6]	34.683	4.13	0.940	1.121	[3]
12		35.034		[6]	34.723	4.10	0.942	1.120	[a]
13		35.049		[6]	34.762	9.56	0.941	1.116	[a]
14	$1,3\text{-}Cl_2C_6H_4$	34.936[b]		[3, 6]	34.627	5.62	0.940	1.122	[3]
15		34.470[b]		[6]	35.117	16.72	0.941	1.111	[a]
16 16′	2,3-dichlorodioxan	34.986 32.176		[3]	34.842 32.912	4.26 1.31	0.940 0.954	1.137 1.190	[a]

Table 1. (Continued)

No.	Molecule	ν_c, MHz	η_c, %	Ref.	ν_c, MHz	η_c, %	$N3p_z$, e	Np_z, e	Ref.
17	$1,4\text{-}Cl_2C_6H_4$	34.918[b]	6.0±2.0	[3]	34.439	5.31	0.942	1.126	[3]
18 18′	$4\text{-}ClC_6H_4CH_2Cl$	34.567 33.754	6.3±0.7 1.2±0.7	[3]	34.261 33.545	5.81 0.90	0.943 0.945	1.128 1.187	[3, 9, 12]
19	ClC_6H_5	34.621		[3, 6]	33.826	5.44	0.946	1.137	[3]
20	$ClOCCOCl$	33.621		[3, 6]	34.576	23.64	0.948	1.133	[9]
21	$2\text{-}Cl\text{-}4,6(NHCH_3)_2(C_3N_3)$	33.900	13.0±2.0	[7]	34.297	18.15	0.947	1.119	[a]
22	$ClCH_2Si(CH_3)_3$	34.320		[3]	32.975	0.16	0.945	1.128	[3, 12]
23	$ClCH{=}CH_2$	33.411		[6]	33.044	7.53	0.953	1.161	[10]
24	$2\text{-}ClC_5H_4N$	34.194		[6]	33.883	10.91	0.948	1.120	[3]
25	$ClCH_2C(CH_3)_3$	33.015		[3]	31.876	1.55	0.960	1.211	[3, 12]
26	$ClCH_2CH_3$	32.702[b]		[6]	32.095	0.11	0.958	1.207	[3, 12]
27	$ClC(CH_3)_3$	31.065		[3, 6]	30.625	0.00	0.968	1.233	[3, 12]
28	$4\text{-}ClOCC_6H_4COCl$	31.134	30.0±2.0	[3]	30.583	20.01	0.975	1.190	[a]
29	2-chlorodioxan (ax)	29.908		[3]	30.429	3.98	0.972	1.233	[a]
30	$ClCH_2OCH_3$	29.814		[3]	30.004	4.28	0.975	1.236	[3, 12]
31	$CH_2{=}CHCOCl$	30.040	22.4±1.0	[3]	29.543	22.78	0.983	1.212	[a]
32	CH_3COCl	28.962	20.0±2.0	[3]	29.125	20.77	0.986	1.227	[3, 9]
33	$ClP(S)(OCH_3)_2$	25.943		[8]	25.467	2.60	1.021	1.389	[a]
34	$ClP(S)(CH_3)C_2H_5$	25.850		[6, 8]	25.708	1.15	1.016	1.382	[13]
35	$ClP(O)(OCH_3)_2$	25.420		[6, 8]	24.217	2.77	1.033	1.415	[a]
36	$ClP(C_2H_5)_2$	25.080		[6, 8]	24.092	2.74	1.023	1.428	[14]
37	$ClP(O)(CH_3)C_2H_5$	23.760		[6, 8]	22.856	0.64	1.040	1.430	[13]
38	$ClP[N(CH_3)_2]_2$	18.508		[8]	19.281	0.77	1.056	1.515	[14]
39	Cl_2SiH_2	18.571		[6]	18.551	9.04	1.070	1.477	[12]
40	$ClSi(CH_3)_3$	16.506		[6]	15.945	0.03	1.090	1.554	[3]
41	$ClSi(OCH_3)_3$	16.870		[6]	15.496	0.01	1.097	1.549	[12]

[a] Calculations of this work [b] Average value

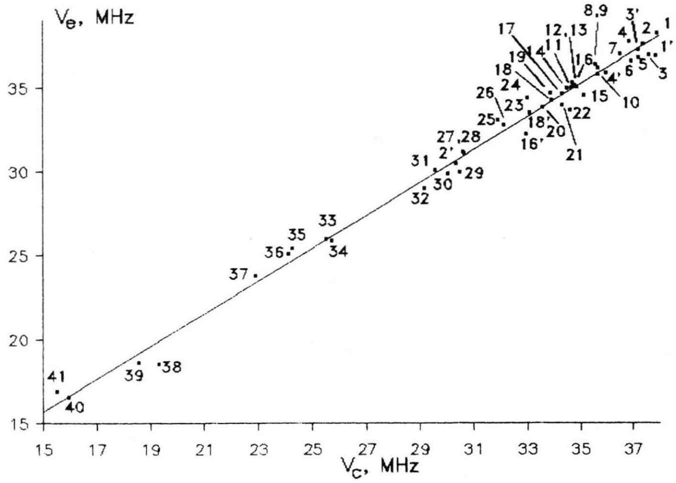


Fig.1. Correlation between the experimental (ν_e) and calculated (ν_c) ^{35}Cl NQR frequencies in organic and organometallic compounds (Table 1).

ue (93.093 MHz) in the equation (1) for the ^{35}Cl NQR frequency estimation were obtained from the Cl_2 molecule calculation at the same level. These calculated ν and η values for nearly all molecules are close to the experimental ones for the corresponding organic and organometallic compounds (Table 1). The linear correlation between the experimental (ν_e) and calculated (ν_c) ^{35}Cl NQR frequencies for them are observed (Fig. 1):

$$\nu_c = 1.020\ (\pm\ 0.030)\ \nu_e - 0.853\ (\pm\ 0.978), \quad r = 0.995, \quad n = 47. \tag{4}$$

This correlation is somewhat improved at exception of the compounds 24, 25, 35, 36, and 41, for which the difference between the calculated and experimental ^{35}Cl NQR frequencies exceeds 1 MHz.

$$\nu_c = 1.001\ (\pm\ 0.030)\ \nu_e - 0.147\ (\pm\ 0.989), \quad r = 0.996, \quad n = 42. \tag{5}$$

The satisfactory correlation is observed as well between the experimental η values and calculated ones using populations of 3p-components of the Cl atom valence p-orbitals.

$$\eta_c = 1.028\ (\pm\ 0.182)\ \eta_e + 0.601\ (\pm 2.290), \quad r = 0.966, \quad n = 13. \tag{6}$$

The η values for the compound 28 not follow this correlation. So far as the calculated in this way NQR parameters are close to the experimental ones the free member in these equations have the small value and the coefficients at ν_e and η_e are close to one. These results show that the analysis of populations of the less diffuse components of the Cl atom valence p-orbitals obtained from *ab initio* calculations of organic and organometallic molecules provides the most reliable interpretation of their NQR parameters.

Recently we have found the satisfactory linear correlation between the experimental ^{35}Cl NQR frequencies for a great number of chloro-containing organic, organometallic and inorganic compounds and the populations of the Cl atom valence p_z-orbital in them obtained from CNDO/2 calculations of these molecules [5]. This correlation confirms the reverse linear dependence between the ^{35}Cl NQR frequencies or the EFG at the ^{35}Cl nucleus on the Cl-M bond direction and the Cl atom p_σ-electron density. Analogous correlation is observed at the using the total populations ($Np_z = N3p_z + N4p_z$) of the Cl atom p_z-orbital obtained from *ab initio* calculations of corresponding molecules:

$$Np_z = -\ 0.024\ (\pm\ 0.001)\ \nu_e + 1.954\ (\pm\ 0.048), \quad r = 0.979, \quad n = 47. \tag{7}$$

Such correlation is considerably improved at the using the populations of the less diffuse 3p-components of the Cl atom valence p_z-orbital.

$$N3p_z = -\ 0.008\ (\pm\ 0.000)\ \nu_e + 1.227\ (\pm\ 0.009), \quad r = 0.993, \quad n = 47. \tag{8}$$

In the molecules studied the range of changes of total populations of the Cl atom p_z-orbitals is approximately 2.7

times as much than that of $3p_z$-components. Therefore, at the varying of substituents in these molecules the most changes occur in the most diffuse part of the Cl atom p-shell while the ^{35}Cl NQR parameters are determined by its less diffuse part which is less sensitive to X influence.

The linear correlation between the populations of $3p_z$-compounents and the half-sums of the populations of $3p_x$- and $3p_y$-components $(N3p_x + N3p_y)/2$ of the Cl atom valence p-orbital in compounds studied follow as well from (7), (8) and (1):

$$N3p_z = -0.329\ (\pm 0.024)\ (N3p_x + N3p_y)/2 + 1.621\ (\pm 0.023),\quad r = 0.971,\quad n = 47. \tag{9}$$

The range of changes of the $N3p_z$ values for these compounds is considerable more (0.182 e) than that of $(N3p_x + N3p_y)/2$ ones (0.061 e). Therefore, the Cl atom p_σ-electrons bring in the main contribution to the ^{35}Cl NQR frequency changes for compounds of the series ClX at X varying, and contribution of the Cl atom unshared electron pairs to them is small.

The compounds of the ClX series with any X substituents follow these correlations with both substituents, which exert only an inductive influence on the Cl atom (alkyl, for instance) and which take part in the p, π-interaction with the Cl atom unshared electron pairs (vinyl, benzyl, etc.) or in some other conjugation effects. These correlations point out that the NQR frequency changes on going from one compound to another depend, in general, on the change of the Cl atom p_σ-electron density in these compounds and, first of all, on the change of population of the less diffuse part of the Cl atom p_z-orbital.

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