Control of *ab initio* calculation correctness of the electron distribution in chlorine-containing molecules using ^{35}Cl NQR data

Valentin P. Feshin and Elena V. Feshina

Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences, 13 Lenin St., Perm, 614990, Russian Federation
E-mail: cheminst@mpm.ru

Abstract

Ab initio calculations of 2-chlorodioxene and 1-chloro-1-methoxycyclohexane were performed with total optimization of their geometry using the Hartree-Fock theory and the split valence basis set 6-31G(d). The ^{35}Cl frequencies at 77K for these compounds were obtained as well. These frequencies were compared with those resulting from *ab initio* calculations. This comparison allows controlling the correctness of *ab initio* calculations of electron distribution in chloro-containing molecules using ^{35}Cl NQR data.

Keywords: *Ab initio* calculations, ^{35}Cl NQR frequencies, 2-chlorodioxene, 1-chloro-1-methoxy-cyclohexane, electron distribution

Introduction

Our investigations have shown that the atomic orbital coefficients in different molecular orbitals, Mulliken's populations of atomic orbitals, etc. may be obtained incorrectly from the analysis of the electron distribution in molecules using quantum mechanical calculations, for instance at the RHF/6-31G(d) level. This incorrectness may result from coordinate origin displacement and molecule rotation in the process of the calculation. The authenticity of calculations carried out on chlorine-containing molecules may be controlled using ^{35}Cl nuclear quadrupole resonance (NQR) data. Recently we have established that the ^{35}Cl NQR frequencies (ν) and asymmetry parameters (η) of the electric field gradient (EFG) at ^{35}Cl nuclei as calculated using equations 1 and 2,[1–3] and populations of the less diffuse 3p-components of the chlorine atom valence p-orbitals in chlorine-containing molecules calculated with the Hartree-Fock method RHF/6-31G(d), satisfactorily conform to the corresponding experimental ^{35}Cl NQR data (e.g. refs[3–5]).

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

$$\eta = |(3Np_x - Np_y)/(Np_z - Np_x - Np_y)| \qquad \textbf{Eq 2}$$

Q is the atomic quadrupole moment, eq_{at} is the electric field gradient of the free atom, h is Planck's constant, Np_x, Np_y and Np_z are the populations of the indicator atom valence p-orbitals along the X-, Y- and Z-axes, respectively.

For a large number of organic and organometallic compounds the correlation between ^{35}Cl NQR parameters estimated in this manner and those experimentally determined has been established. For instance, the correlation between the calculated (v_c) and experimental (v_e) ^{35}Cl NQR frequencies has been observed for 42 compounds (equation 3).[5]

$$v_c = 1.001(\pm0.030)v_e - 0.147(\pm0.989), \quad r = 0.996 \qquad \textbf{Eq 3}$$

The conformity between estimated and experimental ^{35}Cl NQR parameters proves the correctness of the *ab initio* calculations on electron distribution in a molecule, and consequently, any substantial difference between these data indicates an erroneous calculation.

Results and Discussion

In this communication we provide the results of *ab initio* calculations on 2-chlorodioxene (**1**) and 1-chloro-1-methoxycyclohexane (**2**) as examples, using the Hartree-Fock theory, the split and polarized valence basis set 6-31G(d), and the Gaussian 94W program.[6] These calculations were performed with total optimization of the molecular geometry. The coordinate origin is chosen to be at the Cl nucleus, the Z-axis coincides with the Cl-C bond.

1   **2**
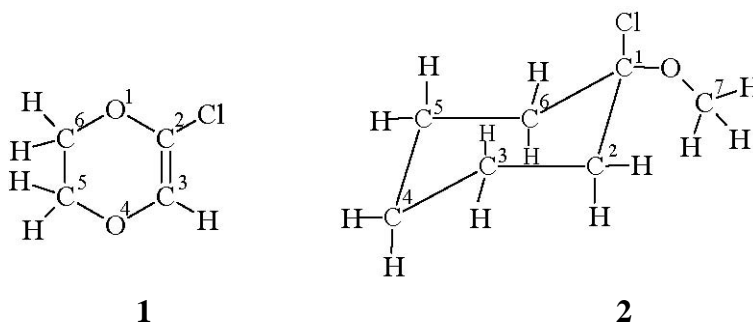
The geometrical characteristics of compounds **1** and **2** are given in Table 1, the atomic charges in Table 2; the populations of the valence p-orbitals of the chlorine atoms and the carbon atoms attached to them (Np), as well the populations of components of these orbitals are listed in

Table 3.

The atoms $O^1ClC^2=C^3HO^4$ in molecule **1** are practically in one plane (the dihedral angles are close to 0° or 180°). The O^4-C^5 and O^1-C^6 bonds deviate from this plane by more than 40° (Table 1). Molecule **2** assumes the chair conformation. The angle C^1OC^7 is substantially greater than the COC angles in **1** (Table 1). In both molecules the charges at the oxygen atoms are practically the same (Table 2).

Table 1. Bond lengths (d), internal (α) and dihedral angles (β) of **1** and **2** obtained from RHF/6-31G(d) calculations

Structure	Bond	d [Å]	Angle	α [°]	Angle	β [°]
1	O^1-C^2	1.347	$O^1C^2C^3$	124.3	$O^1C^2C^3O^4$	−1.4
	Cl-C_2	1.723	O^1C^2Cl	113.0	$ClC^2C^3O^4$	178.4
	C^2-C^3	1.317	$C^2C^3O^4$	122.6	$C^2C^3O^4C^5$	−13.8
	C_3-C_4	1.357	$C^2O^1C^6$	112.5	$C^3O^4C^5C^6$	43.05
	O^4-C^5	1.406	$C^3O^4C^5$	113.7	$C^5C^6O^1C^2$	45.5
	C_5-C_6	1.518	$O^4C^5C^6$	109.9	$O_4C_5C_6O_1$	−60.4
	C_6-O_1	1.412	$C_5C_6O_1$	109.6		
2	C^1-Cl	1.861	ClC^1O	108.5	$ClC^1C^2O^3$	−69.5
	C^1-O	1.369	$C^1C^2C^3$	113.9	$OC^1C^2O^3$	174.3
	C^1-C^2	1.525	C^1OC^7	120.1	$ClC^1C^6O^5$	70.2
	C_2-C_3	1.529	$C_2C_3C_4$	111.3	ClC^1OC^7	68.3
	C^3-C^4	1.530	$C^3C^4C^5$	111.1	$C_2C_3C_4C_5$	55.3
	O_4-C_5	1.530	$C^4C^5C^6$	111.9	$C^3C^4C^5C^6$	−55.3
	C^5-C^6	1.532	$C_5C_6C_1$	113.4	$C_4C_5C_6C_1$	52.2
	C_6-C_1	1.529				
	O-C_7	1.405				

Table 2. Charges (q) at the atoms of **1** and **2** obtained from RHF/6-31G(d) calculations

1	Atom	O^1	C^2	Cl	C^3	O^4	C^5	C^6		
	q [e]	−0.606	0.170	0.020	0.111	−0.611	−0.031	-0.041		
2	Atom	Cl	C^1	C^2	C^3	C^4	C^5	C^6	O	C^7
	q [e]	−0.161	0.254	−0.310	−0.331	−0.318	−0.325	−0.341	−0.606	−0.179

The ^{35}Cl NQR frequencies and the asymmetry parameters of the electric field gradient at the ^{35}Cl nuclei were estimated using the populations of 3p-components of the chlorine atom valence p-orbitals in molecules **1** and **2** and equations 1 and 2. For comparison, the experimental ^{35}Cl NQR frequencies at 77K have been measured for these compounds. The ^{35}Cl NQR spectra exhibit one line each at the frequency 35.814 MHz and 28.984 MHz, respectively (the signal to noise ratio for both lines is 10). The calculated NQR frequency for **1** (28.062 MHz) turned out to

be considerably lower, and the asymmetry parameter (32.8%) is considerably higher than the experimental ones for the chlorine atoms bonded to the sp^2-hybridized carbon atom in unsaturated molecules; the majority of the latter is in the range of ~5–15% (see, e.g.[3, 7]).

The ^{35}Cl NQR frequency calculated for molecule **2** (24.385 MHz) turned out considerably lower than the experimental value, and the estimated asymmetry parameter (14.4%) is considerably higher than the experimental values measured for saturated chlorine-containing organic compounds, usually being close to zero.[3, 7]

Table 3. Populations (Np, e) valence p-orbitals of the chlorine atom and the attached carbon atom in **1** and **2** as well as their (3p- and 4p-) and (2p- and 3p-) components, respectively, resulting from incorrect (**1a** and **2a**) and correct (**1** and **2**) RHF/6-31G(d) calculations

Atom	Orbital	1a	1	2a	2
Cl	$3p_x$	1.321	1.320	1.264	1.293
	$3p_y$	1.256	1.314	1.289	1.289
	$3p_z$	1.992	0.935	1.016	0.987
	$4p_x$	0.637	0.637	0.632	0.679
	$4p_y$	0.575	0.648	0.675	0.673
	$4p_z$	0.251	0.177	0.338	0.293
	Np_x	1.958	1.957	1.896	1.972
	Np_y	1.831	1.962	1.964	1.962
	Np_z	1.243	1.112	1.354	1.280
C	$2p_x$	0.676	0.683	0.669	0.722
	$2p_y$	0.623	0.642	0.665	0.647
	$2p_z$	0.621	0.594	0.500	0.465
	$3p_x$	0.090	0.074	0.198	0.215
	$3p_y$	0.390	0.451	0.192	0.174
	$3p_z$	0.269	0.224	0.255	0.256
	Np_x	0.766	0.757	0.867	0.937
	Np_y	1.013	1.093	0.857	0.821
	Np_z	0.890	0.818	0.755	0.721

Comparison of the experimental ^{35}Cl NQR parameters with those resulting from RHF/6-31G(d) calculations of the investigated molecules shows that the calculations of the populations of the chlorine atom valence p-orbitals are incorrect. The incorrectness may be caused by the displacement of the coordinate origin and by the deviation of the symmetry axes of the chlorine atom valence p-orbitals from the directions of the coordinate axes during the calculation process. The reason for this may be the long calculation time. The displacement of the coordinate origin can be seen from the output file. At the end of the calculation process the coordinates of the chlorine atom in **1** became –0.051, 1.128 and 0.439Å, in **2** –0.801, 0.359 and –0.417Å. A*b initio*

calculations of **1** and **2** at the RHF/6-31G(d) level have been repeated with the estimated geometrical characteristics as in the parameters. As a consequence, the coordinates of the chlorine atoms in **1** and **2** remained unchanged (0.000, 0.000 and 0.000 Å) or close to these values. The recalculated geometrical characteristics of these molecules (Table 1) and the atomic charges (Table 2) remained the same within the limits of calculation errors. The total energies for each of the molecules **1** and **2** in both calculations coincide as well. However, the coefficients at the atomic orbitals in different molecular orbitals, the populations of the atomic valence p-orbitals, as well as their components have substantially changed (Table 3). The recalculated ^{35}Cl NQR frequencies obtained when using the populations of 3p-components of the chlorine atom valence p-orbitals in **1** and **2** (35.64 MHz and 28.301 MHz, respectively) are close to the experimental values (see above). The asymmetry parameter of the EFG at the ^{35}Cl nuclei in **1** estimated using the recalculated populations of 3p-components of the chlorine atom valence p-orbitals in this molecule (2.0%) is close to the η-value for the *trans* chlorine atoms in molecules of the type $Cl_2C=CHOR$.[3] For the recalculated molecule **2**, the asymmetry parameter is close to zero too (2.1%). This is characteristic for chlorine atoms bonded to a sp^3-hybridized carbon atom.[3, 7] The estimated ^{35}Cl NQR frequencies and asymmetry parameters of the EFG at the ^{35}Cl nuclei for the recalculated molecules **1** and **2** allow the conclusion that the estimation of the electron density distribution is correct.

Thus, the correctness of *ab initio* calculations at the RHF/6-31G(d) level of electron distribution in chlorine-containing molecules may be proven using ^{35}Cl NQR data and does not require experimental NQR data. At present, a large number of chlorine-containing organic, inorganic and organometallic compounds is studied by this method (e.g. refs[3, 8–10]). Therefore the range of frequencies and of asymmetry parameters in which these NQR parameters for the molecule calculated should be easily estimated using available ^{35}Cl NQR data. The comparison with those estimated using the populations of 3p-components of the given chlorine atom valence p-orbitals allows to judge the correctness of the calculations of electron distribution in these molecules.

Acknowledgements

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