

Ab initio calculation of 4-ClC₆H₄CH₂Cl and peculiarities of electron density distribution in this molecule

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Ab initio calculation of the 4-ClC₆H₄CH₂Cl molecule was performed by the restricted Hartree—Fock method in the split valence 6-31G* basis set with complete optimization of its geometry. Populations of p-orbitals of atoms of this molecule were analyzed. ³⁵Cl NQR frequencies and asymmetry parameters of the electric field gradient on ³⁵Cl nuclei were estimated on the basis of the populations of valent p-orbitals of Cl atoms and their components. Good conformity with the experimental values was obtained when only less diffuse components of p-orbitals were used in calculations of populations.

Key words: *ab initio* calculations, 4-ClC₆H₄CH₂Cl, p-orbital populations, p,π-conjugation, asymmetry parameters, ³⁵Cl NQR frequencies.

According to the present views, the asymmetry parameter (η) of the electric field gradient (EFG) on ³⁵Cl nuclei is a quantitative measure of the dual character of the C—Cl bond in planar molecules, for example, in chloroethylene and chlorobenzene derivatives.^{1–3} For the latter compounds, the η value is ~5–17 % (see, for example, Refs. 3–13). This agrees with the concepts of the classical theoretical chemistry about p,π-conjugation between a lone electron pair of the Cl atom (or other heteroatom) and the π-electronic system of the double bond or the aromatic ring.^{14,15}

The η value for Cl atoms bound to the sp³-hybridized carbon atom, including the Cl atom in the CH₂Cl group of substituted benzyl chlorides, is equal or close to zero.^{3,7,13,16,17} This does not contradict the assumption about the existence of π,σ-conjugation between the π-electronic system of the aromatic ring and the C—Cl bond of the chloromethyl group in XC₆H₄CH₂Cl molecules. This conjugation is assumed on the basis of a lower ³⁵Cl NQR frequency of this group compared to that of methyl chloride (see, e.g., Ref. 18). However, these experimental data, in our opinion, are due to other reasons.^{7,16,17}

The analysis of asymmetry parameters of EFG on ³⁵Cl nuclei allowed us to conclude that they are not a quantitative measure of the dual character of the C—Cl bond even for planar fragments of molecules.⁸ The fact that the η parameter does not equal zero cannot be a proof for the participation of a lone electron pair of the Cl atom in any interaction, because, first, it characterizes the asymmetry of the electron distribution of the Cl atom only in a certain spatial area around its nucleus. This is quite reasonable, because EFG at the site of location of the nucleus of the indicator atom is inversely proportional to the cubic distance to the charges that created this EFG.^{1,2} Second, $\eta = (q_{xx} - q_{yy})/q_{zz}$ is

determined by three EFG components. Therefore, the η value alone, without additional information, cannot indicate which of three p-orbitals of the Cl atoms participates in the interaction with other AO and to what extent.

In order to study further the electronic effects in aromatic molecules, their manifestation in experimental data of ³⁵Cl NQR, and correlation of these data with the spatial electron density distribution of the Cl atom, we performed calculations of the molecule by the MNDO and *ab initio* methods with complete optimization of its geometry by the program Gaussian 92 for Windows (Gaussian Inc.).¹⁹ The calculation in the MNDO approximation was performed in the valence sp-basis set, and the *ab initio* calculation was performed by the restricted Hartree—Fock method in the split valence 6-31G* basis set, in which each valent orbital is presented as a combination of two orbitals of different sizes (for example, it consists of 3p- and 4p-functions for the Cl atom). The latter basis set is polarized, which makes it possible to take into account the change in the forms of orbitals of heavy atoms affected by various factors. When the 4-ClC₆H₄CH₂Cl molecule was calculated, the beginning of the system of coordinates was chosen at the site of location of the nucleus of the Cl(1) atom. The Z axis of this system is directed along the Cl(1)—C(2) bond, and the X axis is perpendicular to the plane of the molecule.

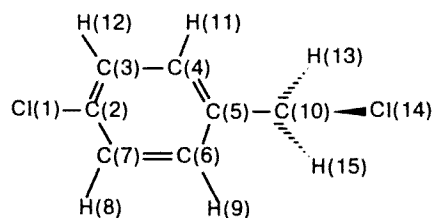


Table 1. Bond lengths (d), bond angles (α), and torsion angles (β) in the 4-ClC₆H₄CH₂Cl molecule optimized by the RHF/6-31G*(I) and MNDO (II) methods

Bond	$d/\text{\AA}$		Angle	α/deg		Angle	β/deg	
	I	II		I	II		I	II
Cl(1)—C(2)	1.742	1.750	Cl(1)C(2)C(3)	119.50	119.58	Cl(1)C(2)C(3)C(4)	179.82	179.88
C(2)—C(3)	1.383	1.407	C(2)C(3)C(4)	119.16	119.28	C(2)C(3)C(4)C(5)	-0.01	-0.11
C(3)—C(4)	1.384	1.406	C(3)C(4)C(5)	120.93	121.14	C(3)C(4)C(5)C(6)	0.08	0.32
C(4)—C(5)	1.388	1.416	C(4)C(5)C(6)	118.83	118.33	C(4)C(5)C(6)C(7)	-0.08	-0.32
C(5)—C(6)	1.388	1.416	C(5)C(6)H(7)	120.93	121.14	C(5)C(6)C(7)H(8)	180.10	180.02
C(6)—C(7)	1.384	1.406	C(6)C(7)H(8)	120.68	119.73	C(4)C(5)C(6)H(9)	179.73	179.54
C(7)—H(8)	1.073	1.090	C(5)C(6)H(9)	119.90	120.35	C(3)C(4)C(5)C(10)	180.34	180.49
C(6)—H(9)	1.076	1.092	C(4)C(5)C(10)	120.59	120.83	C(2)C(3)C(4)H(11)	179.80	179.75
C(5)—C(10)	1.503	1.502	C(3)C(4)H(11)	119.18	118.51	C(7)C(2)C(3)H(12)	180.03	179.80
C(4)—H(11)	1.076	1.092	C(2)C(3)H(12)	120.16	120.99	C(6)C(5)C(10)H(13)	-28.62	-28.37
C(3)—H(12)	1.073	1.090	C(5)C(10)H(13)	111.66	112.79	C(6)C(5)C(10)Cl(14)	90.20	90.10
C(10)—H(13)	1.078	1.108	C(5)C(10)Cl(14)	112.42	111.03	C(6)C(5)C(10)H(15)	209.02	208.57
C(10)—Cl(14)	1.806	1.810	C(5)C(10)H(15)	111.66	112.79			
C(10)—H(15)	1.078	1.108						

According to the *ab initio* calculation, the total energy E of the 4-ClC₆H₄CH₂Cl molecule is equal to -1187.539 eV. The results of optimization of its geometry by the RHF/6-31G* and MNDO methods are similar (Table 1). Dihedral angles indicate that the framework of the molecule is almost planar. The H and Cl atoms of the chloromethyl group are out-of-plane. The plane in which the C—Cl bond of this group lies is nearly perpendicular to the plane of the molecule.

According to the *ab initio* calculation of the aforementioned molecule, the total population of the p_x -orbital of its Cl(1) atom is somewhat lower (by 0.008, Table 2) than that of its p_y -orbital. The population of a less diffuse component of the p_x -orbital of this atom (3p-orbital) is also lower than that of the p_y -orbital (by 0.014). It can be supposed that the somewhat lower population of the p_x -orbital of the Cl atom is caused by its participation in p, π -conjugation with the π -electronic system of the aromatic ring. However, the population (both the total population and the 3p-component) of the p_y -orbital of the Cl atom, which is almost unable to participate in such a conjugation, is only slightly higher than that of the p_x -orbital. The overall population of both p_x - and p_y -orbitals of this Cl atom is considerably lower than 2. It is likely that the deficiency of electrons on the orbitals is due to reasons other than p, π -conjugation.

In carbon atoms of the aromatic ring, p_x -orbitals are also electron-deficiency (their total deficiency is 0.077). The only exception is the p_x -orbital of the C(2) atom bound with the Cl(1) atom, which possesses an excess of electrons (0.030). This excess is lower than the deficiency (0.043) of the p_x -electron density of the Cl(1) atom and lower than the total deficiency of electrons on other carbon atoms of the aromatic ring. This is due to the fact that the p_x -electron density of the atoms in the 4-ClC₆H₄CH₂Cl molecule is prone to redistribution not only between p_x -orbitals: their other orbitals participate in this redistribution as well.

The populations of valent p-orbitals of the Cl atoms in the 4-ClC₆H₄CH₂Cl molecule determined by *ab initio* calculation make it possible to estimate their ³⁵Cl NQR frequencies and asymmetry parameters of EFG on ³⁵Cl nuclei by the following equations (see, e.g., Refs. 1—3 and 8).

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

$$\eta = |3(N_{p_x} - N_{p_y}) / (2N_{p_z} - N_{p_x} - N_{p_y})|.$$

The ³⁵Cl NQR frequencies calculated from the overall populations of the p-orbitals of Cl atoms or of only the 4p-components of these orbitals differ substantially from

Table 2. *Ab initio* calculated partial (N_p) and overall (ΣN_p) populations of valent p-orbitals of atoms in the 4-ClC₆H₄CH₂Cl molecule

Orbital	Atom										
	Cl(1)			C(2),	C(3,7),	C(4,6),	C(5),	C(10),	Cl(14)		
	N_{p_x}	N_{p_y}	N_{p_z}	N_{p_x}	N_{p_x}	N_{p_x}	N_{p_x}	N_{p_x}	N_{p_x}	N_{p_y}	N_{p_z}
2p	—	—	—	0.569	0.531	0.516	0.545	0.536	—	—	—
3p	1.304	1.318	0.943	0.461	0.459	0.457	0.452	0.319	1.304	1.306	0.945
4p	0.653	0.647	0.185	—	—	—	—	—	0.674	0.672	0.242
ΣN_p	1.957	1.965	1.128	1.030	0.990	0.973	0.997	0.855	1.978	1.978	1.187

Table 3. ³⁵Cl NQR frequencies (ν) and asymmetry parameters (η) of EFG on ³⁵Cl nuclei in the 4-ClC₆H₄CH₂Cl molecule obtained experimentally¹⁷ and calculated from populations of p-orbitals of Cl atoms

Orbital	Atom							
	Cl(1)				Cl(14)			
	ν_{calc}	ν_{exp}	η_{calc}	η_{exp}	ν_{calc}	ν_{exp}	η_{calc}	η_{exp}
	/MHz		(%)		/MHz		(%)	
3p	34.261	34.567	5.81	6.3±0.7	33.545	33.754	0.90	1.2±0.7
4p	61.942		1.94		57.410		0.70	
ΣN_p	45.647		1.44		43.343		0.00	

the corresponding experimental values. However, the frequencies calculated from the populations of less diffuse 3p-components of valent p-orbitals of the Cl atoms are close to the experimental values. The same concerns asymmetry parameters η (Table 3).

It is noteworthy that no satisfactory correspondence between the experimental parameters η and those calculated from the populations of valent p-orbitals of Cl atoms (determined by semiempirical methods for the corresponding molecules) has been obtained. All previously calculated parameters η are considerably lower than the experimental values.^{8,20} This is due first of all to a slight difference in populations of valent p_x - and p_y -orbitals of Cl atoms in all the molecules studied, including those in which these atoms are bound with the sp^2 -hybridized C atoms, whose π -orbitals, according to the existing concepts, should participate in p, π -conjugation with one of the lone electron pairs of the Cl atom.

The dimensions of the 3p-components of valent p-orbitals of Cl atoms in the split valence 6-31G* basis set are considerably lower than those of the 4p-components. This difference in sizes of p-orbitals is not taken into account in the expressions for ν and η (see above). Therefore, the ν and η values calculated by these expressions using populations of individual components of valent p-orbitals of the Cl atoms (see Table 3) cannot be considered as individual contributions to the total values of ν and η . Since EFG in the site of location of the nucleus of the indicator atom is inversely proportional to the cubic distance to the charges that create this EFG, it can be assumed that the contribution of the 4p-components of the valent p-orbitals of this atom (more diffuse and less populated than 3p-components) to EFG and to ν and η is insignificant. This is confirmed by the good agreement between the experimental values and the ν and η values calculated from the populations of 3p-components of valent p-orbitals of the Cl atoms of 4-ClC₆H₄CH₂Cl (see Table 3) and other chlorine-containing molecules.^{21,22}

Thus, to calculate ³⁵Cl NQR frequencies and asymmetry parameters of EFG on ³⁵Cl nuclei by the known expressions (see above), the populations of the components of p-orbitals that determine this EFG to the greatest extent (closest to the nucleus) should be used

rather than the overall populations of diffuse valent p-orbitals of the Cl atoms. Substantially larger sizes of more diffuse 4p-components should be taken into account in calculations of their ν and η , these components contributing relatively little to these values.

The populations of the 3p_x-components of valent p-orbitals of both Cl atoms in the 4-ClC₆H₄CH₂Cl molecule are equal. This contradicts the consideration of asymmetry parameters of EFG on ³⁵Cl nuclei in derivatives of chlorobenzene. According to this consideration, the nonzero asymmetry parameter of the Cl atom is caused by p, π -conjugation between its lone electron pair and the π -electronic system of the aromatic ring. This conjugation should result in a lower population of the p_x -orbital of the Cl atom linked to the aromatic ring compared to that of the Cl atom in the CH₂Cl group. In the 4-ClC₆H₄CH₂Cl molecule, the orbital populations of the 3p_z-components of both Cl atoms are also almost equal. The difference in frequencies ν and parameters η of these Cl atoms is caused only by the difference in populations of their 3p_y-orbitals.

The populations of the corresponding components of valent p_x - and p_y -orbitals of the Cl atom in the CH₂Cl group are almost equal as well as their overall populations. The electron density distribution of this Cl atom has the axial symmetry along the whole distance from the nucleus corresponding to the size of 4p-components of its p-orbitals. Taking this into account, as well as the geometry of the 4-ClC₆H₄CH₂Cl molecule (see above), it can be assumed that the p_x - and p_y -orbitals of the given Cl atom almost do not interact directly with substituents near the adjacent C atom. This interaction can hardly be the same for both orbitals.

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