Ab initio calculations of p-Cl$_2$C$_6$H$_4$ molecule and its ^{35}Cl NQR parameters

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Ab initio calculations of p-dichlorobenzene molecule were carried out using the Hartree—Fock method in the 6-31G* valence-split basis set. The molecule was also calculated by the MNDO method in the valence sp-basis set for comparison. The populations of the valent p-orbitals of the C and Cl atoms were analyzed. The optimized geometry of the molecule as well as its ^{35}Cl NQR frequency and the asymmetry parameter of the electric field gradient at the ^{35}Cl nuclei calculated using the populations of the less diffuse components of the valent p-orbitals of the Cl atoms are in agreement with the corresponding experimental values for the α-modification of 1,4-Cl$_2$C$_6$H$_4$.

Key words: p-dichlorobenzene, *ab initio* calculations; p-orbital populations; ^{35}Cl NQR frequency, asymmetry parameter of the electric field gradient at the ^{35}Cl nuclei.

In accordance with the Townes—Dailey theory, the electric field gradient (EFG) at the nucleus of the "indicator" atom, the nuclear quadrupole resonance (NQR) frequency, and the EFG asymmetry parameter (η) are primarily determined by the valent p-electron shell of the atom in question. Charges exterior to this atom contribute only slightly to the EFG at the nucleus.[1,2] According to this approximation, the NQR frequency of ^{35}Cl (ν) and the asymmetry parameter η at the ^{35}Cl nucleus are related with populations (N) of the valent p-orbitals of the chlorine atom by the following relationships (z axis coincides with the direction of the M—Cl bond):[1—3]

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

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

Usually, the ^{35}Cl NQR frequencies and the EFG asymmetry parameters at the ^{35}Cl nuclei are estimated using the valent p-orbital populations of Cl atoms obtained *via* semiempirical calculation methods (CNDO, MNDO, *etc.*). Unfortunately, the agreement between the experimental values of ν and η and the values calculated by these methods is, as a rule, poor, in particular for the asymmetry parameters.[3—7] This brings some uncertainty into the interpretation of the NQR data, casting doubt upon the reliability of quantum-chemical estimations of the populations of the atomic valent p-orbitals in the molecules. Recently,[8—10] this inconsistency between experimental and calculated ν and η values has been found to be due to the fact that the strong dependence of the EFG at the nucleus of the

indicator atom on the distance (r) to the charges creating this gradient was not taken into account in the estimation of the full population of the valent p-orbitals of the chlorine atoms. The dependence in question is described by the following expression:[1,2]

$$eq_{zz} = -e\int \psi^*[(3\cos^2\theta - 1)/r^3]\psi d\tau. \quad (3)$$

From Eq. (3) one can assume that not only charges exterior to the indicator atom contribute slightly to the EFG (as follows from the Townes—Dailey approximation), but the populations of the most diffuse parts of the valent p-orbitals of the indicator atom itself[8—10] contribute as well. Therefore, when estimating the values of ν and η from Eqs. (1) and (2), there is no need to use the full populations of the valent p-orbitals of the indicator atom, but only their less diffuse parts which can be obtained from quantum-chemical calculations of the molecules in the split basis set.

Recently, this estimation of the ^{35}Cl NQR frequencies and the EFG asymmetry parameters at the ^{35}Cl nuclei has been carried out for a relatively small number of organic and inorganic molecules.[8—10] Therefore, the extension of the range of the objects calculated using this procedure is of fundamental importance for the correct interpretation of NQR data from the viewpoint of the characteristic features and the mechanism of the mutual influence of the atoms in the molecules. In this communication, the results of *ab initio* calculations of the p-dichlorobenzene molecule (the numbering of the atoms is given below) and its ^{35}Cl NQR parameters are presented.
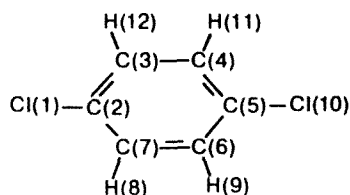
p-Dichlorobenzene was chosen because its experimental ³⁵Cl NQR frequencies and EFG asymmetry parameters

Table 1. Bond lengths (d) and bond angles (ω) in the 1,4-Cl₂C₆H₄ molecule optimized by the RHF/6-31G* and MNDO methods and their experimental values

Bond,	Calculation		Experiment[15]
angle	RHF/6-31G*	MNDO	
	d/Å		
Cl—C	1.741	1.749	1.74
C(2)—C(3)	1.383	1.409	1.39
C(3)—C(4)	1.384	1.406	1.39
C(4)—C(5)	1.383	1.408	1.37
C—H	1.073	1.090	—
	ω/deg		
Cl(1)—C(2)—C(3)	119.5	119.4	118.5
C(2)—C(3)—C(4)	119.5	119.4	119.3
C(3)—C(4)—C(5)	119.5	119.6	119.2
C(4)—C(5)—C(6)	120.9	120.9	121.5
C(2)—C(3)—H(12)	120.2	120.9	—
C(3)—C(4)—H(11)	120.3	119.6	—
C(4)—C(5)—Cl(10)	119.5	119.6	120.0

Table 2. The orbital energies (E) of the six HOMO in 1,4-Cl₂C₆H₄ molecule and the vertical ionization potentials (IP) of this compound[17,18]

MO	−E	IP
	eV	
1	9.20	8.95
2	9.97	9.87
3	12.37	11.38
4	12.50	11.45
5	12.65	11.51
6	13.99	12.77

at the ³⁵Cl nuclei are known (see Refs. 11—14). In addition, the data of X-ray studies of this compound are available.[15]

The *ab initio* calculations of the 1,4-Cl₂C₆H₄ molecule were carried out by the Hartree—Fock method in the split 6-31G* basis set with full optimization of geometry. This molecule was also calculated in the MNDO approximation using the valent sp-basis set with full optimization of geometry to compare both results. In all calculations, the origin of coordinates was placed at the nucleus of the Cl(1) atom. The *x* axis was perpendicular to the molecular plane, while the *z* axis was directed along the Cl—C bond. The calculations were carried out using the GAUSSIAN-92 for Windows[16] program package.

The optimized and experimental geometric parameters of the 1,4-Cl₂C₆H₄ molecule are listed in Table 1. The orbital energies of the six highest occupied MO obtained from the *ab initio* calculations and the energies of six vertical ionization potentials obtained from the photoelectron spectrum of *p*-dichlorobenzene[17,18] are given in Table 2. The populations of the valent p-orbitals of the chlorine and carbon atoms in this molecule are listed in Table 3. Along with the total populations (ΣN_p), the populations of components of the valent p-orbitals for the Cl and C atoms in the split basis set are given: for the less diffuse orbitals (2p for the C atom and 3p for the Cl atom) and for the more diffuse orbitals (3p for the C atom and 4p for the Cl atom).

Results and Discussion

Three crystalline modifications, α, β, and γ are known for *p*-dichlorobenzene. The geometric parameters of the molecules in these modifications are somewhat different. For instance, the C—Cl bond lengths in the α-modification of 1,4-Cl₂C₆H₄ are 1.74 Å, those in the β-modification are equal to 1.79 Å, the C(2)—C(3) and the C(3)—C(4) bonds in the α-modification are equal (1.39 Å), while they differ in the β-form (1.34 and 1.44 Å, respectively), *etc.*[15] The molecular geometry of 1,4-Cl₂C₆H₄ optimized by the RHF/6-31G* and MNDO methods (see Table 1) is closest to that in the α-modification for which the bond lengths and bond angles are given. This molecule is nearly planar: all its dihedral

Table 3. The populations (N) of the valent p-orbitals of the Cl and C atoms and their components in the 1,4-Cl₂C₆H₄ molecule calculated by the RHF/6-31G* and MNDO methods and the estimated ³⁵Cl NQR frequencies (v), and the EFG asymmetry parameters (η) at the ³⁵Cl nuclei

Method	Orbital	Cl(1,10)					C(2, 5)	C(3, 4, 6, 7)
		N_x	N_y	N_z	v/MHz	η (%)	N_x	
RHF/6-31G*	2p	—	—	—	—	—	0.576	0.527
	3p	1.305	1.318	0.942	34.439	5.31	0.466	0.453
	4p	0.652	0.647	0.184	62.030	1.75	—	—
	ΣN_p	1.957	1.965	1.126	45.755	1.44	1.042	0.980
MNDO	3p (2p)	1.974	1.933	1.150	45.672	3.42	(1.048)	(0.989)

angles are equal to 0 or 180°. In accordance with the symmetry type of the molecule its C—Cl bonds are equivalent as well as all C—H and C—C (C=C) bonds. The molecular geometry optimized by the RHF/6-31G* method is closer to the experimental geometry than that optimized in the MNDO approximation.

The planar structure of the molecule favors the participation of the unshared electron pairs of the Cl atoms (p_x-AO) in p,π-conjugation with the π-electron system of the aromatic ring. The populations of the p_x-AO of the Cl atoms, which are substantially less than 2, are in agreement with their participation in the conjugation. The deficiency of p_x-electron density on each chlorine atom (0.043) is, according to the *ab initio* calculations, equal to its excess on the bonded C atom. However, the p_y-orbitals of the chlorine atoms (p_y-AO), which lie in the molecular plane and not capable of p,π-conjugation, are also electron-deficient. Their deficiency (0.035) is only slightly less than that for the p_x-AO. The electron density deficiency is observed for the p_x-orbitals of all C atoms not bonded to Cl atoms. The p_x-orbitals of the Cl and C atoms contribute to the formation of MO with $E = -9.20$, -12.37, and -12.65 eV. Only the C(3), C(4), C(6), and C(7) atoms participate in the formation of the second occupied MO ($E = -9.97$ eV). The energies of these two highest occupied MO are close in their absolute value to two first vertical ionization potentials of *p*-dichlorobenzene. However, beginning with the third occupied MO, the difference between the calculated absolute values of the MO energies and the experimental ionization potentials increases (see Table 2).

The chlorine atoms are the most electronegative atoms in the $1,4$-$Cl_2C_6H_4$ molecule. Nevertheless, according to the *ab initio* calculations, they have a small positive charge (0.007). This might be due to the p_x- and p_y-electron density deficiency on these atoms. However, the negative charges (−0.137) on the C(2) and C(5) atoms to which, as one can assume, the p_x-electron density of the corresponding chlorine atoms is transferred, are much smaller than that on the carbon atoms not bonded to chlorine (−0.174). It seems likely that these carbon atoms accept electron density from the hydrogen atoms, which have a large positive charge (0.240).

The experimental ^{35}Cl NQR frequencies for the three crystal modifications of $1,4$-$Cl_2C_6H_4$ (α, β, and γ) differ somewhat (ν = 34.780, 34.765, and 35.208 MHz, respectively[19]) as do their EFG asymmetry parameters at the ^{35}Cl nuclei. The values of the EFG asymmetry parameters for the α- and β-modifications of $1,4$-$Cl_2C_6H_4$ reported in Ref. 11 are η = 6±2%; for the γ-modification η = 7.4%. The value of η obtained for the same compound by other authors[12,13] equals 7.16%, *etc.* (see, *e.g.*, Ref. 14). The ^{35}Cl NQR frequency and EFG asymmetry parameter at the ^{35}Cl nuclei of that molecule estimated according to Eqs. (1) and (2) using fully populated valent p-orbitals of the chlorine atoms (obtained from quantum-chemical calculations by both

MNDO and RHF/6-31G* methods) differ substantially from those found experimentally (see Table 3). However, if only the populations of the less diffuse components (3p) of the valent p-orbitals of the chlorine atoms calculated by the *ab initio* method are used, they appear to be close to the experimental values, in particular, for the α-modification (which is also the case with geometric parameters, see above).

These results are evidence that the estimation of the Mulliken populations of the valent p-orbitals of the chlorine atoms in the $1,4$-$Cl_2C_6H_4$ molecule calculated by the *ab initio* method in the 6-31G* basis set are correct. These populations, adequately describing the real spatial distribution of the electron density at the chlorine atoms, can serve as a good basis for drawing the conclusion that the atoms in the molecule have an effect on one another.

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