

# *Ab initio* calculations of *o*- and *m*-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> molecules and their <sup>35</sup>Cl NQR parameters

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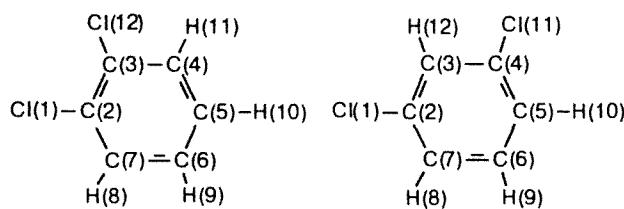
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The MNDO and *ab initio* (Hartree-Fock method, split 6-31G\* basis set, full optimization of geometry) calculations for the *o*- and *m*-dichlorobenzene molecules have been performed. The populations of the valent p-orbitals of the carbon and chlorine atoms have been analyzed. Estimations of the <sup>35</sup>Cl NQR frequencies and the asymmetry parameters of the electric field gradient at the <sup>35</sup>Cl nuclei have been made. It was confirmed that these values are not determined by the contribution of the whole valent p-shell, but only by its less diffuse component.

**Key words:** *o*- and *m*-dichlorobenzene, *ab initio* calculations; p-orbital populations; <sup>35</sup>Cl NQR frequency, asymmetry parameter of the electric field gradient at the <sup>35</sup>Cl nuclei.

The *ab initio* and MNDO calculations for a number of molecules of organic and inorganic compounds<sup>1-4</sup> have been carried out to study the peculiarities of the mutual influence of the atoms in the molecules and to establish the relations between the results of quantum-chemical calculations and the parameters of nuclear quadrupole resonance (NQR). It has been shown that the <sup>35</sup>Cl NQR frequencies ( $\nu$ ) and the asymmetry parameter ( $\eta$ ) of the electric field gradient (EFG) at the <sup>35</sup>Cl nuclei of chlorine-containing molecules calculated using the populations of the valent p-orbitals of the chlorine atoms significantly differ from the experimental values. This discrepancy is caused by disadvantages in the calculation procedure, which neglects the strong dependence of the EFG at the "indicator" atomic nucleus (and, hence, of the <sup>35</sup>Cl NQR frequencies and the EFG asymmetry parameters) on the distance to the charges creating the gradient. To remove this inconsistency in estimating the NQR parameters one can use the less diffuse components of the chlorine valent p-orbitals, which can be obtained from quantum-chemical calculations of the molecules in the valence-split basis set (see, e.g., Refs. 1-4), instead of the overall populations (as is required by Townes-Dailey theory).

In a continuation of our investigations we performed *ab initio* calculations of the *o*-dichlorobenzene and *m*-dichlorobenzene molecules (the numbering of the atoms is given below).



The origin of coordinates was set at the Cl(1) nucleus; the  $z$  axis was directed along the Cl(1)-C(2) bond, and the  $x$  axis was perpendicular to the molecular plane. The calculations were carried out both by the Hartree-Fock method in the split 6-31G\* basis set with full optimization of the molecular geometry using the GAUSSIAN-92 for Windows<sup>5</sup> program and by the MNDO approximation in the valent sp basis set. The optimized geometric parameters of these molecules are listed in Table 1, and the Mulliken charges on the

**Table 1.** Bond lengths ( $d$ ) and bond angles ( $\omega$ ) in the 1,2- and 1,3-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> molecules optimized by the *ab initio* (RHF/6-31G\*) and MNDO methods

Bond, angle	1,2-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>		1,3-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	
	RHF/6-31G*	MNDO	RHF/6-31G*	MNDO
<i>d</i> /Å				
Cl-C	1.735	1.747	1.741	1.751
C(2)-C(3)	1.387	—	1.383	—
C(3)-C(4)	1.387	1.410	1.383	1.409
C(4)-C(5)	1.385	1.404	1.383	1.406
C(5)-C(6)	1.385	1.409	1.384	1.406
C(6)-C(7)	1.385	1.383	1.383	1.407
C(7)-H(8)	1.073	1.091	1.073	1.090
$\omega$ /deg				
Cl(1)-C(2)-C(3)	121.8	—	119.0	—
C(2)-C(3)-C(4)	119.8	—	118.4	—
C(3)-C(4)-C(5)	120.3	120.0	121.5	120.8
C(4)-C(5)-C(6)	119.9	120.1	118.3	120.1
C(5)-C(6)-C(7)	119.9	120.1	120.8	120.8
C(6)-C(7)-H(8)	120.7	—	121.0	—
C(5)-C(6)-H(9)	120.4	—	119.6	—
C(4)-C(5)-H(10)	119.6	—	120.2	—
C(3)-C(4)-H, Cl(11)	119.0	—	119.0	—
C(2)-C(3)-Cl, H(12)	121.8	—	120.8	—

**Table 2.** Charges (*q*) on the atoms in the 1,2- and 1,3-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> molecules calculated by the *ab initio* method

1,2-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>		1,3-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	
Atom	<i>q/e</i>	Atom	<i>q/e</i>
Cl(1, 12)	0.036	Cl(1, 11)	0.010
C(2, 3)	-0.125	C(2, 4)	-0.130
C(4, 7)	-0.174	C(3)	-0.161
C(5, 6)	-0.193	C(5, 7)	-0.181
H(8, 11)	0.237	C(6)	-0.190
H(9, 10)	0.219	H(8, 10)	0.237
		H(9)	0.223
		H(12)	0.255

atoms (calculated by the *ab initio* method) are given in Table 2. The results of quantum-chemical calculations of the populations of the valent p-orbitals of the C and Cl atoms and their components (2p, 3p, and 4p) as well as the <sup>35</sup>Cl NQR frequencies and the EFG asymmetry parameters at the <sup>35</sup>Cl nuclei are listed in Tables 3 and 4.

## Results and Discussion

In accordance with *ab initio* and MNDO calculations, the 1,2- and 1,3-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> molecules are planar: all their dihedral angles are equal to 0 or 180°. The lengths of the relevant bonds and bond angles in these molecules differ insignificantly. Only the Cl(1)—C(2)—C(3) and C(2)—C(3)—Cl(12) angles in 1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> are significantly larger than the corresponding angles in

1,3-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> due to mutual repulsion of the chlorine atoms. The C—Cl bond lengths in each of these molecules are equal.

The most electronegative atoms in the molecules under study are the chlorine atoms. However, according to the *ab initio* calculations, the Cl atoms have small positive charges; the C atoms bear a large negative charge, whereas, as should be expected, the H atoms are positive. The negative charges on the C atoms increase as the distance between the carbon and chlorine atoms increases, which is in agreement with the damping induction effect of the chlorine substituent.

*Ab initio* calculations have shown that the populations of the orbitals of the lone electron pairs of the chlorine atoms perpendicular (p<sub>x</sub>-AO) to the molecular plane in the 1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> molecule are 0.048 less than 2. The populations of the p<sub>x</sub>-orbitals of the carbon atoms bonded to chlorine exceed 1 by the same value (see Table 3). It can be assumed that the electron density of the p<sub>x</sub>-orbitals of the chlorine atoms is delocalized on the adjacent carbon atoms. The populations of the orbitals of the lone electron pairs of the chlorine atoms, lying in the molecular plane (p<sub>y</sub>-AO) and incapable of p,π-conjugation with the aromatic π-system of the ring, are almost the same as those of p<sub>x</sub>-AO. A deficiency of π-electron density is observed for the C atoms not bonded to chlorine atoms in this molecule. However, if the populations of the p<sub>x</sub>-orbitals of all the C atoms are considered, the aromatic ring has an excess of π-electron density.

In the 1,3-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> molecule, the p<sub>x</sub>-orbitals of the Cl atoms are electron deficient, like those in

**Table 3.** Populations (*N*) of the valent p-orbitals of the Cl and C atoms in the 1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> molecule and their components (2p, 3p, and 4p), the <sup>35</sup>Cl NQR frequencies (*v*), and the EFG asymmetry parameters (*η*) at the <sup>35</sup>Cl nuclei, calculated by *ab initio* and MNDO methods

Method	Orbital	Cl(1, 12)				<i>v</i> /MHz	<i>η</i> (%)	C(2, 3)	C(4, 7)	C(5, 6)
		<i>N</i> <sub>x</sub>	<i>N</i> <sub>y</sub>	<i>N</i> <sub>z</sub>	<i>N</i> <sub>x</sub>			<i>N</i> <sub>x</sub>	<i>N</i> <sub>x</sub>	<i>N</i> <sub>x</sub>
RHF/6-31G*	2p	—	—	—	—	—	—	0.585	0.527	0.517
	3p	1.304	1.326	0.933	35.633	8.50	0.463	0.455	0.462	—
	4p	0.648	0.631	0.176	61.815	5.43	—	—	—	—
	$\Sigma N_p$	1.952	1.957	1.109	46.330	0.89	1.048	0.982	0.970	—
MNDO	<i>N</i> <sub>p</sub>	1.973	1.993	1.133	46.577	3.53	1.054	0.989	0.984	—

**Table 4.** Populations (*N*) of the valent p-orbitals of the Cl and C atoms in the 1,3-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> molecule and their components (2p, 3p, and 4p), the <sup>35</sup>Cl NQR frequencies (*v*), and the EFG asymmetry parameters (*η*) at the <sup>35</sup>Cl nuclei, calculated by *ab initio* and MNDO methods

Method	Orbital	Cl(1, 11)					<i>v</i> /MHz	<i>η</i> (%)	C(2, 4)	C(3)	C(5, 7)	C(6)
		<i>N</i> <sub>x</sub>	<i>N</i> <sub>y</sub>	<i>N</i> <sub>z</sub>	<i>N</i> <sub>x</sub>	<i>N</i> <sub>x</sub>			<i>N</i> <sub>x</sub>	<i>N</i> <sub>x</sub>	<i>N</i> <sub>x</sub>	<i>N</i> <sub>x</sub>
RHF/6-31G*	2p	—	—	—	—	—	—	—	0.570	0.543	0.533	0.512
	3p	1.305	1.319	0.940	34.627	5.62	0.460	0.451	0.460	0.455	—	—
	4p	0.651	0.645	0.182	62.036	1.90	—	—	—	—	—	—
	$\Sigma N_p$	1.956	1.964	1.122	45.919	1.43	1.030	0.994	0.993	0.967	—	—
MNDO	<i>N</i> <sub>p</sub>	1.975	1.993	1.150	45.700	3.24	1.058	0.983	0.979	0.993	—	—

**Table 5.** Total (3p + 4p) populations ( $N$ ) of the valent p-orbitals of the Cl atoms in the  $\text{ClC}_6\text{H}_5$  and  $1,4\text{-Cl}_2\text{C}_6\text{H}_4$  molecules calculated by the *ab initio* method

$N$	$\text{ClC}_6\text{H}_5$	$1,4\text{-Cl}_2\text{C}_6\text{H}_4$
$N_x$	1.959	1.957
$N_y$	1.966	1.965
$N_z$	1.137	1.126

$1,2\text{-Cl}_2\text{C}_6\text{H}_4$ ; the  $p_x$ -orbitals of the C atoms bonded to chlorine atoms have excess electron density (see Table 4). The deficiency of  $p_x$ -electron density on the chlorine atoms in  $1,3\text{-Cl}_2\text{C}_6\text{H}_4$  is somewhat greater than its excess on the corresponding carbon atoms. The  $p_x$ -orbitals of the other C atoms are electron deficient. As a result, the aromatic ring of this molecule has an excess of  $p_x$ -electron density while the  $p_y$ -orbitals of the Cl atoms are only slightly less electron deficient than their  $p_x$ -AO.

The populations of the  $p_x$ -orbitals of the chlorine atoms in the 1,2- and  $1,3\text{-Cl}_2\text{C}_6\text{H}_4$  molecules calculated by the MNDO method, in principle, coincide with those computed by the *ab initio* method; only the ratios of these populations are different (cf. Tables 3 and 4).

The electron density of the  $p_\sigma$ -orbitals of the chlorine atoms (Table 5) decreases when passing from  $\text{ClC}_6\text{H}_5$ \* to  $1,4\text{-, }1,3\text{-, and }1,2\text{-Cl}_2\text{C}_6\text{H}_4$  (cf. Tables 3 and 4), which is in agreement with the electron-acceptor properties of chlorine substituents. The electron density of the  $p_x$ - and  $p_y$ -orbitals of the Cl atoms in all these molecules is much less than 2, and also decreases slightly in the same sequence. Thus, the introduction of a second chlorine atom into the  $\text{ClC}_6\text{H}_5$  molecule and the close approach of these atoms when passing from 1,4- to 1,3- and  $1,2\text{-Cl}_2\text{C}_6\text{H}_4$  affects the redistribution of the electron density of all the valent p-orbitals of the carbon atoms, and change their populations in the same way.

It is possible to calculate the  $^{35}\text{Cl}$  NQR frequencies and the EFG asymmetry parameters at the  $^{35}\text{Cl}$  nuclei of *o*- and *m*-dichlorobenzene molecules using the populations of the valent p-orbitals of the chlorine atoms and Eqs. (1) and (2) (see, for instance, Refs. 6-9).

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

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

Comparing the obtained values with the corresponding experimental data one can verify the correctness of the quantum-chemical calculations of those populations and the adequacy of the description of the spatial distri-

bution of the electron density on the chlorine atoms in the molecules based on those populations.

The  $^{35}\text{Cl}$  NQR frequencies in the 1,2- and  $1,3\text{-Cl}_2\text{C}_6\text{H}_4$  molecules calculated by the MNDO method using the populations of the valent p-orbitals of the chlorine atoms are close to those found by the *ab initio* method from the total populations ( $N_{3p} + N_{4p}$ ) of those orbitals (see Table 3, 4). Those values differ substantially from the corresponding experimental values, whose average values at 77 K are equal to 35.720 and 34.905 MHz (see Ref. 6). However, if only the less diffuse 3p-components of the chlorine valent p-orbitals are used, the  $^{35}\text{Cl}$  NQR frequencies obtained from the *ab initio* calculations are close to the experimental values. This is in agreement with previously obtained data.<sup>4</sup>

The experimental values of the EFG asymmetry parameters at the  $^{35}\text{Cl}$  nuclei in 1,2- and  $1,3\text{-Cl}_2\text{C}_6\text{H}_4$  are not available. An analysis of these values for other derivatives of chlorobenzene showed them to lie in the interval  $\sim 5\text{-}16\%$ . The EFG asymmetry parameters at the  $^{35}\text{Cl}$  nuclei in the molecules under study calculated using the populations of only the less diffuse 3p-components of the valent p-orbitals of the chlorine atoms lie in the same interval (see Tables 3, 4). If the total populations of these orbitals obtained from MNDO and *ab initio* calculations are used, the asymmetry parameters for  $1,2\text{-Cl}_2\text{C}_6\text{H}_4$  and  $1,3\text{-Cl}_2\text{C}_6\text{H}_4$  appear to be much smaller than those for other substituted chlorobenzenes.

These results confirm the previously drawn conclusion<sup>1-4</sup> that the  $^{35}\text{Cl}$  NQR frequency and the EFG asymmetry parameter at the  $^{35}\text{Cl}$  nucleus are not determined by the whole valent p-electron shell of the chlorine atom (as is assumed by the Townes-Dailey theory<sup>6,7</sup>), but only by its less diffuse component. The good agreement between the experimental and calculated values of the  $^{35}\text{Cl}$  NQR frequencies and the EFG asymmetry parameters at the  $^{35}\text{Cl}$  nuclei (see Refs. 1-4) for *o*- and *m*-dichlorobenzene and other molecules when the aforesaid points are taken into account indicates the validity of evaluating the populations of the valent p-orbitals of the chlorine atoms by using the RHF/6-31G\* method and the adequacy of the description of the spatial distribution of p-electron density based on them.

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\* The results of the *ab initio* (RHF/6-31G\*) calculations for these molecules are published elsewhere.

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