# Spatial Electron Density Distribution of Chlorine Atoms in Molecules of the Series 4-$XC_6H_4MCCl_2C(O)C_6H_5$ (M = S and Se)

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The $^{35}$Cl NQR frequencies and EFG asymmetry parameters at the $^{35}$Cl nuclei have been measured for compounds of the series 4-$XC_6H_4MCCl_2C(O)C_6H_5$ (M = S and Se, X = H and $CH_3$) at 77 K. The electron distribution at the Cl atoms in all the compounds studied differs from axial symmetry, and is unequal for the two Cl atoms of the $CCl_2$ group. The results of the measurements imply $p_\sigma$-electron density nonequivalence of Cl atoms in the $CCl_2$ group of these molecules.

*Key words:* NQR spectroscopy, Electron distribution, Organometallic compounds.

## Introduction

The M atom occupying a geminal position to the Cl atom in the $ClCH_2M$ group (M = $C_{sp^2}$, 0, Si, etc.) does not cause a deviation from axial symmetry of the electron distribution at the Cl atom [1–3], but it influences the $p_\sigma$-electron density of the Cl atom [1–6]. However, the electron distribution of the Cl atom attached to an sp$^3$-hybridized carbon atom may deviate from axial symmetry if this Cl atom takes part in a nonbonded interaction with other atoms (e.g., in $Cl(CH_2)_3SnCl_3$ [7]).

In molecules of the series XCOCl the geminal oxygen atom influences the chlorine electron density both along the C–Cl bond and normal to the direction of this bond. Thus electric field gradient (EFG) asymmetry parameters ($\eta$) at the chlorine nuclei have rather large values in all compounds of the series XCOCl [3].

For molecules of the series $Cl_2C = CXX'$, the geminal interaction of the Cl atoms does not lead to a deviation of their electron distribution from axial symmetry. At the same time such deviation takes place in related molecules under the influence of the more remote vicinal (cis) oxygen and chlorine atoms (X = OR or Cl) [8–12].

These results show that the deviation of Cl atom electron distribution from axial symmetry does not depend on hybridization of the carbon atom to which the Cl atom is attached. The large asymmetry of the Cl atom electron distribution in molecules of the series XCOCl is apparently due to the influence of the oxygen atom.

In the present work we have studied the electron distribution at the Cl atoms attached to sp$^3$-hybridized C atoms in molecules containing the carbonyl group. The deviation of the electron distribution from axial symmetry was revealed by measurements of the $\eta$ parameters [13].

## Experimental

Compounds of the series 4-$XC_6H_4MCCl_2C(O)C_6H_5$ (M = S and Se, X = H and $CH_3$) have been investigated. The syntheses of these compounds were carried out as described in [14]. The $^{35}$Cl NQR frequencies ($\nu$) and the EFG asymmetry parameters ($\eta$) were measured at 77 K (Table 1). The measurements were performed on polycrystalline substances using a pulse NQR spectrometer. The $\eta$ values were determined by use of the beats spectra of quadrupole spin echo envelopes in an external magnetic field, the intensity of which was $(2.4-6.4) \cdot 10^3$ A/m. The spectra of the beats were obtained from experimental interferograms by a program of fast Fourier transformation [15]. The relative error in the $\eta$ values was calculated at the 95% level of the beats spectrum.

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Table 1. $^{35}$Cl NQR frequencies at 77 K ($\nu^{77}$) of compounds of the series 4-$XC_6H_4MCCl_2C(O)C_6H_5$, their average values ($\nu_{av}$), the NQR line splitting ($\Delta\nu$) and EFG asymmetry parameters ($\eta$) at the $^{35}$Cl nuclei.

| M | X | $\nu^{77}$ (MHz) | $\nu_{av}$ (MHz) | $\Delta\nu$ (MHz) | $\eta$ (%) |
|---|---|---|---|---|---|
| S | H | 38.228 | 38.218 | 0.020 | 4.1 ± 1.0 |
| | | 38.208 | | | |
| | $CH_3$ | 38.407 | 37.737 | 1.341 | 3.2 ± 0.3 |
| | | 37.066 | | | 4.5 ± 0.2 |
| Se | H | 38.090 | 37.967 | 0.247 | 5.2 ± 0.5 |
| | | 37.843 | | | 3.5 ± 0.7 |
| | $CH_3$ | 38.359 | 37.710 | 1.298 | 2.6 ± 0.3 |
| | | 37.061 | | | 4.5 ± 0.5 |

## Results and Discussion

The $^{35}$Cl NQR spectra of all compounds of the series 4-$XC_6H_4MCCl_2C(O)C_6H_5$ (M = S and Se, X = H and $CH_3$) consist of two lines at 77 K (the number of the NQR lines is equal to the number of the Cl atoms in the molecule). In compounds of this series with M = S the $^{35}$Cl NQR frequency average values are rather higher than the ones for the corresponding compounds with M = Se. This correlation corresponds to an inductive effect of the geminal S and Se atoms, which have different electronegativities (2.6 and 2.5, respectively [16]). The electron donor influence of the $CH_3$ group on the Cl atoms corresponds to smaller average $^{35}$Cl NQR frequencies for the compounds with X = $CH_3$ than for the ones with X = H. However in all of the above mentioned cases, the difference between the $^{35}$Cl NQR frequency average values (see Table 1) is sufficiently small that it might arise from crystal effects [17].

In $C_6H_5SCCl_2C(O)C_6H_5$ the spectral splitting was so small that in the presence of magnetic field, the two $^{35}$Cl NQR lines coalesce owing to their broadening, and only one $\eta$ value was obtained for this compound (Table 1).

In the compound with X = $CH_3$ the $^{35}$Cl NQR spectrum splitting (Table 1) is much larger than can be expected for a pure crystallographic origin. Such a large spectral splitting of the $CCl_2$ group could arise from different orientations of two C–Cl bonds relative to the neighbouring molecular fragments. This orientational nonequivalence of the C–Cl bonds causes unequal spatial electronic interactions of the two Cl atoms with atoms adjacent to them. The unshared electron pairs of the geminal M atom and of the carbonyl oxygen atom at the vicinal position can also polarize C–Cl bonds. For example, in molecules of the series 4-$XC_6H_4OCHCl_2$ the different orientations of C–Cl bonds relative to the geminal 4-$XC_6H_4O$ group (the different interactions of the C–Cl bonds with the unshared electron pair of the oxygen atom) raise the splitting of the $^{35}$Cl NQR spectra of these compounds from 0.27 MHz (X = $NO_2$) to 2.85 MHz (X = F) [18]. In compounds of the series $Cl_2CHC(O)X$, a large value of the $^{35}$Cl NQR splitting (e.g., 0.51 MHz for X = $NH_2$ and 0.83 MHz for X = COOH [17]) is apparently produced by the influence of the C(O)X group.

It can be supposed that in molecules of the series 4-$XC_6H_4MCCl_2C(O)C_6H_5$ (M = S and Se) the orientational influence of the 4-$XC_6H_4M$ group is the main cause of the $^{35}$Cl NQR frequency splitting of the $CCl_2$ group, i.e. the C–Cl bond orientations relative to the 4-$XC_6H_4M$ group are approximately equivalent for X = H, but are essentially different for X = $CH_3$. At the same time the $C(O)C_6H_5$ group orientation influences the $\eta$ values, which are different for two Cl atoms of the $CCl_2$ group both for X = H and X = $CH_3$ (see Table 1).

As is seen from the $\eta$ values for the compounds studied (Table 1), the elctron distribution symmetry for the Cl atoms of the $CCl_2$ group deviates from axial, and is not equivalent for the pair of Cl atoms. A similar pattern was observed for the Cl atoms of the $CCl_3$ group in $CCl_3COCl$ ($\eta$ = 1.4, 2.3 and 3.2% [3]). In both cases the deviation of the electron distribution from axial symmetry is due to the influence of carbonyl oxygen atom at the vicinal position on the Cl atoms (similar to that for the cis-Cl atom in $Cl_2C = CHOR$ compounds [10–12]).

As was mentioned above, an EFG asymmetry parameter non-equivalence of the Cl atoms of the 4-$XC_6H_4MCCl_2C(O)C_6H_5$ compounds has been found. In the compounds with X = $CH_3$ the larger $\eta$ value belongs to the Cl atom which has the lower NQR frequency (see Table 1). The same correlation between the $\nu$ and $\eta$ quantities was observed in the compounds of the series $Cl_2C = CHOR$ [8–12]. In these compounds the Cl cis-atom, which has the lower NQR frequency and the larger EFG asymmetry parameter, is more approachable for the influence of the vicinal oxygen atom directly through the field. By analogy with the $Cl_2C = CHOR$ compounds, one can suppose that in the 4-$CH_3C_6H_4MCCl_2C(O)C_6H_5$ series, the Cl atom possessing the lower NQR frequency and the larger $\eta$ value (Table 1) is effected by the carbonyl oxygen atom through the field more strongly than the other Cl atom of the $CCl_2$ group. This suggests that the former Cl atom lies in the C–Cl bond forming the smaller dihedral angle with the C = O bond.

It should be noted that in $C_6H_5SeCCl_2C(O)C_6H_5$ the mentioned correlation between the quantities of $\nu$ and $\eta$ is not observed. The absence of such a correlation is explained by crystallographic effects which are dominant at the small $^{35}$Cl NQR spectral splitting in this compound.

## Conclusions

The present investigation shows that the electron density distribution of the Cl atom attached to the $sp^3$-hybridized carbon atom can deviate from axial symmetry as a result of the vicinal carbonyl oxygen atom influence. From the measurements of the $^{35}$Cl NQR frequencies and the EFG asymmetry parameters one can draw conclusions about intramolecular interaction geometry of the C–Cl bonds and the molecular fragments (ArM and C(O)Ph) in the compounds under investigation.

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