Spatial Electron Density Distribution of Chlorine Atoms in Molecules of the Series $Cl_2C=CXX'$

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Z. Naturforsch. **47a,** 150–152 (1992); received June 29, 1991

The EFG asymmetry parameters at ^{35}Cl nuclei have been measured for polycrystalline compounds of series $Cl_2C=CHX$ (X = OR, OCOR) and $Cl_2C=C(Cl)OCOR$ at 77 K. For the Cl trans-atoms in molecules $Cl_2C=CHX$, the η values are equal or close to zero. For the Cl cis-atom of these compounds and for all Cl atoms of compounds $Cl_2C=C(Cl)OCOR$, $\eta \sim 6$–9%. It was shown that the deviation from the axial symmetry of electron distribution of Cl atoms in these compounds is due to the influence not of the geminal, but of a vicinal atom or group directly through the field. The expected p, π-conjugation between the unshared electron pair of halogen and the π-electron system of double bond is absent in the molecules studied.

Introduction

In order to describe the features of the electron distribution in the $Y-C=C\langle$ group and to explain several properties of compounds containing such a group, the representations of the p, π-conjugation between the unshared electron pair (u.e.p.) of the Y heteroatom and the π-electron system of the double bond have often been used (see, e.g., [1–3]). Some scientists believe that such an interaction really exists (see, e.g., [1]). It may be experimentally tested how adequately these representations reflect the actual electron distribution in a plane $Y-C=C\langle$ fragment and thus how appropriate their use is in explaining the properties of compounds containing such a fragment. According to the available representations, when Y is halogen the p, π-conjugation involves one u.e.p. of the halogen atom, which is located in a plane perpendicular to the plane of the $Y-C=C\langle$ fragment, while the other u.e.p. is not involved in this interaction. The measure of such an interaction may be the asymmetry parameter (η) of the electric field gradient (EFG) at the halogen atom nucleus: $\eta=(q_{xx}-q_{yy})/q_{zz}$ (the z axis being directed along the C–Hal bond) (see, e.g., [4]). When the halogen atom is involved in the p, π-conjugation, the components of the EPG tensor along the x and y axes (q_{xx} and q_{yy}) will be unequal, and $\eta>0$. However, it is to be kept in mind that the same result may also be obtained from other reasons, which will be shown below. When the Hal atom is not involved in such a conjugation, then in the absence of other reasons that cause the deviation of the electron distribution of the halogen atom from axial symmetry, the q_{xx} and q_{yy} components will be the same, and the η value will be zero.

Therefore, the value of the EFG asymmetry parameter at the halogen atom nucleus in the $Hal-C=C\langle$ group gives ground for estimating the character of interactions involving the halogen atom, including its ability to be involved in the suggested p, π-conjugation.

Results and Discussion

We measured at 77 K the EFG asymmetry parameters at ^{35}Cl nuclei, of polycrystalline compounds of the series $Cl_2C=CHX$ (X = OR, OCOR), $Cl_2C=C(Cl)OCOR$, and cis-$ClCH=CHOC_6H_4Cl$-4 (Table 1) by envelope beats of the quadrupole spin echo in the external magnetic field [5]. The measuring error

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Table 1. ^{35}Cl NQR frequencies at 77 K and EFG asymmetry parameters at ^{35}Cl nuclei of some unsaturated compounds.

Compound	Assignment	ν^{77} (MHz)	η (%)
cis-$ClCH=CHOC_6H_4Cl-4$	cis	34.264	8.2±2.0
	arom	35.339	3.0±0.5
$Cl_2C=CHOCH_3$	cis	36.904	7.3±1.5
	trans	37.188	0.0±0.5
$Cl_2C=CHOC_6H_5$	cis	37.146	7.3±1.5
	trans	37.552	2.7±1.0
$Cl_2C=CHOC_6H_4Cl-4$	cis	36.753	7.5±0.8
	trans	38.561	0.0±0.5
	arom	35.315	4.2±0.8
$Cl_2C=CHOCH_2OCH(CH_3)_2$	cis	36.540	8.0±0.6
	trans	37.433	0.8±0.4
$Cl_2C=CHOCOCH_3$	cis	36.876	7.3±1.8
	trans	38.220	1.2±0.6
$Cl_2C=CHOCOOCH_3$	cis	37.166	8.1±2.0
	trans	37.870	3.5±2.0
$Cl_2C=CHOCOC_6H_5$	cis	37.306	8.1±2.0
	trans	37.796	1.1±0.2
$Cl_2C=CHOCOC_6H_4NO_2-4$	cis	37.778	6.7±2.4
	trans	37.484	1.4±0.2
$(Cl_2C=CHO)_2Si(CH_3)_2$	cis	36.521	7.7±0.5
	cis	36.664	
	trans	37.506	1.5±0.3
	trans	37.548	
$Cl_2C=CHOCOCOOC_2H_5$	cis	37.310	9.0±2.7
	trans	38.017	6.6±1.6
$Cl_2C=C(Cl)OCOC_2H_5$		36.807	9.2±1.4
		38.297	7.6±0.8
		38.600	7.7±0.6
$Cl_2C=C(Cl)OCOC(CH_3)_3$		36.88	8.3±0.7
		38.19	6.5±0.5
		38.55	8.6±0.4

of η was determined to be at a 95% level of the corresponding beat spectrum. The assignment of η values to Cl atoms in cis- and trans-positions to the X group of molecules $Cl_2C=CHX$ was unambiguously performed by the ^{35}Cl NQR frequencies corresponding to these atoms. But the assignment of NQR frequencies to these atoms is performed using the ratio of experimental ^{35}Cl NQR frequencies of corresponding cis- and trans-isomers $ClCH=CHX$ [6–8], as well as taking into account the regularity in the change of NQR frequencies of the Cl cis-atom in such compounds depending on the character of substituent X. According to this regularity, in the $ClC=CM$ group the partially negative charged M atom (M = N, O, Cl, etc.) lowers, and the positive charged M atom (M = H, Si, Ge, etc.) raises the NQR frequency of the Cl cis-atom [7]. This is due to the polarization of the C–Cl cis-bond under the action of the M atom charge directly through the field. Such an interaction and experimentally observed regularity of the M atom influence on the Cl cis-atom in the $ClC=CM$ group are also confirmed by the calculated results of the contribution to the ^{35}Cl NQR frequency of the influence of Cl and H atom charges on the NQR frequency of the Cl cis-atom in cis- and trans-$ClCH=CHCl$ [8]. In accordance with the regularity mentioned above, for example, the ^{35}Cl NQR frequencies of cis-$ClCH=CHOR$ when $R=CH_3$ ($\nu^{77}=34.219$ MHz) and $C(CH_3)_3$ ($\nu^{77}=33.828$ MHz) are noticeably lower than those of trans-isomers (35.003 and 34.689 MHz, respectively) [6, 7].

Hence, the available experimental data imply that the NQR frequency of the Cl cis-atom in ^{35}Cl NQR spectra of compounds $Cl_2C=CHOR$ and $Cl_2C=CHOCOR$ must generally be lower than that of the trans-atom [7, 9–11]. The quadrupole spin-lattice relaxation times T_1 are also consistent with such an assignment of NQR frequencies for the latter compounds, and for Cl cis-atoms they are much shorter than those for trans-atoms [12]. Thus a lower NQR frequency and smaller T_1 value usually correspond to the Cl cis-atom in these compounds as compared to those for the trans-atom. The exception is $Cl_2C=CHOCOC_6H_4NO_2-4$, whose low frequency line in the NQR spectrum corresponds to the larger T_1 values [12]. Taking into account the insignificant difference in NQR frequencies and the large difference in T_1 values for Cl cis- and trans-atoms in the latter compound, the line assignment in its NQR spectrum is better made by the T_1 values. In tis case the ratio of the NQR frequencies of Cl cis- and trans-atoms in this compound is anomalous, which is explained by the crystalline effect [12].

The η values corresponding to the low frequency lines in the NQR spectra of studied compounds of series $Cl_2C=CHOR$ and $Cl_2C=CHOCOR$ are markedly larger than those of high frequency ones. The exception is for $Cl_2C=CHOCOC_6H_4NO_2-4$, which confirms the line assignment in the NQR spectrum of this compound to Cl cis- and trans-atoms by the T_1 values for them and the anomalous ratio of the NQR frequencies of these atoms. Thus, for all studied compounds of the series $Cl_2C=CHOR$ and $Cl_2C=CHOCOR$ the η value of the Cl trans-atom is much lower than that of the cis-atom, and for the Cl trans-atom the η value is zero or close to it. This indicates an essentially axial symmetry of electron distribution of the Cl trans-atom of the compounds studied. In turn, this makes it possible to conclude that the Cl trans-atom of these compounds is essentially not involved in the suggested p, π-conjugation with the π-electron system of the double bond. Since in the molecules $Cl_2C{=}CHX$ both Cl atoms possess the same ability for such an interaction, it should be supposed that the Cl cis-atom is not involved in such an interaction either. A relatively large η value for the latter is due to the influence of the OR or OCOR group and, first of all, to their oxygen atoms, directly through the field [10, 11]. The same holds for the monohalogenoderivatives $HalCH{=}CHX$, which is indicated by their η values. Thus, the EFG asymmetry parameter at the ^{127}I nuclei in trans-$ICH{=}CHI$ is close to zero ($\eta = 2.5\%$) [13], while for cis-$ClCH{=}CHOC_6H_4Cl$–4 the EFG asymmetry parameter at the ^{35}Cl nucleus has a relatively large value (8.2% [10]) (Table 1). For Cl atoms bonded to the aromatic ring in the latter compound and $Cl_2C{=}CHO{-}C_6H_4Cl$–4, the NQR frequencies and asymmetry parameters are similar, which is quite natural because in passing from one of these compounds to another the changes occur far from these chlorine atoms (certainly, when the conformation of these molecules is the same).

In all studied compounds of the series $Cl_2C{=}CHOR$ and $Cl_2C{=}CHOCOR$ the η values for the Cl cis-atom vary within a small range (~6–9%). For the Cl trans-atom, η is zero or close to it, but in the molecule $Cl_2C{=}CHOCOCOOC_2H_5$ the η value of the Cl trans-atom is close to the η values of the Cl cis-atom in the molecules $Cl_2C{=}CHOR$ and $Cl_2C{=}CHOCOR$. Apparently, this is due to the influence of the oxygen atoms of the substituent $COCOOC_2H_5$ on the electron distribution of the Cl trans-atom in this molecule directly through the field. Such an influence is possible when this substituent moves out of the dichlorovinyl group plane and its oxygen atoms approach the Cl trans-atom.

The data presented above show that in the molecules $Cl_2C{=}CHOR$ and $Cl_2C{=}CHOCOR$ the oxygen atom influences directly through the field not only the p_σ-electron density of the Cl cis-atom, but also its electron distribution in directions perpendicular to the C–Cl bond, and so here $\eta > 0$. It may be expected that the same influence on the Cl cis-atom will be produced by other substituents X in molecules $Cl_2C{=}CXX'$. This is supported by large values of the EFG asymmetry parameters at ^{35}Cl nuclei for all Cl atoms in molecules $Cl_2C{=}CClOCOR$ (Table 1) and $Cl_2C{=}C(Cl)COOH$ (16.91, 16.07 and 15.52% [14]), as well as by the large EFG η values at ^{127}I nuclei in the molecules $I_2C{=}Cl_2$ (20.3 and 18.7% [13]) and $(F_3CS)IC{=}ClNO_2$ (12.05 and 15.9%) [13]). The large η values for these compounds are due to the interaction of the vicinal heteroatoms. Strange as it may seem, the interaction of geminal heteroatoms bonded to the same carbon atom, causing a significant change in p_σ-electron density of each other, practically do not distort their axial symmetry. This is indicated by the fact that the η values for the Cl trans-atom in molecules of the series $Cl_2C{=}CHOR$ and $Cl_2C{=}CHOOCR$ is close to zero and that the η values of their Cl cis-atoms are essentially the same as for cis-$ClCH{=}CHOC_6H_4Cl$–4 and for all Cl atoms in compounds of the series $Cl_2C{=}CClOCOR$ (Table 1).

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