The EFG Asymmetry Parameters at ^{35}Cl Nuclei and the Electronic Effects in Chlorine-Containing Organic and Complex Compounds of Group IVA and VA Elements*

Valentin P. Feshin and Mikhail G. Voronkov

Institute of Organic Chemistry, Siberian Branch of the USSR Academy of Sciences, Irkutsk, USSR

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The ^{35}Cl NQR method and, in particular, the EFG asymmetry parameters at ^{35}Cl nuclei were used for the solution of a number of principal problems of theoretical organic and organometallic chemistry, such as the mechanism of non-induction influence of the heteroatom M on the atom Y in the non-linear Y–Z–M or Y–Z=M group, M–Cl bond multiplicity in planar molecular fragments and the asymmetry of halogen atom electron distribution in organic and organometallic molecules. In tetrahedral molecules this distribution is nearly axially symmetric for different M. This symmetry is also characteristic for axial chlorine atoms in trigonal-bipyramidal and octahedral molecules, independently of M. The deviation of the electron distribution of equatorial chlorine atoms from axial symmetry in the two latter cases depends essentially upon M and does not depend much on the peculiarity of the formation of these polyhedra and the character and number of substituents.

Introduction

It is well known that NQR frequencies and electric field gradient (EFG) asymmetry parameters at halogen nuclei (η) provide valuable information concerning the electron density distribution of these atoms and enclosing molecules (see, for example, [1, 2]). Unfortunately, the asymmetry parameters at nuclei with spin $I=3/2$ are not as accessible as NQR frequencies. Therefore, electron distribution in molecules cannot often be obtained as fully as possible. Fairly reliable and convenient measurements of η values for ^{35}Cl nuclei became possible after the development of a technique for the η determination of polycrystalline compounds from the modulation spectrum of the quadrupole spin echo envelope [3]. This technique has been used by us to solve a number of fundamental problems of theoretical organic and organometallic chemistry. These results are summarized in the present work.

Experimental

Table 1 shows the ^{35}Cl NQR frequencies and η values at ^{35}Cl nuclei measured at 77 K with a pulsed NQR spectrometer of the IS-3 type. The η values of polycrystalline substances are determined by use of the spectra of quadrupole spin echo envelopes modulated with a constant outer magnetic field, the intensity of which is about $5 \cdot 10^3 \text{ A m}^{-1}$. The modulation spectrum was obtained from an experimental interferogram by a routine program of fast Fourier transformation. The relative error in η was calculated at the 95% level of the modulation spectrum [3].

Results and Discussion

The experimental data characterizing the distribution of the chlorine atom electron density in the molecule of various organic compounds and complexes of IVA and VA group elements have made it possible to outline a number of principal problems of theoretical chemistry and to contribute to the solution of these problems. In particular, these data have been used to solve the problem of non-induction influence of heteroatom M on the Y indicator atom in the Y–Z–M or Y–Z=M group (Z=C, Si, Ge, P etc.; M=atom

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Reprint requests to Prof. V. P. Feshin, Institute of Organic Chemistry, USSR Academy of Sciences Siberian Branch, 1 Favorsky Street, 664033 Irkutsk/USSR.

Table 1. ^{35}Cl NQR frequencies ν , and EFG asymmetry parameters η at ^{35}Cl nuclei of organic compounds and complexes of group IVA and VA elements (77 K).

No.	Compound	ν , MHz	η , %	No.	Compound	ν , MHz	η , %	Bond
1	$\text{ClCH}_2\text{OC}_3\text{H}_7$	29.987	0.0 ± 0.8	20	$\text{Cl}(\text{CH}_2)_3\text{SnCl}_3$	31.750	8.7 ± 2.0	C–Cl
2	$\text{ClCH}_2\text{Si}(\text{CH}_3)_3$	34.320	0.5 ± 0.4			20.352	6.3 ± 1.0	eq
3	$\text{ClCH}_2\text{SiCl}_3$	36.786	2.0 ± 1.0			20.160	10.7 ± 1.0	eq
4	$\text{ClCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$	32.700	1.0 ± 0.7			19.668	0.4 ± 1.0	ax
5	CH_3COCl	29.070	20.0 ± 1.0	21	$\text{C}_6\text{H}_5\text{PCl}_4$	33.774	33.5 ± 2.5	eq
		28.855	20.0 ± 2.0			33.588	33.5 ± 2.5	eq
6	ClCH_2COCl	30.437	17.6 ± 1.0			25.510	1.4 ± 1.0	ax
		37.517	1.2 ± 1.0			24.608	4.5 ± 1.5	ax
7	$\text{C}_6\text{H}_5\text{COCl}$	29.918	22.0 ± 1.0	22	$(\text{C}_6\text{H}_5)_2\text{PCl}_3$	33.450	28.5 ± 2.0	eq
8	$\text{cis-ClCH=CHOC}_6\text{H}_4\text{Cl-4}$	34.264	8.2 ± 2.0			22.336	2.5 ± 1.5	ax
		35.339	3.0 ± 0.5	23	$(\text{CH}_3)_3\text{N} \cdot \text{SiCl}_4$	21.502	42.1 ± 7.2	eq
9	$\text{Cl}_2\text{C=CHOCH}_3$	36.904	7.3 ± 1.5			21.296	36.6 ± 4.0	eq
		37.188	0.0 ± 0.5			18.857	1.7 ± 0.5	ax
10	$\text{Cl}_2\text{C=CHOC}_6\text{H}_5$	37.146	7.3 ± 1.5	24	$(\text{CH}_3)_3\text{N} \cdot \text{GeCl}_4$	24.829	25.3 ± 3.9	eq
		37.552	2.7 ± 1.0			24.657	24.2 ± 3.3	eq
11	$\text{Cl}_2\text{C=CHOC}_6\text{H}_4\text{Cl-4}$	36.753	7.5 ± 0.8			20.585	2.0 ± 0.9	ax
		38.561	0.0 ± 0.5	25	$\text{C}_6\text{H}_5\text{OCH}_3 \cdot \text{SnCl}_4$	23.851	12.0 ± 1.0	eq
		35.315	4.2 ± 0.8			23.656	9.2 ± 1.0	eq
12	OPCl_3	28.95*	4.0 ± 0.8			23.391	13.3 ± 1.0	eq
13	$\text{OP}(\text{C}_6\text{H}_5)\text{Cl}_2$	26.70*	0.4 ± 0.5			20.182	0.9 ± 0.5	ax
14	SPCl_3	29.800	5.4 ± 2.0	26	$2\text{Cl}_3\text{PO} \cdot \text{SnCl}_4$	30.217	5.1 ± 0.6	P–Cl
		29.675	3.3 ± 1.5			30.117	5.1 ± 0.6	P–Cl
15	$\text{SP}(\text{C}_6\text{H}_5)\text{Cl}_2$	27.840	0.6 ± 0.6			21.132	2.3 ± 0.5	ax
16	$[\text{PCl}_4]^+[\text{AlCl}_4]^-$	32.180	0.8 ± 0.5			19.794	11.1 ± 2.0	eq
17	SiCl_4	20.39*	2.9 ± 0.5			19.030	11.1 ± 2.4	eq
18	GeCl_4	25.66*	2.2 ± 0.5	27	$2\text{ClCH}_2\text{COOCH}_3 \cdot \text{SnCl}_4$	37.756	1.1 ± 0.5	C–Cl
19	SnCl_4	24.10*	2.9 ± 0.5			21.913	1.7 ± 0.5	ax
						19.593	9.0 ± 1.6	eq
						18.566	1.1 ± 0.5	ax

* NQR frequency average values.

with lone electron pairs or with vacant d-orbitals). Usually, this influence has been explained in terms of different conjugation effects depending on the character of the Y, Z and M atoms (see, for example, [1, 2, 4]). On the basis of experimental data available we suggested this non-induction influence to be mainly due to one and the same mechanism with any Y, Z and M, that of the Z–Y bond polarization upon through field action of the charge of M. Some scientists [1, 5] erroneously consider this to be dipole-dipole interaction of the Y–Z and Z–M bonds. However, the latter should lead to the same change in the Y atom electron density as that induced by the inductive effect of heteroatom M or the involved substituent. The suggested “through field” interaction of the charge of M with the Z–Y bond electron cloud leads to an opposite effect and explains well the experimental data from a single viewpoint (see, for example, [2, 4, 6]).

The participation of Y atom p_σ -electrons (Y=Cl) with any M in the above interaction serves as an argument for a single electrostatic mechanism of the

non-induction effect of M on Y with any Y, Z, and M. This participation is also in agreement with zero or close to zero η values at the ^{35}Cl nuclei of compounds containing a Cl–C–M group (M=C, O, Si) (Table 1) [7] and with CNDO/2 quantum-chemical calculation of these molecules [8]. In all these molecules the population of Cl p_x - and p_y -orbitals is close to 2. With varying the substituents at the sp^3 -hybridized carbon atom only the chlorine p_z -orbital population changes noticeably. The data obtained show the electron density distribution of the chlorine atom attached to the sp^3 -hybridized carbon atom to be nearly axially symmetric. The latter cannot be distorted even by bulky groups such as trichlorosilyl and silatranyl groups (Table 1). Evidently, deviation from the axial symmetry of the chlorine atom electron distribution of this kind can only be caused by its participation in additional interaction with some other atoms. This situation seems to be the case in 3-chloropropyl-trichlorostannane. According to X-ray diffraction, the tin atom in this molecule is pentacoordinated due to

its interaction with the chlorine atom of the 3-chloropropyl group. The η value of this chlorine atom is 8.7% (Table 1) [9].

In molecules of the series XCOCl an overlapping of the Cl lone pair electron orbital with the carbonyl group π -orbital is suggested. Therefore, a large η value can be expected for these compounds, and this is observed in fact (Table 1) [10]. This p_π -conjugation is not confirmed, however, by the C–Cl bond lengths in these molecules. For example, the C–Cl bond length in CH_3COCl is nearly the same as that in CH_3Cl , and considerably longer than in CH_2Cl_2 . The lengths of the two C–Cl bonds in ClCH_2COCl and $\text{ClCH}_2\text{OCOCl}$ molecules are the same within the error limits of the measurements [10]. These experimental data enable a question to be posed: which quantity, is the best measure of the double bond character of C–Cl in planar molecules? Is this the bond length or η of the ^{35}Cl nucleus or neither? CNDO quantum-chemical calculations on molecules of the XCOCl series do not imply any significant p_π -conjugation in these molecules. The η value calculated for these molecules, by use of Cl p-orbital population [10, 11] is much lower than the measured value (Table 1). This allows the conclusion that usually only a small portion of η can be related to the C–Cl double bond character.

The main contribution to the deviation of chlorine electron distribution from axial symmetry seems to be due to the polarization of the lone pairs of Cl induced by the through field of the surrounding atoms. In this case, a polarization of this kind is suggested if Cl is bonded with the sp^2 -hybridized C atom rather than with the sp^3 -hybridized one. In order to check this suggestion, we measured η for a series of chloro-substituted ethylenes [12]. In $\text{ClCH}=\text{CHX}$ and $\text{Cl}_2\text{C}=\text{CHX}$ molecules the cis- and trans-Cl atoms should be involved in p_π -conjugation with the π -bond electrons to the same extent. However, the degree of their participation in through field interaction with the substituent X is quite different. If the chlorine cis-atom can readily be involved in this interaction, the trans-atom is shielded from the substituent X by the molecular skeleton and does not seem to be prone to this interaction. The η value of the Cl cis-atom turned out to be quite high, whereas that of the transatom is equal or close to zero (Table 1). This suggests that the p_π -interaction involving Cl atoms disappears in these molecules whereas the polarization of Cl cis-atom lone pairs induced through the field of the substituent X does take place. The polarization in fact manifests

itself in the relatively high η value. However this value is significantly lower than that for compounds of the XCOCl series, where polarization of this kind should be more efficient.

The absence of p_π -conjugation in the Cl–C=C-group contradicts the ideas generally accepted in theoretical chemistry concerning the interaction of atoms in unsaturated molecules. Therefore this conclusion needs further investigation with a wider set of compounds containing various heteroatoms at the double bond. Nevertheless, this conclusion is quite true and not so unexpected since it should be borne in mind that the conceptions of σ - and π -electrons are conventional. Bond length, the analysis of which gave rise to the conception of bond order, is far from being a unique and convincing parameter of this order (see, for example [13, 14]). Investigation of η on halogen nuclei in unsaturated compounds can throw light on this fundamental problem of theoretical chemistry.

The idea of conjugation of various atom orbitals is widely accepted for the explanation of various experimental data in organic and organometallic chemistry. However, explanations of this kind are lacking in good ground. Thus, slightly higher ^{35}Cl NQR frequencies for compounds of the ClP(S)XX' series compared with those of ClP(O)XX' are explained in terms of unequal conjugation between Cl lone pairs and vacant d-orbitals of the P atom [15, 16]. However, the asymmetry parameters measured by us for the corresponding compounds of these series (Table 1) [17] turned out to be nearly identical. They are close to zero, as is the case for other tetrahedral molecules of the ClCXX'X'' series, MCl_4 (M = Si, Ge, Sn), PCl_4^+ cation in $\text{PCl}_4^+ \cdot \text{AlCl}_4$ (Table 1). The electron distribution of the halogen atom in the M-Halogen bond seems to be of nearly axial symmetry in all the molecules with a tetrahedrally coordinated polyhedron of the central M atom (in the absence of an extra intra- or intermolecular interaction involving the halogen atom).

Some interesting information concerning the electron distribution of Cl atoms can be provided by η values of chlorophosphoranes [17]. These show a trigonal-bipyramidal structure. The NQR frequencies of their axial Cl atoms are considerably lower than those of equatorial Cl atoms. The η values of these atoms also differ much. The axial chlorine atoms display an axial or close to axial symmetry of electron distribution, the symmetry of distribution of equatorial atoms being considerably different from the axial ones

(Table 1). This is due to interaction of lone pairs of equatorial Cl atoms either with the phosphorus p-orbital located along the molecular axial fragment axis, or with the whole fragment. In analogy to organic planar molecules, this interaction is likely to be considered as a result not only of overlapping of the corresponding atomic orbitals, but also of their mutual polarization directly through field as well. At present, the electron density distribution in trigonal-bipyramidal molecules is often described in terms of hypervalent three-centre bonds involving p-orbitals of the three atoms of the axial fragment. Taking into account the higher η value of the equatorial Cl atoms of chlorophosphoranes, it seems better to make use of a hypervalent multicentre bond (instead of a three-centre one) involving the equatorial atoms of the molecule too. The hypervalent interaction with the p-orbital of the central atom (or with the p-orbitals of the whole axial fragment atoms) is also confirmed by X-ray emission P K_β - and Si K_β -spectra recorded by us as well as quantum-chemical calculations of chlorophosphoranes [18] and 1-substituted silatranes. In the latter, this interaction makes some contribution to most lines of the Si K_β -spectrum.

The electron distribution pattern, similar to that in chlorophosphoranes, is also observed in 3-chloropropyltrichlorostannane (Table 1) whose Sn atom coordination polyhedron is also trigonal-bipyramidal [9]. The prominent difference in the NQR frequencies and η values of axial and equatorial Cl atoms in Cl-containing trigonal-bipyramidal molecules may serve as a fairly reliable indication of the above structure.

One can also find a relationship of ^{35}Cl NQR frequencies with the lengths of the corresponding M–Cl bonds in tetrahedral and trigonal-bipyramidal molecules, with the length of coordination $\text{M} \cdots \text{X}$ bond in complexes, etc. This makes it possible to determine the lengths of some bonds by use of NQR spectra. Thus NQR spectroscopy of polycrystalline compounds is a helpful tool for the elucidation of molecular structure. We used this technique for establishing the structure of organyltrichlorogeromanes Cl_3GeX in which Ge can be pentacoordinated due to interaction with the substituent heteroatom of the ligand X [19]. This method was also used in studying trigonal-bipyramidal and octahedral MCl_4 complexes ($\text{M} = \text{Si, Ge, Sn}$) coordinated with organic compounds (see, for example, [20–25]). From the data obtained, the electron density distribution in trigonal-bipyramidal $\text{B} \cdot \text{MCl}_4$ complexes is of the same character as in

structurally similar chlorophosphoranes, 3-chloropropyltrichlorostannane and organyltrichlorogeromanes (Table 1). Axial Cl atoms are nearly axially symmetric. Their η values are close to zero and the NQR frequencies are much lower than those of equatorial Cl atoms. The electron distribution symmetry of the latter differs much from axial. Their η values are significantly larger than zero. Thus, the character of electron distribution in trigonal-bipyramidal molecules does not depend much on the peculiarities of the coordination polyhedron formation. The electron distribution can be described in terms of the same model, a hypervalent model, for instance. Nevertheless, atranes ($\text{XM}(\text{OCH}_2\text{CH}_2)_3\text{N}$; $\text{M} = \text{Al, B, Si, Ge, P}$ etc.) which show the same coordination polyhedron structure, are usually regarded as unique compounds in many respects, including electron distribution (see, for example, [26]). This does not make sense if the above data are taken into account.

Previously, it has been assumed [24] that the ^{35}Cl NQR spectra of trans-octahedral $2\text{B} \cdot \text{MCl}_4$ complexes contain one or several signals of similar frequencies, whereas those of cis-octahedral complexes show two signals or two groups of signals essentially different in frequency. However, the observed NQR spectra of these complexes often differ considerably from the expected ones and do not make it possible to distinguish cis- and trans-isomers and to assign the spectral lines to axial or equatorial chlorine atoms, etc. Analyses of the ^{35}Cl NQR spectra of octahedral complexes, especially η at ^{35}Cl nuclei in these complexes, and X-ray structural data show that the isomers cannot be determined by NQR spectra [22, 24]. The frequencies of the spectra as well as the lengths of axial M–Cl bonds for axial Cl atoms can be either larger or smaller than those for the equatorial ones (see, for example, data for the $2\text{ClCH}_2\text{COOCH}_3 \cdot \text{SnCl}_4$ complex in the Table 1). This gives rise to contradictory opinions concerning the ratio of NQR frequencies, charges etc. of axial and equatorial Cl atoms in octahedral complexes [25]. Due to the different character of interaction of axial and equatorial Cl atoms with the central atom, the asymmetry parameters provide a more reliable information about the position of Cl atoms in the octahedron than NQR frequencies do. In octahedral as well as in trigonal-bipyramidal molecules, the electron density distribution of axial Cl atoms is close to axially symmetric, whereas that in equatorial Cl atoms is quite different (Table 1).

Analysis of the η values at the ^{35}Cl nuclei of the M–Cl bonds in the compounds studied shows that with given M, the η value of equatorial Cl atoms does not differ much in compounds dissimilar in character. This value for intracomplex 3-chloropropyltrichlorostannane, for example, is nearly the same as that for trigonal-bipyramidal and octahedral SnCl_4 complexes. The value for the equatorial Cl atoms in octahedral and trigonal-bipyramidal compounds changes considerably only with a change of the M atom. The asymmetry parameters of the equatorial Cl atoms in $\text{Cl}(\text{CH}_2)_3\text{SnCl}_3$ and SnCl_4 complexes are significantly lower than in chlorophosphoranes. The η value of these Cl atoms in $\text{B} \cdot \text{MCl}_4$ complexes decreases fast in going from $\text{M}=\text{Si}$ to $\text{M}=\text{Ge}$ and Sn (Table 1). Thus, the deviation from the axial symmetry of the equatorial Cl electron distribution is greatly dependent upon the central atom character and does not depend much on the peculiarities of polyhedron formation and the character and number of substituents attached to the central atom. The electron distribution of the axial Cl atoms in trigonal-bipyramidal and octahedral molecules as well as that of Cl atoms in tetrahedral molecules is close to axially symmetric and usually does not depend much on the M character.

The significant decrease in η of equatorial Cl atoms in going from $\text{M}=\text{Si}$ or P to $\text{M}=\text{Ge}$ and Sn is caused by a decreased interaction of Cl and M atoms during the above transition. According to the theory of chem-

ical structure (see, for example, [27]), the strength of this interaction is determined by the degree of overlapping of interaction orbitals, which depends on how close the energies, size and symmetry of these orbitals are. The difference in p-orbital energies of Cl atoms (13.7 eV [28]) and M atoms ($\text{M}=\text{Si}$, Ge and Sn , 7.8, 7.5 and 6.8 eV, respectively [28]) increases slightly in going from $\text{M}=\text{Si}$ to $\text{M}=\text{Ge}$ and Sn ; the same is observed with the difference in size of their valent p-orbitals (the covalent radii of Cl, Si, Ge, and Sn atoms are 0.99, 1.17, 1.22 and 1.40 Å, respectively [29]). This is in agreement with the observed order of change of the η value in compounds of group IVA elements. However, both the 3p-orbital energy of the P atom (9.6 eV [28]) and its covalent radius (1.10 Å [29]) are even closer to the corresponding values of the Cl atom than those for the Si atom. Nevertheless, the η values of the equatorial Cl atoms in phenylchlorophosphoranes and SiCl_4 complexes are similar (within the limits of error of the asymmetry parameter determination) or even slightly lower for phosphorus compounds than in the SiCl_4 complexes studied. Evidently, the strength of interaction of equatorial M–Cl bond atoms is prominently affected by other factors, such as the ability of the M atom to attract electrons, the partial positive charge on the M atom, etc. Further, an interaction of this kind seems to be determined by not only overlapping of the corresponding orbitals but also by through field interaction of atoms.

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