

THE STUDY OF THE INTERACTION BETWEEN GEMINAL CHLORINE AND OXYGEN ATOMS IN ALKOXYCHLOROSILANES BY NQR SPECTROSCOPY

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The measurement and the discussion of ^{35}Cl -NQR spectra of some alkoxychlorosilanes $\text{Cl}_n\text{-(CH}_3\text{)}_{3-n}\text{SiOR}$ and some chlorosilanes is presented. The ^{35}Cl -NQR frequencies of these compounds are consistent with the usual frequency changes observed for compounds containing the Cl-Y-M group, when M is varied. The transmission of polar effects through the silicon atom in alkoxychlorosilanes depends on the group R.

The study of ^{35}Cl -NQR spectra of compounds with Cl—C—M bonding, where M = C, Si, Ge, Sn, F, O, N, etc., has revealed^{1,2}, that the ^{35}Cl -NQR frequency in these compounds is, as a rule, higher than that of their carbon analogues when atom M disposes of vacant *d*-orbitals, but it is lower when atom M disposes of *n* orbitals. It was also recognized that ^{35}Cl -NQR frequency in the compounds $\text{ClP(M)RR}'$ (M = O, S, Se) gradually increases²⁻⁴ on going from O to Se, in spite of the decrease in electronegativity of the atom M. The interpretation of these values of ^{35}Cl -NQR frequency, which are not in harmony with the electronegativity of atoms M do not seem to be convincing². General character of-from the standpoint of the electronegativity of M atom-anomalous values of ^{35}Cl -NQR frequency⁴⁻⁹ could speak for the same mechanism of the interaction between M and Cl atoms. This interaction can be assumed to be through space interaction between M and Cl atoms that operates in the opposite direction compared to the interaction between these atoms through σ bonds.

The regularity in the NQR frequency changes, when atom M being varied, is believed to hold for other compounds with X—Y—M bonding, where X stands for an indicative atom and Y is any atom separating both X and M geminal atoms. To justify the above hypothesis and to examine the mechanism of the interaction between geminal M and X atoms, the ^{35}Cl -NQR spectra of some chlorosilanes and alkoxychlorosilanes have been recorded in this work and their discussion is presented.

EXPERIMENTAL

^{35}Cl -NQR spectra of chlorosilanes and alkoxychlorosilanes were measured as reported earlier⁹. Preparation of the compounds will be described in a subsequent paper¹⁰.

RESULTS AND DISCUSSION

The ^{35}Cl -NQR spectra of the chlorine atoms directly bonded to the silicon consist in case of alkoxymonochlorosilanes of one signal, while the spectra of alkoxydichlorosilanes have different multiplicity. Thus the NQR spectrum of $\text{Cl}_2\text{Si}(\text{CH}_3)\text{OC}_2\text{H}_5$ has singlet character, and the spectrum of the other compounds of the type $\text{Cl}_2\text{Si} \cdot (\text{CH}_3)\text{OR}$ are of doublet character. The elementary crystal cell of these compounds contains likely one molecule. Quadruplet character of NQR spectra of $\text{Cl}_2\text{Si} \cdot [\text{OC}(\text{CH}_3)_3]_2$ speaks likely for two molecules in the elementary crystal cell. If one assumes that splitting of the signals in ^{35}Cl -NQR spectra of $\text{Cl}_2\text{Si}[\text{OC}(\text{CH}_3)_3]_2$ molecule is the same as in the other alkoxydichlorosilanes, the two, close lines of the low frequency in the quadruplet spectra of this compounds belong likely to the chlorine atoms of one molecule, and another two lines of the high frequency belong to the second molecule in the elementary crystall cell. ^{35}Cl -NQR spectra of the alkoxytrichlorosilanes Cl_3SiOR with $\text{R} = \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2$ consist of the three lines of about the same intensity. The two low frequency lines are close to one another, and the third, high frequency line is separated. Splitting of all the three lines is approximately unique when $\text{R} = \text{CH}_2\text{Si}(\text{CH}_3)_3$, the NQR spectrum has singlet character when $\text{R} = \text{CH}_2\text{CCl}_3$. Splitting between the lines of the chlorine atom belonging to the Si—Cl bonds in multiplet NQR spectrum of $\text{Cl}_3\text{SiO}(\text{CH}_2)_3\text{Cl}$ is within crystallographic limits. The NQR spectra of alkoxytrichlorosilanes do not show therefore specific features when compared to the NQR spectra of other trichlorosilanes.

Small splitting in the NQR spectra of some alkoxytrichlorosilanes indicates about the same σ electronic environment of the chlorine atom in these molecules, and also about the same extent of the interaction of the alkoxy substituents with all three chlorine atoms bonded to the silicon.

The ^{35}Cl -NQR frequency of the chlorosilanes $\text{RR}'\text{R}''\text{SiCl}$, depends linearly^{4,6,8,9} on the $\sum\sigma_{\text{R},\text{R}',\text{R}''}^*$ value (Fig. 1, line *a*). This type of the correlation equation including all the known ^{35}Cl -NQR frequencies ($\nu^{77} = 16.567 + 0.416 \sum\sigma^*$) differs only little from the equation calculated earlier⁶. The ^{35}Cl -NQR frequency of all the alkoxy-monochloro- and alkoxydichlorosilanes deviates from that correlation line in the low-frequency region (Fig. 1). Similar deviations from the ν^{77} vs $\sum\sigma_{\text{R},\text{R}',\text{R}''}^*$ plot for $\text{RR}'\text{R}''\text{CCl}$ compounds show also the ν^{77} frequencies of the compounds containing the fragment Cl—C—OR (ref.^{4,8}).

Anomalous values of the ^{35}Cl -NQR frequency of the compounds ClCH_2M where $\text{M} = \text{F, OR, NR}_2, \text{etc.}$ have been explained in several different ways; by interaction of n_{M} orbital with the antibonding C—Cl orbital (p - σ conjugation)¹¹⁻¹³ or by the

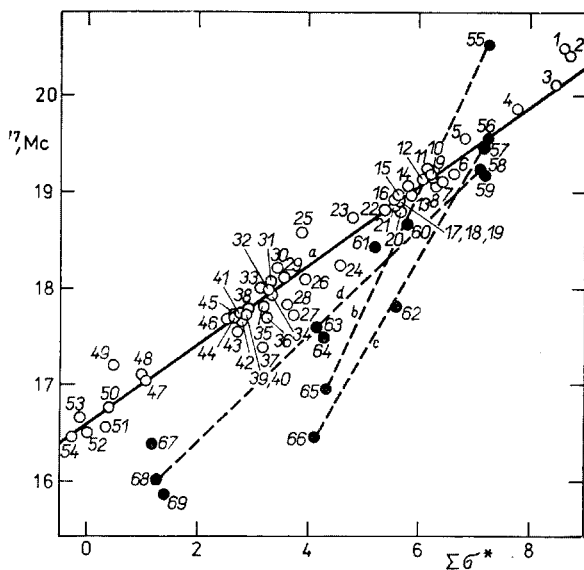


FIG. 1

The $^{35}\text{Cl-NQR}$ Frequency (ν^{77}) vs $\sum\sigma_{R,R',R''}^*$ Plot for ClSiRR'R''

R, R', R'' = Cl, Cl, Br(1); Cl, Cl, Cl(2); Cl, Cl, CCl_3 (3); Cl, Cl, CHCl_2 (4); Cl, Cl, CH_2Cl (5); Cl, Cl, $\text{CH}_2\text{CH}_2\text{CN}$ (6); Cl, Cl, C_6H_5 (7); Cl, Cl, H(8); Cl, Cl, $\text{CH}=\text{CH}_2$ (9); Cl, Cl, $\text{CH}_2\text{CH}_2\text{Cl}$ (10); Cl, Cl, $\text{CH}_2\text{CH}_2\text{CN}$ (6); Cl, Cl, C_6H_5 (7); Cl, Cl, H(8); Cl, Cl, $\text{CH}=\text{CH}_2$ (9); Cl, Cl, $\text{CH}_2\text{CH}_2\text{Cl}$ (10); Cl, CCl_3 , C_6H_5 (11); Cl, Cl, $\text{CH}_2\text{CH}_2\text{Br}$ (12); Cl, Cl, $\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ (13); Cl, Cl, CH_3 (14); Cl, Cl, $(\text{CH}_2)_3\text{Br}$ (15); Cl, Cl, C_5H_2 (16); Cl, Cl, $(\text{CH}_2)_3\text{Cl}$ (17); Cl, Cl, C_4H_9 (18); Cl, Cl, C_3H_7 (19); Cl, Cl, C_2H_5 (20); Cl, Cl, $\text{CH}(\text{CH}_3)_2$ (21); Cl, C_6H_5 , CHCl_2 (22); Cl, CHCl_2 , CH_3 (23); Cl, CH_2Cl , C_6H_5 (24); Cl, H, H(25); Cl, CH_2Cl , CH_3 (26); Cl, CH_3 , $\text{CH}_2\text{CH}_2\text{CN}$ (27); Cl, $\text{CH}_2\text{CH}_2\text{CF}_3$, $\text{CH}_2\text{CH}_2\text{CF}_3$ (28); Cl, C_6H_5 , CH_3 (29); Cl, H, CH_3 (30); Cl, H, C_2H_5 (31); Cl, $\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CH}=\text{CH}_2$ (32); Cl, $\text{CH}_2\text{C}_6\text{H}_5$, CH_3 (33); Cl, $\text{CH}=\text{CH}_2$, CH_3 (34); Cl, $\text{CH}_2\text{CH}_2\text{Cl}$, C_2H_5 (35); Cl, $\text{CH}_2\text{CH}_2\text{CF}_3$, CH_3 (36); Cl, $(\text{CH}_2)_3\text{CN}$, CH_3 (37); Cl, CH_3 , CH_3 (38); Cl, $\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, C_2H_5 (39); Cl, CH_3 , C_2H_5 (40); Cl, $(\text{CH}_2)_3\text{Cl}$, CH_3 (41); Cl, CH_3 , C_3H_7 (42); Cl, C_2H_5 , C_2H_5 (43); Cl, $(\text{CH}_2)_3\text{Cl}$, C_2H_5 (44); Cl, C_4H_9 , C_4H_9 (45); Cl, $\text{CH}(\text{CH}_3)_2$, $\text{CH}(\text{CH}_3)_2$ (36); CH_2Cl , CH_3 , CH_3 (47); $\text{CH}_2\text{CH}_2\text{CF}_3$, $\text{CH}_2\text{CH}_2\text{CF}_3$, $\text{CH}_2\text{CH}_2\text{CF}_3$ (48); H, CH_3 , CH_3 (49); $\text{CH}=\text{CH}_2$, CH_3 , CH_3 (50); $\text{CH}_2\text{CH}_2\text{CF}_3$, CH_3 , CH_3 (51); CH_3 , CH_3 , CH_3 (52); $(\text{CH}_2)_3\text{Cl}$, CH_3 , CH_3 (53); C_2H_5 , C_2H_5 , C_2H_5 (54); Cl, Cl, OCH_3 (55); Cl, Cl, OC_2H_5 (56); Cl, Cl, OC_3H_7 (57); Cl, Cl, $\text{OCH}(\text{CH}_3)_2$ (58); Cl, Cl, OC_4H_9 (59); Cl, OCH_3 , OCH_3 (60); Cl, $\text{OC}(\text{CH}_3)_3$, $\text{OC}(\text{CH}_3)_3$ (61); Cl, OC_2H_5 , OC_2H_5 (62); Cl, CH_3 , $\text{OCH}(\text{CH}_3)_2$ (63); Cl, CH_3 , OC_2H_5 (64); OCH_3 , OCH_3 , OCH_3 (65); OC_2H_5 , OC_2H_5 , OC_2H_5 (66); CH_3 , CH_3 , $\text{OC}(\text{CH}_3)_3$ (67); CH_3 , CH_3 , $\text{OCH}(\text{CH}_3)_2$ (68); CH_3CH_3 , OC_2H_5 (69).

The line *a* was constructed according the equation $\nu^{77} = 16.567 + 0.416 \sum\sigma^*$, valid for compounds 1–54. The lines *b*, *c*, and *d* were constructed for compounds with $\text{R}=\text{OCH}_3$, OC_2H_5 , and $\text{OCH}(\text{CH}_3)_2$ respectively. The data used in these correlations are from this work and papers^{4,6,8,9}.

TABLE I
The ^{35}Cl -NQR Frequency (ν^{77}) of the Compounds $\text{RR}'\text{R}''\text{SiCl}$

No	R	R'	R''	ν^{77} , MHz	s/n^a
1	CH_3	CH_3	OC_2H_5	15-860	5
2	CH_3	CH_3	$\text{OCH}(\text{CH}_3)_2$	16-004	6
3	CH_3	CH_3	$\text{OC}(\text{CH}_3)_3$	16-370	2
4	CH_3	CH_3	$\text{OCH}_2\text{CHCl}_2$	36-336	4
				36-181	6
				35-932	1-5
				16-299	2
				16-454	3
5	CH_3	OC_2H_5	OC_2H_5	16-454	3
6	Cl	CH_3	OC_2H_5	17-523	20
7	Cl	CH_3	$\text{OCH}(\text{CH}_3)_2$	17-682	10
				17-514	10
				17-514	10
8	Cl	CH_3	OCH_2CCl_3	38-848	10
				38-662	11
				38-514	10
				17-868	4
				17-750	4
9	Cl	CH_3	$\text{OCH}_2\text{Si}(\text{CH}_3)_3$	17-624	5
				17-440	5
10	Cl	$\text{OC}(\text{CH}_3)_3$	$\text{OC}(\text{CH}_3)_3$	18-827	4
				18-551	4
				18-196	4
				18-138	4
11	Cl	Cl	OC_2H_5	19-921	4
				19-353	5
				19-298	4
				19-745	25
12	Cl	Cl	$\text{OCH}(\text{CH}_3)_2$	19-126	23
				18-945	25
				18-945	25
13	Cl	Cl	$\text{O}(\text{CH}_2)_3\text{Cl}$	33-588	5
				33-475	5
				19-750	3
				19-739	6
				19-450	2
				19-360	3
				19-232	2
				19-228	6
				19-180	6

TABLE I
(Continued)

No	R	R'	R''	ν^{77} , MHz	s/n^a
14	Cl	Cl	$\text{OCH}_2\text{Si}(\text{CH}_3)_3$	19-604	8
				19-348	10
				19-000	3
15	Cl	Cl	OCH_2CCl_3	39-618	6
				38-346	2
				19-168	10
16	Cl	$\text{CH}(\text{CH}_3)_2$	$\text{CH}(\text{CH}_3)_2$	17-756	10
				17-573	5
17	Cl	CH_3	$(\text{CH}_2)_3\text{CN}$	17-408	8
				17-338	8

^a Signal to noise ratio.

three-center bond¹⁴. The mechanism of the interaction between Cl and M atoms suggesting the participation of the unshared electron pair on the atom M in organosilicon molecules with Cl—Si—OR bonding does not seem to be in harmony with generally accepted ideas on the $(p-d)_\pi$ conjugation in Si—O bond. Thus participation of the n_0 -orbital in $(p-d)_\pi$ bonding would prevent its participation in $p-\sigma$ conjugation or three-center bond. But, in spite of the considered inclusion of n_0 orbitals of the compounds $\text{ClSi}(\text{CH}_3)_2[\text{OSi}(\text{CH}_3)_2]_n\text{OSi}(\text{CH}_3)_2\text{Cl}$ in $(p-d)_\pi$ interaction, from the NQR spectra of these compounds it follows that their ν^{77} frequency is lower than that of appropriate compounds $\text{ClSi}(\text{CH}_3)_2\text{R}$ where R is not an alkoxy group. (For $n = 0$, $\nu^{77} = 16.33$ MHz; $n = 1$, $\nu^{77} = 16.28$ MHz; (ref.^{4,5,14}). For $\text{R} = \text{CH}_3$, $\nu^{77} = 16.506$ MHz; $\text{R} = (\text{CH}_2)_3\text{Cl}$, $\nu^{77} = 16.68$ MHz (ref.^{4,5,14})).

The electrostatic mechanism of the interaction between geminal atoms in Cl—C—M molecules proposed earlier² can however explain unusual frequency values also in Cl—Si—M molecules, even if n_0 orbitals ($\text{M} = \text{OR}$) participate in $(p-d)_\pi$ bonding. Significantly smaller deviations of NQR frequencies for the alkoxychlorosilanes from the linear correlation $\nu^{77} = \nu_0 + \rho \sum \sigma_{\text{R},\text{R}',\text{R}''}^*$ for the compounds $\text{RR}'\text{R}''\text{SiCl}$, compared to the deviations of their carbon analogue, alkoxychloromethanes from the same type of correlation for $\text{RR}'\text{R}''\text{CCl}$, can be, in harmony with this electrostatic mechanism, explained by the greater size of the silicon compared to the carbon. This mechanism can be also used to explain an increase in the NQR frequency of the compounds $\text{RR}'\text{P}(\text{M})\text{Cl}$ when going from $\text{M} = 0$ to $\text{M} = \text{S}$ or Se , *i.e.* when the electronegativity of the atom M decreases^{15,16}.

The $(p - d)_\pi$ conjugation of an unshared electron pair on the oxygen atom with d -orbitals of the silicon atom might be suggested to cause an increase of the electron density on silicon and a decrease of the electronegativity of oxygen. This results in an increase of the p_σ -electron density of the chlorine atom and a decrease of the NQR frequency. Based on the fact, that ability of the oxygen to participate in $(p - d)_\pi$ conjugation with d orbitals of the phosphorus is much higher than that of sulphur or selenium^{3,17}, this mechanism was proposed to explain lower ³⁵Cl-NQR frequencies for compounds, of the series RR'P(O)Cl as compared to those of RR'P(S)Cl (ref.^{3,17}) and RR'P(Se)Cl series³. However, anomalously low NQR frequencies are observed for phosphorous compounds and alkoxychlorosilanes and organic compounds as well. The mechanism of the effect of the oxygen or another heteroatom on the chlorine could be in all cases the same, and if so, one can not assume $(p - d)_\pi$ conjugation to be the main factor responsible for anomalously low NQR frequencies in alkoxy chlorosilanes, because such interaction is absent in organic molecules.

Turning now to the correlation $\nu^{77} = f(\sum\sigma^*)$ for RR'R''SiCl (Fig. 1, line a) one can see that most of the points corresponding to alkoxytrichlorosilanes deviate from the correlation line only little toward the low frequency region. The point for Cl₃SiO·CH₃ is, however, located above the correlation line⁷. This is not in accordance with the above mentioned general regularity of the dependence of ν^{77} value on the nature of the atom M in the compounds Cl—Y—M. This unusual frequency for Cl₃SiOCH₃ can not be fortuitous and should not be the consequence of some specific interaction proper to this molecule which is absent in other Cl—Si—OR compounds, because of linear increase in the NQR frequency of the compounds Cl_nSi(OCH₃)_{4-n} with increasing n or $\sum\sigma^*$ (Fig. 1, line b). The same type of linear dependance holds also for the other compounds of type Cl_nSi(OR)_{4-n} (Fig. 1, line c and d). Moreover, transmission of the polar effect of the group R depends significantly on the character of the group. (An increase in the polarizability of groups R decreases transmission of the polar effect). The unusually high NQR frequency of Cl₃SiOCH₃ is thus consistent with the higher transmittance of polar effects in Cl_nSi(OR)_{4-n} relative to RR'R''SiCl.

Based on these data general regularity between ³⁵Cl-NQR frequency and the nature of the M atom in the compounds Cl—Y—M is influenced by transmission of inductive effects through the atom Y, and is obligatory fulfilled only when this transmission is the same or very similar for various Y and M (ref.¹⁸). This is the case with the compounds ClP(O)RR' and ClP(S)RR' (ref.²), and also XCOCl (X = OR, NR₂ or X ≠ OR, NR₂) (ref.²). The way how, different polar effect transmission makes for deviations from general regularity was demonstrated with ClCH₂MRR'R'' compounds¹⁸ (M = C, Si).

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