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Abstract

Full Text

Physical Chemistry

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Investigation of Organosilicon Compounds Containing Si–Cl and C–Cl Bonds by the Method of Nuclear Quadrupole Resonance

(Presented by Academician Ya. K. Syrkin, 17 XI 1964)

Studies of organic and inorganic compounds by the method of nuclear quadrupole resonance (n.q.r.) have recently begun to acquire a systematic character. This has been manifested above all in the fact that, alongside model objects or objects interesting in one respect or another, the choice of which was partly accidental, many investigators working in this comparatively new field at the boundary between physics and solid-state chemistry have begun to study series and homologous rows of molecules containing one definite type of bond. In studying the nature of the chemical bond with the use of n.q.r., such a tendency promises definite success, since this method is distinguished by its high sensitivity to rearrangement of the electronic shell of molecules, which makes it possible to establish unambiguously the features of a given bond in various classes of organic, organoelement, and inorganic compounds.

In previous investigations (¹⁻⁴) the n.q.r. method was used to study tetrahedral molecules of the type $R_{4-n}MX_n$, containing at the center of the tetrahedron an atom of an element of group IVB ($M = \text{Si, Ge}$), and at its vertices a halogen atom ($X = \text{Cl}$) and various other substituents (R).

In the solid state, under the influence of the resultant forces of intermolecular interaction, some crystalline structures of compounds of the above-indicated type prove to be nonuniform owing to differences in the positions of like atoms X in the lattice. This is indicated by the multiplicity of the n.q.r. spectrum for a large number of the molecules investigated by us (about fifty) that contain two or more $M\text{—Cl}$ bonds.

For this reason such structures would more correctly be called quasi-tetrahedral.

In the present communication we give the results of an investigation by the pulsed n.q.r. method at the temperature of liquid nitrogen (-77°K) of seven chlorine-substituted organochlorosilanes containing from one to three chlorine atoms in the aliphatic radical. The method of investigation and the purification of the starting compounds have been described earlier (⁵). The results obtained are summarized in Table 1.*

Fig. 1

Figure 1: Fig. 1

It was shown earlier (^{2,3}) that the change in the average n.q.r. frequency ν_m^{77} for tetrahedral molecules of the series $R_{4-n}\text{SiCl}_n^{35}$ obeys an additivity law and that, for compounds of the type $RR'R''\text{SiCl}^{35}$, the quantity ν_m^{77} , characterizing the polarity of the Si–Cl bond, is a linear function of the polar (inductive) constants of the substituents R , R' , and R'' :

$$\nu_m^t = \alpha + \beta \Sigma \sigma^* \quad (1)$$

* For all the chlorosilanes studied (except $\text{Cl}_2\text{CHSiCl}_3^{35}$ and $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3^{35}$) the n.q.r. line width lies within the limits 25–100 kHz. For $\text{Cl}_2\text{CHSiCl}_3^{35}$ and $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3^{35}$ an n.q.r. signal with $\Delta\nu > 100$ kHz is observed.

Table 1

Data from the study of chloroalkylorganosilanes by the N.Q.R. method

No.	Compound	N.Q.R. frequencies at 77° K, MHz: Si–Cl	N.Q.R. frequencies at 77° K, MHz: C–Cl	ν_m^{77} , MHz: Si–Cl	ν_m^{77} , MHz: C–Cl	$\Sigma\sigma^*$
1	$\text{Cl}^{35}\text{CH}_2\text{SiCl}_3^{35}$	35,519,47	36,77	19,51	36,77	6,85
2	$\text{Cl}^{35}\text{CH}_2(\text{CH}_3)_2\text{SiCl}_2^{35}$	35,197,98	36,12	18,085	36,12	3,95
3	$\text{Cl}^{35}\text{CH}_2(\text{CH}_3)_2\text{SiCl}_2^{35}$	35,092,023	34,8534,80	17,056	34,825	1,05
4	$\text{Cl}_2\text{CHSiCl}_3^{35}$	35,19,75	—	19,75	—	7,740
5	$\text{Cl}_2^{35}\text{CH}(\text{CH}_3)_2\text{SiCl}_2^{35}$	35,36,76	36,76	18,74	36,76	4,840
6	$\text{Cl}_3^{35}\text{C}(\text{C}_6\text{H}_5)_2\text{SiCl}_2^{35}$	35,19,310	38,7839,10	19,20	38,44	6,150
7	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3^{35}$	35,18,75	—	18,97	—	5,94

This makes it possible to construct a unified theory relating the nuclear quadrupole interaction to the polarity of the chemical bond, and to give a quantitative estimate of the influence of the number and nature of substituents in molecules of the type $R_{4-n}\text{MX}_n$ on the magnitude of ν_m^{77} . Regularities analogous to those indicated above are also observed in the case of molecules simultaneously containing Si–Cl and C–Cl bonds. Fig. 1 illustrates that, for molecules of the series

Fig. 1. Dependence between the mean value of the N.Q.R. frequency (ν_m^{77}) and the number of Si–Cl or C–Cl bonds (n) in molecules: I –

Fig. 2

Figure 2: Fig. 2

$\text{ClCH}_2 \cdot (\text{CH}_3)_{3-n}\text{SiCl}_n^{35}$ (points 2–4), **II** $-\text{Cl}^{35}\text{CH}_2(\text{CH}_3)_{3-n}\text{SiCl}_n$ (points 2–4), **III** $-(\text{CH}_3)_{4-n}\text{SiCl}_n^{35}$ (points 1, 5–7), **IV** $-(\text{CH}_3)_{4-n}\text{CCl}_n^{35}$ (points 8–11)

Fig. 2. Dependence between the mean value of the N.Q.R. frequency (ν_m^{77}) and Taft's polar (inductive) constant σ^* . The numbering of the points corresponds to the number of the compounds in the table

$\text{Cl}^{35}\text{CH}_2(\text{CH}_3)_{3-n}\text{SiCl}_n^{35}$ the dependence between the mean value of the N.Q.R. frequency ν_m^{77} and the number of Si–Cl bonds (n) is close to linear. This applies to ν_m^{77} not only in the case of the Si–Cl bond (**I**), but also for the C–Cl bond (**II**). For comparison, analogous dependences are also given here for molecules of the type $(\text{CH}_3)_{4-n}\text{SiCl}_n^{35}$ (**III**) and $(\text{CH}_3)_{4-n}\text{CCl}_n^{35}$ (**IV**)^{1,6–8} (ν_m^{77} is a strictly linear function only in the case of molecules of the series $(\text{CH}_3)_{4-n}\text{SiCl}_n^{35}$). It is interesting that the slopes of **I** and **II** are almost identical, which indicates approximately

an analogous increase in the polarity of the Si–Cl and C–Cl bonds in the molecules $\text{ClCH}_2(\text{CH}_3)_{4-n}\text{SiCl}_n$ with decreasing n . In contrast to this, slopes **III** and **IV** differ sharply, indicating that, as the number of bonds n decreases in the molecules of the series $(\text{CH}_3)_{4-n}\text{CCl}_n$, the polarity of the C–Cl bond increases considerably more rapidly than in the case of their silicon analogs $(\text{CH}_3)_{4-n}\text{SiCl}_n$.^{*} Figure 2 illustrates the linear character of the dependence between the quantities ν_m^{77} and $\Sigma\sigma^*$ for all the compounds studied, considered as molecules of the type $\text{RR}'\text{R}''\text{SiCl}$ ($\Sigma\sigma^*$ is the sum of the polar constants σ^* of the substituents R, R', and R'').

The data obtained show that in chloralkylchlorosilanes of the type $\text{Cl}_{m\text{H}_{3-m}}\text{C}(\text{R})_{3-n}\text{SiCl}_n$ the Si–Cl bond is in all cases more polar than the C–Cl bond. In all molecules of the series $\text{ClCH}_2(\text{CH}_3)_{3-n}\text{SiCl}_n$ ($n = 1-3$) the polarity of the C–Cl bond is small (for example, lower than in $\text{CH}_3\text{CH}_2\text{Cl}$, but higher than in CCl_4 , CH_3CCl_3 , or HCCl_3). The polarity of the C–Cl bond in chloromethyldimethylchlorosilane, $\nu_m^{77} = 34.825$ MHz, the smallest for molecules of the series $\text{ClCH}_2(\text{CH}_3)_{3-n}\text{SiCl}_n$, may be compared with the polarity of the C–Cl bond in $\text{CH}_3\text{Cl}^{35}$, for which $\nu_m^{77} = 34.029$ MHz (6). At the same time, replacement of hydrogen atoms in the methyl groups of molecules of the type $(\text{CH}_3)_{4-n}\text{SiCl}_n$ by chlorine lowers the polarity of the Si–Cl bond, as indicated by the smaller values of ν_m^{77} for the SiCl bond in methylchlorosilanes than in the corresponding constructed C-chloro derivatives.

The linear dependence established in (2) and in the present work for molecules of the type $\text{RR}'\text{R}''\text{SiCl}$ between ν_m^{77} and the sum of the polar (induction) constants of the substituents R, R', and R'' ($\Sigma\sigma^*$), described by equation (1)**, makes it possible to relate the inductive effect of substituents to the quadrupole-coupling constant (K_z). The relation obtained (for spin 3/2) has the following form:

$$K_z = \frac{2}{(1 + \frac{1}{3}\varepsilon^2)^{1/2}}(\alpha + \beta\Sigma\sigma^*) \quad (2)$$

or, for $\varepsilon \rightarrow 0$,

$$K_z = 2(\alpha + \beta\Sigma\sigma^*), \quad (3)$$

where $K_z = eQq_{zz}$, ε is the electric-field-gradient parameter, α and β are constants, and σ^* is the Taft polar (induction) constant (9), Thomson' s constant (10), or another quantity characterizing the inductive influence of substituent R on the polarity of the given Si–Cl bond. In this case the dependence between the values of the polar constants determined on different scales is, of course, linear.

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* This indicates that the inductive influence of the substituents is transmitted through the silicon atom more strongly than through the carbon atom.

** An analogous dependence has also been established by us for chlorogermanes of the type $RR'R''GeCl$.

Note: Figure translations are in progress. See original paper for figures.

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