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Abstract

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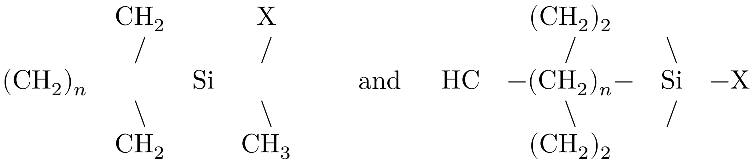
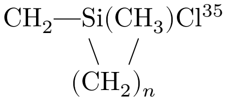
STUDY OF THE NUCLEAR QUADRUPOLE RESONANCE OF 1,1-DICHLORO- AND 1-METHYL-1-CHLORO-1-SILACYCLOALKANES

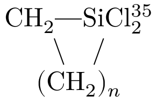
The study of the reactivity of functional groups bonded to the silicon atom in silacarbocyclic systems has attracted the attention of a number of authors ([1]-[9]). They have found an increased reactivity of heterocyclic organosilicon compounds of the type



$(X = Cl,\ H,\ n = 1 \div 3)$

in alcoholysis, hydrosilylation ([3], [4], [7]), ammonolysis ([8]), reduction ([2], [3]), etc. In comparing the reactivity of 1-methyl-1-chloro-1-silacycloalkanes and their acyclic analogs, the chlorine atom bonded to silicon and located in a four-membered heterocycle proved to be the most labile. The reason for the enhanced reactivity of the substituents located at the silicon atom in the above heterocyclic compounds, especially those having a strained ring, may be due either to a steric effect or to an increase in the polarity of the Si—Cl bond when the silicon atom is incorporated into the cyclic system. Since establishing this reason is of exceptional importance for elucidating the not yet fully clear mechanism of nucleophilic substitution reactions at the silicon atom in silacycloalkanes ([9]), we undertook an investigation of the polarity of the Si—Cl bond in 1-methyl-1-chloro-1-silacycloalkanes (I) and 1,1-dichloro-1-silacycloalkanes (II)





I $a)\ n = 2;\ b)\ n = 3$ II $a)\ n = 2;\ b)\ n = 3;\ c)\ n = 4$

by the method of nuclear quadrupole resonance (NQR). The data obtained were compared with the NQR spectra of acyclic analogs of compounds of types I and II—$(CH_3)_3SiCl^{35}$, $(CH_3)_2SiCl_2{}^{35}$, and $(C_2H_5)_2SiCl_2{}^{35}$.

The pulsed measurement technique and the methods of purification of the starting compounds were close to those described earlier ([10]). Spin-echo signals were observed at 77°K. The optimal pulse parameters were as follows: $\tau_1 \approx 10$ μsec and $\tau_2 \approx 20$ μsec (pulse durations of 90 and 180°, respectively). The interval between pulses in a pair was 100–300 μsec; the repetition frequency of the probing pulses was 0.5–5 Hz; the voltage on the circuit with the sample was 2–2.5 kV. The data obtained are summarized in Table 1.

In the case of $(CH_2)_3SiCl_2{}^{35}$ (IIa), a doublet of the NQR signal was observed. When one chlorine atom in it is replaced by a methyl group, the NQR spectrum becomes a singlet, and the mean value of the NQR frequency (ν_m^{77}) decreases—

is observed, which indicates a comparative increase in the polarity of the Si—Cl bond in $\overline{(CH_2)_3Si}(CH_3)Cl$ (Ia).

For $(CH_2)_4SiCl_2^{35}$ (IIb) a singlet NQR signal was observed. In this case as well, replacement of one chlorine atom by a CH_3 group lowers the value of ν_m^{77}, which indicates a greater polarity of the Si—Cl bond in Ib. The multiplet signal in Ib listed in Table 1 is observed in a more weakened form than the singlet in IIb.

Upon rapid cooling of a sample of $\overline{(CH_2)_5Si}Cl_2$ (IIc), one broad line ($\Delta\nu \geqslant 200$ kHz) was found in the NQR spectrum of this compound,

Table 1

NQR spectra of 1-methyl-1-chloro- and 1,1-dichloro-1-silacycloalkanes

Compound	Formula	NQR frequency at 77 °K, MHz	$\Sigma\sigma^*$	ν_m^{77}, MHz found	ν_m^{77}, MHz calculated	Discrepancy***
Ia	$\overline{(CH_2)_3Si}(CH_3)Cl^{35}$	16.60	−0.24	16.60	16.498	−0.102
Ib	$\overline{(CH_2)_4Si}(CH_3)Cl^{35}$	16.80*	−0.26	16.80	16.489	−0.313
IIa	$\overline{(CH_2)_3Si}Cl_2^{35}$	17.840 17.523	+2.66	17.68	17.712	+0.032
IIb	$\overline{(CH_2)_4Si}Cl_2^{35}$	17.775	+2.64	17.775	17.704	−0.071
IIc	$\overline{(CH_2)_5Si}Cl_2^{35}$	17.83**	+2.72	17.83	17.738	−0.092
III	$(CH_3)_2Si(CH_3)Cl^{35}$	16.465[11]	0.00	16.465	16.598	+0.133
IV	$(CH_3)_2SiCl_2^{35}$	17.800[10] 17.762	+2.9	17.781	17.813	+0.032
V	$(CH_3CH_2)_2SiCl_2^{35}$	17.735[12] 17.521	+2.70	17.628	17.595	+0.033

* Mean frequency of the multiplet.
** Line width $\Delta\nu \geqslant 200$ kHz.

*** The mean discrepancy between the calculated and found values of ν_m^{77} (not counting compound Ib) is ±0.071.

which is possibly due to disorder of the crystal lattice.

The NQR spectra of $(CH_3)_2SiCl_2^{35}$, $(CH_3)_3SiCl^{35}$, and $(C_2H_5)_2SiCl_2^{35}$ have been studied previously (10-12). The tabulated data show that replacement of a chlorine atom in $(CH_3)_2SiCl_2$ by a methyl group here also shifts the mean NQR frequency to the lower part of the chlorine frequency range.

The polarity of the Si—Cl bond in organochlorosilanes increases with decreasing mean NQR frequency (ν_m^{77}). This makes it possible to compare the polarity of this bond in compounds of types I and II and in their acyclic analogues. Using the data in Table 1, the compounds studied can be arranged, in order of decreasing polarity of the Si—Cl bond, in the following series (the value of ν_m^{77} in MHz is given in parentheses): 1. $CH_3(C_2H_5)Si(CH_3)Cl^{35}$ (16.3*)* > $(CH_3)_2Si(CH_3)Cl^{35}$ *(16.465)* > $\overline{(CH_2)_3Si}(CH_3)Cl^{35}$ *(16.60)* > $\overline{(CH_2)_4Si}(CH_3)Cl^{35}$ *(16.80). 2.* $(CH_3CH_2)_2SiCl_2^{35}$ *(17.628)* > $CH_3(C_2H_5)SiCl_2^{35}$ *(17.65)* > $\overline{(CH_2)_3SiCl_2^{35}}$ (17.68) > $\overline{(CH_2)_4SiCl_2^{35}}$ (17.775) > $(CH_3)_2SiCl_2^{35}$ (17.781) > $\overline{(CH_2)_5SiCl_2^{35}}$ (17.83).

Thus, the polarity of the Si—Cl bond in silacycloalkanes decreases with increasing ring size. At the same time, it differs appreciably little from

* Calculated value.

the polarity of the Si—Cl bond in similarly constructed acyclic compounds with the same number of carbon atoms in the molecule, and is even somewhat smaller. This is quite understandable, since the polarity of the Si—Cl bond in molecules of the type RR′R″SiCl (apparently all the compounds considered above may also be assigned to this type) is determined primarily by the overall inductive effect of the substituents R, R′, and R″.

It should be noted that comparison of the experimental values of ν_m^{77} with the sums of the polar (induction) Taft constants σ^* (13) of the substituents R, R′, and R″ in the molecules indicates the existence of a linear dependence between them, described by the equation $\nu_m^{77} = \alpha + \beta\Sigma\sigma^*$. In the present case the parameters of this linear equation were calculated from the values of ν_m^{77} given in the table by the method of least squares ($\alpha = 16.598$, $\beta = 0.419$).

The mean discrepancy between the values found and those calculated from the above equation is ±0.071 MHz.

Compound 16 deviates somewhat from this dependence and requires additional study.

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

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