THE MANIFESTATION OF THE α-EFFECT IN ^{35}Cl-NQR SPECTRA OF RR′R′Si($CH_{3-n}Cl_n$), (n = 1—3)

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The ^{35}Cl-NQR frequencies for the silanes RR′R″Si($CH_{3-n}Cl_n$) depend linearly on the sum of Taft σ^* constants of the groups R, R′, R″. The inductive effect of these groups is transmitted to the chlorine atom to a lesser extent in RR′R″MCH_2Cl (M = Si) than in the analogous compounds with M = C, Ge, Sn reported earlier. The α-effect plays a role in all the members of the above series, decreasing with increasing *n*.

A number of experimental data on the reactivity and IR, NMR and NQR spectra of organic compounds of silicon, germanium and tin show that the properties of the compounds with the M—C—X arrangement (M = Si, Ge, Sn; X = halogen, O, N *etc.*) are not in harmony with the electronegativity of the atoms M (ref.[1,2]). This discrepancy was explained by the intramolecular interaction between M and X which was called the α-effect[3-5]. The α-effect in the compounds RR′R″MCH_2Cl (M = Si, Ge, Sn) has been detected by NQR spectroscopy as an increase in the ^{35}Cl-NQR frequency of the organometallic compounds (ref.[1,4]) (M = Si, Ge, Sn) relative to their carbon analogues (M = C) (ref.[1,4]).

The aim of this work was to examine whether an increase in the ^{35}Cl-NQR frequency of RR′R″MCH_2Cl observed when going from M = C to M = Si is common for a wide range of the R, R′, R″ substituents.

EXPERIMENTAL

Model compounds. All the compounds RR′R″$SiCH_2Cl$ were prepared by reported procedures[6,7], except $C_6H_5O(CH_3)_2SiCH_2Cl$ and $(SCN)_3SiCHCl$.

Dimethyl(phenoxy)chloromethylsilane was prepared by the reaction of dimethyl(chloro)-chloromethylsilane with stoichiometric amount of phenol in the presence of pyridine in dry diethyl ether and was separated by rectification as a fraction boiling at 132°C/27 Torr; n_D^{20} 1·5017; 58% yield. For $C_9H_{13}ClOSi$ (200·8) calculated: 17·50% Cl; found: 17·66% Cl.

Tris(isothiocyanato)chloromethylsilane was prepared by the reaction of trichloro(chlormethyl)-silane with silver thiocyanate. Both compounds (0·5 mol) were mixed in heptane (150 ml) and

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shaked in a sealed reaction vessel for 2 days. The liquid layer was separated by filtration, the salts were extracted with benzene and the combined extract and filtrate was distilled (all the operations were carried out under nitrogen). Tris(isothiocyanato)chloromethylsilane was obtained by rectification as a fraction boiling at 155°C/8 Torr; n_D^{20} 1·6430; nearly quantitative yield. For $C_4H_2ClN_3Si$ (248·8) calculated: 19·31% C, 0·81% H, 14·25% Cl; found: 18·82% C, 0·99% H, 15·10% Cl. The purity of all the compounds was checked by gas–liquid chromatography and their physical constants agreed with reported data[6,7].

^{35}Cl-NQR *Spectroscopy.* ^{35}Cl-NQR spectra of studied compounds were measured at 77 K with NQR spectrometer, model ISSCH-1-12 (Institute of Radiotechnics and Electronics, Academy of Sciences of the U.S.S.R.).

TABLE I

The ^{35}Cl-NQR Frequencies of the Compounds RR'R"$SiCH_2Cl$ at 77 K and $\sum\sigma^*$ Values for Groups R, R', R"

Comp.	R	R'	R"	ν^{77}, MHz	$\sum\sigma^{*\,a}$
1	SCN	SCN	SCN	37·145	9·54[b]
2	F	F	F	36·886	9·3
3[c]	Cl	Cl	Cl	36·786	8·7
4[c]	Cl	Cl	CH_3	36·108	5·8
5	F	F	CH_3	36·045	
				36·000	6·2
6	Cl	Cl	C_6H_5	36·024	6·4
7	$OCOCH_3$	$OCOCH_3$	$OCOCH_3$	35·975	6·72[b]
8	Cl	CH_2Cl	CH_3	35·248	3·95
				17·570	
9	OC_2H_5	OC_2H_5	OC_2H_5	35·122	4·11
10	OC_6H_5	CH_3	CH_3	34·886	2·38
11[d]	Cl	CH_3	CH_3	34·827	2·9
12	F	CH_3	CH_3	34·658	3·1
13	OC_2H_5	OC_2H_5	CH_3	34·583	2·74
14	$OCOCH_3$	CH_3	CH_3	34·537	2·24[b]
15	C_6H_5	C_6H_5	C_6H_5	34·715	1·8
16	OC_2H_5	CH_3	CH_3	34·691	1·37
17[d]	CH_2Cl	CH_3	CH_3	34·519	1·05
18[d]	H	CH_3	CH_3	34·192	0·49
19[d]	CH_3	CH_3	CH_3	34·320	0·0
20[c]	C_2H_5	C_2H_5	CH_3	34·592	−0·2
21	$OSi(CH_3)_3$	CH_3	CH_3	34·355	

[a] Taft σ^* constants have been calculated from the relation $\sigma^* = 6{\cdot}23\sigma_I$ where σ_I constants were determined[8] from p*K*'s of α-substituted *p*-toluic acids. [b] For the correlation equation see[9]. [c] The same value of frequency was found in[10]. [d] *cf.* ref.[4].

RESULTS AND DISCUSSION

The ^{35}Cl-NQR frequencies for RR′R″MCH$_2$Cl (M = C, Si, Table I) depend linearly on the sum of Taft σ^* constants of the R, R′, R″ groups (Table II). Deviation of $CH_3(C_2H_5)_2SiCH_2Cl$ from the correlation line for RR′R″SiCH$_2$Cl may be consistent with the fact that the compounds RR′R″SiCH$_2$Cl where R, R′ and R″ are hydrogen or alkyl groups form separate linear correlation. This was also observed with some series of organic compounds (*e.g.* RCl) (ref.[11]). The NQR frequencies increase with increasing $\sum\sigma^*$ R, R′, R″ value (Fig. 1). The correlation lines corresponding to the relationship $\nu^{77} = \nu_0 + \varrho\sum\sigma^*$ for RR′R″MCH$_2$Cl (M = C and Si) bisect one another at about $\sum\sigma^* \sim 6$ (Fig. 1). The ^{35}Cl NQR frequencies for the organosilicon compounds (M = Si) are up to $\sum\sigma^* \sim 6$ higher and for $\sum\sigma^* > 6$ lower than the frequencies for their carbon analogues (M = C). The latter situation could be expected on the basis of the electronegativities of C and Si atoms or of the inductive effects of RR′R″C- and RR′R″Si-groups.

The fact that the lines in the ν^{77} *vs* $\sum \sigma^*_{R,R',R''}$ plot for RR′R″MCH$_2$Cl (M = = C, Si) bisect one another differentiates α-carbofunctional organosilicon chlorides from α-carbofunctional organogermanium and organotin chlorides, the ^{35}Cl NQR frequency of which is always higher than that of the respective carbon derivatives[4]. This arises from the fact that the inductive effect is transferred through —CH$_2$Ge≡ and —CH$_2$Sn≡ groups very similarly as through —CH$_2$C≡ groups. (ref.[4]).

The ϱ value of the equation $\nu^{77} = \nu_0 + \varrho\sum\sigma^*$ for RR′R″SiCH$_2$Cl (Table II) is somewhat lower than the value for RR′R″SiCl (ϱ = 0·404, ref.[11]). This can be expected as a result of the insulating effect of the methylene group. This effect is, however, significantly decreased compared to the carbon derivatives. This can be seen from the ratio of the values obtained from the equations $\nu^{77} = \nu_0 + \varrho\sum\sigma^*$ for RR′R″SiCH$_2$Cl and RR′R″SiCl (ref.[12]) (z = 0·73) and from the ratio of the values obtained from the equations $\nu^{77} = \nu_0 + \varrho\sum\sigma^*$ for RR′R″CCH$_2$Cl and RR′R″CCl (ref.[12]) (z = 0·53).

TABLE II

Parameters of Correlation Equations $\nu^{77} = \nu_0 + \varrho\sum\sigma^*$ for R R′R″M(CH$_{3-n}$Cl$_n$) (n = 1–3; M = C, Si)

n	M = C				M = Si			
	ν_0	ϱ	r	s	ν_0	ϱ	r	s
1	32·039	0·594	0·964	0·223	34·053	0·308	0·981	0·188
2	35·062	0·409	0·988	0·206	35·279	0·279	0·999	0·016
3	37·529	0·408	0·987	0·193	37·586	0·166	0·950	0·211

The ^{35}Cl-NQR frequencies for the series RR'R"$SiCHCl_2$ and RR'R"$SiCCl_3$ can be also satisfactorily correlated with $\sum\sigma^*_{R,R',R''}$ Taft values (Table II). Having at present at our disposal only limited number of such data (Tables III and IV), we must, however, admit that these correlations are less accurate and may serve only for preliminary information. The slopes of the ν^{77} *vs* $\sum\sigma^*_{R,R',R''}$ plots for the compounds RR'R"$SiCH_{3-n}Cl_n$ decrease with increasing n, in agreement with the sequence of the slopes when going from RR'R"CCl to $RCCl_3$ *via* $RRCCl_2$ (ref.[11]). As one can expect, the inductive effect transfer from the substituents attached to the silicon decreases when going from RR'R"$SiCH_2Cl$ to RR'R"$SiCHCl_2$. In the case of RR'R"$SiCHCl_2$ and RR'R"$SiCCl_3$ the inductive effect is transferred to about the

TABLE III

^{35}Cl-NQR Frequencies of RR'R"$SiCHCl_2$ at 77°K (ν^{77}) and $\sum\sigma^*$ Values for Groups R, R', R"

n	R, R', R"	ν^{77}, MHz	$\sum\sigma^*$	n	R, R', R"	ν^{77}, MHz	$\sum\sigma^*$
1[a]	Cl,Cl,Cl	38·160	8·7	3[c]	Cl,Cl,CH_3	37·084	5·8
		37·240				36·752	
		19·963				18·748	
		19·871		4[b]	CH_3,CH_3,CH_3	35·539	0·0
		19·699				35·379	
2[b]	Cl,Cl,C_6H_5	37·060	6·4			34·903	
				5	CH_3,CH_3,Cl	37·083	2·9
						36·745	

[a] The earlier reported[9] NQR frequencies ν^{77} = 38·171, 37·240 and 19·75 MHz. [b] cf. ref.[10]. [c] The earlier reported[9,10] NQR frequencies ν^{77} = 36·76 and 18·74 MHz.

TABLE IV

Average ^{35}Cl-NQR Frequencies for R R' R"$SiCCl_3$ at 77°K (ν^{77}) and $\sum\sigma^*$ Values for Groups R, R', R"

n	R, R', R"	ν^{77}, MHz	$\sum\sigma^*$
1	Cl, Cl, Cl	39·02	8·7
2	Cl, Cl, $CH_2C_6H_5$	38·88	6·0
3	Cl, Cl, C_6H_5	38·55	6·4
4	OC_2H_5, OC_2H_5, CCl_3	38·29	5·4
5	C_2H_5, C_2H_5, C_2H_5	37·54	−0·3

same extent. This can be explained by saturation effect[1]. The transmission of the inductive effect of the groups R to the chlorine atom of $RR'R''SiCH_{3-n}Cl_n$ is always significantly lower compared to the respective carbon derivatives, $RR'R''CCH_{3-n}Cl_n$ (Fig. 1, Table II). The lines of the ν^{77} *vs* $\sum\sigma^*_{R,R',R''}$ plot for both $RR'R''MCHCl_2$ and $RR'R''MCCl_3$ (M = C, Si) bisect one another at the lower $\sum\sigma^*$ values than those for the compounds $RR'R''MCH_2Cl$ (M = C, Si).

The point on $\sum\sigma^*$ scale at which the α-effect begins to be clearly manifested thus shifts toward lower $\sum\sigma^*$ values for $RR'R''SiCH_{3-n}Cl_n$ when *n* increases.

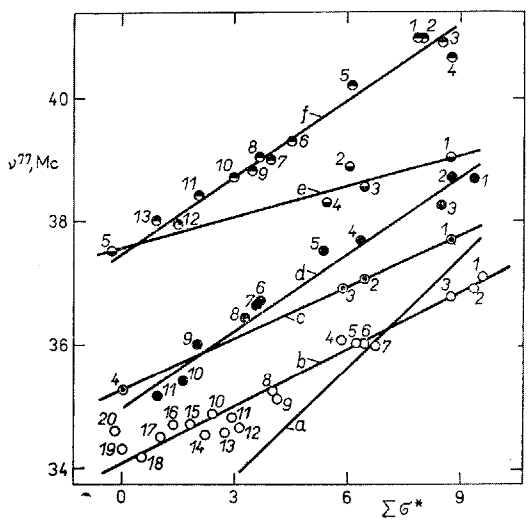

FIG. 1

The ^{35}Cl-NQR Frequency (ν^{77}) *vs* $\sum\sigma^*$ Plot for $RR'R''CCH_2Cl$ (*a*), $RR'R''SiCH_2Cl$ (*b*), $RR'R''SiCHCl_2$ (*c*), $RR'R''CCHCl_2$ (*d*), $RR'R''SiCCl_3$ (*e*) and $RR'R''CCCl_3$ (*f*)

Correlation lines have been derived from the appropriate equations, parameters of which are included in Table II. The numbering of the points corresponds to the numbering of compounds in Tables I, III, and IV. For compounds $RR'R''CCHCl_2$ and $RR'R''CCCl_3$ the points are numbered as follows:

Correlation d. R, R', R'' = F, F, F (1); Cl, Cl, Cl (2); Cl, Cl, CCl_3 (3); H, Cl, Cl (4); H, Cl, $CHCl_2$ (5); H, H, CCl_3 (6); H, H, CF_3 (7); H, OC_2H_5, OC_2H_5 (8); H, H, CH_2Br (9); H, H, H (10); H, H, C_2H_5 (11).

Correlation f. R, R', R'' = Cl, Cl, $CHCl_2$ (1); CCl_3, CCl_3, CCl_3 (2); Cl, Cl, CCl_3 (3); Cl, Cl, Cl (4); H, Cl, CCl_3 (5); H, Cl, CH_2Cl (6); H, H, Cl (7); H, OH, OH (8); H, OH, OC_2H_5 (9); H, H, $CHCl_2$ (10); H, H, CH_2Cl (11); H, H, H (12); H, H, C_2H_5 (13).

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