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Abstract

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CORRELATION OF THE MEAN FREQUENCY OF NUCLEAR QUADRUPOLE RESONANCE WITH THE INDUCTION CONSTANT OF SUBSTITUENTS IN ORGANYLCHLOROSILANES

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Data from the study of the spectra of nuclear quadrupole resonance (NQR) of organylchlorosilanes ($^{1-7}$) make it possible to conclude that the mean NQR frequency is an approximately additive quantity and can be used for a quantitative estimate of the influence of the polar (inductive) effect of substituents on the Si —Cl bond.

In the present work* we consider the dependence of the mean value of the NQR frequency at 77° K (ν_m^{77}) of organylchlorosilanes of the type $RR'R''SiCl^{35}$ (Table 1) on the polar (inductive) constants, associated with the central silicon atom, of any substituents R, R', and R'', σ_i^*, of Taft (^{8,9}). The total induction effect of these substituents can be represented by the sum of the corresponding polar constants $\sum_i \sigma_i^*$.

The correlation dependence between the quantities ν_m^{77} and $\sum_i \sigma_i^*$ approximately follows an additive law and can be represented by the linear equation:

$$\nu_m^{77} = \nu_0^{77} + k \sum_i \sigma_i^*, \tag{1}$$

or

$$\sum_i \sigma_i^* = k^{-1}(\nu_m^{77} - \nu_0^{77}) = \alpha \nu_m^{77} - \beta. \tag{2}$$

The results of calculating the parameters of equations (1) and (2) by the method of least squares for organylchlorosilanes belonging to the series $RSiCl_3^{35}$, $RR'SiCl_2^{35}$, $RR'R''SiCl^{35}$, are given in Table 2.

* The linear dependence between the quantities ν_m^{77} and σ_i^* was first reported in 1964 (4).

Table 1

Values of the mean NQR frequencies ν_m^{77} of ^{35}Cl in organochlorosilanes in comparison with calculated values

No.	Compound	ν_m^{77}, MHz: experimental value I	ν_m^{77}, MHz: calculated II	ν_m^{77}, MHz: calculated III	ν_m^{77}, MHz: calculated IV	Discrep., MHz I—II	Discrep., MHz I—III	Discrep., MHz I—IV
1	$SiCl_4$	20,39	20,31	20,18	20,15	+0,08	+0,21	+0,24
2	$Cl_2CHSiCl_3$	19,75	19,85	19,78	19,76	−0,10	−0,03	−0,01
3	$ClCH_2SiCl_3$	19,52	19,42	19,41	19,40	+0,10	+0,11	+0,12
4	$C_6H_5(Cl_3C)SiCl_2$	19,20		19,12	19,12		+0,08	+0,08
5	$F_3CCH_2CH_2SiCl_3$	19,19	19,06	19,11	19,10	+0,13	+0,08	+0,09
6	$NCCH_2CH_2SiCl_3$	19,17	19,30	19,31	19,30	−0,13	−0,14	−0,13
7	$ClCH_2CH_2SiCl_3$	19,15	19,10	19,14	19,13	+0,05	+0,01	+0,02
8	$CH_2{=}CHSiCl_3$	19,13	19,10	19,14	19,14	+0,03	−0,01	−0,01
9	$C_6H_5SiCl_3$	19,11	19,20	19,23	19,22	−0,09	−0,12	−0,11
10	CH_3SiCl_3	19,11	18,91	18,98	18,97	+0,20	+0,13	+0,14
11	$HSiCl_3$ (α-phase)	19,06	19,15	19,18	19,17	−0,09	−0,12	−0,11
12	$ClCH_2CH_2CH_2SiCl_3$	18,86	18,98	19,03	19,03	−0,12	−0,17	−0,17
13	$(CH_3)_2CHSiCl_3$	18,84	18,82	18,90	18,90	+0,02	−0,06	−0,06
14	$C_2H_5SiCl_3$ (α-phase)	18,77	18,86	18,94	18,93	−0,09	−0,17	−0,16
15	$CH_3(Cl_2CH)SiCl_2$	18,74		18,58	18,59		+0,16	+0,15
16	$H(CH_3)SiCl_2$	18,22		17,98	18,00		+0,24	+0,22
17	$C_6H_5(CH_3)SiCl_2$	18,13		18,02	18,05		+0,11	+0,08
18	$ClCH_2(CH_3)SiCl_2$	18,09		18,21	18,23		−0,12	−0,14
19	$H(C_2H_5)SiCl_2$	18,07		17,94	17,96		+0,13	+0,11
20	$CH_2{=}CH(CH_3)SiCl_2$	17,91		17,94	17,97		−0,03	−0,06
21	$(CH_2)_5SiCl_2$	17,83		17,70	17,73		+0,13	+0,10
22	$(F_3CCH_2CH_2)_2SiCl_2$	17,81		18,04	18,06		−0,23	−0,25
23	$(CH_3)_2SiCl_2$	17,78		17,77	17,80		+0,01	−0,02
24	$(CH_2)_4SiCl_2$ (α-phase)	17,77		17,67	17,70		+0,10	+0,07
25	$C_2H_5(CH_3)SiCl_2$	17,73		17,69	17,76		+0,04	−0,03

No.	Compound	ν_m^{77}, MHz: experimental value I	ν_m^{77}, MHz: calculated II	ν_m^{77}, MHz: calculated III	ν_m^{77}, MHz: calculated IV	Discrep., MHz I—II	Discrep., MHz I—III	Discrep., MHz I—IV
26	$(CH_2)_3SiCl_2$	17,68		17,67	17,71		+0,01	−0,03
27	$F_3CCH_2CH_2(CH_3)SiCl_2$	17,68		17,91	17,91		−0,23	−0,25
28	$(C_2H_5)_2SiCl_2$ (α-phase)	17,62		17,69	17,72		−0,07	−0,10
29	$(F_3CCH_2CH_2)_3SiCl$	17,09			17,02			+0,07
30	$H(CH_3)_2SiCl$	17,09			16,83			+0,26
31	$ClCH_2(CH_3)_2SiCl$	17,06			17,06			−0,00
32	$(CH_2)_4Si(CH_3)Cl$ (α-phase)	16,77			16,53			+0,24
33	$CH_2{=}CH(CH_3)_2SiCl$	16,77			16,79			−0,02
34	$(CH_2)_3Si(CH_3)Cl$	16,60			16,53			+0,07
35	$F_3CCH_2CH_2(CH_3)_2SiCl$	16,53			16,76			−0,23
36	$(CH_3)_3SiCl$	16,47			16,63			−0,16
	Mean value					±0,095	±0,109	**±0,114**

Table 2

Parameters of equations (1) and (2)

Series	ν_0^{77}	k	α	β	Correlation coefficient, %
$RSiCl_3^{35}$	18,999	0,484	2,065	39,047	∼ 0,99
$RR'SiCl_2^{35}$	17,775	0,415	2,411	42,861	∼ 0,96
$RR'R''SiCl^{35}$	16,632	0,404	2,476	41,169	∼ 0,96

For the majority of the organochlorosilanes we studied, the magnitude σ^*_{Cl} proves to be considerably larger than the induction constants σ^*_R of the other substituents (except for CCl_3**). Therefore it is quite natural that, in accordance with the number of Si—Cl bonds in the molecule, the values of ν_m^{77} are arranged on the correlation straight line in the form of three principal groups (the dependence

** Since $\sigma^*_{CCl_3} \simeq \sigma^*_{Cl}$, the value of ν^{77}_m for $C_6H_5(CCl_3)SiCl_2$ lies in the group of compounds with three chlorine atoms.

$\nu^{77}_m = f(\Sigma_i \sigma^*_i)$ is graphically presented in Fig. 1). The centers of these groups correspond to the following averaged values of ν^{77}_m (R, R′ R″ $\neq$ Cl): 19.0 ($RSiCl_3$); 17.9 ($RR'SiCl_2$) and 16.8 MHz ($RR'R''SiCl$), with an index of 1.1 MHz, and are separated from one another by $\simeq 2.9$ (σ^*_{Cl}) units of the σ^* scale.

The average discrepancy between the values of ν^{77}_m calculated from equation (1) and the values found (Table 1) is ±0.5-0.6% (±0.53% for $RSiCl_3$; 0.60% for $RR'SiCl_2$ and ±0.63% for $RR'R''SiCl$).

Earlier ([4]) we noted that equation (2) can be used to calculate unknown values of σ^* and to correlate known values of σ^*. Table 3 gives calculated values of σ^* for several substituents bonded to the silicon atom in molecules of the $RSiCl_3$ series. The average discrepancy between the calculated and literature values of σ^* is ±0.15*.

The data presented here indicate that the inductive effect of substituents (with the exception of the CH_3 group) bonded to the silicon atom generally remains the same as in the case when they are attached to a carbon atom.

The effect of $p_\pi - d_\pi$ interaction, which is so substantially reflected in the properties of silicon bonds with the most electronegative atoms (F, O, Cl, N) and with aryl and α-alkenyl groups, is not noticeably manifested in the data obtained by the NQR method. This considerably distinguishes it from nuclear magnetic resonance, which is very sensitive to the phenomenon of $p_\pi - d_\pi$ interaction ([10]). Consequently, comparison of the NQR and NMR data, which will be carried out elsewhere, proves very useful for solving certain questions concerning the nature of the chemical bond.

Table 3

Values of σ^*_R of substituents R bonded to the central silicon atom in molecules of the $RSiCl_3$ series, calculated from ν^{77}_m by equation (2)

R	σ^*_R source ([8,9]) I	σ^*_R calculated from (2) II	Discrepancy I − II
Cl_3Si	+2.9	+3.05	−0.15
Cl_3SiO	–	+2.02	
Cl_2CH	+1.94	+1.73	+0.21
$ClCH_2(CH_3)CCl$	–	+1.67	
$CH_2 = CCl$	–	+2.00	
2,5-$Cl_2C_6H_3$	–	+1.47	
$ClCH_2$	+1.05	+1.26	−0.21

R	σ_R^* source (^{8,9}) I	σ_R^* calculated from (2) II	Discrepancy I − II
$BrCH_2 = CHBr$	–	+1.20	
Cl_3Si	–	+0.78	
$3\text{-}ClC_6H_4$	–	+0.62	
$F_3C(CH_2)_2$	+0.32	+0.58	−0.26
$NC(CH_2)_2$	+0.80	+0.54	+0.26
$Cl(CH_2)_2$	+0.39	+0.50	−0.11
Cl_3SiCH_2	–	+0.50	
$CH_2 = CH$	+0.40	+0.45	−0.05
C_6H_5	+0.60	+0.41	+0.19
CH_3	+0.00	+0.41	−0.41
H	+0.49	+0.39	+0.10
$Cl_3Si(CH_2)_2$	–	+0.16	
$Cl(CH_2)_3$	+0.14	+0.10	+0.04
C_2H_5	−0.10	−0.29	+0.19
$(CH_3)_2CH$	−0.19	−0.15	−0.04
Average discrepancy			$±$0.15

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* The rather substantial discrepancy in the value of σ^*_{CH3} (-0.41), as we shall show subsequently, is regular (this discrepancy was not taken into account in deriving the average discrepancy).

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

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