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G. N. KARTSEV, Corresponding Member of the Academy of Sciences of the USSR Ya. K. SYRKIN, V. F. MIRONOV

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Abstract

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G. N. KARTSEV, Corresponding Member of the Academy of Sciences of the USSR Ya. K. SYRKIN, V. F. MIRONOV
and E. A. CHERNYSHEV

DIPOLE MOMENTS OF SOME ORGANOSILICON COMPOUNDS

We have measured the dipole moments of a number of organosilicon compounds by the heterodyne method at 25° in benzene. The extrapolated polarizations were calculated by the Hedestrand formula. In the case of compounds containing silicon, it is necessary to take atomic polarization into account, since neglect of this quantity may introduce an error into the value of the dipole moment. In a number of works the atomic polarization was taken as equal to 5% of the electronic polarization or was not taken into account at all. The known atomic polarizations of a number of substances $SiCl_4$ 5.3 (^{1}); Si_2H_6 4; SiH_4 2; SiF_4 5.4 (^{2}); $(CH_3)_3SiCH_2CH_2 \cdot C_6H_5$ 6.5; $(CH_3)_3SiCH_2CH_2C_6H_4NO_2$ 10; $(CH_3)_3Si—O—Si(CH_3)_3$ 7.9 cm^3 (^{3}), show that these quantities must be taken into account in calculating dipole moments. In the case of SiH_4 and $SiCl_4$ the atomic polarization amounts to 16 and 18% of the electronic. We measured the temperature dependence of the total polarization of $(CH_3)_3SiCH_2CH_2C_6H_4NO_2$ (*p*-isomer) in the range from 280.5 to 333° K and found that the total polarization is satisfactorily represented by the equation:

$$P_{\text{tot}} = 77 + 126\,950/T. \tag{1}$$

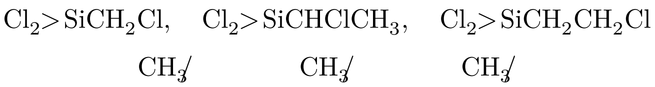
Hence, according to Debye' s equation, the atomic polarization is approximately equal to 10 cm^3, which in this case amounts to 15% of P_{el}. In this connection we estimated the value of P_{at} and introduced the corresponding corrections in determining the dipole moments. For P_{el}, refractivities for the yellow sodium line were used without extrapolation to infinite wavelengths, in order to compensate to a certain extent for the underestimated values of the atomic polarization.

The experimental data obtained are given in Table 1.

A distinctive feature of silicon compounds is the increased polarity in comparison with the corresponding bonds for carbon. From the available data one may estimate the moment of the Si—H bond at 1 D, and that of Si—C at 0.6 D (^{4}). In both cases the positive end of the dipole is directed toward silicon. In the bonds Si—O, Si—Hal, the contribution of the ionic state is greater. The electropositivity of silicon is also evident from the fact that its ionization potential is considerably smaller than that of carbon (186 kcal and 258 kcal, respectively). Another feature of silicon is that, in contrast to carbon, in which the outer electrons $2s^2 2p^2$ are in a shell where there are no d-orbitals, silicon, in the shell of peripheral electrons $3s^2 3p^2$, has empty d-orbitals. We note that, according to various data, the electron affinity of the silicon atom is estimated at 62 ± 11 kcal. Thus, along with polar bonds $\mathrm{Si^+}$—$\mathrm{X^-}$, silicon is also characterized by states with the reverse direction of the moment. This is consistent with the fact that $\mathrm{N(SiH_3)_3}$ is a much weaker base than $\mathrm{N(CH_3)_3}$. In addition, there are data indicating that in $\mathrm{N(SiH_3)_3}$ the nitrogen atom and the three surrounding silicon atoms lie in one plane, as in those cases where the central atom gives three σ-bonds (sp^2) and one π-bond.

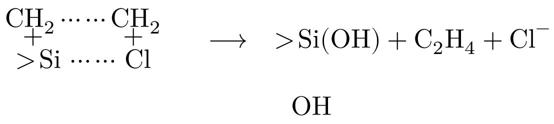
It should be noted that the difference between the moments of $\mathrm{CH_3SiCl_3}$ and $\mathrm{HSiCl_3}$ is 0.97 D, whereas the difference between $\mathrm{CH_3CCl_3}$ and $\mathrm{HCCl_3}$ is equal to

only 0.35 D. It should be noted that the difference between the moments of $\mathrm{(CH_3)_2SiCl_2}$ and $\mathrm{H_2SiCl_2}$ is 0.7 D. This is connected with the larger value of the moment of Si—H. On going to the next element of the fourth group—germanium—the polarity naturally increases. According to our data, the moment of $\mathrm{CH_3GeCl_3}$ is 2.63 D, whereas the moment of $\mathrm{CH_3SiCl_3}$ is 1.87 D, and that of $\mathrm{CH_3CCl_3}$, 1.57 D. Comparison of the moment of $\mathrm{(CH_3)_3SiCH = CHCl}$ (1.71 D) with the moment of vinyl chloride (1.44 D) shows that in the former compound the moment of the C—Cl bond is closer to its normal value. In vinyl chloride, conjugation of chlorine with the $\mathrm{CH_2}$ group, which is capable of drawing an electron toward itself, lowers the moment of the $\mathrm{C^+}$—$\mathrm{Cl^-}$ bond. In $\mathrm{(CH_3)_3SiCH = CH_2}$, the carbon of the $\mathrm{CH_2}$ group is already partially negatively charged owing to the $\mathrm{Si^+}$—$\mathrm{C^-}$ bond. The somewhat reduced value of the moment in $\mathrm{(CH_3)_3SiCH = CCl_2}$ (1.64 D) is due to the presence of two chlorine atoms at one carbon. The compound $\mathrm{Cl_3SiCH = CHCl}$ is probably a mixture of cis- and trans-isomers, with predominance of the trans form, since for the cis compound one may expect a moment of about 2.3 D, and for the trans form, approximately 0.3 D. A large difference is observed in the moments of $\mathrm{Cl_3SiCH_2Cl}$ (1.61 D) and $\mathrm{Cl_3SiCHClCH_3}$ (2.30 D), although vectorially the moments should be identical. Replacement of the C—H bond by C—$\mathrm{CH_3}$ in organosilicon compounds often has a large effect on the moment. Indeed, the moment of $\mathrm{(CH_3)_2SiCl_2}$ is 1.88 D, whereas the moment of $\mathrm{(CH_3)(C_2H_5)SiCl_2}$ is 2.31 D,



$$\begin{array}{ccc} \mathrm{Cl_2}\!>\!\mathrm{SiCH_2Cl}, & \mathrm{Cl_2}\!>\!\mathrm{SiCHClCH_3}, & \mathrm{Cl_2}\!>\!\mathrm{SiCH_2CH_2Cl} \\ \mathrm{CH_3}\diagup & \mathrm{CH_3}\diagup & \mathrm{CH_3}\diagup \end{array}$$

i.e., greater by 0.43 D. Meanwhile, even in this case, it would seem that replacement of the C—H bond by C—$\mathrm{CH_3}$ should not affect the resultant vector. Of the three compounds, the largest moment is observed for the last, where chlorine is in the β-position. It may be assumed that alternating polarity is manifested in the chain of bonds Si—CH$_2$—CH$_2$—Cl (^{5}). If this is so, then the evenness or oddness of the number of links may affect reactivity. Indeed, substituents in the β-position have a strong influence on kinetics. This "silicone" effect is well known in the chemistry of organosilicon compounds. Thus, the β-chlorine atom in Cl$_3$SiCH$_2$CH$_2$Cl can be titrated with 0.5 N aqueous alkali. We think that the alternating polarity, which is reflected in the dipole moment, is manifested in the kinetics of the reaction, which proceeds through a five-membered cyclic complex (with six electrons in the field of five nuclei).



$$\begin{matrix} \mathrm{CH_2} \cdots\cdots \mathrm{CH_2} \\ + \qquad\quad + \\ >\mathrm{Si} \cdots\cdots \mathrm{Cl} \end{matrix} \longrightarrow \; >\mathrm{Si(OH)} + \mathrm{C_2H_4} + \mathrm{Cl^-}$$

$$\mathrm{OH}$$

In the case of an odd number of methylene groups, the reaction proceeds under more severe conditions.

From the moment of $(CH_3)_2Si(CH_2—CH = CH_2)_2$, equal to 0.54 D, it follows that the moment of the group Si—CH$_2$—CH = CH$_2$ has a magnitude of about 0.65 D, either owing to alternating polarity or owing to displacement of electrons toward the CH$_2$ group at the double bond. Comparison of these data with the nearly zero moment of $(C_2H_5)_3SiCH_2—CH = CH_2$ indicates an increase in polarity on going from the group Si—CH$_3$ to Si—C$_2$H$_5$. Here too the specificity of organosilicon compounds is manifested, namely, a change in properties on going from one to two links in the hydrocarbon chain. Comparison of Cl$_3$SiCH$_2$CH$_2$Cl and Cl$_3$SiCH$_2$CHCl$_2$ shows that the presence of two chlorine atoms at one carbon causes a decrease of the moment by 0.16 D, though less than in the case of CH$_3$Cl and CH$_2$Cl$_2$. From the compounds CH$_3$SiCl$_3$ one may estimate the moment of the SiCl$_3$ group as 2.07 D; from the moment of HSiCl$_3$—as 1.90 D. From $(CH_3)_2SiCl_2$, the moment of the SiCl$_2$ group may be estimated as 2.11 D. So-

the compound Cl$_3$SiCH$_2$Cl has a moment of 1.61 D. Meanwhile, the vector sum of the moments Cl$_3$Si 2.07 D; C—Si 0.6 D; C—Cl 1.46 D, C—H 0.4 D leads to a resultant moment of 2.26 D. We note that the compound Cl$_3$SiCHClCH$_3$ with the same vector sum has a moment of 2.3 D, i.e., very close to the calculated value. The discrepancy in the case of Cl$_3$SiCH$_2$Cl must be the subject of additional investigation.

Table 1

No.	Compound	P_{obs}, cm^3	R_D	$\sim P_{\text{at}}$, cm^3	$\mu \cdot 10^{18}$, D
1	Cl$_3$SiCH$_2$Cl	93.8	34.5	5.0	1.61
2	Cl$_3$SiCH$_2$CH$_2$Cl	91.4	38.5	5.1	1.51
3	Cl$_3$SiCH$_2$CH$_2$CH$_2$Cl	129.1	43.3	5.2	1.97
4	CH$_3$(CI$_2$=Si)CH$_2$Cl	109.2	34.2	5.7	1.82
5	CH$_3$(CI$_2$=Si)CH$_2$CH$_2$Cl	123.9	38.5	5.8	1.96

No.	Compound	P_{obs}, cm^3	R_D	$\sim P_{at}$, cm^3	$\mu \cdot 10^{18}$, D
6	$CH_3(CI_2{=}Si)CHClCH_3$	118.5	38.7	5.8	1.87
7	$Cl_3SiCH{=}CHCl$	60.1	38.4	5.5	0.88
8	$(CH_3)_3SiCH{=}CHCl$	106.4	39.4	6.0	1.71
9	$(CH_3)_3SiCH{=}CCl_2$	108.0	44.0	8.0	1.64
10	$(CH_3)_3SiCH{=}CH_2$	38.6	34.6	4.0	0
11	$Cl_3SiCH_2CHCl_2$	89.1	43.4	7.5	1.35
12	$Cl_3SiCHClCH_3$	154.1	38.6	5.2	2.30
13	$Cl_3SiCH_2CHClCH_3$	138.7	43.2	5.3	2.08
14	$CH_3(C_2H_5)SiCl_2$	149.9	34.1	5.0	2.31
15	CH_3SiCl_3	106.2	29.1	4.5	1.87
16	$(CH_3)_2SiCl_2$	108.5	29.6	4.5	1.89
17	CH_3GeCl_3	183.2	31.7	8.0	2.63
18	$(CH_3)_2Si(CH_2CH{=}CH)_2$	58.3	47.2	5.0	0.54
19	$(C_2H_5)_3SiCH_2CH{=}CH_2$	59.6	53.0	5.0	~ 0.2
20	$(CH_3)_3SiCH_2C_6H_5$	66.9	54.7	5.9	0.55
21	$(CH_3)_3SiCH_2CH_2C_6H_5$	65.5	59.3	6.0	0
22	$CH_2{=}CH—CH_2—Si(CH_3)(H)(C_6H_5)$	66.0	54.5	5.0	0.55
23	$Cl_3SiC_6H_5$	155.0	48.9	4.8	2.21
24	$Cl_3SiCH_2C_6H_5$	125.5	54.5	4.9	1.78
25	$Cl_3SiCH_2CH_2C_6H_5$	131.5	58.1	5.0	1.81
26	$Cl_3SiCH_2C_6H_4Br$ (*para*)	136.0	60.9	5.5	1.83
27	$(CH_3)_3SiCH_2C_6H_4NO_2$ (*ortho*)	343.2	60.8	10	3.62
28	$(CH_3)_3SiCH_2CH_2C_6H_4NO_2$ (*ortho*)	349.3	65.4	10	3.63
29	$(CH_3)_3SiCH_2C_6H_4NO_2$ (*para*)	563.5	62.4	10	4.86
30	$(CH_3)_3SiCH_2CH_2C_6H_4NO_2$ (*para*)	504.3	67.0	10	4.53
31	$(C_2H_5)_3SiC_6H_4Br$ (*para*)	143.3	71.4	7.0	1.77
32	$(C_2H_5)_3SiCH_2C_6H_4Br$ (*para*)	173.1	76.0	7.1	2.08
33	$(C_2H_5)_3SiCH_2CH_2C_6H_4Br$ (*para*)	162.3	80.6	7.2	1.89

Owing to the possibility that the free 3*d* orbitals of silicon participate in bonds, states of Si^- with five bonds can be realized. This circumstance plays a certain role in aromatic derivatives, for example, in the bonds of silicon with the benzene ring. From the value of the moment of $(CH_3)_3SiC_6H_5$, 0.42 D, the moment of the $Si—C_6H_5$ group may be estimated as 0.62 D. From the compound $(CH_3)_2Si(CH_2—CH{=}CH_2)$, $\mu = 0.54$ D, and the moment of the Si–allyl group, equal to 0.65 D, one may calculate the moment

$$CH_2{=}CH{—}CH_2{—}Si(CH_3)(H)(C_6H_5)$$

in good agreement with experiment.

The moment of the compound $(CH_3)_3SiCH_2CH_2C_6H_5$ is probably close to zero, since

the total polarization in the temperature interval 288–318° K remains constant. The moment of $Cl_3SiC_6H_5$ differs sharply from the additive value of the moments $SiCl_3$ (2.07) and $Si - C_{ar}$. This is apparently connected with the withdrawal of electrons toward the chlorine atoms through the ring and through the silicon atom, as well as with the above-noted ability of the silicon atom to acquire a negative charge by means of an empty orbital. This indicates the inadequacy of estimating bond polarities solely from electronegativities. Depending on the valence states, one and the same atom in different bonds may be either the positive or the negative end of the dipole. On going from $Cl_3SiC_6H_5$ to $Cl_3SiCH_2C_6H_5$, the conjugation chain is disrupted and the moment is closer to the additive value. The same applies to the moment of $Cl_3SiCH_2CH_2C_6H_5$. In two compounds containing a nitro group in the ortho position (27 and 28, Table 1), the moments are identical. We note that ortho-nitrotoluene and ortho-$(CH_3)_3SiC_6H_4NO_2$ have identical moments (3.66 and 3.67 D). The experimental moments of the para-bromo derivatives $(C_2H_5)_3SiC_6H_4Br$, $(C_2H_5)_3SiCH_2C_6H_4Br$, and $(C_2H_5)_3SiCH_2CH_2C_6H_4Br$ are greater than those calculated from vector sums. It is possible that this reflects the inductive influence of the bond moments $Si^+ - C_{ar}$ and $C_{ar}^+ - Br^-$.

Moscow Institute of Fine Chemical Technology
named after M. V. Lomonosov

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