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Abstract

Full Text

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Electron-Diffraction Study of the Structure of the Phenylmonochlorosilane Molecule

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In previous works (^{1}, ^{2}) on determining the structure of derivatives of trichlorosilanes R—SiCl$_3$ (R = C_2H_3, C_6H_5), an increase in the length of the Si—Cl bond by 0.02–0.04 Å was found in comparison with the mean value r(Si—Cl) = 2.020 Å in compounds of the type R—SiCl$_3$, where R is a saturated radical (see Table 2 in work (^{2})). It is known, however, that the influence of a substituent on the change in the length of any bond is closely connected with the number of bonds considered (^{3}). Therefore it was of interest to investigate the structure of the phenylmonochlorosilane molecule C_6H_5—SiH$_2$Cl (PMCS) in order to determine the magnitude of the influence of the phenyl group on the single Si—Cl bond.

Fig. 1. Experimental and theoretical curves $M(s)$ for the $C_6H_5SiH_2Cl$ molecule. The parameters of the theoretical curves correspond to the experimentally found structure of the molecule (Table 1): 1–4 correspond to the rotational-isomeric forms I–IV; 5 is a 1 : 1 mixture of forms III and IV; 6 is free rotation of the phenyl group

Fig. 2. Experimental and theoretical curves $f(r)$ for the $C_6H_5SiH_2Cl$ molecule. The numbering of the theoretical curves corresponds entirely to the numbering of the curves $M(s)$

Experimental Part

Electron diffraction patterns of PMCS vapors were obtained by the method described earlier (^{4}). The sector r^3 was used in exposures at two nozzle-plate distances (140 and 260 mm). The scattering intensity $I(s)$ was taken equal to the blackenings S for $S < 1$. The experimental curve $M(s)$ was calculated on the basis of a smooth background line drawn on the $I(s)$ curves. The experimental radial-distribution curve $f(r)$ was

calculated after introducing into the $M(s)$ curve a correction for inelastic scattering. Further corrections of the $M(s)$ curve were made on the basis of Fourier inversions from the nonstructural part of the $f(r)$ curve ($0 < r < 0.8$ Å). The final form of the curves is given in Figs. 1 and 2.

The PhMChS molecule is characterized by five principal structural parameters, assuming preservation of the geometry of the benzene ring: r(C—C), r(Si—C), r(Si—Cl), ∠ClSiC, and the angle determining the mutual orientation of the SiH_2Cl and C_6H_5 groups. These parameters were determined mainly from the $f(r)$ curve. The first peak corresponds to r(C—C) and includes r(Si—H). Taking r(Si—H) = 1.48 Å, l(Si—H) = 0.08 Å, and r(C—C) = 1.40 Å, l(C—C) = 0.05 Å, agreement was obtained in the theoretical $f(r)$ curves for the position of this peak (1.405 Å) with experiment (1.407 Å). An additional source for determining r(C—C) is the peak r(C ... C) =

[Figure 3 and Figure 4 are visible on the page.]

Fig. 3. Schemes of models of the rotational isomers of the $C_6H_5SiH_2Cl$ molecule relative to the Si—C axis

Fig. 4. Variation of the Si—Cl distance in chlorosilanes as a function of the number of chlorine atoms n and the nature of the substituent.
1–$SiCl_4$, 2–$C_6H_5SiCl_3$, 3–$(C_6H_5)_2SiCl_2$, 4–$C_6H_5SiH_2Cl$, 5–$SiHCl_3$, 6–SiH_3Cl

= 2.43 Å on the experimental $f(r)$ curve, from which r(C—C) = 1.403 Å follows. The characteristics of the Si—C and Si—Cl bonds were obtained by successive refinement of variables from the complex peak at 2.07 Å, taking into account r(C ... H) = 2.12 Å. It was found that r(Si—C) = 1.81 ± 0.02 Å, l(Si—C) = 0.06 Å, and r(Si—Cl) = 2.076 ± 0.01 Å, l(Si—Cl) = 0.07 Å. Errors in determining internuclear distances were estimated from the approximate equation (12a) of work (5), taking into account the scale error ($\sim 0.2\%$). Determination of the valence angle ∠ClSiC is difficult, since the internuclear distances depending on this parameter are included in complex peaks. In addition, the contribution to scattering from distances determining the orientation of the SiH_2Cl and C_6H_5 groups is very large. The estimate of the angle ∠ClSiC = 110 ± 3° was made on the basis of the small peak r(C ... Cl) = 3.20 Å and confirmed by comparison of $M(s)$ curves calculated for different rotational isomers and valence angles ∠ClSiC.

Table 1

Structural parameters of the $C_6H_5SiH_2Cl$ molecule

Bond	r, Å	Angles
CC	1.40 ± 0.01	ClSiC 110° ± 3
SiCl	2.076 ± 0.01	∠ClSiH = CSiH 110° accepted
SiC	1.81 ± 0.03	∠CCC = CCH 120°
SiH	1.48 accepted	accepted
CH	1.08 accepted	accepted

It also proved difficult to determine the mutual orientation of the C_6H_5 and

SiH_2Cl groups. Earlier, in studying the structure of the $C_6H_5SiCl_3$ molecule, we were unable to make a strict choice between free rotation of the phenyl group relative to the Si—C bond or a parallel arrangement of C_6H_5 and Cl ... Cl (^{2}). In the molecule $C_6H_5SiH_2Cl$ under study, the symmetry of the rotation potential is reduced in comparison with $C_6H_5SiCl_3$. We made calcu-

calculations of the curves $M(s)$ and $f(r)$ for four possible rotational forms (Fig. 3), an equimolecular mixture of two forms III and IV (the choice of precisely these isomeric forms is justified below), and free rotation of the C_6H_5 group about the Si—C bond (Figs. 1 and 2). The curves $M(s)$ and $f(r)$ for free rotation were obtained by averaging the curves for isomers I-IV with statistical weights $1:2:2:1$, respectively.

Examination of these curves and comparison with experiment indicate poor agreement for the individual isomeric forms, and also

Table 2

Comparison of the values of r(Si—Cl) (in Å) in chlorosilanes of different structures

R	R—$SiCl_3$	R_2SiCl_2	$RSiH_2Cl$
H	2.021 ± 0.002 (^{7})	(2.034)*	2.0479 ± 0.0007 (^{10})
C_6H_5	2.04 ± 0.01 (^{2})	2.057 ± 0.015 (^{9})	2.076 ± 0.01 (this work)
C_2H_3	2.06 ± 0.005 (^{1})	·	
Cl	2.017 ± 0.005 (^{8})		

* Obtained by linear interpolation of the data for r(Si—Cl) relative to $HSiCl_3$ and H_2SiCl.

for a $1:1$ mixture. In the curves $M(s)$ and $f(r)$ for free rotation, although complete coincidence is not achieved, better agreement with experiment is nevertheless observed. The difficulty in determining the isomeric composition is due to the fact that the contribution to the total scattering from the interatomic distances that determine the mutual coordination of the SiH_2Cl and C_6H_5 groups is small; this is especially clearly seen in the $f(r)$ curve.

The results of the study of the phenylmonochlorosilane molecule are given in Table 1. The model of free rotation was adopted as the best in terms of agreement.

Discussion of the results

The value obtained by us, $r(\text{C—C}) = 1.40 \pm 0.01$ Å, is in good agreement with the data for benzene, $r(\text{C—C}) = 1.397$ Å (^{6}). This indicates the absence of

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noticeable errors in the experiment and is a good supplement to the approximate error estimates made for the determination of the principal geometrical parameters.

The most important and interesting result is the determination of the value $r(\mathrm{Si—Cl}) = 2.076 \pm 0.01$ Å. Comparison of the data for H_3SiCl and $C_6H_5SiH_2Cl$ (Table 2) makes it possible once again to confirm the previously drawn conclusion about the increase in the length of the Si—Cl bond upon introduction into the chlorosilane molecule of an unsaturated or aromatic substituent. It should be noted that the influence of multiple carbon-carbon bonds on the carbon-halogen bond has not been reliably established because of the lack of agreement among the data of different authors (^{1}). The results of the study of the $C_4H_4Ge_2Cl_4$ molecule indicate that the indicated effect of multiple bonds, if it exists for compounds containing germanium, is considerably smaller (^{11}). The data of Table 2, presented graphically in Fig. 4, also show that the phenyl group causes lengthened Si—Cl bonds in the corresponding molecules by $\Delta r = 0.02$-0.03 Å, which, with an experimental error of 0.01 Å, does not, however, make it possible to speak of a dependence of Δr on the number of chlorine atoms. Obviously, the influence of the substituent on the Si—Cl bond will be expressed most fully in monochlorosilanes: indeed, for F_3SiCl, $r(\mathrm{Si—Cl}) = 1.989 \pm 0.018$ Å (^{12}), i.e., the difference in bond lengths from the case of C_6H_5—SiH_2Cl is 0.087 Å. For comparison we give the value $r(\mathrm{Si—Cl})$, calculated according to the Schomaker-Stevenson rule (^{13}), which is equal to 2.05 Å.

The interatomic distance obtained in the present work, $r(\mathrm{Si—C}) = 1.81 \pm 0.03$ Å, agrees quite well with the values 1.81±0.02 Å for CH_2=CH—$SiCl_3$ $^{(1)}$, 1.82±0.03 Å for C_6H_5—$SiCl_3$ $^{(2)}$, and 1.826_3 Å for HC≡C—SiH_3 $^{(14)}$, but is noticeably smaller than the distance $r(\mathrm{Si—C})$ in saturated organosilicon compounds: 1.867 Å in CH_3—SiH_3 $^{(15)}$, 1.868 Å in $HSi(CH_3)_3$ $^{(16)}$, and 1.889 Å in CH_2Cl—SiH_3 $^{(16)}$. Moreover, the shortening of the Si—C bond is equal in magnitude to the shortening of the C—C bonds in the corresponding hydrocarbon derivatives.

In the molecule C_6H_5—SiH_2Cl, apparently, free or nearly free rotation of the groups about the Si—C bond takes place. It should be noted that at present the question of the rotational potential about bonds of the type $> A—B <$ has been insufficiently studied experimentally and theoretically. The available experimental data only for toluene CH_3—C_6H_5 $^{(18)}$ and trifluorotoluene CF_3—C_6H_5 $^{(19)}$ indicate free rotation about the bond $> C—C <$. Theoretically, the role of the interaction of bonds and nonbonded atoms in the rotational potential is not clear.

Of the numerous semiempirical equations available for the interaction of nonbonded atoms, the Magnasco equation $^{(20)}$ leads to fairly good agreement between calculated and experimental values of the rotation barriers for a number of the simplest molecules.

Calculation of the interaction energy of nonbonded atoms in phenylmonochlorosilane using this equation gives, for configurations I and II,

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values approximately 4 kcal/mole greater than for configurations III and IV. This served as the basis for calculating the curves $M(s)$ and $f(r)$ for a mixture of forms III and IV.

From the results of this calculation it follows that there is substantially hindered rotation in the molecule C_6H_5—SiH_2Cl, which is not consistent with the data obtained. This indicates the approximate nature of the equation used. We shall subsequently consider the applicability of equations of this type to problems of rotational isomerism.

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