

NATURE OF THE SILICON-PHENYL AND SILICON-OXYGEN BONDS IN HEXAPHENYLDISILOXANE: AN ELECTRIC DIPOLE MOMENT STUDY*

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The finite dipole moments of disiloxane¹, $\text{H}_3\text{SiOSiH}_3$, and its derivatives in which all of the hydrogen atoms have been replaced by alkyl groups² have confirmed the existence of a bent configuration for the Si-O-Si grouping in those molecules. The use of such symmetric derivatives should also be greatly advantageous in other dipole moment studies of the disiloxanes because of the difficulty encountered with unsymmetric derivatives in the assignment of the directions and magnitudes of the group and bond moments present¹. This is especially true of the disiloxanes because of the great possibility that a change in the extent of $(p \rightarrow d)_\pi$ bonding between oxygen and silicon may readily occur when substituents on either of the silicon atoms are changed. The change in π -bonding will affect particularly the hybridization of the lone pairs of electrons at the oxygen and hence their important contribution¹ to the effective moments of the groups in the molecule. For example, an increase in $(p \rightarrow d)_\pi$ bonding in the Si-O linkage will tend to increase the Si-O-Si angle, increase the strength of the Si-O bonds, decrease the $\overline{\text{Si}-\text{O}}$ bond moment, decrease the contribution of the oxygen lone pair moments to the effective Si-O moment, decrease the effective R-Si-O moment, and, from symmetry considerations, decrease the molecular dipole moment¹.

Hexaphenyldisiloxane possesses the desired symmetry, and its dipole moment was measured to obtain a direct comparison of the $\text{C}_6\text{H}_5\text{-Si-O}$ group moment with the H-Si-O and $\text{CH}_3\text{-Si-O}$ moments when these groups are present in a symmetric disiloxane structure. Earlier studies³ of unsymmetric compounds, such as $(\text{C}_6\text{H}_5)_3\text{-SiOC}_2\text{H}_5$ and $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiOC}_2\text{H}_5$, have revealed the difficulties of interpretation mentioned above.

RESULTS AND DISCUSSION

The dipole moment of $[(\text{C}_6\text{H}_5)_3\text{Si}]_2\text{O}$ determined here is 1.03 ± 0.02 D. The moments for disiloxane¹, $\text{H}_3\text{SiOSiH}_3$, and hexamethyldisiloxane⁴, $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$, are 0.24 ± 0.005 D and 0.66 ± 0.05 D, respectively, both in the gas phase. The moments of such disiloxanes appear to be the same in the gas phase as in non-polar solvents².

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Due to the symmetry of these molecules, their molecular moments, μ , readily yield the values of the effective moments, m , of the different groups in them, C_6H_5-Si-O , $H-Si-O$, and CH_3-Si-O , by the equation $m = \mu / (2 \cos \frac{1}{2}\theta)$, where θ is the $Si-O-Si$ angle. The largest uncertainty in this calculation comes in the choice of θ , a matter which, for these molecules, causes no difficulty in establishing the relative values of group moments.

The value $144.1 \pm 0.9^\circ$ has been found by electron diffraction⁵ for the $Si-O-Si$ angle in $(SiH_3)_2O$. In $[(CH_3)_3Si]_2O$, the angle has the value $130 \pm 10^\circ$ according to an electron diffraction study⁶, and the value 135° used by Lazarev and Tenisheva⁷ gave good agreement between calculated and observed values of band frequencies in the vibrational spectra of that molecule. Kriegsmann⁸ measured the Raman and infrared spectra of both $[(CH_3)_3Si]_2O$ and $[(C_6H_5)_3Si]_2O$. For $[(CH_3)_3Si]_2O$, he found considerable double-bond character in the $Si-O$ bonds, and his measurements were compatible with an $Si-O-Si$ angle near 150° . With $[(C_6H_5)_3Si]_2O$, the splitting of the antisymmetric and symmetric $Si-O-Si$ stretching frequencies was greater than in $[(CH_3)_3Si]_2O$, and it was noted that the shift of the antisymmetric stretching to higher frequency in the hexaphenyl derivative could be attributed to an increase in the $Si-O-Si$ angle or in the strength of the $Si-O$ bonds. The effect of increased $(p \rightarrow d)_\pi$ bonding between O and Si would be an increase in both of these quantities.

In view of these findings for the $Si-O-Si$ angle, it is best to make the comparisons of the group moments over the range of values $130^\circ-145^\circ$ for that angle. This yields the corresponding ranges in the group moment values: $\overrightarrow{H-Si-O} = 0.28$ to 0.40 , $\overrightarrow{CH_3-Si-O} = 0.78$ to 1.10 , and $\overrightarrow{C_6H_5-Si-O} = 1.22$ to 1.71 D. It is interesting to note that Freiser and co-workers³ estimated a value of 0.95 D for the $\overrightarrow{CH_3-Si-O}$ moment from the molecular moment of ethoxytrimethylsilane, $(CH_3)_3SiOC_2H_5$, a value that falls in the range of values found above. These values show clearly that the group moments lie in the order $\overrightarrow{H-Si-O} < \overrightarrow{CH_3-Si-O} < \overrightarrow{C_6H_5-Si-O}$, in these disiloxanes.

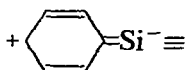
It has been shown from other dipole moment studies and by direct chemical evidence* that the $Si-H$ bond has a large moment (~ 1.0 D), with the negative end toward the hydrogen. This reduces the group moment for $\overrightarrow{H-Si-O}$ to a small value, the large $\overrightarrow{Si-H}$ and $\overrightarrow{Si-O}$ bond moments being in direct opposition along the $Si-O$ axis. The $\overrightarrow{Si-CH_3}$ moment is much smaller than the $\overrightarrow{Si-H}$ moment, being of the order of 0.2 D, with the negative end toward the methyl group⁹⁻¹¹.

Huheey¹² has recently calculated values of the inherent group electronegativities and charge coefficients of the SiH_3 and $Si(CH_3)_3$ groups and has shown how the low charge coefficient of the latter group would be expected to lead to a reversal of the relative electronegativities of these groups when they are attached to oxygen. This result is consistent with the relative values found here for the $\overrightarrow{CH_3-Si-O}$ and $\overrightarrow{H-Si-O}$ moments.

Using the moments given above for $\overrightarrow{Si-H}$ and $\overrightarrow{Si-CH_3}$, a value of $1.28-1.40$ D is obtained for the $\overrightarrow{Si-O}$ bond moment in $(SiH_3)_2O$ and a value of $0.98-1.30$ D for this bond moment in $[(CH_3)_3Si]_2O$. Thus the $\overrightarrow{Si-O}$ bond moments in these compounds are not greatly different.

* For a review of the dipole moment and chemical evidence, see ref. 9.

If it is assumed in the first instance that the $\overrightarrow{\text{Si-O}}$ bond moment in the $\text{C}_6\text{H}_5\text{Si-O}$ group is similar in both direction and magnitude to that in the H-Si-O and $\text{CH}_3\text{-Si-O}$ groups, then it is apparent that the phenyl group must transfer electrons to the silicon ($\text{C}_6\text{H}_5\text{-Si}$ moment, -0.18 to $+0.73$ D) to a greater extent than a hydrogen atom and to an equal or greater extent than a methyl group. If the negative end of the $\overrightarrow{\text{C}_6\text{H}_5\text{-Si}}$ moment lies towards silicon, then the moment lies in the same direction as the $\overrightarrow{\text{Si-O}}$ moment and adds to it to produce the high $\overrightarrow{\text{C}_6\text{H}_5\text{-Si-O}}$ moment. Such a conclusion is consistent with that arrived at by Freiser and co-workers³ from an evaluation of the dipole moment values of $(\text{C}_6\text{H}_5)_3\text{SiOC}_2\text{H}_5$, $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{SiOC}_2\text{H}_5$, and $(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$. It is also in agreement with other evidence¹³, which shows that resonance structures such as



play a very important role in the bonding of a phenyl group to silicon. Indeed, Coleman and Freiser⁹, from a dipole moment study of *m*- and *p*-chlorophenyl trimethylsilanes, -dimethylsilanes, -methylsilanes, and -silanes, concluded that there was a large amount of $(p \rightarrow d)_\pi$ bonding of the phenyl ring into the silicon. Earlier studies of the direction of release of electrons between silicon and phenyl groups have been made by several different techniques with a variety of phenylsilanes. The results of these studies have been summarized by Goodman, Konstam, and Sommer¹⁴ as indicating that silicon has a small $+I$ effect and a slightly greater $-T$ effect. Because of the small differences of these effects in the phenylsilanes, Goodman *et al.*¹⁴ devised a spectroscopic method which permitted direct observation of the electronic distortions in the benzene rings as a more definitive test of the net transfer. Their results show clearly that the SiH_3 group withdraws electrons from the phenyl groups.

Although the base strength of $[(\text{C}_6\text{H}_5)_3\text{Si}]_2\text{O}$ has not been determined, hydrogen bonding base strength studies of $(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$ ¹⁵, $(\text{C}_6\text{H}_5)_3\text{SiOC}_2\text{H}_5$, $[\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2]_2\text{O}$, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$, $[(\text{CH}_3)_2\text{SiH}]_2\text{O}$, $[(\text{C}_6\text{H}_5)_2\text{SiH}]_2\text{O}$, and $(\text{SiH}_3)_2\text{O}$ ¹⁶, have been carried out. In these studies, steric effects are reduced to a minimum. In each case the replacement of a methyl by a phenyl group appeared to lower the base strength of the species.

If, as seems likely, the group moments $\overrightarrow{\text{H-Si-O}}$ (0.28 – 0.40 D) and $\overrightarrow{\text{CH}_3\text{-Si-O}}$ (0.78 – 1.10 D) are more directly related to the base strengths of $(\text{SiH}_3)_2\text{O}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ respectively, than are the corresponding $\overrightarrow{\text{Si-O}}$ moments (1.28 – 1.40 D and 0.98 – 1.30 D), then it is not surprising to find that the base strength of $(\text{SiH}_3)_2\text{O}$ is considerably less than that of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ ^{15,16}. The relative inductive effects of the H and CH_3 groups appear to be largely responsible for the observed base strengths. However, in view of the large $\overrightarrow{\text{C}_6\text{H}_5\text{-Si-O}}$ moment (1.22 – 1.71 D) it might be expected that replacement of methyl groups by phenyl groups would if they had any significant effect at all, bring about an increase in the base strengths of disiloxanes rather than a substantial decrease, as is found experimentally. The observed decrease in base strength might be interpreted as suggesting that when a phenyl group replaces a methyl group in a disiloxane, there is a significant increase in $(p \rightarrow d)_\pi$ bonding in the Si-O bond, and the oxygen lone pair electrons are then less available for acid-base interactions and the base strength of the disiloxane is therefore decreased. This

increase in $(p \rightarrow d)_\pi$ bonding would tend to lower the $\overrightarrow{\text{Si}-\text{O}}$ moment and hence the -0.18 to $+0.73$ D value for the $\overrightarrow{\text{C}_6\text{H}_5-\text{Si}}$ moment given above would represent a lower limit value for that group. Changes which occur in $(p \rightarrow d)_\pi$ bonding between silicon and a given attached atom or group when a non- π -bonding group on the silicon is replaced by a potentially π -bonding group are not fully understood but they probably depend on a variety of factors¹⁷.

EXPERIMENTAL

Materials

Matheson Coleman and Bell "Spectroquality" grade carbon tetrachloride was dried over P_2O_5 .

Hexaphenyldisiloxane (m.p. obs. 225.9 – 226.2° ; lit.^{18,19} 226°) was prepared by condensing triphenylsilanol in boiling anhydrous acetic acid containing 3–4 drops of nitric acid per 100 ml. It was purified by recrystallizing twice from glacial acetic acid and dried *in vacuo*.

Measurements

The apparatus and methods used in determining the dielectric constant, specific volume, and refractive index of the solutions of hexaphenyldisiloxane in carbon tetrachloride at $30.000 \pm 0.005^\circ$ were the same as described earlier²⁰. Five different weight fractions were used, covering the range from 0.001 to 0.014.

The dielectric constant, ϵ_{12} , specific volume, v_{12} , and square of the refractive index for the sodium D line, n_{12}^2 , for the solutions of hexaphenyldisiloxane in CCl_4 at 30° , were treated as linear functions of the weight fraction, w_2 , of the solute. The results were $\epsilon_{12} = 2.21714 + 0.9977 w_2$, $v_{12} = 0.63504 + 0.22985 w_2$, and $n_{12}^2 = 2.11550 + 0.73156 w_2$. The slope and intercept terms of those linear equations were then used to calculate the infinite dilution values of both the molar polarization, P_{20} , and molar refraction, MR_D , of the solute by the method of Halverstadt and Kumler²¹. The values, $P_{20} = 190.65 \pm 0.97$ cc and $MR_D = 169.37 \pm 0.22$ cc, were obtained, the probable errors being computed from the propagation of the probable errors found in the least-squares evaluation of the slope and intercept terms used. The MR_D value obtained compares with the value 168.71 calculated from the group refractions²², 27.515 for $\text{Si}-\text{C}_6\text{H}_5$ and 3.62 for $\text{Si}-\text{O}-\text{Si}$. It is also close to the value of the distortion polarization, $P_E + P_A = 169.6$ cc., obtained by estimating²³ the electronic polarization, P_E , as $0.96 MR_D$, and taking $P_A = 7.0$ cc, as an average of the P_A values found^{1,4} for $(\text{SiH}_3)_2\text{O}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$.

The dipole moment, μ , of the hexaphenyldisiloxane, obtained from the formula $\mu = 0.01281 [(P_{20} - MR_D)T]^\frac{1}{2}$, has the value 1.03 ± 0.02 D.

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SUMMARY

The electric dipole moment of hexaphenyldisiloxane, $(C_6H_5)_3SiOSi(C_6H_5)_3$, has been measured in CCl_4 at 30° . The value, $\mu = 1.03 \pm 0.02$ D, shows that in the disiloxanes $(R_3Si)_2O$ ($R = H, CH_3, C_6H_5$) the group moments are in the order $\overrightarrow{H-Si-O} < \overrightarrow{CH_3-Si-O} \ll \overrightarrow{C_6H_5-Si-O}$. Possible relationships between these data and the base strengths of selected disiloxanes are discussed.

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