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AN ELECTRIC DIPOLE MOMENT STUDY OF METHYLSILYL AND SILYLMETHYL HALIDES*

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SUMMARY

The electric dipole moments of the isomeric monohalogeno derivatives of methylsilane, SiH_3CH_2X and CH_3SiH_2X have been determined in cyclohexane solution at 30°. The magnitudes of the molecular dipole moments and of the bond dipole moments are compared with those of analogous compounds, and are interpreted, in part, in terms of intramolecular interactions between the halogen and the *d* orbitals of silicon.

INTRODUCTION

The importance of electric dipole moments in the investigation of $(p\rightarrow d)\pi$ bonding between a lone pair of *p* electrons and the vacant low energy *d* orbitals of an adjacent Group IV atom is apparent from recent studies which have considered possible effects of backbonding on bond moments or molecular moments in organosilicon[1,2] organogermanium[3,4] and organotin[5] compounds. In the present study the electric dipole moments of the methylsilyl halides, CH_3SiH_2X, and the silylmethyl halides, SiH_3CH_2X, were measured as part of a study of isomeric compounds in which a $(p\rightarrow d)\pi$ interaction between a directly bound substituent and a Group IV atom is possible in one isomer only (the CH_3SiH_2X species); while in the isomeric SiH_3CH_2X compounds, the halogen is attached to the carbon atom and thus no $(p\rightarrow d)\pi$ interaction between directly bound atoms is possible.

EXPERIMENTAL

The electric dipole moments were calculated from the dielectric constants, specific volumes, and refractive indices of solutions of the compounds in cyclohexane

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* Because the names of the isomers are verbally indistinguishable when the standard nomenclature *e.g.* (chloromethyl)silane and chloromethylsilane, is used, the use of the name silylmethyl halide for the carbon-functional series, SiH_3CH_2X, and methylsilyl halide for the silicon-functional series, CH_3SiH_2X, is preferred.

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at 30° over a concentration range of approximately 1×10^{-3} to 6×10^{-3} weight fraction (approximately 10^{-2} *M*).

The preparation of the SiH_3CH_2X (X=Cl, Br, I) compounds has been described previously[6]. The isomeric CH_3SiH_2X (X=Cl, Br, I) compounds were prepared by a method similar to that used in the synthesis of CH_3SiH_2Cl by Stock[7]. The SiH_3I was donated by Dr. T. Yoshioka. The SiH_3CH_2X compounds were purified by gas chromatography. The purity of all species was checked by obtaining a Dumas molecular weight which was within 1% of the calculated value and by the absence of extraneous peaks larger than the ^{13}C satellites in the proton NMR spectra.

Trace amounts of moisture were rigorously excluded by manipulating the compounds in a high-vacuum system and by manipulating the solutions in a glove-bag filled with dry nitrogen which had been passed through drying columns before entering the glove-bag. Any remaining trace amounts of water in the solvent (MC and B "Spectroquality" cyclohexane) were removed by shaking of the solvent over P_2O_5 for four days and subsequent fractionation through a Todd column.

Dielectric constants were measured using a previously described capacitance bridge circuit[8]. The capacitance of each of five solutions of varying weight fraction was measured at seven oscillator frequencies in the range of 0.5 MHz to 1.6 MHz in a 30 ml glass cell which contained a capacitor made of three concentric platinum cylinders one millimeter apart. The replaceable capacitance of the cell was 168 pF. The refractive index of the Na_D line was determined in a Pulfrich refractometer equipped with an air-tight glass sample cell. Density was determined pycnometrically.

All measurements were conducted at a temperature of 30.00°, except that the temperature of the cell in which the refractive indices were measured was found to be a constant 0.18° lower than the oil bath in which the other measurements were made.

The constancy of parameters measured against time, and linearity of the parameters measured against weight fraction, confirmed that the thermostatting of the dilute solutions prior to and during the dipole moment determination apparently did not result in any evaporation loss of the more volatile compounds studied in this investigation. The dipole moments were calculated by computer program from the experimental data according to the procedure of Halverstadt and Kumler[9]. Calculation of the probable error of the dipole moments followed the approach of Rittenhouse[10] and amounted to ± 0.02 D or less for each compound studied. The critical constants and dipole moments of the compounds studied are given in Table 1.

DISCUSSION

In this study the dipole moments of the silicon functional CH_3SiH_2X compounds, in which $(p \rightarrow d)\pi$ bonding between the directly bound halogen and silicon atoms can occur, and the isomeric carbon functional SiH_3CH_2X compounds, in which the halogen and silicon atoms are not directly bound, were experimentally measured and compared to those of the CH_3CH_2X compounds, in which no intramolecular bonding interactions would be expected because of the lack of available *d* orbitals in carbon.

If a CH_3 group replaces a hydrogen in CH_3X and SiH_3X compounds respectively, the dipole moments of the CH_3MH_2X (M=C, Si) compounds thus formed might be expected to show trends which are analogous to those of the parent MH_3X

TABLE 1

CRITICAL CONSTANTS[a] AND DIPOLE MOMENTS[b] OF COMPOUNDS IN CYCLOHEXANE SOLUTION

Compound	ε_1	V_1	η_1^2	α	β	γ	MR_D	P_{20}	μ
$CH_3CH_2I^c$	2.0084	1.2949	2.0176	1.71174	0.76846	0.13658	86.563	145.512	1.71
SiH_3CH_2Cl	2.00788	1.30091	2.01763	2.66692	−0.09362	−0.05734	23.52080	76.66736	1.626
SiH_3CH_2Br	2.00866	1.30163	2.01686	1.64171	−0.73018	−0.01301	17.69601	67.86796	1.580
SiH_3CH_2I	2.00811	1.30102	2.01781	1.42753	−0.68735	0.19032	34.66370	86.22686	1.602
CH_3SiH_2Cl	2.00619	1.30037	2.01760	3.75790	0.05167	−0.09921	25.65929	100.95347	1.935
CH_3SiH_2Br	2.00796	1.30041	2.01756	2.22218	−0.32806	−0.02882	29.92533	98.06570	1.841
CH_3SiH_2I	2.00717	1.30160	2.01778	1.82575	−0.84915	−0.00936	19.32989	95.95280	1.952
SiH_3I	2.00684	1.30179	2.01708	1.47403	−0.80547	0.09533	23.50123	76.36277	1.622

[a] ε_1, V_1 and η_1^2 are the dielectric constant, the specific volume, and the square of the refractive index, respectively, each extrapolated to infinite dilution; α, β, and γ are the slopes of the concentration dependencies of ε_1, V_1 and η_1^2, respectively; MR_D and P_{20} are the molar refraction and the molar polarization, respectively, at infinite dilution; and μ is the dipole moment in Debyes at 30.0°. [b] In Debyes, ±0.02 D. [c] Calculation to fewer significant figures; not done by computer program.

TABLE 2

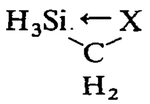
ELECTRIC DIPOLE MOMENTS[a] OF CH_3CH_2X, CH_3SiH_2X, AND SiH_3CH_2X COMPOUNDS

X	CH_3X^b	CH_3CH_2X	$CH_3SiH_2X^c$	$SiH_3CH_2X^c$	SiH_3X
Cl	1.87	2.03[e]	1.93	1.63	1.30[d]
Br	1.80	1.85[e]	1.84	1.58	1.32[d]
I	1.65	1.71[c,e]	1.95	1.60	1.62[c]

[a] In Debyes, ±0.02 D. [b] Ref. 11; gas phase (Stark Effect). [c] In cyclohexane solution at 30.0°, this work. [d] Ref. 12; gas phase (Stark Effect). [e] Ref. 23; solution values.

compounds. From Table 2 it can be seen that the molecular moments of the CH_3CH_2X compounds, in which no intramolecular interaction is expected, do indeed decrease with decreasing electronegativity of the substituent, as do the molecular moments of the parent CH_3X compounds[11]. Analogously the molecular moments of the CH_3SiH_2X compounds, in which $(p\rightarrow d)\pi$ bonding from X to silicon might be expected, follow the overall general trend shown by the parent SiH_3X compounds[12,13]. This behavior is consistent with a reduction in molecular polarity due to a decrease in the effective electronegativity[14] of the halogen by $(p\rightarrow d)\pi$ bonding between the halogen and silicon. The extent of this π bonding is believed to decrease as the size of the halogen increases[15].

It might be expected that the molecular dipole moments of the isomeric carbon functional SiH_3CH_2X species, in which the halogen and the silicon are not directly attached, would show a trend in molecular moments similar to the other carbon functional compounds, *i.e.*, a decrease with decreasing electronegativity of the halogen substituent. However, it can be seen from Table 2 that such is not the case. Instead, the pattern of the molecular moments of the SiH_3CH_2X compounds is rather similar to that of the isomeric CH_3SiH_2X series, *i.e.*, the molecular moments are relatively constant. It is possible that this pattern found in the SiH_3CH_2X isomers may be caused by a $(p\rightarrow d)\sigma$ or π interaction between the halogen and the silicon which is in a β position to it, *e.g.*:



Similar non-bonded interactions have been postulated previously. For example the unexpectedly small base strength of $(CH_3)_3SiCH_2OCH_3$ has been interpreted in terms of an interaction of this type between the oxygen and silicon[16].

Using the $\overrightarrow{\text{Si–H}}$ (1.0 D), $\overrightarrow{\text{Si–C}}$ (0.6 D), and $\overrightarrow{\text{Si–Alkyl}}$ (0.2 D) bond moments customarily assigned for organosilicon compounds as listed by Eaborn[17], the C–X bond moments in the SiH_3CH_2X isomers have been calculated. Tetrahedral angles at carbon and silicon were used since microwave studies of CH_3SiH_2F[18] and SiH_3CH_2Cl[19] indicate that these angles do not deviate significantly from the tetrahedral angle. In addition, calculations show that a change of a few degrees in the central angle will have only a negligible effect on the molecular moment.

It can be seen from Table 3 that the C–Cl bond moment in SiH_3CH_2Cl is substantially less than its value in the analogous ethyl compound. The values of the C–X bond moments in the SiH_3CH_2X isomers become increasingly similar to the values found for the CH_3CH_2X compounds as the size of the halogen increases. Although it may be completely fortuitous, it is interesting that these relative values and their trends are exactly what would be expected, in view of the decreasing π bonding ability of a halogen as its size increases[15], if a β X→Si interaction which decreased on going from chlorine to iodine were present in the SiH_3CH_2X isomers.

TABLE 3

C–X BOND MOMENTS[a] CALCULATED FROM CH_3CH_2X AND SiH_3CH_2X COMPOUNDS

C–X	CH_3CH_2X	SiH_3CH_2X	Diff.
C–Cl	1.63	1.32	0.31
C–Br	1.45	1.27	0.18
C–I	1.31	1.29	0.02

[a] In Debyes.

Certain changes in the dipole moments of the SiH_3CH_2X isomers are somewhat analogous to those reported in some $(CH_3)_3Si$ compounds by other investigators[20]. For example it has also been found necessary to assign a variable moment to the $(CH_3)_3Si$ group in various $(CH_3)_3Si$–(aromatic) compounds, and this variability has been correlated with the extent of $(p\rightarrow d)\pi$ bonding between the phenyl group and the silicon[20]. Similarly if one wishes to assume that the C–X bond moments in the SiH_3CH_2X isomers have the same values as in CH_3CH_2X, then these values may be employed to calculate SiH_3 group moments in the SiH_3CH_2X isomers. These values also vary from compound to compound within the series and could again be interpreted as being consistent with an interaction between the halogen and the β silicon atom. In the case of a compound such as $(ClCH_2)_2Si(CH_3)_2$[21], which has been reported to have a molecular moment which is less than that calculated by the Eyring equation[22], it is of course very much more difficult to calculate a meaningful group moment in view of the difficulty in assigning a definitive conformational form to the molecule.

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REFERENCES

1 V. Vaisarova, V. Bažant and V. Chvalovský, *Collect. Czech. Chem. Commun.*, 33 (1968) 850.
2 V. Vaisarova and V. Chvalovský, *Collect. Czech. Chem. Commun.*, 33 (1968) 859.
3 D. F. Van de Vondel, *J. Organometal. Chem.*, 3 (1965) 400.
4 K. Ulbricht, V. Vaisarova, V. Bažant and V. Chvalovský, *J. Organometal. Chem.*, 13 (1968) 343.
5 H. H. Huang, K. M. Hui and K. K. Chiu, *J. Organometal Chem.*, 11 (1968) 515.
6 J. M. Bellama and A. G. MacDiarmid, *J. Organometal. Chem.*, 18 (1968) 275.
7 A. Stock and C. Somieski, *Chem. Ber.*, 52 (1919) 695.
8 R. A. Prosser, Ph.D. Dissertation, University of Pennsylvania, 1960.
9 I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 64 (1942) 2988.
10 J. Rittenhouse, Ph.D. Dissertation, University of Pennsylvania, 1957.
11 R. G. Shulman, B. P. Dailey and C. H. Townes, *Phys. Rev.*, 78 (1950) 145.
12 J. M. Mays and B. P. Dailey, *J. Chem. Phys.*, 20 (1952) 1695.
13 A. H. Sharbaugh, V. G. Thomas and B. S. Pritchard, *Phys. Rev.*, 78 (1950) 64.
14 C. H. Van Dyke and A. G. MacDiarmid, *Inorg. Chem.*, 3 (1964) 1071.
15 V. Bažant, V. Chvalovský and J. Rathouský, *Organosilicon Compounds*, Vol. 1, Academic Press, New York, 1965, p. 20.
16 E. W. Abel, D. A. Armitage and S. P. Tyfield, *J. Chem. Soc. A*, (1967) 554.
17 C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, p. 483.
18 L. C. Krisher and L. Pierce, *J. Chem. Phys.*, 32 (1960) 1619.
19 R. H. Schwendeman and G. D. Jacobs, *J. Chem. Phys.*, 36 (1962) 1251.
20 H. Soffer and T. de Vries, *J. Amer. Chem. Soc.*, 73 (1951) 5817.
21 H. Freiser, M. V. Eagle and J. Speier, *J. Amer. Chem. Soc.*, 75 (1953) 2821.
22 H. Eyring, *Phys. Rev.*, 39 (1932) 746.
23 A. L. McClellan, *Tables of Experimental Dipole Moments*, Freeman, San Francisco, 1963.