[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Electric Moments of Organosilicon Compounds. II. Bromides

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Electric moments have been obtained for the completely substituted methyl-, ethyl- and phenylbromosilanes, for the partially substituted phenylbromosilanes and for *p*-methoxyphenyltribromosilane. The moments are interpreted as indicating contributions of doubly bonded structures of the type $\overset{-}{\mathrm{Si}}{=}\overset{+}{\mathrm{Br}}$, $^{+}\mathrm{C_6H_5}{=}\overset{=}{\mathrm{Si}}\mathrm{Br}$, and hyperconjugative structures of the type $\mathrm{H}^{+}\mathrm{C}{=}\overset{-}{\mathrm{Si}}\mathrm{Br}$. The large moment of *p*-methoxyphenyltribromosilane reveals resonance interaction between the methoxy and tribromosilyl groups.

In the first paper[1] of this series the electric moments of some organochloro- and organofluorosilanes were reported. An interpretation was made of the moments of the alkyl compounds on the basis of the effect of contributing structures of the type $\mathrm{H}^{+}\mathrm{C}{=}\overset{-}{\mathrm{Si}}{-}\mathrm{Cl}$ and $\overset{-}{\mathrm{Si}}{=}\overset{+}{\mathrm{X}}$. Moments of the aryl compounds were interpreted as indicating contributions of structures of the type $^{+}\mathrm{C_6H_5}{=}\overset{-}{\mathrm{Si}}$. The moments of the corresponding bromo compounds have now been obtained and the results are presented and discussed in the present paper.

Experimental

The preparation and purification of the compounds have been previously described.[2]

Measurements and Calculations.—Dielectric constants were measured at 25° by the heterodyne beat method, using a crystal controlled standard oscillator having a frequency of one megacycle. The dielectric cell, constructed by J. C. Balsbaugh, Cambridge, Mass., and having a capacity of 25 $\mu\mu$f. was modified by the addition of inlet and outlet tubes. Molar refractions and densities were measured as previously described.[2] Polarizations at infinite dilution were calculated by the method of Hedestrand[3] as modified by LeFevre and Vine.[4] The dielectric slopes used in the calculations of moments are average values of at least four measurements on benzene solutions in the weight fraction range, 0.01 to 0.08. Atomic polarizations were taken as 5% of the electronic polarizations. The calculated moments are believed to be accurate to ±0.04 Debye unit. These are listed with the data from which they were calculated in Table I.

TABLE I

AVERAGE DIELECTRIC CONSTANT AND DENSITY SLOPES OF BENZENE SOLUTIONS AT 25°. POLARIZATIONS AND ELECTRIC MOMENTS

Compound	$\frac{\Delta\epsilon}{\mathrm{wf}_2}$	$\frac{\Delta d}{\mathrm{wf}_2}$	$P_{2\infty}$	MR_D	μ
$(\mathrm{CH_3})_3\mathrm{SiBr}$	3.80	0.23	148.8	33.00	2.36
$(\mathrm{CH_3})_2\mathrm{SiBr_2}$	3.00	.43	160.7	35.88	2.45
$\mathrm{CH_3SiBr_3}$	1.44	.56	111.2	38.17	1.86
$(\mathrm{C_2H_5})_3\mathrm{SiBr}$	3.30	.19	169.3	46.70	2.42
$(\mathrm{C_2H_5})_2\mathrm{SiBr_2}$	2.81	.39	176.5	44.70	2.51
$\mathrm{C_2H_5SiBr_3}$	1.60	.52	113.9	43.11	1.99
$(\mathrm{C_6H_5})_3\mathrm{SiBr}$	1.98	.30	192.8	92.37	2.26
$(\mathrm{C_6H_5})_2\mathrm{SiBr_2}$	2.70	.41	236.1	75.41	2.77
$\mathrm{C_6H_5SiBr_3}$	1.94	.51	175.0	58.12	2.36
$\mathrm{C_6H_5SiHBr_2}$	2.60	.44	175.1	51.05	2.33
$\mathrm{C_6H_5SiH_2Br}$	2.65	.31	134.2	44.09	2.07
p-$\mathrm{CH_3OC_6H_4SiBr_3}$	3.44	.49	299.1	66.82	3.34

Discussion

The relatively large moments of triethyl- and triphenylchlorosilane compared to the corresponding fluoro compounds, previously noted,[1] were ascribed to the decreased contribution to the chloro compounds of structures of the type $\overset{-}{\mathrm{Si}}{=}\overset{+}{\mathrm{X}}$. Such structures should be even less important in the bromosilanes because the larger bromine atom does not readily form a double bond. If the contribution of the $\overset{-}{\mathrm{Si}}{=}\overset{+}{\mathrm{X}}$ structures exert an appreciable effect on the polarity of the alkyl- and arylhalogenosilanes, the bromides should have the largest moments. The list of moments in Table II reveals that this is the case for the mono- and dihalides. The reverse order is seen to hold for the trihalides. This is probably a result of the high polarizability of the carbon-to-bromine bond: the decrease in polarity of each C–X bond from the mono- to the trihalides is greatest for the bromides. The moments of alkylchloromethanes decrease from the mono- to the trichloro compounds. In the analogous silanes both the dichloro and dibromo compounds have the largest moments, indicating that the $\mathrm{R_2Si}$ group is more polarizable than the $\mathrm{R_2C}$ group.

TABLE II

ELECTRIC MOMENTS OF SOME ORGANOHALOGENOSILANES

X =	F	Cl	Br
$(\mathrm{C_2H_5})_3\mathrm{SiX}$	1.72	2.07	2.42
$(\mathrm{C_2H_5})_2\mathrm{SiX_2}$	2.23	2.39	2.51
$\mathrm{C_2H_5SiX_3}$	..	2.04	1.99
$(\mathrm{C_6H_5})_3\mathrm{SiX}$	1.84	2.14	2.26
$(\mathrm{C_6H_5})_2\mathrm{SiX_2}$	2.57	2.56	2.77
$\mathrm{C_6H_5SiX_3}$	2.77	2.41	2.36

The ethylbromosilanes have slightly higher moments than the corresponding methylbromosilanes, indicating that the greater inductomeric polarizability of the ethyl group more than offsets the more favorable conditions for hyperconjugation in the methylbromosilanes. The moments of the phenylhalosilanes are larger than those of the alkylhalosilanes for the di- and trihalides, showing, as expected, that electron release due to structures of the type $\overset{+}{\mathrm{C}}_6\mathrm{H_5}{=}\overset{-}{\mathrm{Si}}\mathrm{X_3}$ is more important than the hyperconjugation effect. Triphenylbromosilane, however, has a slightly smaller moment than triethylbromosilane, suggesting that in the former compound the spatial requirements of the bromine atom and the three benzene rings may force the rings into planes unfavorable for maximum over-

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(1) C. Curran, R. M. Witucki and P. A. McCusker, THIS JOURNAL, **72**, 4471 (1950).

(2) P. A. McCusker and E. L. Reilly, *ibid.*, **75**, 1583 (1953).

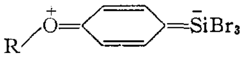
(3) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

(4) R. J. W. LeFevre and H. Vine, *J. Chem. Soc.*, 1805 (1937).

lapping of carbon and silicon π-orbitals. In line with this interpretation, the changes in moments from ethyl- to phenylhalogenosilanes decrease from the tri- to the monohalides for both the chloro and bromo compounds.

The moment of phenyltribromosilane, 2.36, is appreciably greater than that reported for tribromosilane, 0.79,[5] revealing the very large polarizability (electron release) of the phenyl group. The replacement of a phenyl group by a hydrogen atom in diphenyl dibromosilane, and of two phenyl groups by two hydrogen atoms in triphenylbromosilane result in decreases in moment of 0.43 and 0.19, respectively. These relatively small changes suggest that these replacements relieve steric strains, permitting more favorable orientation of the benzene rings for π-orbital overlapping.

A comparison of the moment observed for *p*-methoxyphenyltribromosilane with a calculated moment, gives evidence of resonance interaction between the *p*-methoxy and tribromosilyl groups. A value for the moment of this compound, assuming no resonance interaction, was calculated assuming[6] an angle of 72° between the anisole (μ 1.2) and phenyltribromosilane moment vectors. This calculation leads to a value of 2.97, compared to the observed moment of 3.34. The difference, 0.37 *D*, indicates an appreciable contribution of the structure



to the *p*-methoxyphenyltribromosilane molecule.

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[5] G. L. Lewis and C. P. Smyth, THIS JOURNAL, **61**, 3063 (1939).

[6] W. Anzillotti and C. Curran, *ibid.*, **65**, 607 (1943).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Molecular Structures of Mono-, Di- and Trimethylsilane[1]

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The sector-microphotometer method has been applied to the electron diffraction study of mono-, di- and trimethylsilane. The results are summarized in Tables II and VI. Notable features are the precision of the Si–C bond length values and their significant increase (~0.015 Å.) in the series, as well as the approximate values determined for some of the interatomic vibrational amplitudes.

The wide range of values reported for Si–C bond lengths—$Si(CH_3)_4$ 1.888 ± 0.02 Å.,[3] $Si_2(CH_3)_6$ 1.90 ± 0.02 Å.,[4] $Si(CH_3)_2Cl_2$ 1.83 ± 0.06 Å.,[5] $Si(CH_3)_3Cl$ 1.89 ± 0.03 Å.,[6] $Si(CH_3)_3CH_2Cl$ 1.88 ± 0.04 Å.,[7] methylbromosilanes 1.92 ± 0.06 Å.,[8] $[(CH_3)_3Si]_2O$ 1.88 ± 0.03 Å.,[9] $[(CH_3)_2SiO]_3$ 1.88 ± 0.04 Å.,[10] carborundum 1.89 Å.[11]—might suggest a considerable sensitivity of this bond length to the nature of the other atoms attached to the silicon atom although, to be sure, the more precise values all lie within 0.01 of 1.89 Å. The present electron diffraction study of the three methylsilanes affords a direct test of the effect of added methyl groups; it was the first study of molecular structure to be made in this Laboratory by the sector–microphotometer method.

Experimental

Preparation of the Silanes.—The corresponding methylchlorosilanes were treated with $LiAlH_4$ in ether in a manner similar to that described[12] for the preparation of SiH_4 from $SiCl_4$

$$(4 - x)\ LiAlH_4 + 4Si(CH_3)_xCl_{4-x} \longrightarrow$$
$$4Si(CH_3)_x H_{4-x} + (4 - x)\ AlCl_3 + (4 - x)LiCl;\ x = 1, 2 \text{ or } 3$$

The volatile products were passed through $AlCl_3$ (which forms a stable, non-volatile etherate) and subjected to repeated fractional condensations until tensiometrically pure. Vapor density measurements checked the calculated values to within 0.5%, and straight line log *p* *vs.* 1/*T* plots of rough vapor pressure measurements (Table I) led to estimated boiling points of 6°, −19° and −57°, in agreement with the literature (9–10°,[13] −20.1°[14] and −56.8°[14]).

TABLE I

VAPOR PRESSURES OF THE METHYLSILANES IN MILLIMETERS OF MERCURY

t, °C.	$Si(CH_3)_3H$	$Si(CH_3)_2H_2$	$SiCH_3H_3$
−78.5	. . .	30.0	244.0
−63.5	25.0	84.0	552.0
−32.0	. . .	411.0	. . .
−22.6	233.5	664.0	. . .
−13.5	334.0	. . .	. . .
0.0	607.0	. . .	. . .

The Sector–Microphotometer Method.—Our apparatus has been described by Bartell.[15] An "r^3" sector (a sector with the angular opening proportional to the cube of the radial distance from the center of the sector) mounted 8 mm. in front of the plate (medium-contrast lantern slide) was rotated at 1200 r.p.m. during the exposures. It covered the ranges $3 < s < 30$ and $1 < s < 13$ at the camera distances, 10 and 25 cm., used; the electron wave length was about 0.059 Å. Five photographs covering a range of exposure times and with maximum optical density usually

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[1] From the Ph.D. dissertation of Arthur C. Bond, University of Michigan, 1951.

[2] Department of Chemistry, University of Rochester, Rochester, N. Y.

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