as those in cyclopentane and cycloheptane, namely, 6 kcal./mole in both cases. The amounts of double-bond resonance in the rings are estimated by comparing the heats of formation of cyclopentadiene and cycloheptatriene as calculated from the data given in Branch and Calvin[11] with the heats of formation as calculated with the group equivalent method. The values thus obtained are 6 and 14 kcal./mole, respectively. The resonance energy calculated for the cyclopentadienyl and cycloheptatrienyl radicals should be the total resonance energy and no further allowance for double bond resonance has been made.

It is difficult to assess the uncertainty in the calculated dissociation energies, but the authors are of the opinion that ±5 kcal./mole would be a reasonable estimate in all cases except those involving the cycloheptatrienyl radical where the uncertainty is somewhat greater.

BAYTOWN, TEXAS

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[11] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice–Hall, New York, N. Y., 1941, pp. 275–279.

[CONTRIBUTION NO. 876 FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH AND MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

Electric Moments and Structures of Organosilicon Compounds. II. The Aromatic Carbon–Silicon Bond[1,2]

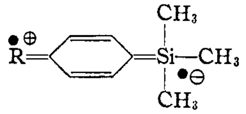
BY HENRY FREISER, MARY V. EAGLE AND JOHN SPEIER

RECEIVED AUGUST 29, 1952

The dielectric constants and densities of benzene solutions of trimethylphenylsilane, trimethyl-*o*-tolylsilane, trimethyl-*m*-tolylsilane, trimethyl-*p*-tolylsilane, *m*-chlorophenyltrimethylsilane, trimethyl-*m*-nitrophenylsilane, chloromethyldimethylphenylsilane, dimethyldiphenylsilane and bis-(chloromethyl)-dimethylsilane have been determined at 30.0°. The dipole moment values of these compounds have been calculated as 0.42, 0.61, 0.50, 0.48, 1.83, 4.28, 1.93, 0.34 and 2.21 *D*, respectively. The results indicate the importance of the so-called "reverse halogen" behavior of silicon and the significance of structures of the type $(CH_3)_3Si^{\oplus}\ominus{:}R$. Other structural implications of the results are also discussed.

In paper I, the dipole moments of some aliphatic organosilicon compounds were discussed in terms of the great ease with which the silicon atom can be electrically distorted. In this report, our work was extended to include compounds containing silicon–phenyl linkages. Two previous publications in this area are of considerable interest. Roberts, *et al.*,[3] had reported the dipole moment values of trimethylphenylsilane and some of its *p*-halogenated derivatives. They considered the value of the $(CH_3)_3Si–C_{arom}$ group moment obtained from the measurement of $(CH_3)_3SiC_6H_5$, 0.44 *D*, too high due to incorrect evaluation of atomic polarization. Since the value calculated from the *p*-halogenated derivatives was considerably less than 0.44 *D* this was taken as evidence of the undue influence of atomic polarization. Because of the ready distortability of silicon referred to,[1] and the presence of the substituent on the benzene ring in position to exert a maximum influence upon the silicon in the compounds used by Roberts, *et al.*, their conclusions are subject to question.

Since the start of the work described in this report a paper by Soffer and De Vries[4] appeared in which the moments of a large number of aryltrimethylsilanes were reported. Soffer and De Vries pointed out how greatly electron-releasing substituents of the benzene ring in the para position affected the $(CH_3)_3Si–C_{arom}$ moment. The results obtained by these workers indicate the great importance of structures of the type



in describing the variation of the $(CH_3)_3Si–C_{arom}$ group moment. While Soffer and De Vries suggest that the importance of this structure is limited to R = alkyl, amino and other electron-releasing groups, we feel that in trimethylphenylsilane itself (R = H) the structure also contributes to the description of the ground state. The dipole moments of trimethylphenylsilane, the three isomeric trimethyltolylsilanes although previously reported were examined as were those of *m*-chlorophenyltrimethylsilane, trimethyl-*m*-nitrophenylsilane, chloromethyldimethylphenylsilane, dimethyldiphenylsilane and bis-chloromethyldimethylsilane.

Experimental

Preparation and Purification of Materials.—Trimethylphenylsilane was prepared by adding an equimolar mixture of chlorotrimethylsilane and chlorobenzene to refluxing toluene containing molten sodium and a small amount of excess chlorotrimethylsilane. The addition was at such a rate as to keep the mixture boiling briskly from the heat of reaction. After the addition was complete, acetic acid was added to destroy any traces of sodium that might have remained. The salts were washed from the organic material with water. Distillation in a 13-mm. Podbielniak Heligrid column afforded trimethylphenylsilane, 90% yield, b.p. 170.6° at 738 mm., $n^{25}D$ 1.4872, d^{25}_4 0.8632; sp. ref. 0.3332, calcd.[5] sp. ref. 0.3334. Roberts, *et al.*,[3] report b.p. 98–99° at 80 mm., $n^{25}D$ 1.4880, d^{25}_4 0.8680.

Tolyltrimethylsilane.—*o*-Chlorotoluene (502.5 g., 3.95 moles) was mixed with trimethylchlorosilane and added slowly to molten sodium (195 g., 8.5 g. atoms) in 400 ml. of boiling toluene containing sufficient trimethylchlorosilane to lower the reflux temperature to 102°. A total of 475 g., 4.4 moles, of the chlorosilane was used. Reaction was very

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[1] Paper I, THIS JOURNAL, **73**, 5229 (1951).

[2] Abstracted from the thesis of M. V. E. submitted in partial fulfillment of the requirements of the M.S. degree in Chemistry, Summer, 1952.

[3] J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

[4] H. Soffer and T. De Vries, *ibid.*, **73**, 5817 (1951).

[5] E. L. Warrick, *ibid.*, **68**, 2455 (1946).

vigorous. When reaction was complete the mixture was diluted with alcohol to destroy the excess sodium, washed with water and distilled to yield 600 g., 86.5% of pure *o*-tolyltrimethylsilane, b.p. 94.4° at 23 mm., $n^{25}\mathrm{D}$ 1.5016, $d^{25}{}_4$ 0.8840; sp. ref. 0.3336, calcd. sp. ref. 0.3331. Soffer and De Vries report[4] b.p. 198° at 760 mm., $n^{25}\mathrm{D}$ 1.5036, $d^{25}{}_4$ 0.8990.

Tolyltrimethylsilane.—The same process employing *p*-chlorotoluene yielded *p*-tolyltrimethylsilane, 87% yield after distillation; b.p. 193° at 740 mm., $n^{25}\mathrm{D}$ 1.4890, $d^{25}{}_4$ 0.8602; sp. ref. 0.3356, calcd. sp. ref. 0.3356. Soffer and De Vries[4] report b.p. 192.5° at 760 mm., $n^{25}\mathrm{D}$ 1.4897, $d^{25}{}_4$ 0.8626.

***m*-Chlorophenyltrimethylsilane.**—*m*-Chloroiodobenzene (Eastman Kodak Co.) (201 g., 0.84 mole) was added to 21 g., 0.86 mole, of magnesium in absolute ether to prepare *m*-chlorophenylmagnesium iodide in the usual manner. This and trimethylchlorosilane were mixed and the mixture was permitted to stand overnight before being heated to reflux for three hours. The mixture was washed with dilute hydrochloric acid, dried and distilled through a simple still to yield 103 ml., 99 g., 64% yield of crude *m*-chlorophenyltrimethylsilane, b.p. 110° at 23.5 mm., $n^{25}\mathrm{D}$ 1.5081–1.5099, $d^{25}{}_4$ 1.04. This material was washed with sodium thiosulfate solution to free it from color, thought to be due to free iodine. The color was removed. The product was then redistilled through a three foot column, one inch in diameter packed with nichrome "Heli-Pak" to yield 65 g., 42% over-all yield of *m*-chlorophenyltrimethylsilane, b.p. 102–104° at 24 mm., $n^{25}\mathrm{D}$ 1.5071–1.5083, $d^{25}{}_4$ 0.9972–1.000. This was partially crystallized, and filtered to produce 25 g. of crystals, m.p. −43°. This material was redistilled and found to be pure so far as fractional distillation could determine, having constant properties, b.p. 105° at 24.5 mm., $n^{25}\mathrm{D}$ 1.5070, $d^{25}{}_4$ 0.9992; sp. ref. 0.2978, calcd. sp. ref. 0.2975. Roberts, *et al.*,[3] prepared this compound by essentially the same method and report, b.p. 97–102.5° at 23 mm., $n^{25}\mathrm{D}$ 1.5070.

Trimethyl-*m*-nitrophenylsilane was isolated by distillation from the product obtained by nitrating trimethylphenylsilane in acetic anhydride solution with fuming (90%) nitric acid. The details of this process may later be published by one of us (J. S.). The compound had the properties b.p. 161° at 40 mm., $n^{25}\mathrm{D}$ 1.5229, $d^{25}{}_4$ 1.051; sp. ref. 0.2906, calcd. sp. ref. 0.2907. Benkeser and Brumfield[6] reported for a sample containing about 5% para isomer, the properties b.p. 126° at 10 mm., $d^{25}{}_4$ 1.055; *MR*D 56.55, calcd. *MR*D 56.34.

Chloromethyldimethylphenylsilane was prepared according to the method of Noll, Speier and Daubert[7] and had essentially the same properties as reported by them, b.p. 121° at 24 mm., $n^{25}\mathrm{D}$ 1.5186, $d^{25}{}_4$ 1.024; sp. ref. 0.2963, calcd. sp. ref. 0.2974.

Dimethyldiphenylsilane was prepared from methylmagnesium bromide and dichlorodiphenylsilane in ether in the usual manner allowing them to react overnight at room temperature; yield 89%, b.p. 177° at 45 mm., $n^{25}\mathrm{D}$ 1.5607, $d^{25}{}_4$ 0.9824; sp. ref. 0.3295, calcd. sp. ref. 0.3298. Kipping[8] reported b.p. 177° at 45 mm.

Bis-chloromethyldimethylsilane was recovered from accumulated residues of chlorinated tetramethylsilane by distillation through a still of about 50 plates. The chlorinations had been carried out in the vapor phase as reported by Speier[9] and the isolated product had the properties[9,10] b.p. 160° at 742 mm., n^{25}_{D} 1.4566, d^{25}_{4} 1.081; sp. ref. 0.2519; calcd. sp. ref. 0.2544. Only the center fraction (100 ml.) from a plateau of 800 ml. was used.

Measurements and Calculations.—The procedure used is described elsewhere.[11] The measurements are summarized in Table I where the dielectric constants, ε, and the densities, *d*, of benzene solutions containing mole fraction f_2 of the substance indicated are given along with the molar polarization, P_2, and the molar refraction at the Na D line, *MR*D. The table also includes the polarization obtained by extrapolation to $f_2 = 0$ of the P_2 values and the dipole moment, μ, calculated therefrom in the usual manner.

TABLE I

DIELECTRIC POLARIZATION DATA AT 30°

f_2	ε	*d*	P_2
Trimethylphenylsilane, *MR*D = 50.16, μ = 0.42 *D*			
0.0000	2.2627	0.86823	(53.63)
.04431	2.2667	.86703	53.51
.06143	2.2683	.86660	53.55
.08700	2.2717	.86592	53.81
Trimethyl-*o*-tolylsilane, *MR*D = 54.81, μ = 0.61 *D*			
0.00000	2.2627	0.86823	(62.23)
.01082	2.2671	.86832	61.92
.01877	2.2699	.86839	61.59
.03068	2.2735	.86849	61.20
Trimethyl-*m*-tolylsilane, *MR*D = 55.09, μ = 0.50 *D*			
0.00000	2.2627	0.86823	(60.01)
.02746	2.2682	.86723	60.28
.03682	2.2695	.86700	59.97
.05504	2.2722	.86643	59.83
Trimethyl-*p*-tolylsilane, *MR*D = 55.14, μ = 0.48 *D*			
0.00000	2.2627	0.86823	(59.82)
.03549	2.2676	.86647	59.77
.04638	2.2698	.86623	59.85
.07723	2.2739	.86489	59.83
m-Chlorophenyltrimethylsilane, *MR*D = 55.0, μ = 1.83 *D*			
0.00000	2.2627	0.86823	(122.7)
.00882	2.3031	.87045	123.3
.01609	2.3352	.87220	122.3
.01932	2.3496	.87297	122.2
.02489	2.3758	.87428	122.9
Trimethyl-*m*-nitrophenylsilane, *MR*D = 56.7, μ = 4.28 *D*			
0.00000	2.2627	0.86823	(425.5)
.003240	2.3438	.86944	421.4
.006559	2.4280	.87063	418.2
.008159	2.4656	.87115	414.2
Chloromethyldimethylphenylsilane, *MR*D = 54.7, μ = 1.93 *D*			
0.00000	2.2627	0.86823	(129.8)
.009409	2.3112	.87109	130.1
.02726	2.4046	.87626	130.6
.02963	2.4154	.87698	129.8
.04188	2.4763	.88037	128.9
Dimethyldiphenylsilane, *MR*D = 70.0, μ = 0.34 *D*			
0.00000	2.2627	0.86823	(72.2)
.02588	2.2766	.87532	72.0
.03056	2.2784	.87640	71.8
.03917	2.2851	.87862	72.8
.04471	2.2864	.87997	72.4
Bis-(chloromethyl)-dimethylsilane, *MR*D = 39.6, μ = 2.21 *D*			
0.00000	2.2627	0.86823	(137.5)
.01122	2.3353	.87194	136.7
.01964	2.3893	.87457	137.7
.03106	2.4655	.87815	138.0
.04249	2.5410	.88169	137.4

Discussion of Results

The value of the dipole moment of trimethylphenylsilane reported here, 0.42 *D*, is in substantial

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[6] R. A. Benkeser and P. E. Brumfield, THIS JOURNAL, **73**, 4770 (1951).

[7] J. E. Noll, J. L. Speier and B. F. Daubert, *ibid.*, **73**, 3867 (1951).

[8] F. S. Kipping, *J. Chem. Soc.*, 104 (1927).

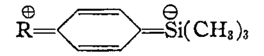
[9] J. L. Speier, THIS JOURNAL, **73**, 824 (1951), reported a b.p. 160–161° at 749 mm., $n^{25}\mathrm{D}$ 1.4573, $d^{25}{}_4$, 1.08.

[10] J. L. Speier and B. F. Daubert, *ibid.*, **70**, 1400 (1948), reported b.p. 160° at 724 mm., $n^{25}\mathrm{D}$ 1.4579, $d^{25}{}_4$ 1.075.

[11] R. K. Keswani and H. Freiser, *ibid.*, **71**, 218 (1949).

agreement with that reported previously.[3,4] That this is a true value, not one in error due to neglect of atomic polarization, can be seen by the comparison of the observed moments of *m*-chlorophenyltrimethylsilane, 1.83 *D*, and trimethyl-*m*-nitrophenylsilane, 4.28 *D*, with the respective calculated values, 1.83 and 4.24 *D*. These were calculated by vector addition of the $(CH_3)_3Si–C_{arom}$ moment found here to be 0.42 *D*, the $Cl–C_{arom}$ moment from chlorobenzene 1.57 *D*,[12] and the $O_2N–C_{arom}$ moment from nitrobenzene 4.01 *D*.[13] The importance of using meta isomers in evaluating the $(CH_3)_3Si–C_{arom}$ lies in the fact that in this meta position the resonance interaction of the two substituents is at a minimum.

Using the value of 0.34 *D* for the $CH_3–C_{arom}$ moment,[14] the moments of the isomeric trimethyltolylsilanes can be interpreted in terms of $(CH_3)_3Si–C_{arom}$ group moment values of 0.37, 0.54 and 0.12 from the measurements of the ortho, meta and para isomers, respectively. The fact that the $(CH_3)_3Si–C_{arom}$ moment in the *o*- and *p*-trimethyltolylsilanes has a lower value than found in the other compounds discussed may be attributed to the influence of the so-called "reverse halogen" effect of silicon which is so named because of the contrasting behavior of chlorine which has a −I but a +T influence, and that of silicon which seems to have a +I and −T influence. This −T effect of silicon has been implicit in the weight given by Soffer and De Vries[4] to resonance structures such as

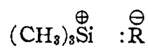


where R is an electron-releasing group such as CH_3, NH_2, etc., to explain the observed moments of the various substituted trimethylphenylsilanes they studied. The relatively small decrease of the $(CH_3)_3Si–C_{arom}$ moment in trimethyl-*o*-tolylsilane might be considered as an indication of possible steric hindrance to structures such as the one shown above by the group in the *o*-position.

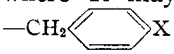
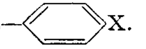
On the basis of comparison of the moments of trimethylphenylsilane and *t*-butylbenzene (0.53 *D*),[15] the importance of such structures in this silicon compound cannot be overlooked since otherwise one might have predicted that because of its lower electronegativity the $(CH_3)_3Si$ group would give rise to a greater moment than would the $(CH_3)_3C$ group.

It is interesting to observe that chlorine and the methyl group in the para position have essentially the same effect on the moment of the $(CH_3)_3Si–C_{arom}$ group indicating that the +T effect and the extent of the double bondedness to the ring carbon is somewhat greater in chlorine than in the methyl group inasmuch as this effect in chlorine operates against a −I effect.

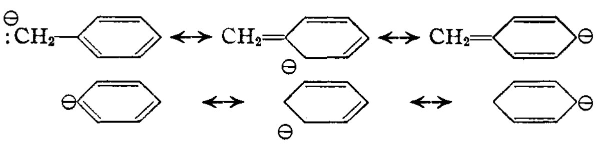
Study of the dipole data of aliphatic and aromatic organosilicon compounds leads to the consideration of resonance structures of the type



$$\overset{\oplus}{(CH_3)_3Si}\quad \overset{\ominus}{:R}$$

where R may be aliphatic such as $–CH_2X$ or  or aromatic such as .

Thus the reason for the greater value of the $(CH_3)_3Si–C$ group moment in trimethylphenylsilane (0.42 *D*) and benzyltrimethylsilane (0.47 *D*)[4] than in chloromethyltrimethylsilane (0.25 *D*)[1] or in dichloromethyltrimethylsilane (0.32 *D*) might be seen in the greater stability of the $:\bar{R}$ portion of the first mentioned compounds due to the great number of resonance structures that can be written for $\overset{\ominus}{:R}$, *e.g.*



In the case of the benzyltrimethylsilane, the $(CH_3)_3Si–C$ moment is somewhat larger than that in the trimethylphenylsilane due to the absence of structures of the "reverse halogen" type that characterize the description of the phenyl derivative.

The ability of phenyl or benzyl [as R in $(CH_3)_3$-Si–R] to accept electrons from $(CH_3)_3Si–$ can, of course, be modified by suitable substituents and, in turn, affect the value of the $(CH_3)_3Si–R$ moment. Electron-releasing substituents on the benzene ring would decrease the electron accepting tendency while those which were electron-drawing would have the opposite effect. These effects are inextricable from the "reverse halogen" effect in substituted trimethylphenylsilanes but are plainly recognized in benzyltrimethylsilanes in which "reverse halogen" structures are not important. Soffer and De Vries reported[4] the moment values of *p*-aminobenzyltrimethylsilane and *p*-nitrobenzyltrimethylsilane as 1.33 and 4.94 *D*, respectively, but do not discuss these in their paper. The values of the $(CH_3)_3Si–C$ group moment were calculated from these data by considering them to represent the vector sum of the moment of the *p*-substituted toluene and of the $(CH_3)_3Si–$ group acting along the tetrahedral bond angle. A value for *p*-aminotoluene of +1.27 *D*[16] and a value of 4.52 *D*[17] for the moment of *p*-nitrotoluene were used. The $(CH_3)_3Si–C$ group moment values were found to be +0.16 and +0.95 *D* for the *p*-amino and *p*-nitro compounds, respectively.

If the moment of trimethylphenylsilane, 0.42 *D*, is assumed to reside in the $Si–C_{arom}$ bond, the moment of dimethyldiphenylsilane may be calculated as the resultant of two $Si–C_{arom}$ moments acting along the tetrahedral bond angle. The calculated value 0.49 *D* is much larger than the observed value of 0.34 *D*. This deviation may be attributed to at least two factors. First, the presence of one

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[12] B. C. Curran, THIS JOURNAL, **64**, 830 (1942); this is also the value obtained a number of times in our own laboratory.

[13] W. Wassiliew and J. Syrkin, *Acta Physiochem. U.R.S.S.*, **14**, 414 (1942).

[14] This value is derived not only from the measurement of the toluene moment (C. G. Le Fevre, R. J. W. Le Fevre and K. W. Robertson, *J. Chem. Soc.*, 480 (1935)) but also from the moments of several meta substituted toluenes.

[15] C. G. Le Fevre, R. J. W. Le Fevre and K. W. Robertson, *ibid.*, 480 (1935).

[16] H. L. Donle and Gehrckens, *Z. physik. Chem.*, **B18**, 146 (1932).

[17] G. R. Paranjpe and D. J. Davar, *Indian J. Physics*, **15**, 173 (1941).

electron-drawing phenyl group will render the silicon electrons less available to the second. Second, structures involving double bond character of the Si–C_{arom} bonds will be sterically hindered because of the necessity of having both phenyl rings coplanar in the resonance hybrid representing the structures of this molecule.

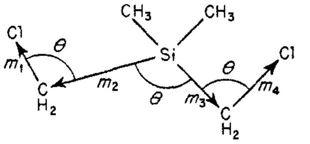
The two other compounds whose dipole moments were measured in this study have to be treated in a special manner because their component moments act in a system involving free rotation of a complex chain of atoms. While the instantaneous value of the over-all moment changes the average value may be calculated by the equation of Eyring[18] developed by the technique of matrix algebra. This equation, with slightly modified notation, is

$$\bar{\mu}^2 = \sum_{j=1}^{n} m_j^2 + 2\sum_{j=1}^{n} \sum_{s>j} {\textstyle\prod}_k^{s-1} \cos \theta_k m_j m_s$$

where m_j is the value of the jth component moment, θ_k is the angle between the jth and the $(j + 1)$th moment vectors (considered to be 0° if the two moments are in the same direction), and the product $m_j m_s$ is considered negative if the direction of the two vectors is not the same along the line of atoms joining them.

In calculating the moments of the two compounds the component moments of the two methyl groups were not considered. The solution of the Eyring equation for bis-(chloromethyl)-dimethylsilane is

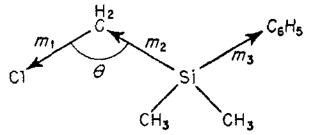
$$\bar{\mu}^2 = 2m_1^2 + 2m_2^2 - 2[m_1^2 \cos^3 \theta + m_2^2 \cos \theta - 2m_1m_2 \cos \theta\,(1 + \cos \theta)]$$



where $m_1 = m_4 = \mu_{C-Cl} = 1.93\ D^1$, $m_1 = m_3 = \mu_{Si-C} = 0.25\,D$,[1] and $\theta = 109°\ 28'$.

Substitution of the numerical values leads to a calculated average value of 2.77 D, as compared to the observed value of 2.21 D. This great negative deviation may be attributed to electrostatic repulsion with a consequently lower moment than that calculated on the basis of free rotation. An analogous explanation was made by Smyth and Walls[19] in comparing the calculated (2.42 D) and observed (2.07 D) moments of 1,3-dichloropropane.

For chloromethyldimethylphenylsilane, it would be predicted that the electrostatic repulsion would not be as strong between the chlorine atom and the phenyl group as between the two chlorine atoms. This should result in much lower hindrance to free rotation, and consequently better agreement between calculated and observed values. For chloromethyldimethylphenylsilane the solution to Eyring's equation is



where $m_1 = \mu_{C-Cl} = 1.93\ D$, $m_2 = \mu_{Si-C\ aliph} = 0.25\,D$, $m_3 = \mu_{Si-C\ arom} = 0.42\,D$, $\theta = 109°\ 28'$.

$$\bar{\mu}^2 = m_1^2 + m_2^2 + m_3^2 - 2[(m_1m_2 - m_2m_3)\cos \theta + m_1m_3 \cos^2 \theta]$$

Upon substitution, the average moment value is calculated to be 2.01 D which, as expected, is in much better agreement with the observed value, 1.93 D, than was found in the case of the bis-(chloromethyl)-dimethylsilane.

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[18] H. Eyring. *Phys. Rev.*, **39**, 746 (1932).

[19] C. P. Smyth and W. S. Walls, THIS JOURNAL, **54**, 2261 (1932).

[CONTRIBUTION NO. 878 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH AND MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

Electron Moments and Structures of Organosilicon Compounds. III. The Oxygen–Silicon Bond[1,2]

BY HENRY FREISER, MARY V. EAGLE AND JOHN SPEIER

RECEIVED AUGUST 29, 1952

The dielectric constants and densities of benzene solutions of ethoxytrimethylsilane, hexamethyldisiloxane, ethoxytriphenylsilane, chloromethylethoxydimethylsilane, diethoxydimethylsilane and ethoxydimethylphenylsilane have been determined at 30.0°. The dipole moment values of these compounds have been calculated as 1.18, 0.79, 1.25, 2.14, 1.36 and 1.30 D, respectively. The results are consistent with an assumed Si–O–Si bond angle of 131° in hexamethyldisiloxane. The effect of the Si–O link upon the Si–carbon bond moment is seen to be quite large, as might be predicted from the electronegative character of oxygen.

In previous papers in this series[1,3] the ease with which silicon is electrically distorted was noted. In the present report, the extension of the study to compounds in which silicon is bonded to the highly electronegative oxygen atom is discussed. The effects noted with various organosilicon compounds are more pronounced when silicon–oxygen bonds are involved.

Experimental

Preparation and Purification of Materials. Ethoxytrimethylsilane was prepared from chlorotrimethylsilane and absolute alcohol. The product was distilled twice, the second time through a column of about 50 plates. The fraction used had the properties: b.p. 74° at 736 mm., $n^{25}{}_D$ 1.3712, $d^{25}{}_4$ 0.7521; sp. ref. 0.3016; calcd. sp. ref. 0.3018. Sauer[4] reported b.p. 75° at 745 mm., $n^{20}{}_D$ 1.3743, $d^{20}{}_4$ 0.7573.

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[1] Paper II, THIS JOURNAL, **75**, 2821 (1953).

[2] Abstracted from the thesis of M. V. E. submitted in partial fulfillment of the requirements of the M.S. degree in Chemistry, Summer, 1952.

[3] Paper I, *ibid.*, **73**, 5229 (1951).

[4] R. O. Sauer, *ibid.*, **66**, 1707 (1944).