[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

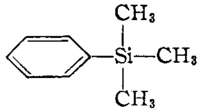
Dipole Moments of Aromatic Derivatives of Trimethylsilane

BY HERBERT SOFFER WITH THOMAS DE VRIES

The dipole moments of aromatic derivatives of trimethylsilane were determined and the resulting data, along with data already existing for similar compounds, were examined. It was found that electron-supplying groups para to the trimethylsilyl group produce a marked decrease in the algebraic value of the moment of this group. Such a decrease seems to be proportional to the ease with which the para groups give up electrons to the ring. The structure which must be postulated to account for this decrease is one which involves a double bond between the carbon and silicon atoms and places ten electrons around the silicon.

Although no compound containing a carbon to silicon double bond has as yet been isolated, structures involving such a bond have occasionally been postulated. Since silicon, in the second row of the periodic table, has *d* orbitals available for bonding, it is not restricted by the octet rule.[1]

The following structures may be posulated for trimethylsilylbenzene[2]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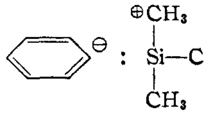
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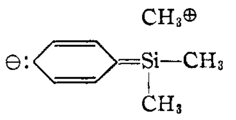
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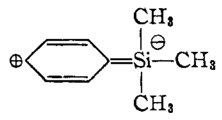
IV

Structure IV is the only one which would make the trimethylsilyl group negative with respect to the ring. Analogous structures have been suggested[3] for aliphatic organosilicon compounds. Since silicon is normally electron releasing with respect to carbon, any contribution of structure IV would tend to decrease the positive moment of the trimethylsilyl group. It is the opinion of the authors that a relatively large contribution of this structure might even result in a negative value for the dipole of the group. Since the dipole moment is proportional to the separation of charge, if structures II and IV contributed equally, the latter would have a much greater influence on the resultant value of the dipole. A small increase in the contribution of such a structure, therefore, would produce a relatively large decrease in the algebraic value of the dipole of the group. The dipole moments of a number of derivatives of trimethylsilylbenzene was determined and these data, together with known moments of other members of this group of compounds, were examined.

Experimental

All compounds whose moments were determined were prepared and purified by Mr. Philip Brumfield of this department. They were redistilled until the fractions from successive distillations showed no difference in refractive index in the fourth decimal place. The benzene used as a solvent was purified by washing with concentrated sulfuric acid followed by dilute sodium hydroxide solution. It was dried over lime, decanted and distilled over calcium hydride. The fraction collected boiled at 80.0° (corrected for standard pressure). The density at 25° was 0.8734 ± 0.0002 g./ml. and the refractive index at that temperature was 1.49748 ± 0.00009.

The changes in dielectric constant with mole fraction were determined in benzene solution at 25° using the heterodyne beat method.[4] The refractive indices were measured at 25° with a Pulfrich refractometer and the densities were determined with an Ostwald pycnometer of about 1-ml. capacity. The dipole moments were calculated using both the Guggenheim equation[5] and a modified form of the Hedestrand equation.[6] The atomic polarization correction was omitted for all molecules whose moments exceeded one debye unit since such a correction is negligible in these cases. For molecules whose moments were less than 1.00 *D*, a correction was made in the calculations with the Hedestrand equation, assuming that the atomic polarization was 5% of the electronic polarization. In the case of benzyltrimethylsilane, the moment calculated was that of the C–Si$(CH_3)_3$ group acting along the carbon–silicon bond. It was assumed that the trimethylsilyl group made an angle of 109° 28′ with the ring in this compound.

The data given in Table I show the boiling points, indices of refraction, densities, molar refractivities (calculated from the densities and refractive indices, wherever possible), changes in dielectric constant with mole fraction (calculated by the method of least squares), changes in density with mole fraction, polarizations at infinite dilution, and the dipole moments calculated by means of the two equations. In Table II are listed the experimentally determined moments of trimethylsilyl compounds together with the moments of the trimethylsilyl group calculated by vector analysis. The moments of the compounds used in these calculations were the average values of the dipoles listed by Wesson.[7]

Discussion

The attempted explanation of the large range in values of the trimethylsilyl group assumes the moments of the other substituents on the ring to be constant with respect to their position on the ring and with respect to other groups present. This is, of course, only a first approximation since there is certainly interaction between the groups. It is believed, however, that a qualitative interpretation can be made despite this simplifying assumption.

The moment of phenyltrimethylsilane itself was found to be approximately 0.45. In this compound structures II, III and IV are possible. In structure IV the silicon group is an electron withdrawer and any group in the para position which supplies electrons to the ring should cause an increase in the contribution of IV to the structure of the compound.

The para-halogen derivatives give a calculated moment of the trimethylsilyl group of approxi-

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[1] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, pp. 228-235.

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

[3] C. Curran, R. M. Witucki and P. A. McCusker, *ibid.*, **72**, 4471 (1950).

[4] P. Brown and T. DeVries, *ibid.*, **73**, 1811 (1951).

[5] E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

[6] R. J. W. LeFevre and P. Russel, *J. Chem. Soc.*, 491 (1936).

[7] L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Massachusetts Institute of Technology, Cambridge, Mass., 1948.

TABLE I

PHYSICAL PROPERTIES AND DIPOLE MOMENTS OF DERIVATIVES OF TRIPHENYLSILANE

	B.p. °C.	Mm.	$n^{22}D$	d^4_{25}	MR_D	$\Delta D/\Delta f_2$	$\Delta d/\Delta f_2$	$P_2\infty$	μ (in Debye) Hedestrand	μ (in Debye) Guggenheim
p-Aminophenyl	113	10	1.5366	0.9379	55.00	3.930	0.105	110.91	1.65	1.66
p-(N,N-Dimethylamino)-phenyl	255	752	1.5319	0.9171	65.31	4.646	.0099	133.88	1.83	1.84
p-Bromophenyl	229.5	752	1.5229	1.1731	59.67	4.463	.613	125.04	1.79	1.78
p-Carboxylphenyl	M.p. 118				56.29[a]	2.07	.230	89.67	1.22	1.36
o-Methylphenyl	198	760	1.5036	0.8990	54.08	0.549	.262	63.31	0.57[b]	0.66
m-Methylphenyl	190	760	1.4907	0.8649	54.99	0.337	− .0380	62.15	.46[b]	.57
p-Methylphenyl	192.5	760	1.4897	.8626	55.04	0.320	− .0439	62.08	.46[b]	.62
o-Aminobenzyl	113.5	10	1.5234	.9385	59.24	4.250	.110	120.24	1.73	1.74
p-Aminobenzyl	119	10	(m.p. 34°)		59.07[a]	2.555	.112	95.23	1.33	1.33
p-Nitrobenzyl	147	10	1.5386	1.0510	62.34	34.13	.387	560.96	4.94	4.98

[a] Calculated from atomic refractivities. [b] Includes correction for atomic polarization.

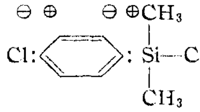
TABLE II

MOMENTS OF DERIVATIVES OF TRIMETHYLSILANE AND OF THE TRIMETHYLSILYL GROUP

	(Compound) in Debye units	(Group) in Debye units
Phenyl	0.44[a]; 0.44[b,f]	
p-Aminophenyl	1.66[c]	−0.13
p-(N,N-Dimethylamino)-phenyl	1.84[c]	− .26
p-Bromophenyl	1.79[c]	+ .27
p-Carboxyphenyl	1.29[c]	+ .46
p-Chlorophenyl	1.70[a]	+ .13
p-Fluorophenyl	1.69[a]	+ .25
o-Methylphenyl	0.57[c,f]	+ .26[d]
m-Methylphenyl	0.46[c,f]	+ .50
p-Methylphenyl	0.46[c,f]	− .06
o-Nitrophenyl	3.67[b]	+ .62[d]
p-Nitrophenyl	4.43[b]	+ .49
Benzyl	0.71[b]	+ .47[e]

[a] Determined by Roberts, *et al.*[2] [b] Determined by A. L. Myers (unpublished work, Purdue University). [c] Determined in this Laboratory. [d] The moments of the group in the ortho compounds were calculated assuming a 60° angle between the group and the ortho carbon. [e] The moment calculated for the C–Si$(CH_3)_3$ group. [f] Correction made for P_A assuming $P_A = 5\% P_E$.

mately +0.2. The structures which can be drawn for these compounds are



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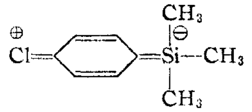
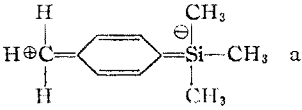


The *p*-methyl derivative gives a result from which the group moment may be calculated to be either +0.86 or −0.06. In view of the fact that no derivative of phenyltrimethylsilane whose moment has been determined gives a group moment greater than +0.62, the value −0.06 is probably the correct one. This is further substantiated by the results obtained with *p*-aminophenyltrimethylsilane. Here, the group moment may be +3.19 or −0.13. A value for the moment of the $(CH_3)_3$-Si–C group as high as three is extremely unlikely so that $\mu = -0.13$ must be taken as the moment of the group in this compound. Structures such as



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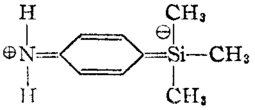
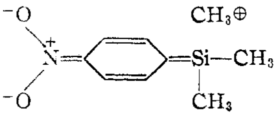


can be drawn for the latter two compounds. It is believed that these forms are possible and that the amino group contributes more than the methyl group. The result of such contributions would be a marked decrease in the moment of the trimethylsilyl group. The N,N-dimethylamino group is even more electron supplying than the unsubstituted amino group. The moment of the trimethylsilyl group in *p*-(N,N-dimethylamino)-phenyltrimethylsilane would therefore be expected to be even more negative than it is in the *p*-amino compound. Its moment in the former compound is −0.26, thus indicating an increased contribution of structure IV.[8] *p*-Nitrophenyltrimethylsilane, on the other hand, would not be expected to undergo such resonance forms because the nitro group is itself electron withdrawing. In fact, resonance of the type IV would be greatly retarded but III might make a larger contribution than it would in phenyltrimethylsilane since the structure



should occur more readily. The moment found for the group in the para nitro derivative was +0.49. This might indicate that structure III makes very little contribution, even in phenyltrimethylsilane. Since it involves no bond resonance with a methyl group, this structure very likely does not exist. The group moment of +0.46 in the para carboxylic acid derivative further illustrates this point, since the carboxyl group is strongly electron withdrawing.

m-Methylphenyltrimethylsilane could not undergo resonance analogous to that of the para compound. The moment of the silicon group would therefore be expected to be at least as high as it is in the unsubstituted ring. The value obtained was +0.50. *o*-Methylphenyltrimethylsilane should give a lower group moment than the meta compound but a higher moment than the para derivative, since the resonance may be restricted

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[8] H. Gilman and G. E. Dunn, THIS JOURNAL, **73**, 3404 (1951), from a study of the effects of substituents on the rate of hydrolysis of triarylsilanes obtained σ-constants for the *p*-dimethylamino group which when compared with values from other sources indicate that its contribution to resonance structures through the conjugated system of the ring depends on the ability of the ring substituent to accept electrons.

due to steric hindrance in the ortho position. We found a value of +0.26 for the moment of the group in the ortho compound. The *o*-nitrophenyltrimethylsilane gives a resultant group moment of +0.62 which is about what we would expect.

If structure IV existed to any appreciable extent in the unsubstituted phenyltrimethylsilane, we would expect the moment of the trimethylsilyl group in this compound to be less than it is in benzyltrimethylsilane since resonance of the silicon group with the ring is not possible in the latter compound. We find, however, a moment of +0.47 for the group in the benzyl compound, a value which is the same as that in the phenyl derivative within experimental error. We are therefore led to believe that structure IV makes practically no contribution to the structure of phenyltrimethylsilane itself but becomes important in derivatives of this compound due to group interaction.

Acknowledgment.—The authors wish to express their gratitude to Mr. Philip Brumfield for the preparation and purification of the compounds and to Dr. R. A. Benkeser under whose direction the preparation of the compounds were undertaken.

LAFAYETTE, INDIANA RECEIVED APRIL 5, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

The Temperature–Interfacial Tension Studies of Some Alkyl Esters of Monofluoroacetic and Monoiodoacetic Acids Against Water

BY JOSEPH J. JASPER AND WILLIAM J. MAYER[1]

This is the third in a series of interfacial tension studies involving the lower esters of the monohalogen acetic acids with water. The present paper reports the results obtained from the ethyl and *n*-propyl esters of monofluoroacetic acid, and the methyl, ethyl, *n*-propyl and *n*-butyl esters of monoiodoacetic acid over an appreciable range of temperature. The method of least squares was applied in formulating empirical equations relating the interfacial tensions to the temperature, and the equations were used to calculate the temperature coefficients, the latent heats, and the enthalpy attending the formation of each sq. cm. of interfacial surface. The data and calculated results are presented in two tables.

Although interfacial tension studies have proved to be of fundamental importance in the interpretation of the behavior of systems having great specific surfaces, the subject has not received nearly as much study as surface tension. This may be due to (a) the experimental difficulties attending accurate measurements, and (b) the failure to understand the significant role that it plays in numerous aspects of theoretical and industrial chemistry. Interfacial tension is undoubtedly a complex phenomenon which is probably capable of resolution and interpretation through experimentally established relationships among the factors which determine the properties of the transition region.

The purpose of this investigation was to obtain interfacial tension data for a series of esters of monofluoroacetic and monoiodoacetic acids with water over an appreciable temperature range, and to formulate empirical equations relating the interfacial tension and temperature. With these data it was possible to determine several thermodynamic properties of the interfacial region. This is the third of a series of such studies which will eventually include other homologous series containing substituted halogen groups.

Experimental

Preparation and Purification of the Esters.—Six esters were studied in this investigation. Owing to experimental difficulties, only the ethyl and *n*-propyl esters of monofluoroacetic acid were used. The remaining four were the methyl, ethyl, *n*-propyl and *n*-butyl esters of monoiodoacetic acid. The two esters of monofluoroacetic acid were prepared from sodium fluoroacetate, sulfuric acid and the corresponding alcohols. For final purification, the esters were subjected to the vacuum fractionation method described by Morton.[2]

A 15-inch column was used. This was packed with single-turn glass helices and fitted with a total reflux variable take-off head. The middle third boiled at a constant temperature and was collected for use.

The methyl, ethyl and *n*-butyl esters of monoiodoacetic acid were prepared by the method of Fisher as described by Fieser and Fieser,[3] and the *n*-propyl ester by halogen exchange. In the latter preparation sodium iodide, *n*-propyl alcohol and *n*-propyl chloroacetate were used. This method gave a very good yield of the *n*-propyl iodoacetate.

The esters of monoiodoacetic acid were purified by fractional distillation in an atmosphere of nitrogen with the aid of an 8-inch column. Since the esters tended to decompose in the light, the fractionations were carried out in the dark. Under these conditions the esters distilled over at a constant temperature with a slight yellow color. Distillation through a Claisen head was then carried out with a small globule of mercury in the receiving flask.[4] The final products obtained were colorless. During the interfacial tension measurements which followed, a small globule of mercury was kept in constant contact with the organic liquids in the receiving container where the tips delivered the drops. The mutually saturated liquids were tested spectroscopically for the presence of mercury, but no traces were detected. Because of their instability, all subsequent operations involving these esters were carried out as rapidly as possible in subdued light.

Determination of the Densities.—Since the density factor appears in the interfacial tension equation as an explicit variable, densities must be determined as accurately as possible. The pycnometers used were a modified form of the "type D" instrument described by Weissberger.[5] Three pycnometers, each having a volume of about 20 ml., were constructed as nearly alike as possible with respect to dimensions and shape. Two of these were used for the respective mutually saturated liquids, and the third as a counterpoise. Repeated trials showed no deviation in the densities greater than 0.05% over the temperature range employed. Several thermoregulators were used, each of which was set at a different temperature. This made it possible and convenient

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[1] Present address: Park Forest, Illinois.

[2] A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, Chapters IV and V.

[3] L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 133.

[4] A. H. Blatt, "Organic Syntheses," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 402.

[5] A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, New York, N. Y., 1945, p. 79.