terms not of the volume of a molecule but rather of the volume occupied by a molecule, which would be given by V/N instead of $4\pi a^3/3$. The omission from consideration of the temperature dependence of τ, therefore, appears to be justified by the results.

The activation energies calculated according to Kauzmann[18] from the temperature dependence of the viscosity and the relaxation time are listed in Table VI. Also included for comparison are the values for pure pyridine,[6] pyridine in benzene solution (*i.e.*, benzene[12]), and γ-picoline.[6] For the planar molecules of benzene and pyridine, $\Delta H_v^{\ddagger}$ is relatively much larger than $\Delta H_\epsilon^{\ddagger}$, indicating that viscous flow involves greater interference by neighbors than does dielectric relaxation. This is to be expected since dielectric relaxation takes place by rotation of the molecule with little or no translation, whereas viscous flow may involve both forms of motion. With increasing dissymmetry and consequently greater mutual interference of the molecules during relaxation, the difference in activation energies decreases nearly to zero as in ethylbenzene and becomes negative in isopropylbenzene. The $\Delta H_\epsilon^{\ddagger}$ and $\Delta H_v^{\ddagger} - \Delta H_\epsilon^{\ddagger}$ values for styrene appear comparable to those of the planar molecules rather than to that of ethylbenzene which has a molecule close to that of styrene in size. This is in accord with the previous indication of the planarity of styrene. The relatively lower value of $\Delta H_\epsilon^{\ddagger}$ for *o*-xylene is also consistent with the previous description of its dielectric behavior. The values for 4-ethylpyridine, however, must be considered anomalous. Free energies and entropies of activation for each process also have been calculated. The values for $\Delta F_\epsilon^{\ddagger}$ lie between 2 and 4 kcal./mole and those for $\Delta S_\epsilon^{\ddagger}$ lie between −1 and −4 e.u. The negative entropy values indicate that the relaxation occurs by the coöperation of nearest neighbors, the molecules maintaining a relatively highly ordered arrangement.

TABLE VI

ACTIVATION ENERGIES FOR VISCOUS FLOW ($\Delta H_v^{\ddagger}$) AND DIELECTRIC RELAXATION ($\Delta H_\epsilon^{\ddagger}$) (KCAL./MOLE)

	$\Delta H_v^{\ddagger}$	$\Delta H_\epsilon^{\ddagger}$	$\Delta H_v^{\ddagger} - \Delta H_\epsilon^{\ddagger}$
Benzene	2.5	(1.4)	(1.1)
Pyridine	2.5	1.4	1.1
Styrene	2.3	1.4	0.9
Toluene	2.2	1.6	.6
α-Picoline	2.2	1.6	.6
γ-Picoline	2.5	1.8	.7
o-Xylene	2.3	1.5	.8
m-Xylene	2.0	1.7	.3
p-Chlorotoluene	2.3	1.7	.6
Ethylbenzene	2.1	1.9	.2
2-Ethylpyridine	2.4	2.0	.4
4-Ethylpyridine	2.5	1.5	1.0
i-Propylbenzene	2.3	2.5	−0.2

PRINCETON, NEW JERSEY

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[18] W. Kauzmann, *Rev. Mod. Phys.*, **14**, 12 (1942).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dipole Moment and Steric Strain in Hexaaryldisilanes[1,2]

BY ANTHONY J. PETRO[3] AND CHARLES P. SMYTH

RECEIVED JULY 1, 1957

The dipole moments of 1,1,2-triphenyl-1,2,2-tri-*p*-tolyldisilane, 1,1,1-triphenyl-2,2,2-tri-*p*-tolyldisilane and 1,1,1-triphenyl-2,2,2-trimethyldisilane have been determined in dilute benzene solution. The measured values 0.80, 0.77 and 0.64×10^{-18}, respectively, have been used to calculate a value of 115° for the aryl–silicon–silicon bond angle. Failure to detect free radicals in solution indicates that the distortion does not lead to measurable dissociation of these compounds. On the basis of available data and the measured moments, the following approximate maximum group moment magnitudes and their directions have been assigned: phenyl$^-$–$^+$Si $= 0.84 \times 10^{-18}$ and tolyl$^-$–$^+$Si $= 0.25 \times 10^{-18}$.

The gift of three substituted disilanes by Professor Henry Gilman of the Iowa State College has made possible the investigation of their molecular dipole moments and of the group moments and bond angles in the molecules. Steric hindrance might be expected among the aryl groups in hexaaryldisilanes analogous to that found in hexaarylethanes.[4] In the case of the latter compounds so much steric hindrance is present between the aryl groups across the ethane linkage that dissociation takes place in solution.[5] Since silicon has a 50% larger covalent radius than carbon[6] it is to be expected that such steric hindrance, if present at all, would be greatly reduced. Dipole moment measurements have been carried out on 1,1,2-triphenyl-1,2,2-tri-*p*-tolyldisilane and 1,1,1-triphenyl-2,2,2-tri-*p*-tolyldisilane, which will hereafter be referred to as I and II, respectively. These two substances form an ideal pair for determining such steric effects, since they contain the same groups but with a different arrangement, allowing the valence angles to be calculated from measured dipole moments without knowledge of the individual group moments.

The phenyl–Si and *p*-tolyl–Si group moments could be determined by measuring the moment of a compound containing either of the above groups

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[1] This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600)1331. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] This paper represents a part of the work to be submitted by Mr. A. J. Petro to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Monsanto Fellow in Chemistry, 1956–1957.

[4] W. A. Waters, "The Chemistry of Free Radicals," 2nd ed., Oxford University Press, London, 1948.

[5] W. A. Waters, ref. 4, pp. 59–60.

[6] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 164.

and a group whose moment has been determined. These requirements were fulfilled by compound III, 1,1,1-triphenyl-2,2,2-trimethyldisilane, which contains the CH_3–Si group whose moment has been reported to be[7] 0.2×10^{-18}.

Experimental

The dipole moments were measured in benzene solution at 30°. "Reagent" grade benzene, obtained from Merck and Co., was dried over sodium hydride and fractionally distilled as needed. The fraction used boiled at 79.9° at 757.8 mm. and had the following physical constants: $n^{30}{}_{\mathrm{D}}$ 1.49521, ϵ_{30} 2.2635, $d^{30}{}_4$ 0.8623.

The disilanes were used without further purification after a check of their melting points. The melting points and ranges of mole fractions used were: I, 226–227°, $3\text{–}4 \times 10^{-3}$; II, 262–264°, $2.5\text{–}4 \times 10^{-3}$; III, 107–108°, $5.5\text{–}7.5 \times 10^{-3}$.

The dielectric constants of the solutions were measured with a heterodyne-beat apparatus and a dielectric cell as previously described.[8–11] The dielectric constants were found to be linear functions of the mole fractions according to the equation

$$\epsilon_{12} = \epsilon_1 + \alpha' c_2$$

Densities were measured with a graduated pycnometer[12] having an accuracy of ±0.002%. The specific volumes were found to be linear functions of the mole fractions according to the equation

$$v_{12} = v_1 + \beta' c_2$$

The values of α' and β' were then used to calculate the polarizations of the solutes at infinite dilution, P_∞, by the method of Halverstadt and Kumler.[13]

Refractive indices were measured with a Pulfrich refractometer and the molar refractions for the sodium D line, R_2 were calculated by the equations

$$R_{12} = \frac{n^2_{12} - 1}{n^2_{12} + 2}\,\frac{(M_1c_1 + M_2c_2)}{d_{12}}$$

and

$$R_2 = \frac{R_{12} - c_1R_1}{c_2}$$

where c is the mole fraction, n the refractive index, d the density and M the molecular weight, with the subscripts 1, 2 and 12 referring to solvent, solute and solution, respectively. The dipole moments were calculated by the Debye equation

$$\mu = 0.01281 \times 10^{-18}\,[(P_\infty - R_2)T]^{1/2}$$

The measured values of R_2 were used directly, despite the fact that the atomic polarization may not be entirely accounted for. The effect of this approximation on the calculation of the bond angles and group moments will be discussed below. The experimental results and the molar refractions calculated from bond refractions[14] are listed in Table I.

TABLE I

EMPIRICAL CONSTANTS AND MOLAR POLARIZATIONS AT 30°, MOLAR REFRACTIONS (SODIUM D LINE) AND DIPOLE MOMENTS

	M_2	α'	β'	P_∞	R_2 Exp.	R_2 Calcd.	$\mu(\times 10^{18})$
I	560.80	3.665	−1.653	207.6	194.8	182.3	0.80 ± 0.02
II	560.80	3.400	−1.590	205.1	193.3	182.3	.77 ± .02
III	332.52	1.675	−0.731	121.5	113.3	109.9	.64 ± .02

Discussion of Results

As can be seen, there is a discrepancy between the experimental and calculated R_2 values. The difference amounts to about 6% in I and II and 3% in III, or about 1% for each aromatic ring contained in each molecule. This would appear to indicate that the differences are due to exaltation. The 0.8% difference between the measured values of R_2 for I and II can be ascribed to the experimental error arising from the high dilution of the solutions.

Calculations of the Valence Angle.—The formulation of equations for the calculation of the dipole moments of I and II from group moments is simplified by the fact that the presence of the methyl group in the *para* position is sterically unimportant. Whether I is considered from the point of view of rotation of each half of the molecule around the Si–Si axis or from the point of view of fixed orientations wherein the potential energy of interaction across the Si–Si bond is at a minimum, the result is the same. The formulation is made by means of the equation for the resultant moment of movable dipoles.[15,16] Two possible cases may arise, depending on the relative directions of the group moments in the molecules, that is, case A, the group moments may be opposed, or, case B, they may add within the molecule. The resulting equations for I and II are

$$\text{Case A: } \mu_{\mathrm{I}}^2 = |\mu_{\mathrm{p}} - \mu_{\mathrm{t}}|^2\,(1 + \sin^2\theta) \qquad (1)$$

$$\text{Case B: } \mu_{\mathrm{I}}^2 = (\mu_{\mathrm{p}} + \mu_{\mathrm{t}})^2(1 + \sin^2\theta) \qquad (2)$$

$$\text{Case A: } \mu_{\mathrm{II}} = 3\,|\mu_{\mathrm{p}} - \mu_{\mathrm{t}}|\cos\theta \qquad (3)$$

$$\text{Case B: } \mu_{\mathrm{II}} = 3\,(\mu_{\mathrm{p}} + \mu_{\mathrm{t}})\cos\theta \qquad (4)$$

where

μ_{I} = dipole moment of I, μ_{II} = dipole moment of II
μ_{p} = phenyl-silicon group moment
μ_{t} = *p*-tolyl-silicon group moment
θ = 180° − Si–Si–C angle

That there is interference among the aryl groups can be seen by substituting the values of μ_{I} and μ_{II} into the above equations and tentatively assuming tetrahedral symmetry. For case A, (1) yields

$$|\mu_{\mathrm{p}} - \mu_{\mathrm{t}}| = 0.47$$

and (3) yields

$$|\mu_{\mathrm{p}} - \mu_{\mathrm{t}}| = 0.77$$

Equations 2 and 4 yield similarly inconsistent results indicating the assumption of tetrahedral symmetry to be incorrect.

Solving each pair of equations, (1) and (3), or (2) and (4), simultaneously, yields

$$\frac{9\mu_{\mathrm{I}}^2}{\mu_{\mathrm{II}}^2} = 1 + 2\tan^2\theta \qquad (5)$$

from which θ can be evaluated to be 64.5° and, therefore, the Si–Si–C bond angle is 115.5° (±1°) or a deformation of about 6 ± 1°. From this result the C–Si–C bond angle can be computed by simple geometry to be 102° or a reduction of about 7.5° from the tetrahedral angle.

An attempt was made to determine whether this distortion is sufficient to cause dissociation of the Si–Si bond analogous to that occurring in hexaphenylethane.[4] If dissociation were taking place

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[7] A. P. Altshuller and L. Rosenblum, THIS JOURNAL, **77**, 272 (1955).

[8] C. P. Smyth and S. O. Morgan, *ibid.*, **50**, 1547 (1928).

[9] L. M. Kushner and C. P. Smyth, *ibid.*, **71**, 1401 (1949).

[10] G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

[11] A. J. Petro, C. P. Smyth and L. G. S. Brooker, THIS JOURNAL, **78**, 3040 (1956).

[12] G. R. Robertson, *Ind. Eng. Chem., Anal. Ed.*, **11**, 464 (1939).

[13] I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

[14] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 409.

[15] C. P. Smyth, ref. 14, p. 234.

[16] H. Eyring, *Phys. Rev.*, **39**, 746 (1942).

in solution, the solution would be expected to be colored, and the evaporation of solvent should yield a mixture because of the statistical recombination of the dissociation products and also because of the reaction of the free radicals with atmospheric oxygen. When this experiment was carried out with each compound, no color was observed even at the boiling point of the solution and no change in melting point of the solid was observed. In addition, an electron-spin resonance experiment carried out by Mr. T. H. Brown and Dr. J. A. Weil of this Laboratory failed to detect the presence of free radicals in either saturated benzene solution or hot naphthalene solution. This evidence of the absence of dissociation is consistent with the conclusions of Gilman and Wu in regard to these compounds.[17] Stuart–Briegleb models show that the three aryl groups must be arranged in the form of a propeller in order to allow a reduction of the C–Si–C bond angle by 7.5° and at the same time prevent dissociation of the Si–Si linkage.

According to equation 5 tan θ is dependent only on the ratio of μ_{I}^2 and μ_{II}^2 and not on the absolute magnitude of either. As a result the absolute magnitude of the induced polarization is of small consequence in the evaluation of the Si–Si–C bond angle. Since the moment of I and II can be considered equal within the experimental error, and any induced polarization which may not have been accounted for in the use of R_{D} to calculate the moments may also be considered to be the same for both compounds, the error introduced by the approximation is within the probable error assigned to the value of the bond angle.

Calculation of Group Moments.—Calculation of the aryl–silicon group moments is more approximate because of the uncertainty in the absolute values of the dipole moments. Furthermore, in III the extent of the distortion of the bond angles is uncertain, but is presumably less than in I and II because of the smaller size of the methyl group as compared to the phenyl. As an approximation, however, tetrahedral symmetry is assumed and the moment of III is expressed by the equation

$$\mu_{\mathrm{III}} = \mu_{\mathrm{p}} \pm \mu_{\mathrm{m}} \qquad (6)$$

where μ_{m} is the $\mathrm{CH_3}$–Si bond moment, estimated by Altshuller and Rosenblum[7] to be 0.2×10^{-18} with direction Si^{+}–$^{-}\mathrm{CH_3}$. When (6) is solved simultaneously with (1) and (2), or (3) and (4), the following results are obtained: For case A, using the − sign in (6), $\mu_{\mathrm{p}} = 0.84 \times 10^{-18}$ with direction Si^{+}–$^{-}$phenyl, and $\mu_{\mathrm{t}} = 0.25 \times 10^{-18}$ with direction Si^{+}–p^{-}-tolyl. For case B, using the + sign in (6), $\mu_{\mathrm{p}} = 0.44 \times 10^{-18}$ with direction Si^{-}–$^{+}$phenyl, and $\mu_{\mathrm{t}} = 0.15 \times 10^{-18}$ with Si^{+}–p^{-}-tolyl.

The result for case A is more reasonable than that for case B because of the fact that the phenyl group is more electronegative than the methyl group,[18] which, in turn, is more electronegative than silicon. However, the effect of adding a *p*-methyl group to the phenyl ring should be to decrease μ_{p} by about[17] 0.3–0.4×10^{-18} instead of 0.6×10^{-18} as obtained above. The source of this discrepancy may lie in the uncertainty of the induced polarization as previously discussed or in the considerable uncertainty of the Si^{+}–$^{-}\mathrm{CH_3}$ moment, or in both. Indeed, reduction of all three moments by 50% would yield the values $\mu_{\mathrm{p}} = 0.5 \times 10^{-18}$ and $\mu_{\mathrm{t}} = 0.2 \times 10^{-18}$, which give the correct difference, but there is no justification for this calculation. The possibility remains that μ_{p} and μ_{t} alter each other's value when both are on the same silicon atom, but this effect cannot be treated quantitatively.

On the basis of the foregoing discussion the following maximum group moment magnitudes and their directions may be assigned: phenyl^{-}–$^{+}$Si = 0.84×10^{-18} and *p*-tolyl^{-}–$^{+}$Si = 0.25×10^{-18}.

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[17] H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 3762 (1953).

[18] C. P. Smyth, ref. 14, p. 253.

[CONTRIBUTION FROM THE MINERAL BENEFICIATION LABORATORY, COLUMBIA UNIVERSITY]

Thermal Analysis of the Ferrous Chloride–Potassium Chloride System[1a]

BY HARRY L. PINCH[1b] AND JACK M. HIRSHON[1c]

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The phase diagram for the system $\mathrm{FeCl_2}$–KCl is presented. Two intermediate compounds exist: $\mathrm{KFeCl_3}$ with a congruent melting point of 399° and $\mathrm{K_2FeCl_4}$ with an incongruent melting point of 380°. There is a eutectic formed between $\mathrm{K_2FeCl_4}$ and $\mathrm{KFeCl_3}$ at 38.2 mole % $\mathrm{FeCl_2}$ and another between $\mathrm{KFeCl_3}$ and pure $\mathrm{FeCl_2}$ at 54.2 mole % $\mathrm{FeCl_2}$. There are also two solid–solid transitions.

The system $\mathrm{FeCl_2}$–KCl was studied as part of the fused-salt program of this Laboratory. The solid–liquid phase diagram has been obtained, and the results of our investigation are reported.

Experimental Procedure

Reagents.—Anhydrous $\mathrm{FeCl_2}$ was prepared from Fisher "Certified" reagent, $\mathrm{FeCl_2 \cdot 4H_2O}$. The hydrated $\mathrm{FeCl_2}$ was heated to 400–500° in a dried HCl stream for several hours. The heating was continued for an hour after the last traces of water had disappeared from a cooled condenser in the exit gas stream. Analysis of the anhydrous salt showed that it was 99.95% $\mathrm{FeCl_2}$.

The KCl was Fisher "Certified" reagent which was vacuum dried while molten. The cooled salt was crushed within a dry-box and then re-dried for several hours at 110° before use in sample preparation.

Preparation of Samples.—The two salts were weighed into Vycor test-tubes. All transferring operations were carried out in the dry-box. The samples were not prefused but were stirred well when molten. The samples ranged in weight from 15 to 25 g. After a determination the samples were dissolved and analyzed. In general, the compositions

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[1] (a) The work reported herewith was performed under contract AT (49-1)-621 between the Atomic Energy Commission and Columbia University. Reproduction in whole or part is permitted for any purpose of the United States Government. (b) RCA Laboratories, Princeton, N. J. (c) Lansdale Tube Co., Lansdale, Penna.