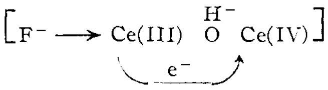
ticular cation between the equilibrium stabilization of an oxidation state by a ligand, and its pure ligand influence on rate can be expected, and is realized in the few data quoted for Cr^{++}. While the pure ligand effect seems obvious enough, its possibilities have not been exploited in conjectures about the geometry of activated complexes for electron transfer. In considering the catalytic effect of F^- [11] on the rate of electron transfer between Ce^{+++} and Ce(IV), taking account of the facts that Ce(IV) has a strong tendency to hydrolyze, and that F^- exerts an enormous stabilizing effect on Ce(IV) over Ce(III), the activated complex corresponding to the rate term $(Ce^{+3})(Ce(IV))$ (F^-) can reasonably be formulated as



$$\left[F^- \longrightarrow Ce(III)\ \overset{H^-}{O}\ Ce(IV)\right]$$

i.e., electron transfer accompanying the movement of F^- into the coördination shell of Ce^{+++}. From this point of view, symmetry in the activated complex is not a necessary condition for electron exchange, even between two ions of the same element; in fact, the act producing electron transfer is approached by F^- in such a manner that the environments of the two Ce ions are made different, thus favoring the change $Ce^{+++} \rightarrow Ce(IV)$. In systems in which an efficient bridging group is not otherwise provided, the role of F^- as simple ligand might be less important than its role as bridging group.

CHICAGO, ILLINOIS

[11] H. C. Hornig and W. F. Libby, *J. Phys. Chem.*, **56**, 869 (1952).

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, NAGOYA UNIVERSITY]

Electron Diffraction Investigation of Tetramethylcyclodi- and Hexamethylcyclotrisilthiane

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The molecular structures of tetramethylcyclodi- and hexamethylcyclotrisilthiane were studied by electron diffraction; the Si–S bond distances were found to be 2.18 ± 0.03 Å. for the former and 2.15 ± 0.03 Å. for the latter compound. Assuming ∠CSiC to be 110°, we estimated the bond angles as follows: ∠SiSS 105° and ∠SiSSi 75° for the disilthiane; ∠SSiS 115° and ∠SiSSi 110° for the trisilthiane.

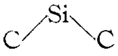
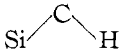
The vapors of tetramethylcyclodi- and of hexamethylcyclotrisilthiane $(Si(CH_3)_2S)_2$ and $(Si(CH_3)_2S)_3$ were studied by electron diffraction to determine the Si–S bond length and the SiSSi bond angle.

Experimental

Tetramethylcyclodisilthiane was prepared by the thermal rearrangement of hexamethylcyclotrisilthiane at 200° in a stream of hydrogen sulfide.[1] Hexamethylcyclotrisilthiane was synthesized[1] by the method of Champetier, *et al.*,[2] who had prepared the ethyl homolog.

The electron diffraction photographs of the vapors of these compounds were taken with a camera of the vertical type at a camera distance of 11 cm. and at an electron wave length of about 0.06 Å. as determined by calibration with gold foil. The samples of disilthiane and trisilthiane were kept at about 30 and 100°, respectively.

Results

The radial distribution functions and the theoretical intensity curves were calculated by the approximation of Spurr and Schomaker.[3] In the temperature factor, $e^{-b_{ij}q^2}$ for the theoretical intensity curves, b_{ij} was assumed to be zero for all bonded distances, 0.0002 for the atom pairs of  and , and 0.0004 for other unbonded long distances. The C–H distance was assumed to be 1.09 Å. and the HCH angle tetrahedral. The parameters which determine the structure are the ratio of the distances Si–C/Si–S, the bond angles ∠SiSSi, ∠SSiS, ∠CSiC, and the form of the ring.

Tetramethylcyclodisilthiane.—The visual (V) and radial distribution curves (R.D.) are shown in Fig. 1. The peaks at 1.87 and 2.18 Å. are due to bonded Si–C and Si–S; the peak at 3.29 Å. may be due to unbonded S . . . C along with Si . . . Si or S . . . S distances. As the total scattering power of S . . . C distances is about three times as large as that of Si . . . Si or S . . . S distances, the S . . . C distance should appear in the neighborhood of this 3.29 Å. peak. If S . . . C is 3.29 Å., ∠SSiS is 113° for ∠CSiC = 110° or 106° for ∠CSiC = 115°, hence ∠SiSSi should be less than 74° to close the four-membered ring of this compound. A comparison of visual and theoretical curves was made with models having the assumed value 110 or 115° for ∠CSiC; these are shown in Fig. 2. The ratio of the distances, Si–C/Si–S, obtained from the R.D. is 1.87/2.18 = 0.86, and bond angles ∠SiSSi and ∠SSiS, were examined with ∠CSiC equal to 110° (curves A to F in Fig. 1) or 115° (curves A′ to F′ in Fig. 1). The parameter values for each model are shown diagrammatically in Fig. 2, in which models situtated on the broken line, *i.e.*, A, A′, B, B′, C and C′, have planar rings. The observed maxima and minima are most satisfactorily reproduced by curves B and B′.

Hexamethylcyclotrisilthiane.—The visual (V) and radial distribution curves (R.D.) are shown in Fig. 3. In the R.D. the peaks representing bonded Si–C and Si–S appear at 1.90 and 2.14 Å., respectively. The peak ranging from 3.1 to 3.6 Å. is attributed to unbonded Si . . . Si, S . . . S and S . . . C

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[1] T. Nomura, M. Yokoi and K. Yamasaki, *Proc. Japan Acad.*, **29**, 342 (1953). Y. Etienne obtained this compound by thiohydrolysis of dimethyldichlorosilane (*Compt. rend.*, **235**, 966 (1952)).

[2] G. Champetier, Y. Etienne and R. Kullmann, *Compt. rend.*, **234**, 1985 (1951).

[3] R. A. Spurr and V. Schomaker, THIS JOURNAL, **64**, 2693 (1942).

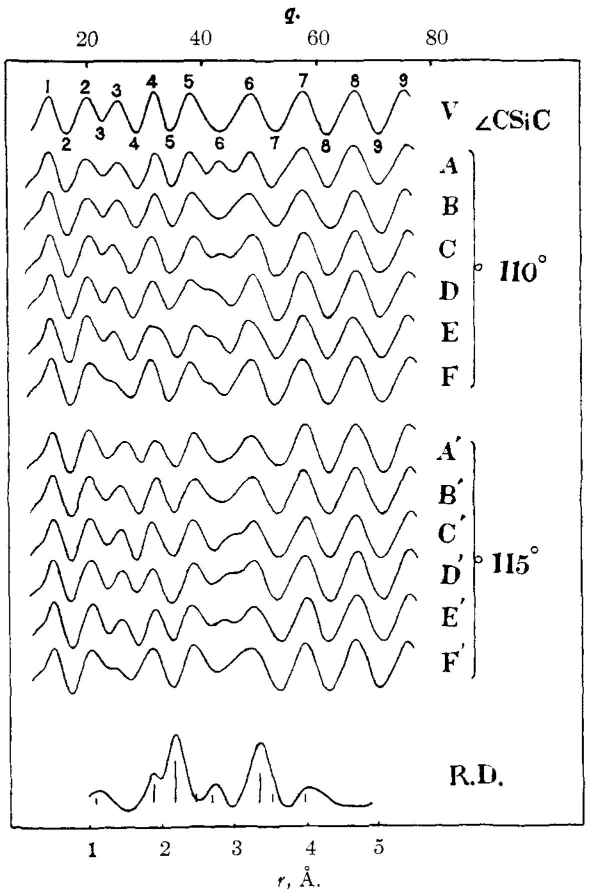

Fig. 1.—Visual, theoretical and radial distribution curves for tetramethylcyclodisilthiane

distances, and the bond angles of silicon and sulfur cannot be estimated from the R.D.

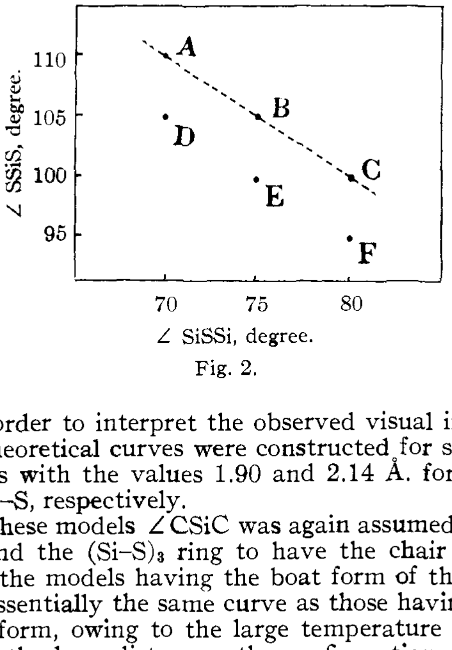

Fig. 2.

In order to interpret the observed visual intensity, theoretical curves were constructed for several models with the values 1.90 and 2.14 Å. for Si–C and Si–S, respectively.

In these models ∠CSiC was again assumed to be 110°and the $(Si–S)_3$ ring to have the chair form. Since the models having the boat form of the ring give essentially the same curve as those having the chair form, owing to the large temperature factor b_{ij} for the long distances, the configuration of the ring cannot be determined. These theoretical curves are shown in Fig. 3 (curves A to I) and the values of ∠SSiS and ∠SiSSi for each model are shown diagrammatically in Fig. 4. The shapes of the 5th, 6th and 7th maxima vary markedly with the change of both ∠SSiS and ∠SiSSi. The shapes of the maxima in the visual curve are best reproduced by model E, but even in this model, the position and the shape of the 7th maximum do not coincide with those of the visual curve. This difficulty can be overcome if a slightly larger temperature factor is used for the unbonded distance of the methyl radical (b_{ij} = 0.0006 or 0.0008 for the unbonded distance to carbon); the modified curve is shown by the broken line superimposed on curve E in Fig. 3.

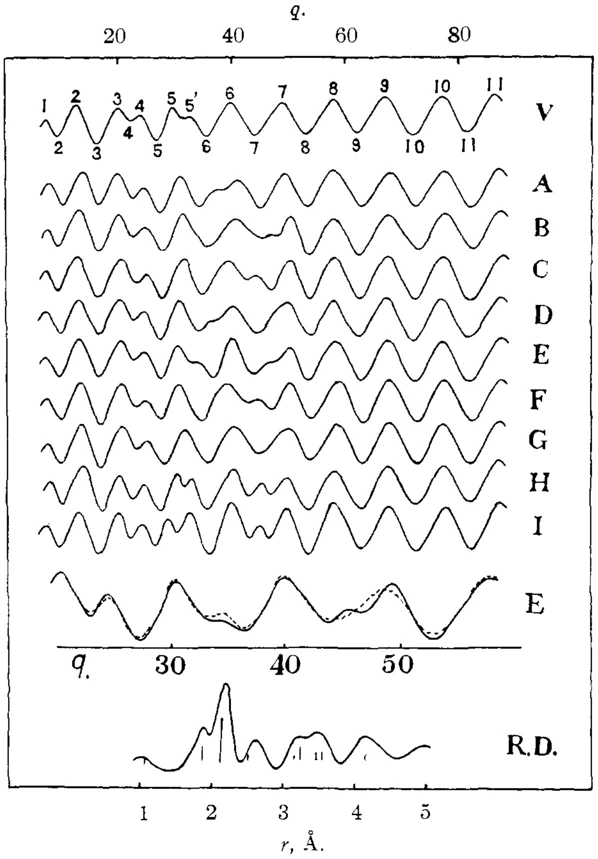

Fig. 3.—Visual, theoretical and radial distribution curves for hexamethylcyclotrisilthiane.

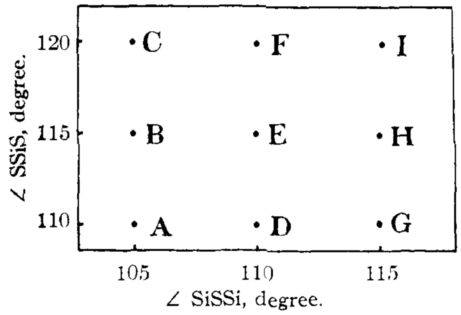

Fig. 4.

The observed and calculated q values for the best curves are compared in Table I. The final results are as follows.

	$[(CH_3)_2SiS]_2$	$[(CH_3)_2SiS]_3$
Si–S, Å.	2.18 ± 0.03	2.15 ± 0.03
∠SSiS	105°	115°
∠SiSSi	75°	110°
∠CSiC	110° (assumed)	110° (assumed)

TABLE I

		$[(CH_3)_2SiS]_2$			$[(CH_3)_2SiS]_3$	
Max.	Min.	$q_{obsd.}$	$q_B/q_{obsd.}$	$q_B'/q_{obsd.}$	$q_{obsd.}$	$q_E/q_{obsd.}$
1		13.4	(0.934)	(0.927)	7.7	(0.934)
	2	17.1	(1.027)	(0.958)	10.4	(0.826)
2		20.1	1.009	1.009	13.1	(0.938)
	3	23.1	1.021	1.013	16.6	(1.005)
3		25.6	1.003	0.996	19.7	1.031
	4	28.7	0.986	.984	22.6	1.017
4		31.6	0.989	.977	25.0	0.968
	5	34.7	0.994	.997	27.5	0.981
5		38.1	1.005	.998	30.0	1.009
5'		..	...	...	33.4	1.008
	6	43.2	1.006	1.002	35.9	1.008
6		48.5	0.988	0.994	39.2	1.026
	7	53.0	0.995	0.987	44.2	0.998
7		57.4	0.993	0.989	48.3	1.009
	8	61.7	1.005	1.011	53.2	1.004
8		66.3	1.004	1.004	57.7	1.000
	9	70.8	1.005	1.003	62.7	0.991
9		75.5	1.003	1.006	67.1	1.010
	10	..	...	...	72.7	0.984
10		..	...	...	76.6	1.003
	11	..	...	...	81.0	1.009
11		..	...	...	86.1	1.007
Av.			1.000	0.998		1.003
Av. dev.			±0.008	±0.008		±0.011

The values 2.18 and 2.15 Å., obtained for the bonded Si–S distance of these compounds, agree within the limits of error with the value of 2.15 Å. given by Schomaker and Stevenson's rule.[4]

The crystal structure of silicon disulfide was studied by Bussen, *et al.*,[5] who found that it had a two-dimensional fibrous structure composed of cyclic four-membered rings $(Si-S)_2$. They obtained 2.14 Å. for the Si–S bond length and 100 and 80° for the bond angles of silicon and sulfur, respectively. Our values for the bond length and bond angles of the disilthiane are in comparatively good agreement with those of silicon disulfide; these data suggest that the Si–S bond of silthianes is largely ionic, a characteristic which may be responsible for the ready cracking of trisilthiane to disilthiane.

Kurita and Kondo,[6] assuming the atomic polarization of trisilthiane to be of the same magnitude as that of the corresponding oxygen compound, hexamethylcyclotrisiloxane, estimated the dipole moment of trisilthiane as 1.03 *D*. As this large moment rules out a planar symmetrical structure similar to that of trisiloxane, they suggest that trisilthiane has predominantly a chair configuration; their conclusion is consistent with the results of our electron diffraction study.

This investigation was supported by the Grant-in-Aid for Fundamental Scientific Research of the Ministry of Education.

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(5) W. Bussen, H. Fischer and E. Gruner, *Naturwissenschaften*, **23**, 740 (1935).

(6) Y. Kurita and M. Kondo, *Bull. Chem. Soc. Japan*, **27**, 161 (1954).

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[CONTRIBUTION NO. 1290 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Dynamic Electrical Birefringence of Rigid Macromolecules

BY IGNACIO TINOCO, JR.[1]

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Benoit's theory of the dynamic electrical birefringence of rigid macromolecules under the action of a rectangular electrical pulse has been extended to include the effect of a transverse component of the permanent dipole moment, and the effective orienting field acting on the permanent dipole has been explicitly considered. The proton polarizability contribution to the induced dipole moment introduced by Kirkwood and Shumaker has also been considered. A new interpretation of Benoit's electrical birefringence measurements on nucleic acid has been made.

Introduction

The theory of the dynamic double refraction in a sinusoidal electric field was developed by Peterlin and Stuart.[2] Subsequently Benoit[3] considered the birefringence produced by a rectangular electrical pulse acting on a dilute solution of rigid macromolecules. As a model for the macromolecule he chose an ellipsoid of revolution with a permanent dipole moment along the axis of revolution whose principal geometrical, optical and electrical axes coincided. His very thorough treatment of this system has been used to interpret the electrical birefringence of protein solutions.[3,4]

Benoit's model of a protein molecule can be improved by removing the restriction that the dipole moment be along the axis of revolution and by including the Kirkwood–Shumaker[5] concept of the mobile proton contribution to the polarizability. Consideration of this model shows that electrical birefringence (Kerr effect) measurements, unlike dielectric dispersion,[5] can be used to determine unambiguously rotary diffusion coefficients for pro-

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(1) Public Health Service Research Fellow of the National Cancer Institute.

(2) A. Peterlin and H. A. Stuart, "Hand und Jahrbuch der Chemischen Physik," Bd. 8, Abs. 1B., Leipzig, 1943.

(3) H. Benoit, *Ann. Phys.*, **6**, 561 (1951).

(4) I. Tinoco, Jr., THIS JOURNAL, **77**, 3476 (1955).

(5) J. G. Kirkwood and J. B. Shumaker, *Proc. Natl. Acad. Sci.*, **38**, 855 (1952).