ever, the curve produced did not break sharply, although extensions of the straight portions of the curve showed a break at the molar ratio of 1:1 for the niobium and pyrogallol. The absence of a sharp break here was further evidence that the niobium pyrogallol complex was partially dissociated.

The above observations, which seem to show that one pyrogallol molecule complexes with one niobium, do not give the nature of the complex formed. It is uncertain whether the pyrogallol simply adds itself to the niobium oxytrioxalato ion already present or whether it displaces one oxalate ion. If the addition compound is formed, the coördination number of niobium would be eight, which is possible according to Sidgwick.[11] Work in progress in this Laboratory, it is hoped, will give more information regarding the relative dissociation constants of the pyrogallol and oxalato complexes of niobium.

[11] N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. I, Oxford University Press, London, 1950, pp. 840–841.

AUBURN, ALABAMA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND SPECTROSCOPY LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Vibrational Spectra and Structure of Disiloxane and Disiloxane-d_6[1]

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Disiloxane and disiloxane-d_6 have been prepared by the hydrolysis of chlorosilane and chlorosilane-d_3. Infrared and Raman spectra have been obtained of the gaseous and liquid samples, respectively, down to about 250 cm.$^{-1}$. In the infrared, the fundamentals have been located at 2169, 1107, 957 cm.$^{-1}$ (parallel) and 2183, 957, 764 cm.$^{-1}$ (perpendicular) in $H_3SiOSiH_3$, and at 1575, 1094, 713 cm.$^{-1}$ (parallel) and 1575, 720, 593 cm.$^{-1}$ (perpendicular) in $D_3SiOSiD_3$. In the Raman effect fundamentals are located at 2174, 1009, 606 cm.$^{-1}$ (sharp) and 2174, 947, 716 cm.$^{-1}$ (diffuse) in $H_3SiOSiH_3$, and at 1575, 771, (555) cm.$^{-1}$ (sharp) and 1546, 699, 532 cm.$^{-1}$ (diffuse) in $D_3SiOSiD_3$. One perpendicular infrared-active fundamental, believed to lie well below 250 cm.$^{-1}$, was not observed. High-resolution spectra were obtained but insufficient rotational structure was found to permit interpretation. Vibrational analysis indicates that the point-group symmetry of the molecule is D_{3d}, that is, the Si–O–Si bond angle equals or approaches 180°. The results are equally compatible with a structure in which the silyl groups undergo free internal rotation about a linear Si–O–Si axis.

Introduction

Although considerable attention has been directed toward spectroscopic and other structural investigations of silicon compounds, it is rather surprising that disiloxane, the parent of silicones, has never been the object of such studies.[3] Spectra of substituted disiloxanes have been reported[4] and electron diffraction,[5] dipole moment,[6] and nuclear magnetic resonance[7] studies have appeared with some structural interpretation. No precise measurements of the Si–O–Si bond angle have been made on these compounds, but the fact has been established that the angles are much greater—probably between 130 and 160°—than those found when first period elements replace silicon. Furthermore, the wide angle is not general for the second period since, for example, the angle in Cl_2O is only 110.8 ± 1°.[8] The present investigation confirms the unexpectedly wide Si–O–Si bond angle in unsubstituted disiloxane.

Experimental

Preparation of Disiloxane and Disiloxane-d_6.—Although many attempts were made to reduce hexachlorodisiloxane to disiloxane using lithium aluminum hydride and other similar reducing agents, in no case could a reaction be found yielding the product sought. The Si–O–Si linkage was always cleaved giving SiH_4 as the only volatile product.[9] Disiloxane was prepared by the method of Stock[10] in which monochlorosilane is hydrolyzed. Silicon tetrachloride[11] was reduced to silane, SiH_4, with lithium aluminum hydride by the method described by Finholt, Bond, Wilzbach and Schlesinger.[12]

The silane was converted to monochlorosilane by heating for about 30 hours at 100° with hydrogen chloride in the presence of aluminum chloride. The monochlorosilane was separated from unreacted silane and hydrogen chloride by fractionation of these more volatile compounds through a trap immersed in allyl chloride slush. It was separated from dichlorosilane by repeated fractionation through a trap immersed in carbon disulfide slush. The monochlorosilane was hydrolyzed with twice the theoretical amount of water at 30°; the resulting disiloxane was then washed with about fifty times as much water at 0°. A total of 0.78 g. of disiloxane was prepared in this manner.

Disiloxane-d_6 was produced by similar reactions with some modifications. Silicon tetrachloride was reduced with lithium aluminum deuteride purchased from Metal Hydrides, Inc. The silane-d_4 formed was then chlorinated with deuterium chloride prepared by hydrolysis of benzoyl chloride with deuterium oxide. However, because long heating

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[1] Based on the Ph.D. thesis of Dean W. Robinson, submitted to the Graduate Department of Chemistry, Massachusetts Institute of Technology, May, 1955.

[2] Du Pont Instructor in Chemistry, 1954–1955.

[3] After the present work was completed, the authors learned of the investigation of Emeléus, MacDiarmid and Maddock (*J. Inorg. Nucl. Chem.*, **1**, 194 (1955)). Their structural conclusion that disiloxane is an asymmetric top based on infrared studies only is somewhat at variance with those drawn in this paper. We believe that the additional evidence of the infrared spectrum of disiloxane-d_6 and of the Raman spectra of both compounds enables firmer conclusions to be drawn.

[4] C. C. Certo, J. L. Lauer and H. C. Beachell, *J. Chem. Phys.*, **22**, 1 (1954); H. Murato and M. Kumada, *ibid.*, **21**, 945 (1953); L. Savidon, *Bull. soc. chim. France*, 411 (1953); I. Simon and H. O. Mahon, *J. Chem. Phys.*, **20**, 905 (1952); N. Wright and M. J. Hunter, THIS JOURNAL, **69**, 803 (1947).

[5] K. Yamasaki, A. Kotera, M. Yokoi and Y. Ueda, *J. Chem. Phys.*, **18**, 1414 (1950).

[6] R. S. Holland and C. P. Smyth, THIS JOURNAL, **77**, 268 (1955).

[7] E. G. Rochow and H. G. LeClair, *J. Inorg. Nucl. Chem.*, **1**, 92 (1955).

[8] J. D. Dunitz and K. Hedberg, THIS JOURNAL, **72**, 3108 (1950).

[9] W. C. Schumb and D. W. Robinson, *ibid.*, **77**, 5294 (1955).

[10] A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919).

[11] Obtained from the City Chemical Company, Brooklyn, New York. The lithium aluminum hydride was kindly donated by Dr. M. D. Banus of Metal Hydrides, Inc., Beverly, Massachusetts.

[12] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

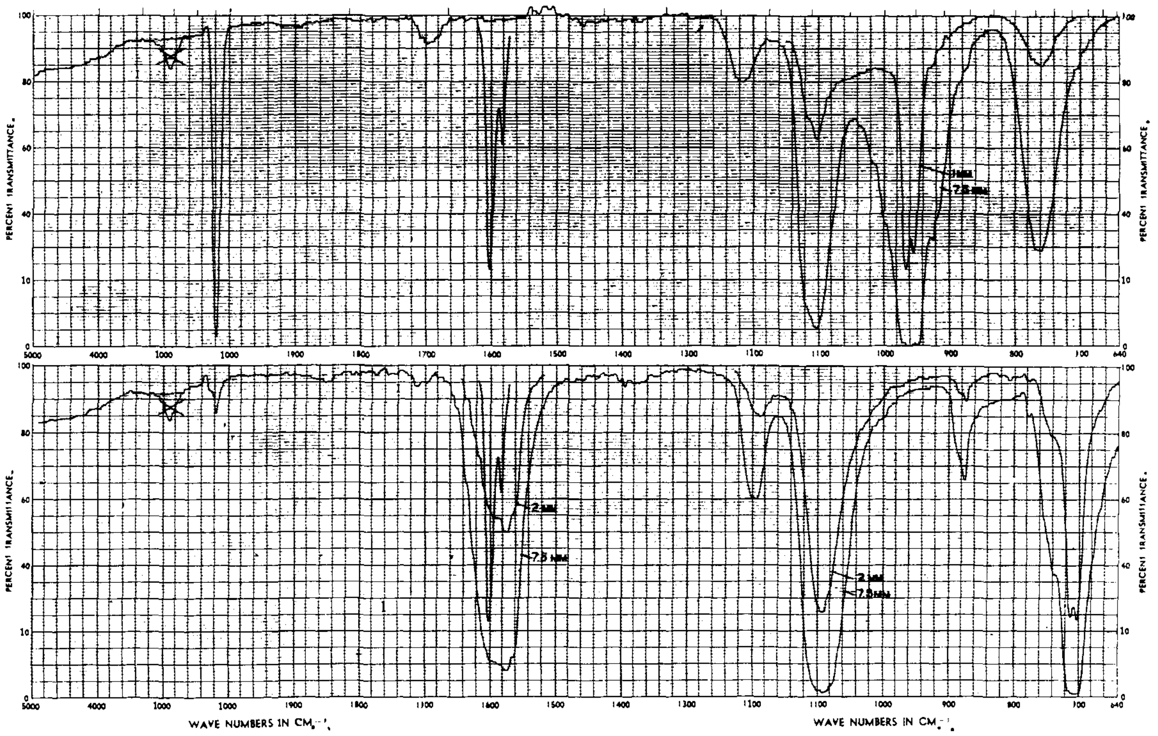

Fig. 1.—Infrared spectra of disiloxane (above curve) and disiloxane-d_6 (bottom curve) vapor. The isolated polystyrene band at 1582–1603 cm.$^{-1}$ in both spectra was recorded as a check on the wave number calibration. Note change of scale at 2000 cm.$^{-1}$.

was found to favor strongly the formation of dichlorosilane, presumably by disproportionation of monochlorosilane, the chlorination was done in batches, each batch being heated to 100° with aluminum chloride for 1–3 hours. This reduced the ratio of dichlorosilane-d_2 to monochlorosilane-d_3. One attempt to chlorinate silane-d_4 with hydrogen chloride showed considerable hydrogen–deuterium exchange on the silicon atom.

The monochlorosilane-d_3 was hydrolyzed with deuterium oxide and washed in the same manner as described for disiloxane. Yields for the hydrolysis step were as high as 94% and the silicon tetrachloride reduction is practically quantitative. The poorest yields were in the chlorination step, where the proportion of dichlorosilane could not be reduced below about 20%. Disiloxane-d_6 amounting to 1.3 g. was prepared. The isotopic purity, as shown by the very weak Si–H infrared band at 2180 cm.$^{-1}$, was about 98 atom-% deuterium.

Disiloxane was found to be reasonably stable at room temperature. Confined as a liquid of vapor pressure about 4.75 atm. and stored in a small Pyrex tube, it decomposed 3% in 4 months. The volatile product contained silane.

Determination of Spectra.—The infrared spectra were obtained with a Baird Associates' Double-Beam Recording Infrared Spectrophotometer with a rock-salt prism and a 10 cm. path length through the gaseous samples and with a Perkin–Elmer Model 12B Single-Beam Spectrometer modified[13] to permit removal of atmospheric carbon dioxide and water from the radiation beam. With the latter instrument gas cells of 5 cm. path length and prisms of CaF_2, NaCl, KBr and TlBr–TlI were used to cover the range 250–5000 cm.$^{-1}$. The band centers were estimated from the single-beam records, each band being measured with the prism of optimum dispersion for the particular frequency. As no unambiguous rotational structure was resolved, the estimates of centers, particularly for oddly shaped bands, are somewhat approximate. Probably the greatest error in the location of any band is 3 cm.$^{-1}$. All spectra were calibrated against known bands in water, carbon dioxide, methanol, ammonia and carbon monoxide, each used in the appropriate spectral region.

High-resolution infrared spectra were obtained of the two perpendicular bands at 2183 and 957 cm.$^{-1}$ in disiloxane. The instrument used for the first band has been described recently,[14] and for the latter a similar instrument was employed which used a Golay radiometer as a detector rather than a refrigerated lead telluride cell. Spectral resolution of 0.3–0.4 cm.$^{-1}$ was achieved.

For the determination of the Raman spectra of the light and heavy compounds in the liquid phase, samples were sealed in tubes constructed of Pyrex with an inside diameter of 3.5 mm. and a wall thickness of 1.4 mm. Flat circular windows 3.0 mm. thick were sealed to the tubes with a tiny oxy-hydrogen flame and then annealed. These easily withstood the vapor pressure of the samples at 40°, the temperature during excitation. Extremely slow photodecomposition was noticed.

The Raman spectra were obtained with a Zeiss three-prism spectrograph and Hg-4358 excitation. Filters of a saturated aqueous sodium nitrite solution and a 0.15 g./l. aqueous rhodamine solution were used. In the case of the more weakly scattering deuterium compound, a saturated solution of praseodymium chloride also was used. Plates were calibrated against the spectrum of an iron arc imposed on either side of the Raman spectra. Spectra were measured by enlargement of the plates and comparison with a millimeter scale. Strong lines are probably accurate to ±2 cm.$^{-1}$, while weak diffuse lines only to ±4 cm.$^{-1}$.

Because of the small sample size and poor Raman scattering power of the compounds, all spectra were weak. The small tube diameter and the necessarily long exposure times caused halation about the exciting line so that no Raman lines could be observed below about 250 cm.$^{-1}$. No depolarization measurements were made.

The infrared spectra above 650 cm.$^{-1}$ obtained with the Baird instrument are shown in Fig. 1, and the only band observed below 650 cm.$^{-1}$, that of disiloxane-d_6 at 593 cm.$^{-1}$, is given in Fig. 2. The numerical values of band transmission minima are listed in Tables I and II and the Raman data in Tables III and IV.

Interpretation of Spectra.—The spectra, if complete, are too simple to be interpreted on the basis

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[13] R. C. Lord, R. S. McDonald and F. A. Miller, *J. Opt. Soc. Am.*, **42**, 149 (1952).

[14] R. C. Lord and T. K. McCubbin, Jr., *ibid.*, **45**, 441 (1955).

TABLE I

INFRARED BANDS OF DISILOXANE VAPOR

Observed between 280 and 5000 cm.$^{-1}$.

Wave no. (cm.$^{-1}$ vac.) and estd. intensity	Assignment	Wave no. (cm.$^{-1}$ vac.) and estd. intensity	Assignment
764 s	ν_{13}	1910 w	$\nu_7 + \nu_9$; $\nu_9 + \nu_{12}$
957 vvs	ν_{12}; ν_7	2169 vs	ν_5
1107 vs	ν_6	2183 vs	ν_{11}
1220 ms	?	3135 w	$\nu_1 + \nu_7$; $\nu_1 + \nu_{12}$; $\nu_5 + \nu_9$; $\nu_7 + \nu_8$; $\nu_8 + \nu_{12}$; $\nu_9 + \nu_{11}$
1465 vw	$\nu_{10} + \nu_{12}$	3320 vvw	$\nu_1 + \nu_6$; $\nu_6 + \nu_8$
1556 w	$\nu_3 + \nu_7$; $\nu_3 + \nu_{12}$	4450 w	$\nu_1 + \nu_5$; $\nu_1 + \nu_{11}$; $\nu_5 + \nu_8$; $\nu_8 + \nu_{11}$
1700 m	$\nu_3 + \nu_6$; $\nu_8 + \nu_{13}$		
1761 vw	$\nu_2 + \nu_{13}$		

TABLE II

INFRARED BANDS OF DISILOXANE-d_6 VAPOR

Observed between 240 and 5000 cm.$^{-1}$.

Wave no. (cm.$^{-1}$ vac.) and estd. intensity	Assignment	Wave no. (cm.$^{-1}$ vac.) and estd. intensity	Assignment
593 s	ν_{13}	1575 vs	ν_5; ν_{11}
713 vvs	ν_7	1710 m	?
720 s	ν_{12}	1862 m	$\nu_2 + \nu_6$
882 w	$\nu_{11} - \nu_9$	2290 m	$\nu_1 + \nu_7$; $\nu_1 + \nu_{12}$; $\nu_5 + \nu_9$; $\nu_7 + \nu_8$; $\nu_8 + \nu_{12}$; $\nu_9 + \nu_{11}$
1094 vs	ν_6	2660 vw	$\nu_1 + \nu_6$; $\nu_6 + \nu_8$
1196 ms	?	3150 w	$\nu_1 + \nu_5$; $\nu_1 + \nu_{11}$; $\nu_5 + \nu_8$; $\nu_8 + \nu_{11}$
1260 vw	$\nu_3 + \nu_7$; $\nu_3 + \nu_{12}$		
1385 m	$\nu_7 + \nu_9$; $\nu_9 + \nu_{12}$		

TABLE III

RAMAN SPECTRUM OF LIQUID DISILOXANE

Wave no. (cm.$^{-1}$ vac.)	Character	Estd. int.	Assignment
2174	Sharp	vs	ν_1
(2174)	Under ν_1	—	ν_8
1009	Sharp	w	ν_2
947	Diffuse	s	ν_9
716	Diffuse	s	ν_{10}
606	Sharp	s	ν_3

TABLE IV

RAMAN SPECTRUM OF LIQUID DISILOXANE-d_6

Wave no. (cm.$^{-1}$ vac.)	Character	Estd. int.	Assignment
1575	Sharp	vs	ν_1
1546	Diffuse	w	ν_8
771	Sharp	w	ν_2
699	Diffuse	w	ν_9
(555)^a	Under ν_{10}	—	ν_3
532	Diffuse	s	ν_{10}
468		vw	Spurious

[a] Approximate.

of C_{2v} or C_s symmetry. The lack of coincidences between infrared and Raman frequencies, apart from those which can be regarded as accidental, implies a symmetry center in the molecule. The only plausible structure with a symmetry center is that of a point group D_{3d}. However, it has been pointed out by Bauman[15] that the vibrational selection rules for a free internal rotator of the ethane type are indistinguishable from those of point group D_{3d}. Thus the interpretation of the spectra in terms of a D_{3d} structure is ambiguous since vibrational spectra cannot serve to distinguish a rigid D_{3d} structure from a freely rotating one.

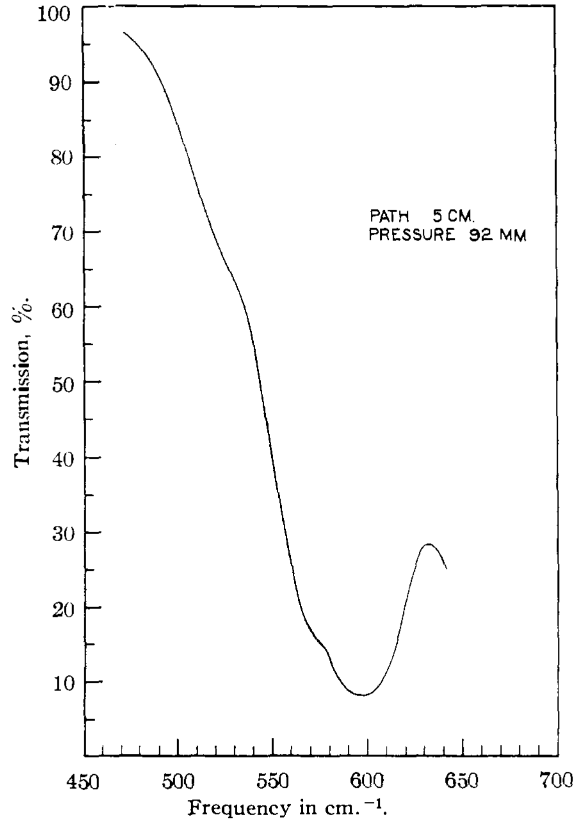

Fig. 2.—Infrared band of disiloxane-d_6 at 593 cm.$^{-1}$.

In Table V is listed an assignment of the infrared and Raman frequencies based on the D_{3d} model. Since the evidence against this model comes mainly from the rotational structure of the infrared bands, that evidence will be discussed below in connection with the results of the high-resolution studies. The assignment of observed frequencies to the various vibrational species was made as follows:

Species A_{1g}.—Since no polarization studies were carried out, totally symmetrical Raman lines were identified by their sharpness and intensity. There is little doubt about the assignment of the Si–H and Si–D stretching frequencies at 2174 and 1575 cm.$^{-1}$, nor about the deformation frequencies at 1009 and 771 cm.$^{-1}$. Comparable but slightly lower values have been observed in the Raman spectrum of disilane vapor by Stitt and Yost.[16] The third A_{1g} vibration, Si–O–Si symmetrical stretching, is observed at 606 cm.$^{-1}$, considerably above the value of 435 found for the analogous vibration in disilane.[17] This difference is not surprising in view of the greater stability of the Si–O bond than that of the Si–Si bond. Unfortunately the corresponding vibration in disiloxane-d_6 cannot be clearly observed. It is expected in the range 550–575 cm.$^{-1}$, which would place it quite close to the broad line centered at 532 cm.$^{-1}$. The estimated value of 555 cm.$^{-1}$ is in satisfactory agreement with the product rule.[17]

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(15) R. P. Bauman, *J. Chem. Phys.*, **24**, 13 (1956).

(16) F. Stitt and D. M. Yost, *ibid.*, **5**, 90 (1937).

(17) Table V, last column. Discussion of the product rule is given by F. Halverson, *Rev. Mod. Phys.*, **19**, 87 (1947).

Table V

Symmetry Species, Selection Rules and Frequency Assignments of Fundamentals of Disiloxane and Disiloxane-d_6 (D_{3d} Structure)

Species	Vibn. no.	Approximate form of vibration	Selection rules		Assignment		Product rule	
			Raman	Infrared	$(SiH_3)_2O$	$(SiD_3)_2O$	Obsd.	Calcd.
A_{1g}	1	Si–H stretching	Active sharp	Silent	2174	1575	1.97	1.999
	2	SiH_3 deformation	(Pol.)		1009	771		
	3	Si–O–Si stretching			606	555		
A_{1u}	4	Torsion	Silent	Silent	..	..	..	1.414
A_{2u}	5	Si–H stretching	Silent	Active parallel	2169	1575	1.87	1.926
	6	Si–O–Si stretching			1107	1094		
	7	SiH_3 deformation			957	713		
E_g	8	Si–H stretching	Active diffuse	Silent	2174	1546	2.56	2.602
	9	SiH_3 deformation	(Depol.)		947	699		
	10	SiH_3 rocking			716	532		
E_u	11	Si–H stretching	Silent	Active perpendicular	2183	1575	..	2.724
	12	SiH_3 deformation			957	720		
	13	SiH_3 rocking			764	593		
	14	Si–O–Si bending			<280	<240		

Species E_g.—This is the only other species active in the Raman effect. The Si–H stretching frequency of this species lies very close to the totally symmetrical one. It was not resolved in the spectrum of disiloxane and thus is given the same frequency, 2174 cm.$^{-1}$. In the deuterium compound the two Raman lines are not superimposed and the E_g stretching frequency is observed at 1546 cm.$^{-1}$. The two remaining vibrations are the SiH_3 deformation and rocking. In the hydrogen compound these are found at 947 and 716 cm.$^{-1}$, respectively, and in the deuterium compound at 699 and 532 cm.$^{-1}$.

A weak line at 468 cm.$^{-1}$ in disiloxane-d_6 cannot be assigned. It occurs only after long exposure (>50 hours) and falls below the lowest observed line in disiloxane by more than a factor $1/\sqrt{2}$. It is believed not to belong to disiloxane-d_6.

Species A_{2u}.—The three infrared-active vibrations of this species, Si–H stretching, Si–O–Si antisymmetric stretching and SiH_3 deformation. can be identified by the parallel structure of the infrared bands. In other silyl compounds such as SiH_3Br[18,19] and in GeH_3Cl and GeD_3Cl,[20] the parallel vibrations occur at very similar but slightly lower frequencies than the corresponding perpendicular vibrations. In disiloxane the parallel Si–H stretching vibration is shown by high-resolution spectra to lie at about 2169 cm.$^{-1}$, just below the perpendicular vibration. The band center was estimated from the band's transmission minimum. In the heavy compound, both parallel and perpendicular Si–D stretching vibrations appear to coincide at 1575 cm.$^{-1}$.

Although in disilane the parallel and perpendicular SiH_3 deformation vibrations are well separated[21] because of close mechanical coupling between the silyl groups, in disiloxane the two vibrations are superimposed at 957 cm.$^{-1}$.[22] This can be seen in Fig. 1. The broad perpendicular band showing rotational fine structure at its edges has at its center an intense relatively narrow band with a missing Q-branch. The Q-branch should be very weak because of the small ratio of I_A to $I_B (I_A/I_B \sim 0.063)$.[23] In disiloxane-d_6 the parallel band moves to 716 cm.$^{-1}$.

The strong band at 1107 cm.$^{-1}$ in disiloxane is assigned to the parallel Si–O–Si stretching vibration. This is in agreement with the strong band at about 1075 cm.$^{-1}$ found in substituted siloxanes.[4] The 1107 cm.$^{-1}$ band moves to 1094 cm.$^{-1}$ in the deuterium compound.

Species E_u.—As indicated above, the perpendicular stretching vibrations are located at 2183 cm.$^{-1}$ in disiloxane and 1575 cm.$^{-1}$ in disiloxane-d_6 while the perpendicular SiH_3 deformation frequency lies near 960 in disiloxane. Although its center is obscured by the parallel band, measurement from its sides places it at 957 cm.$^{-1}$. In the deuterium compound the perpendicular deformation vibration appears to be displaced to slightly higher frequency than the parallel band. The best estimate of its center is 720 cm.$^{-1}$. The SiH_3 rocking vibration is found at 764 cm.$^{-1}$ in disiloxane and 593 cm.$^{-1}$ in disiloxane-d_6. This may be compared with the values of 666.2 cm.$^{-1}$ in SiH_3Cl[22] and 629 in SiH_3Br.[18]

The remaining E_g vibration is the Si–O–Si bending mode. This would be expected to lie below 280 cm.$^{-1}$ in disiloxane and is certainly not observed above this frequency in either compound.

High-resolution Spectra.—Although the grating instruments used for high-resolution work on the perpendicular fundamentals at 2183 and 957 cm.$^{-1}$ are capable of resolving lines spaced as closely as 0.3 cm.$^{-1}$ or less, no clear-cut rotational structure of the usual Q sub-band sort was observed for either band. If there were no complications such as those discussed below, the expected sub-band spacing (with ζ assumed nearly zero) is well above 2 cm.$^{-1}$. The lack of the expected rotational detail was the basis for the conclusion of Emeléus, Mac-

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(18) D. W. Mayo, H. E. Opitz and J. S. Peake, *J. Chem. Phys.*, **23**, 1344 (1955).

(19) See also R. N. Dixon and N. Sheppard, *ibid.*, **23**, 215 (1955).

(20) R. C. Lord and C. M. Steese, *ibid.*, **22**, 542 (1954).

(21) H. S. Gutowsky and E. O. Stejskal, *ibid.*, **22**, 939 (1954).

(22) In the infrared spectrum of monochlorosilane the appearance of the 960 cm.$^{-1}$ region is quite similar to that in disiloxane, indicating that the parallel and perpendicular SiH_3 deformation vibrations are also superimposed in that molecule. The band in SiH_3Cl at 1097.5 cm.$^{-1}$ attributed by Monfils (*ibid.*, **19**, 138 (1951); *Compt. rend.*, **236**, 795 (1953)) to the parallel deformation vibration is probably the overtone of the fundamental at 551 cm.$^{-1}$.

(23) E. Teller, *Hand- und Jahrbuch Chem. Physik*, **9**, [II] 43 (1934).

Diarmid and Maddock[3] that disiloxane is an asymmetric top.

There are, however, numerous complications present in disiloxane which may make the rotational structure of any observed perpendicular band too complex to resolve even if the equilibrium structure is that of a rigid or internally rotating symmetrical top. These are: (a) superposition of a parallel band; (b) "upper-stage" bands of high intensity; (c) vibration-rotation interaction of various kinds. There is little question that all of these complicating factors are present in disiloxane. The over-lapping of the parallel and perpendicular bands already has been discussed. Upper-stage bands, that is, bands due to vibrational transitions originating on excited vibrational levels, are to be expected because of the presence of a doubly degenerate vibration of low frequency (the Si–O–Si bending mode). Such bands are unusually strong if the Boltzmann population factor of the excited vibrational level is high, and for the Si–O–Si bending vibration this requirement is certainly satisfied. The effect of such bands is to wash out rotational structure because their vibrational frequencies are shifted slightly from those of fundamental bands and the rotational structure of the upper-stage bands fills in the transmission windows in the rotational structure of the fundamental. Other vibrations than the Si–O–Si bending, particularly the Si–O–Si symmetrical stretching, can give rise to upper-stage bands of appreciable intensity, but the bending mode is certainly the most important.

Vibration–rotation interaction is also an important factor. If disiloxane is truly a free internal rotator, even without vibration–rotation interaction the rotational structure will have a more complex structure than would be expected for a rigid D_{3d} model.[24] Rotation–vibration interaction can affect resolution by cutting down on the Q sub-band spacing if the value of the Coriolis coupling constant has a positive sign[23] in a molecule like disiloxane. In addition Howard[25] has pointed out that Coriolis coupling between analogous vibrations of species E_g and E_u, provided their frequencies are close together (as is the case for the observed bands in disiloxane), can cause a splitting in the degenerate frequencies. This splitting need not be large ($\sim$1 cm.$^{-1}$) to result in serious interference with the resolution of the rotational fine structure.

Finally it should be remarked that some structure was resolved on the very edges of both the 2183 and 957 bands. The former showed twelve moderately prominent peaks with a regular spacing of 5.2 cm.$^{-1}$. This value is too large for a rigid rotator, but is possible for a completely free internal rotator with $I_A << I_B$. The 957 band also showed structure at the edges when examined at fairly high pressure (5–10 cm. Hg with 10 cm. path), and even showed indication of strong-weak-weak intensity alternation. This rather regular structure was obtained with the Baird double-beam spectrometer, but was not observable at lower pressures near the band center either with the prism instrument or with the grating. The grating spectrum showed only irregular spacings, though considerable structure was resolved.

NOTE ADDED IN PROOF.—Through the courtesy of Professor J. S. Peake and Mr. D. W. Mayo of Indiana University, the authors have had the opportunity to see an infrared spectrum of disilylacetylene (DSA), which presumably has a strictly linear structure. Bands of DSA analogous to the bands of ν_6, ν_7 and ν_{13} in disiloxane are closely similar in appearance to these latter. A displacement of ν_7 from ν_{12} by about 35 cm.$^{-1}$, however, enables the resolution of a portion of ν_{12}, the sub-band structure of which displays the amazingly large spacing of 7 cm.$^{-1}$.

Discussion of Results

From the preceding remarks it is our conclusion that the absence of the usual rotational fine structure found in trigonally symmetrical molecules is not sufficient evidence to rule out a linear Si–O–Si arrangement in disiloxane. The positive arguments for this structure are the following.

1. Raman lines at 1009, 716 and 606 cm.$^{-1}$ in disiloxane and at 1546, 771 and 532 cm.$^{-1}$ in disiloxane-d_6 have no infrared counterparts, and infrared bands centered at 1107 and 764 in disiloxane and at 1094 and 593 in disiloxane-d_6 do not appear in the Raman effect. The remaining Raman and infrared frequencies coincide within the rather broad limits which must be allowed because the two kinds of spectra were not studied in the same state, but all coincidences are readily explicable as accidental in the sense that similar modes of vibration belonging to different species often are found to have nearly identical frequencies. If the lack of genuine coincidences is taken to indicate a symmetry center, the Si–O–Si group must be linear.

2. The number of infrared and Raman bands is small, indicating considerable symmetry. The infrared spectrum of disiloxane is similar to that of disilane[21] apart from the extra bands at 1107 and 1220 cm.$^{-1}$ which are presumed to arise from the addition of the oxygen atom, and from the rotational structure which is expected to differ for the reasons discussed above.

3. The frequencies in disiloxane and disiloxane-d_6 obey the product rule for the A_{2u} and E_g frequencies (Table V) with the expected 1–2% deviation in the correct direction due to an anharmonicity.[26] The value for species A_{1g} is less meaningful because ν_3 in disiloxane-d_6 is overlaid by ν_{10}, and no experimental value can be obtained for species E_u because ν_{14} lies below the observational limit. The product-rule agreement is evidence for the presence of considerable symmetry, since agreement is possible for a postulated structure of *lower* symmetry, but improbable for a structure of higher symmetry than the true one.

The chief evidence against the D_{3d} structure in our data appears to be the pair of infrared bands at 1220 and 1196 cm.$^{-1}$ in light and heavy disiloxane, respectively. These bands differ so little in frequency that they must arise from skeletal vibrations. If they are not due to a fundamental, the simplest combination allowed on the D_{3d} basis would be $\nu_6 + 2\nu_{14}$. This would place ν_{14} at 56 and

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(24) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand and Co., Inc., New York, N. Y., 1945, pp. 491 ff.

(25) J. B. Howard, *J. Chem. Phys.*, **5**, 451 (1937).

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52 cm.$^{-1}$ in the two compounds. The difficulty with this interpretation is the absence of a difference tone $\nu_6 - 2\nu_{14}$ in either spectrum. However, a similar difficulty arises with structures of lesser symmetry, including a non-linear Si–O–Si model, in which the band could be attributed to $\nu_6 + \nu_{14}$. Possibly the absence of a difference band may be due to a slightly bent structure in the vibrationless ground state, which becomes linear on the average when the Si–O–Si bending mode is excited to the first quantum state above ground. On this basis the summation tone might be much more intense than the corresponding difference tone. In this event ν_{14} would be placed at 112 cm.$^{-1}$ in disiloxane and at 105 cm.$^{-1}$ in disiloxane-d_6.

The other combination bands in the infrared spectra are readily explicable (Tables I and II) on the basis of D_{3d} selection rules, with the exception of the 1710 band in disiloxane-d_6. It is possibly due to an impurity.

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The Infrared Spectra of Aromatic Compounds. II. Evidence Concerning the Interaction of π-Electrons and σ-Bond Orbitals in C–H Out-of-plane Bending Vibrations[1]

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In certain monosubstituted and *para*-disubstituted benzenes the frequency of one of the C–H out-of-plane bending vibrations falls above the characteristic frequency range assigned to that vibration. A property common to all of the substituents which cause this positive shift in frequency is that they are electrophilic in nature, *i.e.*, they tend to deplete the aromatic nucleus of π-electronic charge. These experimental observations are consistent with the theory of orbital following during molecular vibrations. The depletion of π-electron density of the aromatic nucleus by electrophilic substituents leads to a decreased ability of the carbon bonding orbitals to follow the out-of-plane movement of the hydrogen atoms. This results in higher bending vibration frequencies because the vibrations occur with greater difficulty as orbital overlap decreases. Applications of this theory to other spectral anomalies are also discussed.

Various observations[2,3] have indicated that the frequencies of one of the out-of-plane C–H bending vibrations in monosubstituted benzenes falls outside of the characteristic frequency range for compounds such as benzoic acid, sodium benzoate, benzoyl chloride and nitrobenzene. It has also been observed that in *para*-disubstituted benzenes the same substituents give rise to anomalous shifts in frequency. The purpose of this paper is to discuss certain other observations on the frequencies of these vibrations and to present a self-consistent explanation for this effect.

Experimental

All the spectra were recorded under the same conditions as were described in the first paper of this series.[1,2a]

I. Results

Spectra of a typical group of monosubstituted benzenes in which the frequency falls in the normal range below 775 cm.$^{-1}$ are shown in the upper portion of Fig. 1, whereas the spectra of the group of compounds in the lower portion of Fig. 1 all exhibit a shift of this frequency above 775 cm.$^{-1}$. A pronounced decrease in intensity with the shift to higher frequency is also generally observed, although a low intensity may also be observed with a normal frequency, as in ethylbenzene. The same groups which give rise to the shifts in monosubstituted benzenes also cause corresponding shifts in the *para*-disubstituted benzenes (Table II). When both *para*-positions are occupied by one of these groups, the shift from the normal frequency range is even larger. The data summarized in Tables I and II show that the increase in frequency caused by certain groups is basically an intramolecular interaction, since there is no significant frequency difference between spectra obtained from the solid state and from dilute solutions.

II. Discussion

A. Orbital Rehybridization during C–H Out-of-plane Bending Vibrations.

A. Orbital Rehybridization during C–H Out-of-plane Bending Vibrations.—A characteristic common to all of the substituents which cause a positive shift in C–H out-of-plane bending frequencies in both mono- and *para*-disubstituted compounds is that they are electrophilic in nature, *i.e.*, the substituents tend to deplete the aromatic nucleus of π-electronic charge. This suggests that the π-electrons located above and below the plane of the benzene ring exert a significant influence on the out-of-plane C–H bending vibrations. Independent supporting evidence for this interaction resides in the theory of the variation of bond hybridization during molecular deformations.[4-6] This theory has provided an explanation for the anomalously large C–H bond moments obtained from the

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

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