104. *The Preparation and Properties of New Chloride, Cyanide, and Oxygen Derivatives of Disilane.*

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The following new derivatives of disilane have been synthesized and characterized: $H_3Si{\cdot}SiH_2Cl$, $Me_3Si{\cdot}SiMe_2{\cdot}CN$, $(Me_3Si{\cdot}SiMe_2)_2O$ and $(Me_3Si{\cdot}SiMe_2{\cdot}O)_2Si_2Me_4$. Evidence is submitted which suggests that $Me_3Si{\cdot}SiMe_2CN$ exists as an equilibrium mixture of the normal cyanide and the isocyanide. The thermal stability of several analogous disilanyl and pentamethyldisilanyl compounds is discussed.

Although the physical and chemical properties of the carbon–carbon bond have been extensively investigated, relatively little is known about the analogous silicon–silicon linkage and compounds containing this bond. As part of a general study of the silicon–silicon linkage we previously reported the synthesis and properties of a number of derivatives containing the disilanyl, $H_3Si{\cdot}SiH_2{\cdot}$, group.[1, 2] These may be considered to be the silicon analogues of ethyl compounds. The present paper describes the preparation of new substances containing either the disilanyl or pentamethyldisilanyl ($Me_3Si{\cdot}SiMe_2$) group.

Stock and Somieski[3] tried to prepare disilanyl chloride, $H_3Si{\cdot}SiH_2Cl$, by treating disilane with hydrogen chloride in the presence of aluminium chloride and, although a mixture was obtained which appeared to be rich in disilanyl chloride, they were not able to isolate this compound since it decomposed rapidly below 0°. Since we have shown[2] that decomposition of disilanyl bromide at 0° is greatly catalyzed by aluminium bromide, and since disilanyl chloride prepared by the above method might contain traces of aluminium chloride which could similarly catalyze its decomposition, its preparation was attempted by a method less likely to permit such contamination.

The chloride was prepared in good yields by reaction at room temperature of the vapour of disilanyl iodide with silver chloride:

$$H_3Si{\cdot}SiH_2I + AgCl \longrightarrow H_3Si{\cdot}SiH_2Cl + AgI$$

It was spontaneously inflammable in air and showed only very slight thermal decomposition at 18°. When mixed with hydrogen chloride, it underwent some decomposition at $-24°$ and it therefore differs from the bromide which appears to be stable at 0° when mixed with

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[1] Ward and MacDiarmid, *J. Amer. Chem. Soc.*, 1960, **82**, 2151.

[2] Ward and MacDiarmid, *J. Inorg. Nuclear Chem.*, 1962, in the press.

[3] Stock and Somieski, *Ber.*, 1920, **53**, 759.

hydrogen bromide.[2] When disilanyl chloride was mixed with aluminium chloride at $-24°$ decomposition was much more rapid. It therefore appears highly likely that the thermal instability of the chloride reported by Stock and Somieski[3] was caused by the presence of aluminium and/or hydrogen chloride in their material and not by any characteristic property of the Si–Si bond in the compound. Disilanyl chloride differs from the iodide, but is similar to the bromide, in not being attacked by mercury at room temperature.

Repeated efforts to obtain pure $H_3Si{\cdot}SiH_2(CN)$ * by passing the vapour of disilanyl iodide over silver cyanide were unsuccessful. Although a material was obtained which appeared to consist chiefly of the desired compound, it appeared to decompose partially during handling in the vacuum system.

Bispentamethyldisilanyl ether was prepared in good yields in an analogous manner to the unmethylated ether,[1] by hydrolysis of the disilanyl halide, $2Me_3Si{\cdot}SiMe_2Cl + H_2O \longrightarrow (Me_3Si{\cdot}SiMe_2)_2O + 2HCl$. An ether, $Me_3Si{\cdot}SiMe_2{\cdot}O{\cdot}SiMe_2{\cdot}SiMe_2{\cdot}O{\cdot}SiMe_2{\cdot}SiMe_3$, was formed by the cohydrolysis of 1-chloropentamethyl- and 1,2-dichlorotetramethyldisilane. It is uncertain whether this is the 1,1- or 1,2-isomer, although the latter is preferred, since demethylation and subsequent chlorination of hexamethyldisilane yields 1,2-dichlorotetramethyldisilane.[4]

Pentamethyldisilanyl (cyanide) was prepared in good yields from the chloride and silver cyanide. Like trimethylsilyl (cyanide),[5] it gave an infrared spectrum indicating that it is probably a mixture of the normal cyanide and the isocyanide since there are maxima at 4·58 and 4·76 μ, the relative intensities being in the ratio ~3·2 : 1. This absorption is almost identical with that of trimethylsilyl (cyanide),[5] whose maxima, at 4·58 and 4·76 μ, are in the ratio 4·5 : 1, these peaks being ascribed, respectively, to the normal cyanide and the isocyanide stretching frequency. The molar refraction of the disilanyl compound lies approximately half-way between the calculated values for the normal cyanide and the isocyanide structure, supporting the infrared data in suggesting that the compound is a mixture of two isomeric forms, which are probably in rapid equilibrium with each other, as postulated for $Me_3Si(CN)$.[5]

With the exception of the cyanide, the presence of a Si–Si bond in the compounds R_6Si_2, R_5Si_2Cl, $R_5Si_2(CN)$, $(R_5Si_2)_2O$ ($R = H$ or Me), and H_5Si_2Br does not cause them to be much less stable thermally than their silyl analogues, insofar as comparable data are available. However, as might be expected, the parent compounds ($R = H$) are less stable thermally than the fully methylated derivatives.† [1, 2, 4, 6] The smaller thermal stability of the parent silyl and disilanyl compounds than of fully methylated species cannot be attributed to weakness of Si–H bonds, compared with Si–C bonds, since both these linkages appear to have almost the same (76 kcal./mole) bond energy.[7] It is probably related to the fact that, when the smaller hydrogen atoms are attached to the silicon, the silicon is more sterically vulnerable to nucleophilic attack by the electronegative substituent on adjacent molecules.

The much smaller thermal stability of the cyanide than of the other disilanyl and pentamethyldisilanyl compounds studied is consistent with the peculiar nature of the bonding in it and possibly also in the unmethylated analogue. If the substance exists as an equilibrium mixture of normal and iso-forms then structures such as (A) are suggested,

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* Parentheses around CN indicate that no assumption is made whether the compound is the normal cyanide or the isocyanide.

† We have observed that little, if any, thermal decomposition occurs when hexamethyldisilane is passed through a tube at 500°.

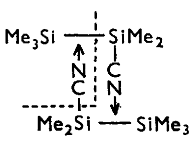
[4] Kumada, Yamaguchi, Yamamoto, Nakajima, and Shiina, *J. Org. Chem.*, 1956, **21**, 1264.

[5] Bither, Knoth, Lindsey, and Sharkey, *J. Amer. Chem. Soc.*, 1958, **80**, 4151.

[6] Hogness, Wilson, and Johnson, *J. Amer. Chem. Soc.*, 1936, **58**, 108; Stokland, *Trans. Faraday Soc.*, 1948, **44**, 545; Shiina and Kumada, *J. Org. Chem.*, 1958, **23**, 139.

[7] Cottrell, " The Strengths of Chemical Bonds," 2nd edn., Butterworths Scientific Publ., London, 1958, pp. 271, 275; Eaborn, " Organosilicon Compounds," Butterworths Scientific Publ., London, 1960, p. 90.

where the filled nitrogen *p*-orbital overlaps a *d*-orbital of one silicon atom or the other, or perhaps, more probably, partly overlaps a *d*-orbital of each silicon atom simultaneously. Such associated structures are consistent with the somewhat high Trouton's constant observed for pentamethyldisilanyl (cyanide). It therefore appears that cleavage could readily occur at the broken line as shown, with breaking of the Si–Si bond to form trimethylsilyl (cyanide) and $Me_3Si{\cdot}[SiMe_2]_x{\cdot}SiMe_2(CN)$. This suggestion is supported by the fact that trimethylsilyl (cyanide) was formed during thermal decomposition of the disilanyl (cyanide). Cleavage of Si–Si bonds in substituted higher silanes under mild conditions is not unusual and has been found to occur when certain chlorodisilanes are treated with traces of tertiary amines. Hexachlorodisilane affords tetrachlorosilane and $Cl_3Si{\cdot}[SiCl_2]_x{\cdot}SiCl_3$ in what appears to be a somewhat analogous reaction.[8] The results of this investigation suggest that the formation of $SiCl_3{\cdot}CN$ from hexachlorodisilane and mercuric cyanide[9] may proceed through the intermediate species, $Si_2Cl_5{\cdot}CN$, which then breaks down to give $SiCl_3{\cdot}CN$ and polymeric chlorides.



(A)

EXPERIMENTAL

Disilanyl chloride and cyanide were prepared and characterized in a vacuum system, with the analytical techniques described for disilanyl bromide.[2] Distillations involving pentamethyldisilanyl derivatives were performed in a Podbielniak high-temperature distillation apparatus (Mini-cal series 3400).

Disilanyl Chloride.—The vapour of disilanyl iodide (0·2134 g.) was passed four times through a tube packed with alternate layers of glass wool and a mixture of reagent-grade silver chloride (17 g.) and fine white sand (60 g.). The tube had been packed in the dark and wrapped with aluminium foil to prevent photodecomposition of the silver chloride. The disilanyl chloride was purified by repeatedly distilling it from a trap at room temperature by way of a trap at −112° into a trap at −196°. The condensate in the −112° trap was impure chloride. This was then repeatedly distilled from a trap at room temperature by way of a trap at −78° into a trap at −196°, giving material which was next distilled slowly from a trap at −96° into a trap at −196°. The condensate in the final −196° trap was pure *disilanyl chloride* (0·0864 g., 68%), m. p., −111·6° ± 0·2° [Found: Si, 57·6; Cl, 36·9%; H_2, 107·1 ml. (S.T.P.); *M*, 96·7. Si_2H_5Cl requires Si, 58·1; Cl, 36·7%; H_2, 107·6 ml. (S.T.P.); *M*, 96·7]. Comparable yields were obtained when larger quantities (∼0·5 g.) of iodide were used.

The vapour pressure of a sample (Found, *M*, 96·7) was measured in an apparatus which had been pretreated with disilanyl chloride, with the results tabulated. Vapour pressures in the range −46·2° to 18·0° are represented by: $\log p(\text{mm.}) = 7{\cdot}76416 - 1529{\cdot}80/(273{\cdot}2 + T)$ (*T* in °c). The extrapolated b. p. is 40·1° and, since the maximum pressure recorded was 316·6 mm., the true b. p. should not differ greatly from the extrapolated value. The molar heat of vaporization is 7·00 kcal. mole^{-1}, and Trouton's constant is 22·4 cal. deg.$^{-1}$ mole^{-1}.

Vapour pressure (mm.) of disilanyl chloride.[a]

Temp.	Obs.	Calc.	Temp.	Obs.	Calc.	Temp.	Obs.	Calc.	Temp.	Obs.	Calc.
−46·2°	10·3	10·6	−25·2°	39·6	39·4	0·0°	146·4	146·1	−24·4°	43·9[b]	41·2
−42·7	13·9	13·4	−21·0	50·0	49·9	4·2	175·9	175·9	−45·5	12·0[b]	11·1
−37·4	18·9	18·9	−17·0	61·8	62·1	8·0	208·3	210·6	−196	0·80[b]	—
−32·2	25·9	26·1	−10·4	87·7	87·7	18·0	316·6	324·1	0·0	145·8[c]	146·1
−28·2	32·9	33·1	−6·0	109·5	109·4	0·0	146·1[b]	146·1			

[a] Duration of the determination: 10 hr. [b] Pressure observed on decreasing the temperature. Pressure observed on warming from −196° to 0° at the conclusion of the experiment (after removal of the small amount of non-condensable gas). Molecular weight of the entire sample at the conclusion of the experiment; found, 97·2.

To test the thermal stability, the chloride (0·1110 g.) was held at 0° for 22 hr. The vapour pressure increased from 145·8 mm. (calc., 146·1 mm.) to 147·5 mm. When the sample was

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[8] Wilkins, *J.*, 1953, 3409; Kacmarczyk and Urry, *J. Amer. Chem. Soc.*, 1960, **82**, 751; Cooper and Gilbert, *ibid.*, p. 5042.

[9] Kaczmarczyk and Urry, *J. Amer. Chem. Soc.*, 1959, **81**, 4112.

cooled to −196° a pressure of 0·8 mm. persisted in the tensimeter. Liquid phase was present throughout the experiment.

When anhydrous hydrogen chloride (0·0049 g.) was added to disilanyl chloride (~0·1 g.; v. p. 37·6 mm. at −24·4°) the total pressure of this system at −24·4° was 49·0 mm. and after 4·5 hr. at this temperature was 64·2 mm. When the mixture was cooled to −196° a pressure of 1·7 mm. was observed. Liquid phase was present throughout the experiment.

Anhydrous aluminium chloride (~20 mg.) was sublimed *in vacuo* into the lower chamber of a magnetic-break-seal tube fused to the tensimeter. Disilanyl chloride (v. p. 44·8 mm. at −23·2°) was distilled into the upper portion of the tube. The seal was then broken, permitting the vapour to come in contact with the solid. After 1·7 hr. at −23·2° the pressure had risen to 50·0 mm. When the sample was cooled to −196° a pressure of 0·50 mm. was noted in the tensimeter. The non-condensable gas was removed and the disilanyl chloride was condensed directly on to the aluminium chloride; during 45 min. at −24·0°, the vapour pressure rose from 50·0 mm. to 61·2 mm.; at −196°, a pressure of 1·0 mm. was present. Liquid phase was present throughout the experiment.

Disilanyl (*Cyanide*).—In a typical experiment, disilanyl iodide (1·0 g.) was passed through a tube packed with a mixture of silver cyanide (15 g.) and fine white sand (90 g.). The tube was wrapped with aluminium foil. The tube became warm and the silver cyanide became yellowish-orange. Separation of volatile materials yielded a small amount of hydrogen cyanide and disilane (identified by infrared spectra [10]), about 100 mg. of disilanyl iodide (identified by its infrared spectrum [1]), and 0·15 g. of impure disilanyl cyanide (Found: *M*, 97·3. Calc. for CH_5NSi_2: *M*, 87·2).

Many lengthy vacuum-distillations on the combined products from a number of preparations afforded 0·04 g. of pure *cyanide* (Found: *M*, 87·4). Since it decomposed fairly rapidly at −23°, as shown by an increase in vapour pressure from 40·0 to 46·0 mm. during 40 min., no attempt was made to characterize it further. Small quantities of hydrogen cyanide (identified by infrared spectrum [10]) appeared to be formed during the decomposition.

Pentamethyldisilanyl Chloride.—Hexamethyldisilane was prepared in good yields by treating a mixture of methylchlorodisilanes with methylmagnesium bromide. It was converted into pentamethyldisilanyl chloride (by concentrated sulphuric acid and ammonium chloride [4]), b. p. 136—137°, n_D^{30} 1·4336, d_4^{30} 0·8537, $[R_L]_D$ 50·83 (calc. by the Lorenz–Lorentz formula). B. p. 134—135°, n_D^{20} 1·4430, and d_4^{20} 0·8684 have been reported.[4] $[R_L]_D$ calc. is 50·71.*

Bispentamethyldisilanyl Ether.—Water (10—15 ml.) was added to pentamethyldisilanyl chloride (5 ml., 4·4 g.) in a small separatory funnel which was shaken for 15 min.; the two layers which were formed were separated. This process was repeated until 29·0 g. of chloride had been used, whereupon the clear upper layers of the *ether* were combined and distilled (yield, 18·40 g., 76%) [Found: C, 43·1; H, 10·7; Si, 40·5%; *M* (cryoscopic in benzene), 280·9. $C_{10}H_{30}Si_4O$ requires C, 43·1; H, 10·85; Si, 40·3%; *M*, 278·7], d_4^{30} 0·8028, n_D^{30} 1·4334, $[R_L]_D$ 90·30 (calc., 90·80). This ether had an odour somewhat similar to that of hexamethyldisiloxane and was immiscible with water. Vapour pressures, determined in a Podbielniak still in an atmosphere of dry nitrogen, are tabulated. Vapour pressures in the range 87·7—182·8° are represented by: $\log p$ (mm.) = 8·15993—2573·89/(273·2 + T) (T in °c). The extrapolated b. p. is 214·4° and should be very close to the true value since the extrapolation is small. The molar heat of vaporization is 11·78 kcal. mole⁻¹, and Trouton's constant is 24·1 cal. deg.⁻¹ mole⁻¹. No sign of thermal decomposition was observed during the above determinations.

Vapour pressure (mm.) of bispentamethyldisilanyl ether.

Temp.	87·7°	100·3°	109·0°	113·9°	119·4°	122·7°	126·5°	129·7°
V. p.: obs.	10·0	18·2	26·1	32·8	40·2	45·5	52·7	59·3
calc.	10·7	18·6	26·6	32·4	40·2	45·6	52·5	59·1
Temp.	132·4°	136·0°	139·8°	145·4°	150·4°	168·4°	182·8°	
V. p.: obs.	64·7	74·5	84·9	102·8	120·6	215·1	329·3	
calc.	65·2	74·1	84·7	102·6	121·3	214·5	327·7	

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* Molar refractions are calculated from the values given by Vogel, Cresswell, and Leicester (*J. Phys. Chem.*, 1954, **58**, 174).

[10] Pierson, Fletcher, and Grantz, *Analyt. Chem.*, 1956, **28**, 1218; Bethke and Wilson, *J. Chem. Phys.*, 1957, **26**, 1107.

Bispentamethyldisilanoxydisilane.—Crude pentamethyldisilanyl chloride resulting from the treatment of hexamethyldisilane with sulphuric acid and ammonium chloride, which still contained other chloromethyldisilanes, was hydrolyzed in a similar manner to the pure chloride. From the several products resulting from the hydrolysis of 78·1 g. of crude material there were obtained 12·5 g. of a *diether* [Found: C, 40·6; H, 10·4; Si, 41·3%; *M* (cryoscopic in benzene), 412·0. $C_{14}H_{42}O_2Si_6$ requires C, 40·9; H, 10·3; Si, 41·05%; *M*, 411·0], d_4^{30} 0·8238, n_D^{30} 1·4395, $[R_L]_D$ 131·36 (Calc., 130·46), as an odourless oil, immiscible with water. Presumably some 1,2-dichlorotetramethyldisilane was present in the crude monochloride. Vapour pressures in the range 168·9—201·0° are represented by the equation log p(mm.) = 8·77697 − 3250·98/(273·2 + T). The extrapolated b. p. is 278·2°. Since no thermal decomposition was observed during distillations the true b. p. probably does not differ greatly from the calculated value. The molar heat of vaporization is 14·88 kcal. mole^{-1}, and Trouton's constant is 27·0 cal. degree^{-1} mole^{-1}.

Vapour pressure (mm.) of bispentamethyldisilanoxydisilane.

Temp.	168·9°	176·8°	179·0°	186·5°	191·0°	201·0°
V. p.: obs.	26·5	36·0	41·0	50·8	58·8	83·3
calc.	26·5	35·7	38·7	50·7	59·4	83·4

Pentamethyldisilanyl (*Cyanide*).—Pentamethyldisilanyl chloride (0·224 mole, 35·4 g.) and silver cyanide (0·149 mole, 20·0 g.) were stirred at room temperature for 24 hr. in a flask (fitted with a drying tube), then filtered, and the residue was washed with anhydrous ether (60 ml.). Distillation separated the ether from a fraction of b. p. 145—190° which was then distilled in the Podbielniak still, giving a *product* (11·0 g., 50% based on AgCN used) [Found: C, 45·6; H, 9·8; N, 8·6; Si, 35·25%; *M* (as above), 157·0. $C_6H_{15}NSi_2$ requires C, 45·8; H, 9·6; N, 8·9; Si, 35·7%; *M*, 157·4], d_4^{30} 0·8136, n_D^{30} 1·43735, $[R_L]_D$ 50·72 (calc. for cyanide,* 50·94, for isocyanide, 50·58). Vapour pressures (see Table) in the range 61·9—108·0° are represented by the equation log p (mm.) = 8·33469 − 2452·00/(273·2 + T). The extrapolated b. p. is 176·4°, the molar heat of vaporization is 11·22 kcal. mole^{-1}, and Trouton's constant is 25·0 cal. degree^{-1} mole^{-1}.

Vapour pressure (mm.) of pentamethyldisilanyl (cyanide).

Temp.	61·9°	73·1°	82·8°	87·4°	90·4°	96·1°	101·4°	105·0°	108·0°	115·4°	129·1°
V. p.: obs.	10·3	18·0	27·9	34·3	40·2	50·6	61·1	71·1	80·0	114·1	195·2
calc.	10·4	18·0	28·0	34·3	39·0	49·6	61·5	71·0	79·9	105·9	173·7

Thermal decomposition of this product was rapid between 115° and 130° as indicated by the non-linearity of the vapour pressure curve in this range and by the fact that the material became black; 3—4 ml. of trimethylsilyl cyanide (b. p. 115—116°; lit.,[11] 117·9—118·2°; confirmed by the infrared spectrum [12]) was recovered from the 6—7 ml. of disilanyl compound used.

Infrared Spectra.—Infrared spectra were taken with a Perkin-Elmer model 134 B Infracord double-beam recording spectrophotometer fitted with a sodium chloride optical system. The spectra of disilanyl chloride were of a gaseous sample at 25° in a 10 cm. cell equipped with 30 mm. potassium bromide windows cemented with glyptal resin. The spectra were observed at pressures of 11·0 and 2·0 mm. All spectra of pentamethyldisilanyl derivatives were made on samples dissolved in CCl_4 (~10% solution) in a 0·05 mm. cell equipped with sodium chloride windows. The spectra are tabulated.

Analyses were done by Galbraith Laboratories, Knoxville, Tenn., and by Micro-Analysis, Inc., Wilmington, Delaware. The sample of mixed methylchlorodisilanes was kindly presented by the General Electric Company, Schenectady, New York. One of us (A. G. MacD.) acknowledges an Alfred P. Sloan Research Fellowship. This work is in part a contribution from the

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[*] A value of 4·82 mole/c.c. (see Vogel, Cresswell, Jeffery, and Leicester, *Chem. and Ind.*, 1950, 358) was used in both cases for carbon triply bonded to nitrogen although other values have been employed in analogous calculations (McBride, *J. Org. Chem.*, 1959, **24**, 2029).

[11] Evers, Frietag, Keith, Kriner, MacDiarmid, and Sujishi, *J. Amer. Chem. Soc.*, 1959, **81**, 4493.

[12] McBride and Beachell, *J. Amer. Chem. Soc.*, 1952, **74**, 5247.

The infrared spectra of derivatives of disilane (cm.$^{-1}$).

Si_2H_5Cl	Si_2Me_5Cl	$Si_2Me_5(CN)$	$(Si_2Me_5)_2O$	$(Si_2Me_5O)_2Si_2Me_4$	Interpretation	Ref.
	3000s	3000s	3000m	3000s	C–H stretch	*a*
	2950m	2950m	2950w	2950m	,,	*a*
		2198m			C–N stretch	5, *b*, *c*
2190vs					Si–H stretch	
		2100w			N–C stretch	5, *b*, *c*
		1940w		1940vw	Unassigned	
		1875vw			,,	
		1715vw			,,	
			1590vw	1580vw	,,	
	1440sh	1440sh	1430sh	1430sh	CH_3 deform.	*d*
	1400m	1400s	1400w	1400m	,,	*a*, *d*
	1312vw	1312w			Unassigned	
	1249vs	1250vs	1245vs	1245vs	CH_3 deform.	*d*, *e*
		1040m †	1045vs	1025vs	Si–O–Si stretch	*e*
962sh					SiH_3 and/or SiH_2 deform. or rock	*b*, *f*
946m					,, ,, ,,	*b*, *f*
936m					,, ,, ,,	*b*, *f*
888s					,, ,, ,,	*b*, *f*
878s					,, ,, ,,	*b*, *f*
	875m	878s	870m	872s	Unassigned	
	842vs	840vs	838vs	838vs	Si–CH_3 stretch in $SiMe_3$	*e*
	829vs	810vs	817s	815vs	Si–CH_3 stretch in $SiMe_2$	*e*
814vs					SiH_3 and/or SiH_2 deform. or rock	*b*, *f*
807vs					,, ,, ,,	*b*, *f*
801vs					,, ,, ,,	*b*, *f*
			787—740 * s		Si–CH_3 stretch in $SiMe_3$	*e*
	770sh	775vs		769sh	Unassigned	
				760sh	Si–CH_3 stretch in $SiMe_3$	*e*
	745s	738s		745vs	Unassigned	
	723m		711w	712m	,,	
707w					,,	
	695s	694s	688m	687s	,,	
	668s	669m			,,	

* Transmittance constant between wavelengths given. † Impurity.

(*a*) Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edition, John Wiley and Sons, New York, 1959, pp. 13—31. (*b*) Linton and Nixon, *Spectrochim. Acta*, 1958, **10**, 299. (*c*) Bellamy, *op. cit.*, pp. 263—266; Linton and Nixon, *J. Chem. Phys.*, 1958, **28**, 990; ref. 11. (*d*) Ebsworth, Onyszchuk, and Sheppard, *J.*, 1958, 1453. (*e*) Bellamy, *op. cit.*, pp. 334—342. (*f*) Linton and Nixon, *Spectrochim. Acta*, 1958, **12**, 41.

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