The Vibrational Spectra of Hexamethylcyclotrisiloxane and Hexamethylcyclotrisilazane

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A detailed Raman study of the title compounds, together with new far-i.r. data, has permitted a more complete assignment than previously available.

PARTIAL i.r. and Raman data for hexamethylcyclotrisiloxane and -silazane, $(Me_2SiO)_3$ (I) and $(Me_2SiNH)_3$ (II), have been reported by several authors[1] but the only detailed Raman study is that of Kriegsmann.[2] I.r. data for the siloxane (I) down to 400 cm^{-1} were obtained by Lazarev;[3] since completion of our work i.r. spectra (down to 250 cm^{-1}) of oriented films of the siloxane (I) have been reported.[4] As we were in possession of more complete Raman and far-i.r. spectra it seemed appropriate to re-examine the assignments, and to test them for consistency with those recently made for hexachlorocyclotriphosphazen (III).[5]

Selection Rules.—In the solid state the $(SiO)_3$ skeleton (I) is planar;[6] we assume that this is also true for solutions and that D_{3h} rules apply throughout. It crystallises with the symmetry of space group $R3m$-(C^5_{3v}) with a unimolecular rhombohedral cell.[6] Consequently there can be no correlation splitting, no optical branch translatory modes, and only three rotatory modes (A_2 and E in C_{3v}) of which only the E mode is optically

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[1] For details see I. Haiduč, ' Inorganic Rings,' Part I, Wiley, London, 1970.

[2] H. Kriegsmann, *Z. anorg. Chem.*, 1959, **298**, 223.

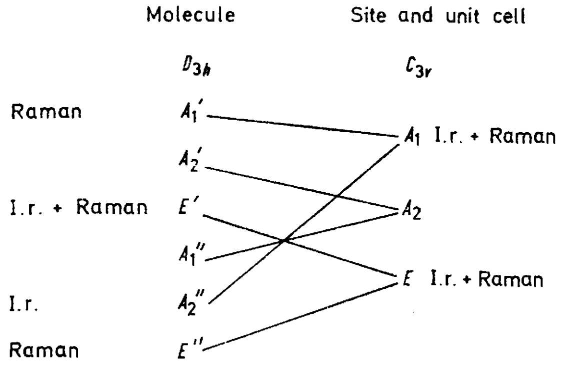
[3] A. N. Lazarev, *Optics and Spectroscopy*, 1962, **18**, 445.

[4] S. Dobos, G. Fogarasi, and E. Castellucci, *Spectrochim. Acta*, 1972, **28**, *A*, 877.

[5] D. M. Adams and W. S. Fernando, *J.C.S. Dalton*, 1972, **2503**.

[6] G. Peyronel, *Atti. Acad. naz. Lincei Rend.*, 1953, **15**, 402; 1954, **16**, 78, 231.

active (i.r. +Raman allowed). Since both site and unit-cell groups are C_{3v} the following correlation scheme applies.



It follows that D_{3h} Raman-active modes can become i.r.-active in the solid (and similarly for i.r. modes) but in a molecular crystal we would not expect this to occur with significant development of intensity.

The structure of the silazane (II) is not entirely settled although non-planarity is indicated by both electron-diffraction and n.m.r.[1] Nevertheless the vibrational spectra are well accounted for on the basis of a planar structure of D_{3h} symmetry, as concluded by Kriegsmann.[2] Possible puckered ring structures are all of lower symmetry and should reveal themselves most clearly in the form of an increased number of polarised lines. We do not find any additional polarised lines, although this does not rule out non-planarity.

For both compounds (I) and (II), methyl being treated as a monatomic group, the vibrational modes are spanned by the representation (1) where R = Raman-active

$$\Gamma = 4a_1'(\mathrm{R}) + 2a_2' + 6e'\ (\mathrm{i.r.} + \mathrm{R}) + a_1'' + 3a_2''\ (\mathrm{i.r.}) + 4e''(\mathrm{R}) \qquad (1)$$

A complicating feature of the assignments is the need to decide which bands are due to methyl vibrations. ν(C–H), δCH_3(s), and δCH_3(a) come at well characterised frequencies and were readily identified for both compounds. The difficulty arises with the rocking and torsional modes which come within the region of the ring skeletal modes. The most probable model for discussion of the methyl motions is one in which an isolated Me_2Si group of C_{2v} symmetry is considered; if the interactions are large the D_{3h} rules apply. On either model only one torsion and three rocking modes are i.r.-active, but there are differences between the two models for the Raman spectrum.

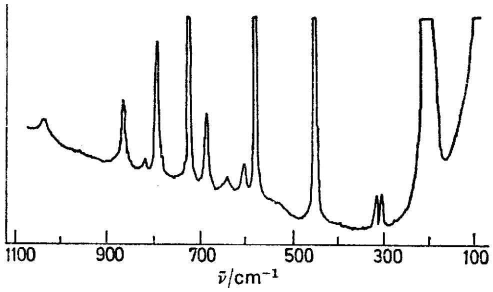
EXPERIMENTAL

Commercial samples were used. The trimeric silazane was found to contain *ca.* 20% of the tetramer: they were separated on a spinning-band column, yielding samples that contained a few percent. impurity as indicated by mass spectroscopy. The spectra of the purified trimer showed no sign of the strongest bands of the tetramer.

Raman spectra were obtained with Coderg PH0 and PH1 instruments with both 632·8 and 488·0 nm excitation and a Cryocirc cold cell. I.r. spectra were obtained with a Perkin-Elmer 225 spectrometer and a Beckman-RIIC FS-620 interferometer.

RESULTS AND DISCUSSION

Results are collected in Tables 1 and 2; the Raman spectrum of the siloxane (I) is illustrated in the Figure.



Raman spectrum of $(Me_2SiO)_3$ at liquid-nitrogen temperature. Spectral slit width 2 cm^{-1}, 488·0 excitation, 300 mW at sample

The data are in good agreement with Kriegsmann's, except that we have rather more Raman detail plus far-i.r. frequencies and that we find no trace of the weak i.r. band at 455 cm^{-1} for the siloxane (I) in carbon disulphide solution.

Hexamethylcyclotrisiloxane.—Apart from the expected ν(C–H)s at 2909 and $\delta(CH_3)$s at 1261 cm^{-1} there are polarised bands at 723, 584, and 453 cm^{-1}. There is little doubt that internal co-ordinates are substantially mixed and that all three are symmetrical deformations of the entire skeleton. It is likely that Si–C stretching is the dominant contribution in the 723 cm^{-1} band. Since ν_4 cannot be higher than 350 cm^{-1}, and is quite possibly lower, it is either very weak or has a depolarisation ratio close to 6 : 7. Exceedingly weak i.r. counterparts have recently been reported for the 453 and 584 cm^{-1} Raman bands.[4]

a_2'' Modes. Bands unique to the i.r. spectrum occur at 162, 232, 391, and 812 cm^{-1}. The positions of these bands correspond with reasonable expectation; they are accordingly labelled ν_5 (391), ν_6 (812), and ν_7 (232). The weak 162 cm^{-1} feature could be the b_2 torsional mode. The symmetry of the 391 and 812 cm^{-1} bands has recently been confirmed from oriented-film i.r. measurements.[4]

e' and e'' Modes. Convincing i.r.–Raman coincidences (e' species) are found at 307, 608, 687, 876, and 1020 cm^{-1}, leaving 189, 199, 209, 319, 644, and 794 cm^{-1} as e'' modes. The e' symmetry of these bands has very recently been confirmed by an oriented-crystal film i.r. study.[4] The weak point in this argument is that a vanishingly weak i.r. or Raman counterpart could lead to mislabelling of a band; and one of the lower frequencies apparently assigned to the e'' class is almost certainly the missing a_1' (ν_4). Also, as shown by the correlation scheme, in the solid *all* vibrations should be both i.r.- and Raman-active so that nothing but coincidences should be found. In addition to the $6e' + 4e''$ skeletal

modes, methyl rocking modes are also bound to be present in the 600—1000 cm^{-1} region.

In the e'' class only ν_{17}, ν(Si–C) is expected to be high in frequency, *ca.* 650—800 cm^{-1}; the other three will almost certainly be below 350 cm^{-1}. The 794 cm^{-1} band is quite strong and is reasonably placed for ν(Si–C), whereas that at 644 cm^{-1} is only found in the Raman spectrum of the cooled solid: the higher band is taken to be ν_{17}. Below 350 cm^{-1} we have to select three of the four Raman-unique bands as e'' fundamentals, without a shred of evidence. Most probably one of these four is ν_4. We arbitrarily place ν_4 at 199 cm^{-1} thereby making three assignments to the e'' class, two of which should be correct.

TABLE 1

Band frequencies/cm^{-1} and assignment for $(Me_2SiO)_3$

	Raman			I.r.		
Assignment[a]	Melt, 80 °C	Cooled solid	Solution[b]	Solution[c]	Solid, Cooled	Solid, Ambient
Torsion, CH_3					162w	162 w
e'' $(+e')$		189sh				
a_1', ν_4	199s,br	199m	199dP			
e''		209sh				
a_2'', ν_7					232m	232m
e'		307w	306?P			306sh
	311w,br					310s
e''		319w	323dP			
a_2'', ν_5						391m
a_1'	454s	452s	453P			
		532vvw				
a_1'	586s	583vs	584P			
e', ν_{13}	606vw	605w	608dP	606m	610m	607s
		644vw				
e', ν_{12}	689wm	684m	689dP	684vw		687wm
a_1'	724m	724s	723P		724w	
e'', ν_{17}	794wm	794ms	799dP			
e', ν_{14}		819w				
a_2'', ν_6				812s	812m,br	810s,br
$e'\rho_r(CH_3)$	876vw	867m	872dP	874wm	876w	874w
e', ν_{11}	~1049vvw,br	1044vw,br	1021dP	1015s	1020vs,br	1012vs,br
		1254w		1255s	1257m	1252m
$\delta(CH_3)s$	1264mw		1261P			
		1269vw				
		1376vvw			1375m	1370m
		1399sh				
$\delta(CH_3)a$		1408w		1400w		1405vw
	1416m	1424m	1411dP			
2 × $\delta(CH_3)a$	2814vw	~2800vw			2850wm	
ν(C–H)	2909s	2909s	2909P	2900vw	2910s	2900w
	2971s	2974s	2969dP	2962s	2945sh	2965s

[a] Modes are labelled only when this is fairly unambiguous; see text. [b] In CCl_4, CH_2Cl_2, or C_6H_6 according to clear range of solvent. [c] In CS_2 and CCl_4.

Six e' skeletal modes are required of which two (ν_{15}, ν_{16}) will be below 350 cm^{-1}: since we have only one in this region we should presumably add an e' label to the complex of Raman bands at *ca.* 200 cm^{-1}. It is likely that one or more of the higher e' modes is a methyl rock: we have only qualitative arguments to help us decide. A band near 1000 cm^{-1} is known to be characteristic of Si–O bonded compounds;[1] we therefore accept 1020 cm^{-1} as ν_{11}. In comparison with other ring systems the second e' ring stretching vibration (ν_{12}) is unlikely to be as close to ν_{11} as 876 cm^{-1}; for this reason we accept this as a methyl rocking mode, and attribute the 687 and 608 cm^{-1} vibrations to the two ring modes ν_{12} and ν_{13}. Finally, we tentatively place ν_{14} at 819 cm^{-1} where a weak, but by no means negligible, Raman band occurs.

Our assignment is summarised in Table 3 and differs from Kriegsmann's principally in being more complete, but also in the treatment of the 454 and 689 cm^{-1} bands. The recent work of Dobos *et al.*[4] supports our assignment to a_2'' and e' classes but we disagree with several of their mode descriptions, as detailed above. We consider that their very weak i.r. band at 450 cm^{-1} is a site-allowed counterpart of the a_1' Raman line at 453 cm^{-1} and not an e' fundamental. Since our Raman and i.r. data are the most complete yet obtained for the siloxane (I), we believe the basis for our assignment is firmer.

Hexamethylcyclotrisilazane.—We confirm Kriegsmann's suspicion that his 582 cm^{-1} band is due to an instrumental feature.[1] Our Raman data for the solid are entirely new, although our discussion is handicapped by ignorance of the crystal structure and unit-cell occupancy.

We confine our discussion to additions to or differences from Kriegsmann's. Owing to the similarity of the compounds (I) and (II) large differences in spectrum are not expected. Accordingly we proceed by analogy with the assignment of the siloxane (I).

Both the 789 and 814 cm^{-1} i.r. bands have exceedingly weak Raman counterparts. We can interpret this to mean *either* that both are e' (coincidences required) *or* that one is e', the other a_2'' with the coincidence resulting from non-planarity of the ring (see correlation scheme). There is no *a priori* means of deciding between these alternatives. We chose the order ν_{14} e' 814; ν_6 a_2'' 789 cm^{-1}, not least because if both are labelled e' there is no other prominent i.r. band in this region to label ν_6. In contrast to the siloxane (I) there are several bands which split at low temperature; this could be due to site and correlation effects if there is more than one molecule per unit cell, or to relaxation of selection rules owing to non-planarity of the ring. Since the doublets concerned are associated with what appear to be e-modes, we attribute the splitting to unit-cell effects, because e-modes cannot split if the symmetry is reduced to C_{3v}.

TABLE 2

Band frequencies/cm^{-1} and assignments for $(Me_2SiNH)_3$

	Raman		I.r.
Assignment	Liquid-nitrogen temp.	Liquid	CS_2 solution
$e''(+e')$		~172sh	
a'_1,ν_4	192m,br	190m	
e''		~208sh	
a_2'',ν_4	233w	232w	
	269vw		
	285vw		282sh
e',ν_{15}	322vw,br		300s
a_2'',ν_5			393wm
a_1'	433s	430s,P	
e',ν_{13}	615sh	613sh	617m,br
a_1'	638s	640vs,P	
e',ν_{12}	678m 688m	682s	677wm
a_1'	712s	715m,P	
	735vvw		
e'',ν_{17}	770sh 777m	774wm	
a_2'',ν_6	790sh		789s
e',ν_{14}	815vvw		814m
$\rho_r CH_3$	853w 865vvw	856vw	864wm
e',ν_{11}	928vw,br 938vw,br	931vw,br	925s
			1008vw
δNH		1167vvw	1162s
$\delta CH_3 s$	1250w 1255sh	1253wm,P	1250s
$\delta CH_3 a$	1410m	1410wm	1400vw
			~1430vvw
	1460vw,br	1462vw,br	
		1550vw,br	
		2860vw,P	
ν(C–H)	2900s	2895s,P	2895vw
	2962s	2955m	2958m
ν(N–H)	3412m	3405m,P	3405wm

Below 300 cm^{-1} the assignment is rather speculative and is made by analogy with (I). We may have missed one or more weak i.r. bands below 200 cm^{-1}.

Comparison of Compounds (I), (II), *and* (III).—Comparison of ring mode assignments for compounds (I) and (II), arrived at independently of those for $(PNCl_2)_3$ (III), are seen to be mutually consistent (Table 4) with the possible exception of two of the lower frequencies. These trends, including comparison with benzene, lend support to the majority of our assignments for (I) and (II).

TABLE 3

Approximate mode descriptions, band frequencies/cm^{-1}, and assignments for skeletal modes of compounds (I) and (II)

			(I)	(II)
a_1'	ν_1	Ring breathing [a]	724	712
	ν_2	Ring in-plane deformation [a]	584	638
	ν_3	ν(Si–C)s [a]	453	433
	ν_4	$\delta(SiC_2)$s [a]	199 [b]	190 [b]
a_2''	ν_5	Ring out-of-plane deformation	391	393
	ν_6	ν(Si–C)a	812	789
	ν_7	ρ_r SiC_2	232	232
a_1''	ν_8	ρ_τ SiC_2	–	–
a_2'	ν_9	Ring stretch	–	–
	ν_{10}	$p\omega$ SiC_2	–	–
e'	ν_{11}	Ring stretch	1020	925
	ν_{12}	Ring stretch	689	677
	ν_{13}	Ring in-plane deformation	608	615
	ν_{14}	ν(Si–C)s	819	814
	ν_{15}	$\rho\omega$ SiC_2 [a]	306	300
	ν_{16}	$\delta(SiC_2)$ [a]	(~200) [c]	(~200)
e''	ν_{17}	ν(Si–C)a	799	774
	ν_{18}	Ring out-of-plane deformation	323	322
	ν_{19}	p_τ SiC_2 [a]	209	208
	ν_{20}	p_r SiC_2 [a]	189	172

[a] Not individually assigned owing to probable internal co-ordinate mixing. [b] Arbitrarily assigned to an observed band; see text. [c] Presumed frequency; see text.

TABLE 4

Comparison of hexatomic ring vibrational frequencies/cm^{-1}

C_6H_6	D_{6h}		D_{3h}	$(PNCl_2)_3$	$(Me_2SiO)_3$	$(Me_2SiNH)_3$
1599	ν	e_{2g}	e'	1226	1020	925
1482	ν	e_{1u}	e'	875	689	677
1309	ν	b_{2u}	a_2'	–	–	–
1010	δ	b_{1u}	a_1'	786	584	638
993	ν	a_{1g}	a_1'	669	453	433
707	π	b_{2g}	a_2''	619	391	393
606	δ	e_{2g}	e'	528	608	615
398	π	e_{2u}	e''	205	323	322

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