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# Characterization of new cyclosiloxazanes using both GC/MS and GC/FT-IR

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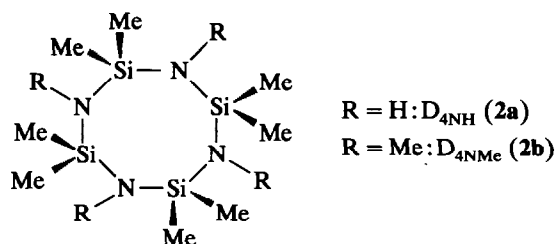
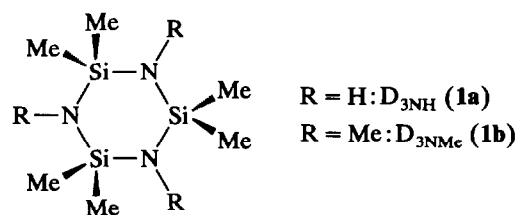
## Abstract

Mixtures of cyclo-silazanes, -siloxanes and -siloxazanes (six- and eight-membered rings) were studied by low- and high-resolution electron-impact and by Fourier transform infrared spectroscopies coupled with gas chromatography (GC/MS and GC/FT-IR). Even though chromatography did not allow us to isolate them, compounds could be characterized from the FT-IR spectra and their frequencies assigned. Where several isomers occurs, different IR bands were assigned to each type of isomer. This study shows the interest of using both GC/MS and GC/FT-IR together for identifying compounds in mixtures.

## 1. Introduction

Cyclotrisilazanes (1) and cyclotetrasilazanes (2) ( $(\text{SiMe}_2\text{-NR})_n$ ) are moisture-sensitive compounds which readily yield cyclosiloxazanes ( $(\text{SiMe}_2\text{-O})_x\text{-(SiMe}_2\text{-NR})_y$ ) and higher cyclic oligomers. Fractional distillation and comprehensive characterization of mixtures of such compounds are difficult. The present work is concerned with their direct analysis by combined GC/MS and GC/FT-IR.

Typical mixtures of cyclosilazanes have been prepared, either *N*-hydrogenated (1a, 2a) or *N*-methylated (1b, 2b).



(Nomenclature: we have extended the well-known *n*-membered cyclosiloxanes abbreviation ( $\text{D}_n$ ) to cyclosilazanes and cyclosiloxazanes as follows:  $(\text{SiMe}_2\text{-O})_n$ ,  $\text{D}_n\text{O}$ ;  $(\text{SiMe}_2\text{-NR})_n$ ,  $\text{D}_{n\text{NR}}$ ).

Reaction mixture A consists of hexamethylcyclotrisilazane ( $\text{D}_{3\text{NH}}$ ) and octamethylcyclotetrasilazane ( $\text{D}_{4\text{NH}}$ ). Reaction mixture B contains nonamethylcyclotrisilazane ( $\text{D}_{3\text{NMe}}$ ) and dodecamethylcyclotetrasilazane ( $\text{D}_{4\text{NMe}}$ ). Each mixture has been characterized by gas chromatography coupled to a mass spectrometer (GC/MS) or a Fourier transform infrared spectrometer (GC/FT-IR).

## 2. GC/MS identification

Low-resolution electron-impact GC/MS, performed with an apolar methyl silicon capillary column, was

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used to identify the different cyclic silicon compounds present in the reaction mixtures. High-resolution electron-impact GC/MS was used complementarily to identify the masses of the major ions.

### 2.1. Reaction mixture A

In the first mixture studied, some cyclosiloxanes (peaks  $O_x$ , Fig. 1, Tab. 1)  $D_{3O}$ ,  $D_{4O}$  and  $D_{5O}$  were present. Beside these cyclosiloxanes, we detected and identified a series of peaks (peaks  $H_x$ , Fig. 1) arising from cyclosilazanes,  $D_{xNH}$ , and cyclosiloxazanes,  $D_{xO}D_{yNH}$  ( $x=0-5$ ,  $y=1-9$ ), with NH substituents. For  $D_{2O}D_{2NH}$  (peaks  $H_5$ ,  $H_6$ ),  $D_{3O}D_{2NH}$  (peaks  $H_{10}$ ,  $H_{11}$ ) and  $D_{2O}D_{3NH}$  (peaks  $H_{13}$ ,  $H_{14}$ ) compounds, two isomers resulting from a different sequence of N-Si and O-Si monomers, are expected. In spite of their very low concentration in the mixture, we observed the GC separation of these isomers, but it was not possible to identify the sequence of the monomers, because of the similarity of the mass spectra. This observation suggests a scrambling of the N-Si and O-Si units by internal rearrangement of the molecular ion. The same occurred for  $D_{4O}D_{2NH}$  and  $D_{2O}D_{4NH}$ , where the three isomers predicted for each were detected (peaks  $H_{15}$ ,  $H_{16}$ ,  $H_{17}$  and  $H_{20}$ ,  $H_{21}$ ,  $H_{22}$ , respectively).

The mass spectra of the cyclosiloxanes ( $D_{xO}$  series) have been described extensively [1]. Several of them ( $D_{3O}$ ,  $D_{4O}$ ,  $D_{5O}$ ) were found in a library search (the NIST library was used for rough identification of the components of the mixtures). The EI mass spectra of these compounds are characteristic: rings smaller than  $D_{6O}$  have base peaks corresponding to  $M-CH_3$  ions; rings larger than  $D_{4O}$  show an intense  $Si(CH_3)_3^+$  ion

( $m/z = 73$ ), accompanied by an ion resulting from a ring contraction after loss of the methyl radical ( $M-CH_3-D_{xO}$ ). Vanden Heuvel [2], for  $D_{4O}$ ,  $D_{5O}$ ,  $D_{6O}$  and later Pickering [3], for the larger rings, explained the ring contraction by a transannular mechanism (Scheme 1).

The mass spectra of  $D_{3NH}$  and  $D_{4NH}$  have been described by Silbiger [5]; the main features of the mass spectra of these lower ring derivatives are (Table 2): methyl radical loss (a) followed by successive losses of methane (b) and ammonia (c). The mass spectra of these compounds are also characterized by the presence of a doubly charged ion, determined by high resolution GC/MS as  $(M-C_2H_6)^{2+}$  (ion j); such ions were commonly found in different silazanes [5] and are explained by the simultaneous elimination of two methyl radicals.

In the spectra of the higher members of the series, the importance of the ammonia loss increased and the ion c became the base peak for  $D_{5NH}$  and  $D_{6NH}$ . Very intense fragments appear for species larger than  $D_{5NH}$  resulting from a ring contraction leading to a six-membered ring ion, after the elimination of a methyl radical: ions h (204) for  $D_{xNH}$  and ions i (205) for the  $D_{xO}D_{yNH}$  derivatives. The mechanism involved here is certainly close to the transannular ring contraction described for the cyclosiloxanes [3], but leads directly to the six-membered species.

In the spectra of the lower members of the series, we observed the ring contraction, but in this case, by loss of one or two six-membered neutral species ( $D_{1NH}$ ,  $D_{2NH}$  and  $D_{1O}$ ). The ions involved (d, e, f) were much less intense than the g or h ions seen before. The

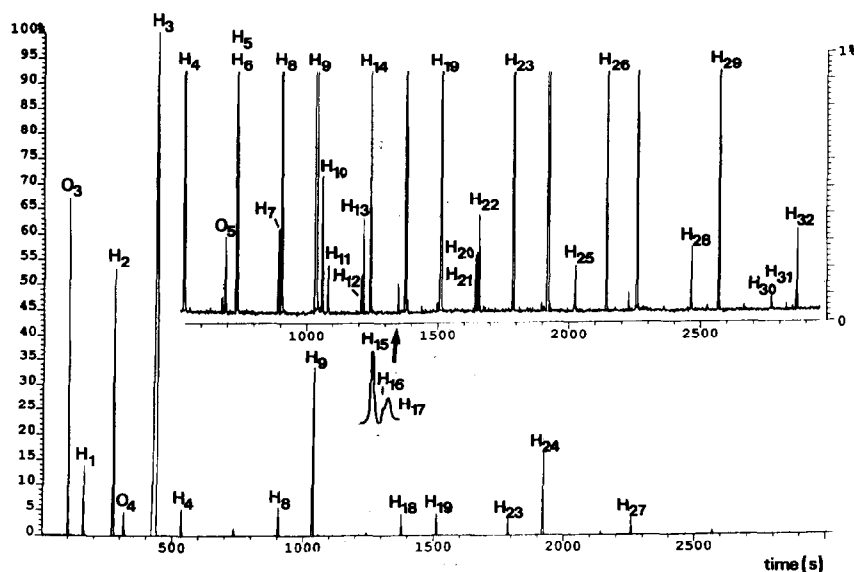


Fig. 1. Chromatogram (GC/MS) of reaction mixture A.



TABLE 1. Kovats index [4] and formulae of the compounds detected in the reaction mixtures A and B

Peak no.	Kovats index	Compound name	Molecular weight	Formula
H <sub>1</sub>	914	D <sub>20</sub> D <sub>1NH</sub>	221	C <sub>6</sub> H <sub>19</sub> O <sub>2</sub> N <sub>1</sub> Si <sub>3</sub>
H <sub>2</sub>	993	D <sub>10</sub> D <sub>2NH</sub>	220	C <sub>6</sub> H <sub>20</sub> O <sub>1</sub> N <sub>2</sub> Si <sub>3</sub>
H <sub>3</sub>	1071	D <sub>3NH</sub>	219	C <sub>6</sub> H <sub>21</sub> O <sub>0</sub> N <sub>3</sub> Si <sub>3</sub>
H <sub>4</sub>	1107	D <sub>30</sub> D <sub>1NH</sub>	295	C <sub>8</sub> H <sub>25</sub> O <sub>3</sub> N <sub>1</sub> Si <sub>4</sub>
H <sub>5</sub>	1197	D <sub>20</sub> D <sub>2NH</sub>	294	C <sub>8</sub> H <sub>26</sub> O <sub>2</sub> N <sub>2</sub> Si <sub>4</sub>
H <sub>6</sub>	1198	D <sub>20</sub> D <sub>2NH</sub>	294	C <sub>8</sub> H <sub>26</sub> O <sub>2</sub> N <sub>2</sub> Si <sub>4</sub>
H <sub>7</sub>	1265	D <sub>40</sub> D <sub>1NH</sub>	369	C <sub>10</sub> H <sub>31</sub> O <sub>4</sub> N <sub>1</sub> Si <sub>5</sub>
H <sub>8</sub>	1281	D <sub>10</sub> D <sub>3NH</sub>	293	C <sub>8</sub> H <sub>27</sub> O <sub>1</sub> N <sub>3</sub> Si <sub>4</sub>
H <sub>9</sub>	1354	D <sub>4NH</sub>	292	C <sub>8</sub> H <sub>28</sub> O <sub>0</sub> N <sub>4</sub> Si <sub>4</sub>
H <sub>10</sub>	1365	D <sub>30</sub> D <sub>2NH</sub>	368	C <sub>10</sub> H <sub>32</sub> O <sub>3</sub> N <sub>2</sub> Si <sub>5</sub>
H <sub>11</sub>	1375	D <sub>30</sub> D <sub>2NH</sub>	368	C <sub>10</sub> H <sub>32</sub> O <sub>3</sub> N <sub>2</sub> Si <sub>5</sub>
H <sub>12</sub>	1429	D <sub>50</sub> D <sub>1NH</sub>	443	C <sub>12</sub> H <sub>37</sub> O <sub>5</sub> N <sub>1</sub> Si <sub>6</sub>
H <sub>13</sub>	1440	D <sub>20</sub> D <sub>3NH</sub>	367	C <sub>10</sub> H <sub>33</sub> O <sub>2</sub> N <sub>3</sub> Si <sub>5</sub>
H <sub>14</sub>	1455	D <sub>20</sub> D <sub>3NH</sub>	367	C <sub>10</sub> H <sub>33</sub> O <sub>2</sub> N <sub>3</sub> Si <sub>5</sub>
H <sub>15</sub>	1510	D <sub>40</sub> D <sub>2NH</sub>	442	C <sub>12</sub> H <sub>38</sub> O <sub>4</sub> N <sub>2</sub> Si <sub>6</sub>
H <sub>16</sub>	1515	D <sub>40</sub> D <sub>2NH</sub>	442	C <sub>12</sub> H <sub>38</sub> O <sub>4</sub> N <sub>2</sub> Si <sub>6</sub>
H <sub>17</sub>	1518	D <sub>40</sub> D <sub>2NH</sub>	442	C <sub>12</sub> H <sub>38</sub> O <sub>4</sub> N <sub>2</sub> Si <sub>6</sub>
H <sub>18</sub>	1532	D <sub>10</sub> D <sub>4NH</sub>	366	C <sub>10</sub> H <sub>34</sub> O <sub>1</sub> N <sub>4</sub> Si <sub>5</sub>
H <sub>19</sub>	1613	D <sub>5NH</sub>	365	C <sub>10</sub> H <sub>35</sub> O <sub>0</sub> N <sub>5</sub> Si <sub>5</sub>
H <sub>20</sub>	1683	D <sub>20</sub> D <sub>4NH</sub>	440	C <sub>12</sub> H <sub>40</sub> O <sub>2</sub> N <sub>4</sub> Si <sub>6</sub>
H <sub>21</sub>	1690	D <sub>20</sub> D <sub>4NH</sub>	440	C <sub>12</sub> H <sub>40</sub> O <sub>2</sub> N <sub>4</sub> Si <sub>6</sub>
H <sub>22</sub>	1697	D <sub>20</sub> D <sub>4NH</sub>	440	C <sub>12</sub> H <sub>40</sub> O <sub>2</sub> N <sub>4</sub> Si <sub>6</sub>
H <sub>23</sub>	1785	D <sub>10</sub> D <sub>5NH</sub>	439	C <sub>12</sub> H <sub>41</sub> O <sub>1</sub> N <sub>5</sub> Si <sub>6</sub>
H <sub>24</sub>	1878	D <sub>6NH</sub>	438	C <sub>12</sub> H <sub>42</sub> O <sub>0</sub> N <sub>6</sub> Si <sub>6</sub>
H <sub>25</sub>	1942	D <sub>20</sub> D <sub>5NH</sub>	513	C <sub>14</sub> H <sub>47</sub> O <sub>2</sub> N <sub>5</sub> Si <sub>7</sub>
H <sub>26</sub>	2032	D <sub>10</sub> D <sub>6NH</sub>	512	C <sub>14</sub> H <sub>48</sub> O <sub>1</sub> N <sub>6</sub> Si <sub>7</sub>
H <sub>27</sub>	2121	D <sub>7NH</sub>	511	C <sub>14</sub> H <sub>49</sub> O <sub>0</sub> N <sub>7</sub> Si <sub>7</sub>
H <sub>28</sub>	2282	D <sub>10</sub> D <sub>7NH</sub>	585	C <sub>16</sub> H <sub>55</sub> O <sub>1</sub> N <sub>7</sub> Si <sub>8</sub>
H <sub>29</sub>	2372	D <sub>8NH</sub>	584	C <sub>16</sub> H <sub>56</sub> O <sub>0</sub> N <sub>8</sub> Si <sub>8</sub>
H <sub>30</sub>	2506	D <sub>10</sub> D <sub>8NH</sub>	658	C <sub>18</sub> H <sub>62</sub> O <sub>1</sub> N <sub>8</sub> Si <sub>9</sub>
H <sub>31</sub>	2540	D <sub>9NH</sub>	657	C <sub>18</sub> H <sub>63</sub> O <sub>0</sub> N <sub>9</sub> Si <sub>9</sub>
H <sub>32</sub>	2630	D <sub>10</sub> D <sub>9NH</sub>	731	C <sub>20</sub> H <sub>69</sub> O <sub>1</sub> N <sub>9</sub> Si <sub>10</sub>
M <sub>1</sub>	958	D <sub>20</sub> D <sub>1NMe</sub>	235	C <sub>7</sub> H <sub>21</sub> O <sub>2</sub> N <sub>1</sub> Si <sub>3</sub>
M <sub>2</sub>	1099	D <sub>10</sub> D <sub>2NMe</sub>	248	C <sub>8</sub> H <sub>24</sub> O <sub>1</sub> N <sub>2</sub> Si <sub>3</sub>
M <sub>3</sub>	1169	D <sub>30</sub> D <sub>1NMe</sub>	309	C <sub>9</sub> H <sub>27</sub> O <sub>3</sub> N <sub>1</sub> Si <sub>4</sub>
M <sub>4</sub>	1263	D <sub>3NMe</sub>	261	C <sub>9</sub> H <sub>27</sub> O <sub>0</sub> N <sub>3</sub> Si <sub>3</sub>
M <sub>5</sub>	1336	D <sub>20</sub> D <sub>2NMe</sub>	322	C <sub>10</sub> H <sub>30</sub> O <sub>2</sub> N <sub>2</sub> Si <sub>4</sub>
M <sub>6</sub>	1336	D <sub>20</sub> D <sub>2NMe</sub>	322	C <sub>10</sub> H <sub>30</sub> O <sub>2</sub> N <sub>2</sub> Si <sub>4</sub>
M <sub>7</sub>	1455	D <sub>10</sub> D <sub>3NMe</sub>	335	C <sub>11</sub> H <sub>33</sub> O <sub>1</sub> N <sub>3</sub> Si <sub>4</sub>
M <sub>8</sub>	1702	D <sub>4NMe</sub>	348	C <sub>12</sub> H <sub>36</sub> O <sub>0</sub> N <sub>4</sub> Si <sub>4</sub>
O <sub>3</sub>	822	D <sub>30</sub>	222	C <sub>6</sub> H <sub>18</sub> O <sub>3</sub> N <sub>0</sub> Si <sub>3</sub>
O <sub>4</sub>	1011	D <sub>40</sub>	296	C <sub>8</sub> H <sub>24</sub> O <sub>4</sub> N <sub>0</sub> Si <sub>4</sub>
O <sub>5</sub>	1173	D <sub>50</sub>	370	C <sub>10</sub> H <sub>30</sub> O <sub>5</sub> N <sub>0</sub> Si <sub>5</sub>
O <sub>6</sub>	1349	D <sub>60</sub>	444	C <sub>12</sub> H <sub>36</sub> O <sub>6</sub> N <sub>0</sub> Si <sub>6</sub>
O <sub>7</sub>	1525	D <sub>70</sub>	518	C <sub>14</sub> H <sub>42</sub> O <sub>7</sub> N <sub>0</sub> Si <sub>7</sub>
O <sub>8</sub>	1697	D <sub>80</sub>	592	C <sub>16</sub> H <sub>48</sub> O <sub>8</sub> N <sub>0</sub> Si <sub>8</sub>
O <sub>9</sub>	1861	D <sub>90</sub>	666	C <sub>18</sub> H <sub>54</sub> O <sub>9</sub> N <sub>0</sub> Si <sub>9</sub>
O <sub>10</sub>	2019	D <sub>100</sub>	740	C <sub>20</sub> H <sub>60</sub> O <sub>10</sub> N <sub>0</sub> Si <sub>10</sub>
O <sub>11</sub>	2176	D <sub>110</sub>	814	C <sub>22</sub> H <sub>66</sub> O <sub>11</sub> N <sub>0</sub> Si <sub>11</sub>
O <sub>12</sub>	2328	D <sub>120</sub>	888	C <sub>24</sub> H <sub>72</sub> O <sub>12</sub> N <sub>0</sub> Si <sub>12</sub>
O <sub>13</sub>	2477	D <sub>130</sub>	962	C <sub>26</sub> H <sub>78</sub> O <sub>13</sub> N <sub>0</sub> Si <sub>13</sub>
O <sub>14</sub>	2625	D <sub>140</sub>	1036	C <sub>28</sub> H <sub>84</sub> O <sub>14</sub> N <sub>0</sub> Si <sub>14</sub>

### 3.1.1. Six-membered ring compounds

Hexamethylcyclotrisilazane D<sub>3NH</sub> has been well studied [6,10–15,17–18]. We also obtained this pure

compound and we recorded the IR and Raman spectra. We compared the FT-IR spectrum of the gas corresponding to the peak H<sub>3</sub> with the IR spectrum of the liquid. We agree with the assignment of an intense absorption at *ca.* 930 cm<sup>-1</sup> to the ν<sub>a</sub>(SiNSi). We attributed the Raman bands at 637 cm<sup>-1</sup> to ν<sub>s</sub>(SiNSi) and that at 710 cm<sup>-1</sup> to ν<sub>s</sub>(SiC<sub>2</sub>), as did Kriegsmann [6].

Recently, Kravchenko [16] confirmed these assignments after a study of D<sub>3NH</sub> and of the two isotopic molecules [(CH<sub>3</sub>)<sub>2</sub>Si<sup>15</sup>NH]<sub>3</sub> and [(CH<sub>3</sub>)<sub>2</sub>SiND]<sub>3</sub>, he assigned the 1170 cm<sup>-1</sup> band to the in-plane deformation vibration, δ(NH), and that at 870 cm<sup>-1</sup> to the out-of-plane deformation γ(NH), according to the rules of symmetry.

Abel [12] agreed with the assignment of δ(NH) after a comparison of D<sub>3NH</sub>, D<sub>3NMe</sub> and D<sub>3NEt</sub>. He did not comment on γ(NH).

The absorption at 1168 cm<sup>-1</sup> is assigned to δ(NH). Since we observe 862 cm<sup>-1</sup> and 815 cm<sup>-1</sup> in the IR spectra and 853 cm<sup>-1</sup> in the Raman, we think that the γ(NH) mode is mixed with the r<sub>||</sub>(CH<sub>3</sub>)<sub>Si</sub>, so that there is always a strong IR band between 900 cm<sup>-1</sup> and 800 cm<sup>-1</sup>.

The mass spectrum showed that the compound corresponding to H<sub>1</sub> is D<sub>20</sub>D<sub>NH</sub>. Its IR spectrum has already been studied [10,11,13,17]. Although most workers assigned the 1025 cm<sup>-1</sup> band to ν<sub>a</sub>(SiOSi), Bush [17] ascribed two bands (1030 and 989 cm<sup>-1</sup>) to this vibration. The comparison of D<sub>20</sub>D<sub>NH</sub> with its *N*-silyl derivative D<sub>20</sub>D<sub>NSiMe<sub>3</sub></sub> led him to attribute the band at 989 cm<sup>-1</sup> to a siloxane mode, as suggested by Murray [10], rather than to a silazane mode. We agree with this interpretation, since two SiOSi groups are present in the molecule. We also found two bands for ν<sub>a</sub>(SiOSi), as shown in Table 4. Assignments for ν<sub>a</sub>(SiNSi) also conflict: 983 [11], 978 [6], 946 [13] or 910 cm<sup>-1</sup> [17]. We observed one absorption at 905 cm<sup>-1</sup>, not far from Bush's value and near the 902 cm<sup>-1</sup> observed for D<sub>20</sub>D<sub>NMe</sub>.

Concerning D<sub>O</sub>D<sub>2NH</sub>, corresponding by mass spectra to H<sub>2</sub>, various workers have made the following proposals: the bands at 1058 [13], 1000 [17], 995 cm<sup>-1</sup> [19] were assigned to ν<sub>a</sub>(SiOSi) and those at 946 [13], 930 [17], and 926 cm<sup>-1</sup> [19] to ν<sub>a</sub>(SiNSi). We think that Haiduc [13] did not obtain the same product as the others. Fink [19] noted that his mixture of siloxane-silazane studied by gas chromatography contained 27% D<sub>O</sub>D<sub>2NH</sub>, 10% D<sub>3NH</sub>, 39% D<sub>20</sub>D<sub>2NH</sub>, 22% D<sub>O</sub>D<sub>3NH</sub> and 2% D<sub>4NH</sub>.

Our results (Table 4) are in fair agreement with those of Fink [19] and Bush [17], since we found very strong absorptions at 1015 and 930 cm<sup>-1</sup> assigned to ν<sub>a</sub>(SiOSi) and ν<sub>a</sub>(SiNSi), respectively. A weak shoulder

TABLE 2. Nature and intensity (I%) of the most important ions found in the mass spectra of the major cyclosiloxazanes (N-H) of reaction mixture A

Compound name	M <sup>+</sup>	a	b	c	d	e	f	g	h		i	j								
									D <sub>3NH</sub>	D <sub>10D<sub>3NH</sub></sub>										
	m/z	I%	M-CH <sub>3</sub>	I%	a-CH <sub>4</sub>	I%	a-NH <sub>3</sub>	I%	a-D <sub>1NH</sub>	I%	a-D <sub>2NH</sub>	I%	a-D <sub>10</sub>	I%	-Me	I%	SiMe <sub>3</sub>	I%	(m-C <sub>3</sub> H <sub>6</sub> ) <sup>2+</sup>	I%
D <sub>20</sub> D <sub>1NH</sub>	221	0.5	206	100	190	11	189	1.6	133	1	-	-	132	4.5	-	-	73	3	95.5	11
D <sub>10</sub> D <sub>2NH</sub>	220	0.1	205	100	189	13	188	4.1	132	2.5	59	1.3	131	4.4	205	100	-	-	95	14
D <sub>3NH</sub>	219	0.3	204	100	188	17	187	10	131	6.7	58	0.1	-	-	205	0	204	100	73	19
D <sub>30</sub> D <sub>1NH</sub>	295	0.7	280	100	264	8.8	263	0	207	1.5	-	-	206	2.5	205	3	204	0.8	73	3.6
D <sub>20</sub> D <sub>2NH</sub>	294	0.6	279	100	263	8.6	262	2.7	206	3.2	133	0.9	205	1.5	205	1.5	-	-	5	3.6
D <sub>10</sub> D <sub>3NH</sub>	293	0.4	278	100	262	9.9	261	4.3	205	2	132	1.7	204	0.5	205	2	204	0.5	73	1.7
D <sub>4NH</sub>	292	0.2	277	100	261	14	260	14	204	1.7	131	7.2	-	-	205	0	204	1.7	4.6	7.2
D <sub>10</sub> D <sub>4NH</sub>	366	0.2	351	79	335	0	334	100	278	1.9	205	8.9	277	0	205	10	204	4	73	13
D <sub>5NH</sub>	365	0.5	350	52	334	0	333	100	277	1.7	204	17	-	-	205	0	204	17	73	0
D <sub>10</sub> D <sub>5NH</sub>	439	1.2	424	10	408	0	407	100	351	0	278	15	350	0	205	7	204	25	73	0
D <sub>6NH</sub>	438	1.7	423	2.4	407	0	406	100	350	0	277	14	-	-	205	0	204	42	73	0

TABLE 3. Nature and intensity (I%) of the most important ions found in the mass spectra of the major cyclosiloxazanes (N-Me) of reaction mixture B

Compound name	M <sup>+</sup>	a	b	c	d	e	f	g	h	i	j	k	l	m						
															M-CH <sub>3</sub>	I%	a-D <sub>1NMe</sub>	I%	a-D <sub>2NMe</sub>	I%
D <sub>20</sub> D <sub>1NMe</sub>	235	7.7	220	100	133	2.2	-	146	0	73	11	102.5	4.1	191	0	177	3	119	0	
D <sub>10</sub> D <sub>2NMe</sub>	248	3.7	233	100	146	1.1	59	4.4	159	0	73	4.6	109	4.7	204	0	190	3.5	132	2.6
D <sub>3NMe</sub>	261	12	246	100	159	10	72	3.5	-	-	73	3.6	115.5	7.3	217	2.2	203	4.9	145	3.5
D <sub>30</sub> D <sub>1NMe</sub>	309	8	294	100	207	10	-	220	0	73	35	139.5	4	265	0	251	7	193	20	
D <sub>20</sub> D <sub>2NMe</sub>	322	7.7	307	100	220	18	133	6.2	233	2.5	73	55	146	6.2	278	6.2	264	3.1	206	12
D <sub>10</sub> D <sub>3NMe</sub>	335	5.6	320	100	233	16	146	16	246	3.4	73	45	152.5	2.9	291	7.4	277	4.5	219	40
D <sub>4NMe</sub>	348	5.9	333	100	246	5.5	159	17	-	-	73	9	159	17	304	2.5	290	2.9	232	15

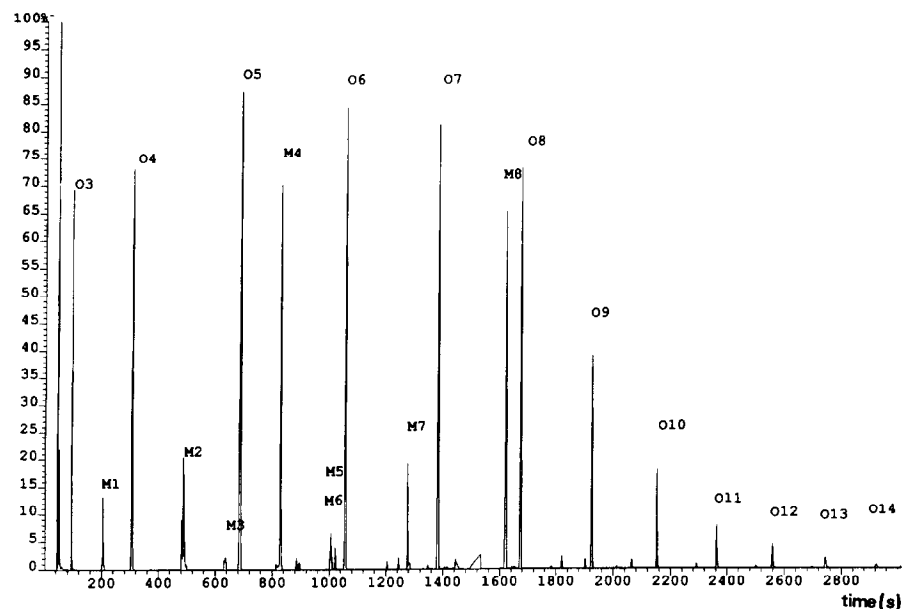


Fig. 2. Chromatogram (GC/MS) of reaction mixture B.

at  $896\text{ cm}^{-1}$  was due to another  $\nu_a(\text{SiNSi})$ . As does Bush [17], we assign the bands at  $1166\text{ cm}^{-1}$  to  $\delta(\text{NH})$  and  $803\text{ cm}^{-1}$  to  $\gamma(\text{NH})$ . Haiduc [13] reported different frequencies, confirming that his compound was not  $\text{D}_0\text{D}_{2\text{NH}}$ .

### 3.1.2. Eight-membered ring compounds

After various authors [10,11,13,14,19] published partial data, Imbenotte [8] reported the IR and Raman spectra of octamethylcyclotetrasilazane ( $\text{D}_{4\text{NH}}$ ) in different states (gas, liquid, crystal). We also recorded the IR and Raman spectra of this molecule in solid state and agree with Imbenotte.

In the mixture studied, we identified peak  $\text{H}_9$  for  $\text{D}_{4\text{NH}}$  (gas),  $\nu_a(\text{SiNSi})$  being at  $945\text{ cm}^{-1}$  (Table 4).

For  $\text{D}_{30}\text{D}_{\text{NH}}$ , corresponding to  $\text{H}_4$  as shown by the mass spectrum, all previous authors [11–13] assigned two bands about  $1065$  and  $1025\text{ cm}^{-1}$  to  $\nu_a(\text{SiOSi})$  and

the absorption at  $926 \pm 2\text{ cm}^{-1}$  to  $\nu_a(\text{SiNSi})$ . As shown in Table 4, we obtained two bands for  $\nu_a(\text{SiOSi})$  and one absorption for  $\nu_a(\text{SiNSi})$ . These results seem logical since three different SiOSi groups and just one SiNSi group are present in the molecule.

The chromatogram (Fig. 1) exhibits two peaks  $\text{H}_5$  and  $\text{H}_6$  for the  $\text{D}_{20}\text{D}_{2\text{NH}}$  molecule. Haiduc [13] prepared the two isomers. When two oxygen atoms and the nitrogen atoms are opposed, he found only a single band ( $1059\text{ cm}^{-1}$ ) assignable to  $\nu_a(\text{SiOSi})$ . In the other case, where the SiOSiSi sequence is present, he observed two bands ( $1038$  and  $1068\text{ cm}^{-1}$ ). We obtained the strongest absorption at  $1040\text{ cm}^{-1}$  and two other bands at  $1070$  and  $1057\text{ cm}^{-1}$  that we assign to  $\nu_a(\text{SiOSi})$ . It seems that we had a mixture of the two isomers. Since two bands ( $943$  and  $930\text{ cm}^{-1}$ ) are still produced by  $\nu_a(\text{SiNSi})$ , the molecule studied is  $\text{D}_{20}\text{D}_{2\text{NH}}$  (Fig. 3).

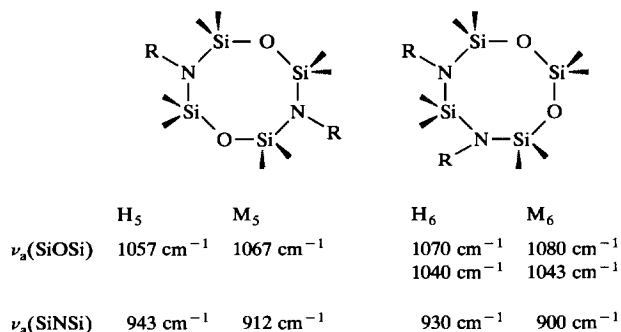


Fig. 3. Isomers of  $\text{D}_{20}\text{D}_{2\text{NR}}$  with  $\text{R} = \text{H}$  ( $\text{H}_5$  and  $\text{H}_6$ ) and  $\text{R} = \text{Me}$  ( $\text{M}_5$  and  $\text{M}_6$ ).

TABLE 4. Frequency assignments for the mixture of cyclic siloxanes, silazanes and siloxazanes with N-H substituents<sup>a</sup>

		$\nu_a(\text{SiOSi})$	$\nu_a(\text{SiNSi})$	$\delta(\text{NH})$	$\delta_s(\text{CH}_3)_{\text{Si}}$	$r_{\parallel}(\text{CH}_3)_{\text{Si}}$	$r_{\parallel}(\text{CH}_3)_{\text{Si}}$ $\gamma(\text{NH})$ $\nu_a(\text{SiC}_2)$
O <sub>3</sub>	D <sub>3O</sub>	1026vs			1264mw	817mw	
H <sub>1</sub>	D <sub>2O</sub> D <sub>NH</sub>	1036vs 995m	905mw	1156m	1263m	806ms	
H <sub>2</sub>	D <sub>O</sub> D <sub>2NH</sub>	1015vs	930vs	1166s	1261m	803s	
H <sub>3</sub>	D <sub>3NH</sub>	-	930vs	1168s	1257m	812mw, sh 795mw	
O <sub>4</sub>	D <sub>4O</sub>	1084vs	-	-	1264m	813ms	
H <sub>4</sub>	D <sub>3O</sub> D <sub>NH</sub>	1069vs 1044s	942m	1184ms	1264s	811s	
H <sub>5</sub> and H <sub>6</sub>	D <sub>2O</sub> D <sub>2NH</sub>	1070sh 1057sh	943m	1185s	1263ms	797s	
H <sub>8</sub>	D <sub>O</sub> D <sub>3NH</sub>	1054m	944vs	1188s	1261ms	813m	
H <sub>9</sub>	D <sub>4NH</sub>	-	945vs	1183ms	1260m	811m	
O <sub>5</sub>	D <sub>5O</sub>	1099vs 1079s, sh	-	-	1264m	808m	
H <sub>18</sub>	D <sub>O</sub> D <sub>4NH</sub>	1070m	941vs	1187s	1259s	812s	
H <sub>19</sub>	D <sub>5NH</sub>	-	936vs 958sh	1197m	1261s	806s	

<sup>a</sup> s, strong; m, medium; w, weak; v, very; sh, shoulder;  $\nu$  in  $\text{cm}^{-1}$ .

In the FT-IR spectrum of the peak H<sub>8</sub> (D<sub>O</sub>D<sub>3NH</sub>), we observed a very strong absorption at 944  $\text{cm}^{-1}$  assigned to  $\nu_a(\text{SiNSi})$  and a medium band at 1054  $\text{cm}^{-1}$  [ $\nu_a(\text{SiOSi})$ ]. Moreover, because the band at 1188  $\text{cm}^{-1}$  is more intense than the 1261  $\text{cm}^{-1}$  band, we conclude that NH groups are more numerous than SiOSi groups, consistent with a D<sub>O</sub>D<sub>3NH</sub> molecule. Haiduc [13] proposed bands at 945  $\text{cm}^{-1}$  for  $\nu_a(\text{SiNSi})$  and at 1047  $\text{cm}^{-1}$  for  $\nu_a(\text{SiOSi})$ .

The strongest band in the H<sub>18</sub> spectrum is at 941  $\text{cm}^{-1}$ . A medium absorption observed at 1070  $\text{cm}^{-1}$  led us to identify this compound as D<sub>O</sub>D<sub>4NH</sub>. It was confirmed by mass spectrometry, but there are no IR data in the literature for this molecule.

Finally, for the last peak H<sub>19</sub>, we observed an intense band at 936  $\text{cm}^{-1}$  with a shoulder at 958  $\text{cm}^{-1}$  that we assign to  $\nu_a(\text{SiNSi})$ . Since no absorption could be assigned to  $\nu_a(\text{SiOSi})$ , we conclude that D<sub>5NH</sub> is present, consistent with the mass spectrometry.

The frequency of  $\nu_a(\text{SiNSi})$  is nearly constant for eight-membered ring compounds.

### 3.2. Reaction mixture B (Table 5)

The chromatogram shows the following sequence: D<sub>3O</sub>, D<sub>2O</sub>D<sub>NMe</sub>, D<sub>4O</sub>, D<sub>O</sub>D<sub>2NMe</sub>, D<sub>3O</sub>D<sub>NMe</sub>, D<sub>5O</sub>, D<sub>3NMe</sub>, D<sub>2O</sub>D<sub>2NMe</sub>, D<sub>6O</sub>, D<sub>O</sub>D<sub>3NMe</sub>, D<sub>7O</sub> and D<sub>4NMe</sub>, which is quite different from the mixture A sequence.

#### 3.2.1. Six-membered ring compounds

Since we prepared D<sub>3NMe</sub> and obtained the IR and Raman spectra of this pure compound (m.p. = 35°C) it was possible to identify this compound easily. Abel [12] published the frequencies for D<sub>3NMe</sub> and found bands at 1210, 1069 and 995  $\text{cm}^{-1}$ . Lienhard [20] also obtained D<sub>3NMe</sub> and gave the frequencies as 1190, 1055 and 930  $\text{cm}^{-1}$ .

For the peak M<sub>4</sub>, we found bands at 1197, 1059 and 924  $\text{cm}^{-1}$  on the FT-IR spectrum of the gas (Table 5). With Lienhard [20], we concur in assigning the band at 924  $\text{cm}^{-1}$  to  $\nu_a(\text{SiNSi})$  but we would rather attribute our band at 1197  $\text{cm}^{-1}$  to the parallel rocking of the methyl-nitrogen bond  $r_{\parallel}(\text{CH}_3)_\text{N}$  and the absorption at

TABLE 5. Frequency assignments for the mixture of cyclic siloxanes, silazanes and siloxazanes with N-Me substituents<sup>a</sup>

		$\nu_a(\text{SiOSi})$	$\nu_a(\text{SiNSi})$	$r_{\parallel}(\text{CH}_3)_\text{N}$	$\nu(\text{CN})$	$\delta_s(\text{CH}_3)_{\text{Si}}$	$r_{\parallel}(\text{CH}_3)_{\text{Si}}$ $\nu_a(\text{SiC}_2)$
O <sub>3</sub>	D <sub>3O</sub>	1026vs	-	-	-	1264mw	817mw
M <sub>1</sub>	D <sub>2O</sub> D <sub>NMe</sub>	1038vs 996ms	902m	1191w	1080m	1263s	809ms
M <sub>2</sub>	D <sub>O</sub> D <sub>2NMe</sub>	1042s	927vs	1200mw	1059s	1260s	815mw, sh 794m
M <sub>4</sub>	D <sub>3NMe</sub>	-	924vs	1197m	1059s	1259s	813mw, sh 785m
O <sub>4</sub>	D <sub>4O</sub>	1084vs	-	-	-	1264m	813ms
M <sub>3</sub>	D <sub>3O</sub> D <sub>NMe</sub>	1049s 1028mw	906mw	1182mw	1085ms	1263m	801ms
M <sub>5</sub> and M <sub>6</sub>	D <sub>2O</sub> D <sub>2NMe</sub>	1080s 1067m 1043s	912m 900mw	1184mw 1169mw	1080s	1265s	806s
M <sub>7</sub>	D <sub>O</sub> D <sub>3NMe</sub>	1080m	910s	1187w	1070vs	1265m	807s
M <sub>8</sub>	D <sub>4NMe</sub>	-	906vs	1185w	1069s	1260ms	810mw 788w

<sup>a</sup> See Table 4.

1059  $\text{cm}^{-1}$  to  $\nu(\text{C-N})$ . Indeed, in the  $(\text{CH}_3)_3\text{N}$  derivative studied by Kress [21] together with  $(\text{CD}_3)_3\text{N}$ , the 1195  $\text{cm}^{-1}$  IR band was assigned to  $r_{\parallel}(\text{CH}_3)_\text{N}$ , ( $A_1$  type); the very intense absorption at 1271  $\text{cm}^{-1}$  and the very strong Raman band at 829  $\text{cm}^{-1}$  were assigned to  $\nu_d(\text{NC}_3)$  (E type) and to  $\nu_s(\text{NC}_3)$  ( $A_1$  type), respectively. The average  $\nu(\text{CN})$  is about 1050  $\text{cm}^{-1}$ . In *N*-methylhexamethylcyclotrisilazane, we assign the 1059  $\text{cm}^{-1}$  band to  $\nu(\text{CN})$ . For  $[(\text{CH}_3)_3\text{Si}]_2\text{NCH}_3$ , Goubeau [18] assigned 1185  $\text{cm}^{-1}$  to  $r(\text{CH}_3)_\text{N}$  and 1065  $\text{cm}^{-1}$  to  $\nu(\text{CN})$ , consistent with our interpretation.

We could find no earlier data on cyclic siloxazanes with a nitrogen-methyl bond. So we identified these compounds by comparison with the GC/MS results. Our interpretation is given in Table 5. The difference in the intensities of the main bands assigned to  $\nu_a(\text{SiOSi})$  and  $\nu_a(\text{SiNSi})$  but also to  $\nu(\text{CN})$  and  $r_{\parallel}(\text{CH}_3)_\text{N}$  were of great help in deciding whether the molecule contains one or more SiOSi or SiNSi groups, and a number of N- $\text{CH}_3$  bonds.

After identification of the  $\text{O}_3$  peak (the compound  $\text{D}_{3\text{O}}$ ) in the  $M_1$  spectrum, two bands were assigned to  $\nu_a(\text{SiOSi})$  (compare Bush [17] and ourselves for  $\text{D}_{2\text{O}}\text{D}_{\text{NH}}$ ). The presence of two SiOSi groups can explain this double band. Moreover, only one band (902  $\text{cm}^{-1}$ ) corresponds to  $\nu_a(\text{SiNSi})$ . The compound could be  $\text{D}_{2\text{O}}\text{D}_{\text{NMe}}$  as suggested by mass spectrometry. The intensities of the 1080 and 902  $\text{cm}^{-1}$  bands are nearly the same, and weaker than the 1263  $\text{cm}^{-1}$  absorption assigned to  $\delta_s(\text{CH}_3)_\text{Si}$ .

On the other hand, since the absorption for the peak  $M_2$  at 1059  $\text{cm}^{-1}$  ( $\nu(\text{CN})$ ) is as strong as the band at 1260  $\text{cm}^{-1}$  ( $\delta_s(\text{CH}_3)_\text{Si}$ ) it is possible that we have more SiNSi groups than in  $\text{D}_{2\text{O}}\text{D}_{\text{NMe}}$ . The strongest band observed in the  $M_2$  spectrum is indeed at 927  $\text{cm}^{-1}$  with a shoulder at 890  $\text{cm}^{-1}$ ; both are assigned to  $\nu_a(\text{SiNSi})$ . As the band at 1042  $\text{cm}^{-1}$  ( $\nu_a(\text{SiOSi})$ ) is less intense than the 927  $\text{cm}^{-1}$  absorption, we conclude that the compound studied is  $\text{D}_{\text{O}}\text{D}_{2\text{NMe}}$ , consistent with the mass spectrum.

### 3.2.2. Eight-membered ring compounds

We synthesized  $\text{D}_{4\text{NMe}}$  and studied the IR and Raman spectra from 4000  $\text{cm}^{-1}$  to 200  $\text{cm}^{-1}$ . In the FT-IR spectrum of the gas, we observed a very strong, broad band with a maximum at 906  $\text{cm}^{-1}$  (peak  $M_5$ ) that we assigned to  $\nu_a(\text{SiNSi})$ .  $\nu(\text{CN})$  corresponding to the band at 1060  $\text{cm}^{-1}$  is very strong, as expected from the number of N- $\text{CH}_3$  groups.

Wannagat [22] has also synthesized  $\text{D}_{4\text{NMe}}$  and proposed for  $\nu_a(\text{SiNSi})$  the 913  $\text{cm}^{-1}$  absorption and for  $\nu(\text{CN})$  the intense absorption at 1078  $\text{cm}^{-1}$ . We agree with this interpretation.

For the  $M_3$  peak of the chromatogram, the mass spectrum shows that the compound is  $\text{D}_{3\text{O}}\text{D}_{\text{NMe}}$ . In its FT-IR spectrum, we assign the two bands, 1049 and 1028  $\text{cm}^{-1}$ , to  $\nu_a(\text{SiOSi})$  as did Krüger [10], Murray [11], and ourselves for  $\text{D}_{3\text{O}}\text{D}_{\text{NH}}$ . The presence of three SiOSi groups can explain this double band. The medium absorption at 906  $\text{cm}^{-1}$  is due to  $\nu_a(\text{SiNSi})$  and the shoulder at 1085  $\text{cm}^{-1}$  is assigned to  $\nu(\text{CN})$ . Those arguments favour a  $\text{D}_{3\text{O}}\text{D}_{\text{NMe}}$  molecule.

On the spectra of peaks  $M_5$ - $M_6$ , we observed three bands at 1080, 1067, and 1043  $\text{cm}^{-1}$  due to  $\nu_a(\text{SiOSi})$  and two bands 912 and 900  $\text{cm}^{-1}$  attributed to  $\nu_a(\text{SiNSi})$ . We think that we have in our mixture the two isomers of  $\text{D}_{2\text{O}}\text{D}_{2\text{NMe}}$  (Fig. 3) which were not separated by chromatography. It was the same for  $\text{D}_{2\text{O}}\text{D}_{2\text{NH}}$ . The rather strong band at 1080  $\text{cm}^{-1}$  is assigned to  $\nu(\text{CN})$ .

The intensities observed for the last siloxazane, corresponding to the peak  $M_7$ , lead us to assign the medium shoulder at 1080  $\text{cm}^{-1}$  to  $\nu_a(\text{SiOSi})$ . The most intense band (1070  $\text{cm}^{-1}$  due to  $\nu(\text{CN})$ ) is at the same position as in  $\text{D}_{4\text{NMe}}$ . The absorption at 910  $\text{cm}^{-1}$ , stronger than in  $\text{D}_{2\text{O}}\text{D}_{2\text{NMe}}$ , is assigned to  $\nu_a(\text{SiNSi})$ .

We conclude that  $\text{D}_{\text{O}}\text{D}_{3\text{NMe}}$  is present, consistent with the mass spectrometry results.

## 4. Discussion

### 4.1. Six-membered series

Comparison of the NH and NMe derivatives shows two bands for  $\nu_a(\text{SiOSi})$  in both  $\text{D}_{2\text{O}}\text{D}_{\text{NR}}$ , whatever the substituent R. On the other hand, in  $\text{D}_{\text{O}}\text{D}_{2\text{NR}}$  the frequency assigned to this vibration is about 30  $\text{cm}^{-1}$  higher for the N-Me compound.

$\nu_a(\text{SiNSi})$  is a little higher in NH compounds, for each pair of molecules  $\text{D}_{2\text{O}}\text{D}_{\text{NR}}$ ,  $\text{D}_{\text{O}}\text{D}_{2\text{NR}}$  and  $\text{D}_{3\text{NR}}$ .

### 4.2. Eight-membered series

The position of the  $\nu_a(\text{SiNSi})$  allows us to distinguish NH compounds from NMe, the former being 30 or 40  $\text{cm}^{-1}$  higher than the latter. In linear molecules  $(\text{Me}_3\text{Si})_2\text{NR}$ , this vibration is at 934 for R = H and 906  $\text{cm}^{-1}$  for R = Me [23].

Tables 4 and 5 show that  $\nu_a(\text{SiNSi})$  frequencies are very similar in each series of compounds R = H or R = Me.

While all three  $\nu_a(\text{SiOSi})$  bands have approximately the same frequency for the  $\text{D}_{2\text{O}}\text{D}_{2\text{NR}}$  pair, we note a 20  $\text{cm}^{-1}$  difference between the frequencies observed in  $\text{D}_{3\text{O}}\text{D}_{\text{NR}}$  pairs. We also find in the case of  $\text{D}_{\text{O}}\text{D}_{3\text{NR}}$ , a frequency for  $\nu_a(\text{SiOSi})$  higher (26  $\text{cm}^{-1}$ ) in the N-Me molecule than in NH compound.



## 5. Cyclic siloxanes

We report here the spectra of many cyclosiloxanes. The first  $O_3$  peak identified in the mixture was  $D_{30}$ . The very intense absorption at  $1026\text{ cm}^{-1}$  was easily assigned to  $\nu_s(\text{SiOSi})$ , consistent with earlier authors [6,7,13,15,24,25].

As shown in Tables 4 and 5, we observe an increase of  $60\text{ cm}^{-1}$  for  $\nu_s(\text{SiOSi})$  when we pass from  $D_{30}$  to  $D_{40}$ . After that, the frequency begins to decrease from five-membered rings to larger cycles (1099–1079,  $D_{50}$ ; 1089–1081,  $D_{60}$ ; 1062,  $D_{70}$ ;  $1056\text{ cm}^{-1}$   $D_{80}$ ). We note a small drop of the band near  $810\text{ cm}^{-1}$  from  $D_{30}$  (817) to  $D_{80}$  ( $805\text{ cm}^{-1}$ ).

Our conclusions are in good agreement with those of Lee Smith [7], ( $D_{30}$ – $D_{40}$ ) and of Fogarasi [24] ( $D_{30}$ – $D_{60}$ ).

We have shown [26] that there is a correlation between the difference of frequencies  $\Delta\nu = \nu_s(\text{SiOSi}) - \nu_s(\text{SiOSi})$  and the size of the Si–O–Si angles in small molecules. It seems that for higher molecules  $D_{nO}$  the Si–O–Si angle is constant if  $n > 3$ .

Oberhammer [27] discussed the structure of different cyclic methyl siloxanes and concluded that the “large ring molecules do not possess any well-defined conformation”.

## 6. Conclusion

Even though chromatography did not allow us to isolate all the compounds present, they could be characterized by the FT-IR spectra and the frequencies assigned. An N–H compound can easily be distinguished from a N–Me derivative by the N–H or N–Me vibrations [especially  $\delta(\text{NH})$  or  $\nu(\text{CN})$ ]. If the frequencies assigned to  $\nu_s(\text{SiNSi})$  or  $\nu_s(\text{SiOSi})$  are no guide to identifying a component in a mixture, since defined structures are not known, the number and the relative intensities of particular absorptions can give information on the composition of the molecules studied. With isomers, FT-IR spectrometry has given complementary data to mass spectrometry; different IR bands were assigned to each type of isomer. With the mass spectra, every siloxazane, siloxane or silazane was identified unambiguously.

A comparison of the Raman and IR spectra of different cyclodisilazanes with  $D_{3\text{NH}}$ ,  $D_{3\text{NMe}}$ ,  $D_{3\text{NEt}}$ ,  $D_{4\text{NH}}$ , and  $D_{4\text{NMe}}$  will be published later.

## 7. Experimental details

Hexamethylcyclotrisilazane ( $D_{3\text{NH}}$ ) and octamethylcyclotetrasilazane ( $D_{4\text{NH}}$ ) are commercial products, and nonamethylcyclotrisilazane ( $D_{3\text{NMe}}$ ) and dodecamethyl-

cyclotetrasilazane ( $D_{4\text{NMe}}$ ) were synthesized according to known methods [12,22,28]. The reaction mixtures A and B were prepared in 1,2-dichloroethane.

GC/MS was performed using a Fisons Instruments AutoSpec-Q hybrid mass spectrometer coupled with a Hewlett Packard 5890 gas chromatograph equipped with split glass injector and a CP-Sil5-CB (Chrompack, Middlebourg, The Netherlands) fused silica capillary column ( $25\text{ m} \times 0.25\text{ mm}$  i.d., film thickness  $0.12\text{ }\mu\text{m}$ ). Injector and interface temperatures were 280 and  $240^\circ\text{C}$ , respectively. The oven temperature was maintained at  $50^\circ\text{C}$  for 5 min and then raised to  $300^\circ\text{C}$  at a rate of  $4^\circ\text{C}/\text{min}$ .

Mass spectra were recorded under electron impact conditions (70 eV, 200  $\mu\text{A}$  ionizing current,  $180^\circ\text{C}$  source temperature). Low-resolution GC/MS mass spectra were obtained under fast scanning conditions: 0.3 s/decade, mass range from  $m/z$  1035 to  $m/z$  35, interscan delay 0.55 s (cycle of 1 s). High-resolution (8000) GC/MS were performed at a lower scan rate: 0.7 s/decade, mass range from  $m/z$  900 to 35, interscan delay 0.51 s (cycle of 1.5 s); perfluorokerosene was used as internal standard for mass calibration. The accuracy of mass measurements was better than 10 ppm.

Kovats indexes [4] were measured by comparing the retention times of the compounds studied with those of n-alkanes contained in a reference mixture.

All manipulation of products was carried out under anhydrous conditions ( $\text{N}_2$  atmosphere) using dried materials.

Infrared spectra were obtained from 4000 to  $200\text{ cm}^{-1}$  on a Perkin-Elmer Model 683 recording spectrometer (accuracy  $\pm 2\text{ cm}^{-1}$ ) in cells with KBr or TlBr (“KRS 5”) plates. Powders were examined as KBr pellets. The experiments were computer-controlled, the spectra being processed and data accumulated for low absorptions.

FT-IR spectra were performed using a Nicolet Model 20 SXB with a GC/IR interface ( $4000$ – $600\text{ cm}^{-1}$ , accuracy  $\pm 4\text{ cm}^{-1}$ ). This spectrometer was coupled with a Carlo Erba 6000 gas chromatograph equipped with a CP-Sil 5-CB fused silica capillary column ( $30\text{ m} \times 0.32\text{ mm}$  i.d., film thickness  $1.0\text{ }\mu\text{m}$ ). The injection temperature was  $250^\circ\text{C}$  and the detection temperature was  $225^\circ\text{C}$ . The oven temperature was maintained at  $50^\circ\text{C}$  for 2 min and then raised to  $200^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ . This apparatus enabled us to obtain FT-IR spectra of each pure product, using only some micrograms without preliminary physical separation. The experiment was repeated several times and proved the reproducibility of the results.

Raman spectra were performed on a Dilor Model XY ( $4000$ – $100\text{ cm}^{-1}$ , accuracy  $\pm 2\text{ cm}^{-1}$ ) with a He–Ne

laser (632.8 nm) under computer control. Pure liquids or powders were used.

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