

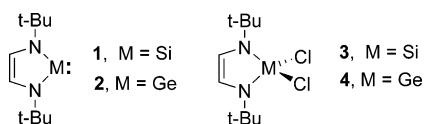
## The Raman Spectrum and Aromatic Stabilization in a Cyclic Germylene

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Silylene **1**, first synthesized in 1994,<sup>1</sup> is remarkably robust, decomposing only at its melting point of 220 °C. The stability of **1** probably results in part from both  $\pi$ -electron donation and  $\sigma$ -electron withdrawal by the two nitrogen atoms attached to silicon. In addition, **1** contains six  $\pi$ -electrons in the ring and thus may be considered to be an aromatic compound. A number of publications, both theoretical<sup>2–5</sup> and experimental,<sup>6–9</sup> dealing with the chemical bonding in **1** have appeared, leading to the general conclusion that aromatic delocalization also contributes to its stability.<sup>10</sup>

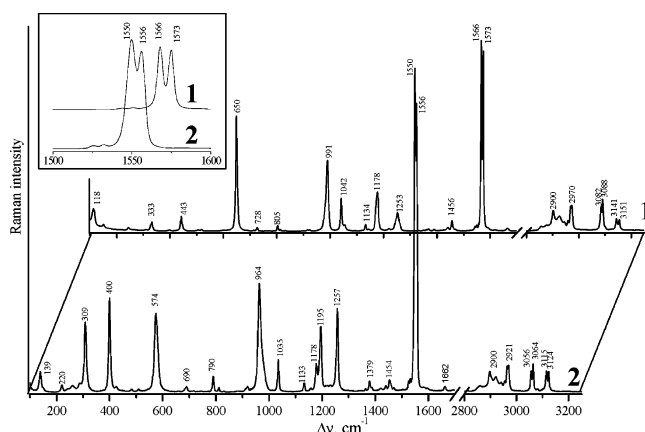


Germylene **2**,<sup>11</sup> the germanium analogue to **1**, is also thermally stable, but its chemical bonding has not been so thoroughly investigated. Three papers have, however, presented theoretical calculations supporting the idea that  $\pi$ -delocalization contributes to the stabilization of **2**,<sup>3,4,11</sup> and a recent paper reports inner shell electron energy loss spectra, also interpreted as indicating aromaticity in **2**.<sup>9</sup>

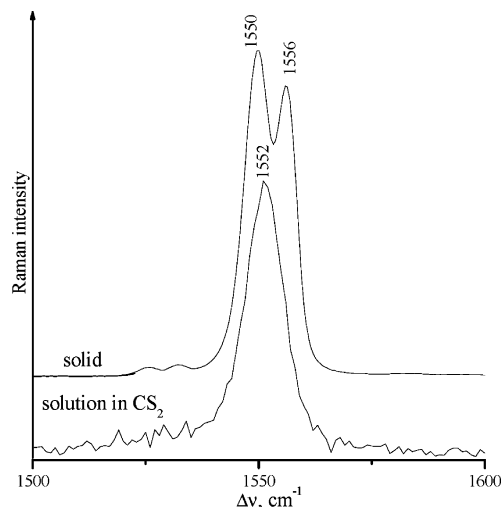
Raman spectra are known to be a highly sensitive indicator of conjugation. The latter leads to a decrease in frequency and a manifold intensity enhancement of polarized lines corresponding to the symmetric stretching vibrations of bonds participating in the conjugation.<sup>12</sup> Our Raman results for **1** showed that the  $\nu_{C=C}$  mode is shifted about 50  $\text{cm}^{-1}$  to lower frequency compared to analogous tetravalent silicon compounds, such as **3**, and is dramatically enhanced, providing strong evidence for cyclic  $\pi$ -conjugation in **1**.<sup>8</sup>

We report here the Raman spectrum of **2**, as a test of aromatic delocalization in this germylene.<sup>13</sup> The spectrum for solid **2** is shown along with that for **1** in Figure 1. The two spectra are quite similar in their overall patterns, but it is noteworthy that the  $\nu_{C=C}$  stretching frequency for **2** is lower than that for **4** by 80  $\text{cm}^{-1}$ .<sup>14</sup> It is also lower than that for **1** (by about 25  $\text{cm}^{-1}$ ) and is strongly enhanced compared to **1** by a factor of about 2 (both spectra are normalized so as to make the intensity of the lines corresponding to the vibrations of the  $\text{CH}_3$  groups, not participating in the conjugation, nearly equal). The  $\nu_{C=C}$  Raman lines for both compounds are split into doublets (1566/1573  $\text{cm}^{-1}$  for **1**, 1550/1556  $\text{cm}^{-1}$  for **2**). This splitting is evidently due to the Davydov effect (correlation field splitting)<sup>15</sup> since it disappears in solution, where only a single polarized band at 1552  $\text{cm}^{-1}$  is observed for **2** (Figure 2).

Before considering the implications of the decrease in  $\nu_{C=C}$ , it is necessary to ascertain that the normal mode associated with the  $C=C$  vibration is well localized and does not involve displacements



**Figure 1.** Raman spectra of solid **1** and **2**, excited by 514.5 nm Ar<sup>+</sup> laser line. The spectra are normalized so as to make the intensity of the bands corresponding to the  $\nu_{\text{CH}}$  and  $\delta_{\text{CH}}$  vibrations in  $\text{CH}_3$  groups nearly equal. The  $\nu_{\text{C}=\text{C}}$  lines are compared in the inset in more detail.



**Figure 2.** The  $\nu_{\text{C}=\text{C}}$  region in the Raman spectra of solid **2** and its solution in  $\text{CS}_2$ .

of the heavier Si or Ge atoms. Therefore, normal coordinate calculations<sup>16</sup> were carried out for **1** and **2** in the  $C_{2v}$  point symmetry group, using the experimental geometries<sup>11,17</sup> and a phenomenological force field model.<sup>18</sup> It is notable that the vibrational spectra of both compounds could best be described with the use of a typical “aromatic” force field, such as that used for benzene, with increased off-diagonal force constants.<sup>16</sup> The resulting eigenvectors allowed assignments to be made. In particular, the intense lines at 650  $\text{cm}^{-1}$  for **1** and 574  $\text{cm}^{-1}$  for **2** were shown to correspond to the stretching vibrations of the M–N bonds, and those at 991  $\text{cm}^{-1}$  for **1** and 964  $\text{cm}^{-1}$  for **2** to complex modes with participation of stretching

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**Table 1.** Frequency and Potential Energy Distribution for the  $\nu_{C=C}$  Mode for **1** and **2**

M	$\nu, \text{cm}^{-1}$	PED, %
Si ( <b>1</b> )	1576	62 C=C, 12 NCH, 9 C-N, 6 CCH, 3.5 N-C <sup>rtBu</sup> , 3 CCN
Ge ( <b>2</b> )	1552	60 C=C, 13 NCH, 9.5 C-N, 6.5 CCH, 4 N-C <sup>rtBu</sup> , 3 CCN

$\nu_{M-N}$  and  $\nu_{N-C}$  (both endo- and exo-cyclic) coordinates along with angle deformations. The eigenvectors of the so-called  $\nu_{C=C}$  vibration are similar for **1** and **2** and show that the Si and Ge atoms do not take any part in this normal mode. The corresponding potential energy distributions are given in Table 1.

Thus, the shift in mode frequency on going from **1** to **2** is purely electronic in nature and reflects a real decrease in the  $K_{C=C}$  force constant. This result, along with the greater Raman intensity enhancement of the  $\nu_{C=C}$  line in **2** than in **1**, suggests that  $\pi$ -delocalization is greater in the germylene than in the silylene.

Other evidence tends to corroborate this conclusion:

1. The C=C distance in **2**, 136.4 (1) pm,<sup>11</sup> is longer than that in **1**, 132.0 (8) pm.<sup>17,19</sup> The vinylic  $\nu_{C-H}$  frequencies in **2** (3056, 3064  $\text{cm}^{-1}$ ) are lower than those for **1** (3082, 3088  $\text{cm}^{-1}$ ). These data suggest a lower C=C bond order in **2** than in **1**.

2. The <sup>1</sup>H NMR resonance for **2**, at 7.05 ppm, is shifted downfield by 1.15 ppm compared with that for the nonconjugated dichloro compound **4**, consistent with a diamagnetic ring current in **2**. The corresponding resonance for **1** at 6.75 ppm is similarly shifted downfield, but by a smaller amount, 1.02 ppm, from the corresponding dichloro compound, **3**.

Finally, some theoretical support for our suggestion that  $\pi$ -conjugation is greater in **2** than in **1** is provided by an NBO analysis by Boehme and Frenking,<sup>3</sup> which gave the following values of occupation of the  $p_z$  orbital: on silicon in **1**, -0.54; on germanium in **2**, -0.63.

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- (13) **2** was synthesized according to the literature preparation<sup>11</sup> and purified by sublimation in high vacuum ( $10^{-5}$  Torr) before spectra registration. The Raman spectra of solid **2** sealed in a capillary and of its solution in CS<sub>2</sub> were obtained using T64000 and U-1000 Jobin-Yvon Raman spectrometers, with 514.5 nm excitation of an Ar<sup>+</sup> laser. Qualitative depolarization ratio measurements were carried out for the solution spectrum. The UV spectra of solid **2** were obtained using a Carl Zeiss M-40 spectrophotometer for a Nujol mull prepared under an atmosphere of purified Ar and for a sample sublimed on a cooled (77 K) quartz target in a vacuum cryostat. Both samples exhibited a UV absorption band with  $\lambda_{\text{max}}$  ca. 350 nm, about 50 nm red-shifted compared to that for **1**.<sup>8</sup>
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- (19) The nitrogen atoms in **2** are farther apart than those in **1**, but only by 0.7 pm.

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