

# Shapes of Simple Silyl Compounds in Different Phases

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*Received April 3, 1986 (Revised Manuscript Received September 18, 1986)*

It is often taken as a good general rule that simple molecular compounds have the same structure in the gas phase and in the crystal. Of course there are some well-known exceptions, such as  $\text{PCl}_5$ , but few systematic studies have been made of the structures of a series of related simple molecules in different phases. There may be enough problems in determining the structure of even quite a simple molecule in the gas phase; it is usually possible to determine the molecular structure in a crystal with modern equipment, so long as a suitable crystal is available, but there may be serious difficulties in growing and keeping crystals, and simple species often melt well below room temperature, which makes things much harder.

The relationship between phase and structure tells us about intermolecular forces: there may be gross differences in structure, so that the units in the crystal are quite different from those in the gas; the units may be the same in both phases, but we may find directed and well-defined secondary interactions, such as hydrogen bonding (which in species like carboxylic acids persists in the gas phase); or there may be subtle changes in structure with phase, changes, perhaps, in conformation in response to crystal forces. Such subtle secondary interactions, sometimes described as "secondary bonding",<sup>1</sup> are now recognized as important in helping to map out models for reaction pathways and in processes of molecular recognition. They may also give us indirect information about electron distribution. X-ray diffraction leads in principle to electron densities. This information is not usually precise enough to provide details about bonds, but we may be able to infer the stereochemical distribution of lone pairs in crystals from the relative positions of atoms within a molecule or its neighbors.

In order to explore the relationship between molecular structure and phase, we have embarked on a study of a series of simple silicon compounds in both gas and crystalline states. We have chosen them partly because the structures of the free molecules show some interesting features and partly because silicon is a second-row element and shows some tendency to secondary bonding. Moreover, a good deal is known about the structures of simple carbon compounds, so some useful comparisons can be made. We believe that the patterns emerging from these comparisons will have general significance.

E. A. V. Ebsworth was born in Richmond, Yorkshire, in 1933. He received his undergraduate education at King's College, Cambridge, where he also received his Ph.D. and M.A. degrees. He was a Fellow of the College for a few years after which he became a Research Associate in Princeton University. He returned to Cambridge as a Demonstrator and then lecturer in Christ's College. Since 1967 he has been the Crum Brown Professor of Chemistry in Edinburgh. His main research interest has been in the chemistry of compounds of silicon, germanium, and phosphorus, including transition-metal derivatives, with particular emphasis on spectroscopic and structural properties.

## Gas-Phase Structures

**General.** Let us consider the geometries of the free molecules first, before placing them in the crystalline environment. Precise gas-phase geometries are determined by microwave spectroscopy or electron diffraction, and the structures of halides  $\text{MH}_3\text{X}$  and cyanides  $\text{MH}_3\text{CN}$  present no special problems. There are some features of interest: bonds to fluorine are well-known to be short; whereas the C-C bonds in  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CCH}$  are almost exactly the same length,<sup>2</sup> the Si-C bond in  $\text{SiH}_3\text{CN}$  is significantly longer<sup>3</sup> than it is in  $\text{SiH}_3\text{CCH}$ . Unfortunately, it is hard to interpret these details quantitatively in simple terms.

With derivatives of N, P, O, S, or Se, questions about the angles at the atom from group V (15)<sup>37</sup> or VI (16) arise. Most chemists feel that they understand the shapes of simple alkyl derivatives of these elements. The shapes fall into a simple and regular pattern, and there are no glaring anomalies. The shapes of analogous simple silyl compounds, with  $\text{M} = \text{Si}$ , are much more varied and less well understood. In the past there has been significant uncertainty as to the ground-state geometry of such species as  $\text{SiH}_3\text{NCO}$ , and the unraveling of the experimental data has proved a testing and instructive process.

As with carbon, the geometry at a saturated silicon atom is essentially tetrahedral. Partly because of experimental difficulties there has been little effort to explore the small and subtle variations in the geometry of the  $\text{SiH}_3$  group in  $\text{SiH}_3\text{Q}$  as Q changes. However, the presence of Si has a striking effect on the angles at N or O directly bound to it. In hydrides or alkyls of N or O, the lone pair at N or O is always stereochemically active, though in ammonia the barrier to inversion is small. The shapes of silylamines and disiloxanes are somewhat different, and they reflect some of the contrasts in chemistry between the silyl compounds and their methyl analogues.

**Silylamines.** Trisilylamine,  $(\text{SiH}_3)_3\text{N}$ , is easily prepared by the reaction between chlorosilane and ammonia; no quaternary silylammonium salts are formed, emphasizing the weakly basic character of trisilylamine.<sup>4</sup> Although not appreciated for 30 years, this observation is associated with planar geometry at N. Indeed, a very large number of compounds containing two silicon atoms bound to saturated nitrogen have now been prepared and studied structurally, and virtually all are planar at N. In contrast, although (dimethylamino)silane is a weaker base than ammonia or trimethyl-

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amine, it is distinctly more basic<sup>5</sup> than di- or trisilylamines. In keeping with this increase in basicity, the coordination around N in gaseous  $\text{SiH}_3\text{NMe}_2$  is distinctly nonplanar,<sup>6</sup> the sum of the angles at N amounting to  $345^\circ$ .

Planarity at N in di- and trisilylamines has been correlated with ( $p \rightarrow d$ )  $\pi$ -bonding from N to Si, and the binding of the lone pair at N has been shown by photoelectron spectroscopy to be tighter in trisilylamine than in trimethylamine, which is consistent with the same hypothesis.<sup>7</sup> However, an alternative explanation in terms of the second-order Jahn-Teller effect has been proposed by Glidewell.<sup>8</sup> In any case, simple explanations do not account for all the structural features of Si-N compounds. The length of the formally single Si-N bond varies over a wide range,<sup>9</sup> from 163 pm in  $(\text{Me}_3\text{Si})_2\text{NLi}$  to 181 pm in  $\text{Me}_3\text{SiN}_2\text{SiMe}_3$ . The shortest bonds are found in neutral molecules, such as  $\text{SiF}_3\text{NMe}_2$  with strongly electron withdrawing substituents at Si, or in species such as  $(\text{Me}_3\text{Si})_2\text{N}^-$  where there is extra electron density at N. Conversely, the longest Si-N bonds are found in species where there are electron-releasing substituents at Si and N is unsaturated.

**Silyl Isocyanate and Related Compounds.** Besides the amino compounds described above, there are some unexpected geometric effects in silyl derivatives of  $\text{N} = \text{X} = \text{Y}$ . There have been no problems in determining the angles at N in gaseous  $\text{SiH}_3\text{N}_3$  and  $\text{SiH}_3\text{NSO}$ , and the molecular shapes are much like those of the analogous methyl compounds;<sup>10</sup> the angle at N in silyl azide is a little wider than in methyl azide, but the difference is small.

**$\text{SiH}_3\text{NCS}$ .** Early studies by microwave and infrared spectroscopy suggested that the heavy-atom skeleton in  $\text{SiH}_3\text{NCS}$  was linear, in contrast to  $\text{CH}_3\text{NCS}$  (where the angle at N is about  $145^\circ$ ). A study of  $\text{SiH}_3\text{NCS}$  by electron diffraction suggested that the molecule was bent at N; the apparently conflicting results from electron diffraction and microwave spectroscopy were reconciled when the effects of the low-frequency bending vibration were appreciated by Glidewell, Robiette, and Sheldrick.<sup>11</sup> The consequence of this was that though the molecule might have a linear ground state, most of the molecules would spend most of their time bent in the gas phase at room temperature. Electron diffraction gives a diffraction pattern based on scattering by pairs of atoms within a molecule and hence determines angles from ratios of internuclear distances; in molecules undergoing large-angle bending vibrations from a linear ground state, the longest internuclear distance will appear shorter than its ground-state value because the atoms spend most of their time at the extrema of the vibration. Hence, the

low-frequency bending vibration might make a molecule with a linear ground state look bent by electron diffraction.

A careful analysis of the shape of the peak in the radial distribution curve for  $\text{SiH}_3\text{NCS}$  due to Si...S scattering allowed Glidewell, Robiette, and Sheldrick to deduce that  $\text{SiH}_3\text{NCS}$  was linear in its ground state but with a bending frequency at N of about  $100\text{ cm}^{-1}$  and a harmonic potential function for bending. Robiette has subsequently confirmed this conclusion by a careful analysis of the microwave spectrum, and Cradock has observed the low-frequency vibrational spectrum directly.<sup>12</sup> This is complicated, but he has been able to analyze it using a potential function like Robiette's.

The ground-state structure of  $\text{SiH}_3\text{NCS}$  is now reasonably well understood: the angle at N is  $180^\circ$  but is easily deformed. The structure of  $\text{SiH}_3\text{NCSe}$  is apparently similar, and the experimental results understood in terms of linear N with a low bending frequency, though the shape of the low-frequency infrared envelope appears very different.

**$\text{SiH}_3\text{NCO}$ .** The case of  $\text{SiH}_3\text{NCO}$  is a little different. The infrared spectrum of the vapor shows rotational fine structure like that observed for  $\text{SiH}_3\text{NCS}$  and  $\text{SiH}_3\text{NCSe}$ , but it is much less well defined. An early study of the microwave spectrum was interpreted in terms of a linear heavy-atom skeleton for the ground state, but there were many features that could not be explained by such a model. The apparent angle as determined by gas-phase electron diffraction was substantially less than in  $\text{SiH}_3\text{NCS}$ . A careful study of the Si...O peak in the radial distribution curve from gas-phase electron diffraction led Glidewell, Robiette, and Sheldrick to conclude that the molecule was bent in its ground state, giving a potential function for bending with a low hump at the linear configuration. The height of the hump was calculated to be about the same as the energy of the ground vibrational state. The low-frequency infrared spectrum, which showed a series of resolved maxima, could also be interpreted in terms of this kind of potential function.<sup>12</sup>

Thus, there are significant differences between the ground-state geometries of  $\text{SiH}_3\text{NCO}$  on the one hand and  $\text{SiH}_3\text{NCS}$  and  $\text{SiH}_3\text{NCSe}$  on the other; but these differences clearly do not correspond to very substantial differences in energy.

**Silyl-Oxygen Compounds.** The shapes of simple  $\text{SiH}_3\text{O}$  compounds show similar effects. The vibrational spectrum of  $(\text{SiH}_3)_2\text{O}$  was originally interpreted in terms of a molecule with linear geometry at O and a center of inversion, because of the absence of coincidences in the infrared and Raman spectra.<sup>13</sup> The failure to observe well-resolved rotational fine structure in the perpendicular bands in the infrared spectrum was not easy to explain, for linear disiloxane should have one small moment of inertia. A study of the molecule by electron diffraction suggested<sup>14</sup> that the skeleton was bent, with an angle at O of  $144^\circ$ ; however, the possibility that this apparent angle might be associated with low-

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frequency bending of a linear skeleton could not initially be excluded, since the bending mode was observed in the infrared spectrum at  $60\text{ cm}^{-1}$ . McKean showed<sup>15</sup> that the skeleton could not be linear by recording the Raman spectrum of a sample containing a substantial proportion of  $(\text{SiH}_3)_2^{18}\text{O}$ . If the skeleton were linear, the frequency of the symmetric skeletal stretching mode should not depend on the mass of the oxygen atom, since this atom would not move in the vibration; in a bent skeleton it would move, and so the frequency of the mode should shift. The line due to the symmetric skeletal stretching mode in the Raman spectrum of McKean's sample showed an additional shoulder, so the skeleton could not be linear.

The question was finally settled by Durig.<sup>16</sup> He observed structure in the band due to the overtone of the skeletal bending mode in the Raman spectrum of the vapor, and he used this to derive a potential function for bending with a low maximum at the linear configuration and its minimum corresponding to an angle at O of  $144^\circ$ , a function very like that proposed by Robiette and Sheldrick for  $\text{SiH}_3\text{NCO}$  but with a higher hump. The symmetry of such a floppy molecule cannot be understood in terms of conventional point groups, but it can be presented by use of permutation group theory, when it transpires that the selection rules are effectively the same as for those of a linear and centrosymmetric molecule. In  $(\text{Me}_3\text{Si})_2\text{O}$  the angle at O is around  $147^\circ$ ; the methyl groups seem to make little difference to the angle at the central atom.<sup>17</sup>

### Crystallography of Silyl Compounds

It therefore appears that there is a group of simple silyl compounds containing Si-N or Si-O bonds whose structures in the gas phase at least show wide but easily deformed angles at N or O. In striking contrast, the gas-phase structures of  $(\text{SiH}_3)_3\text{P}$ ,  $(\text{SiH}_3)_2\text{S}$ , and  $(\text{SiH}_3)_2\text{Se}$  are very like those of their methyl analogues,<sup>18</sup> and the angles at the central atom are all less than tetrahedral. We wondered whether the shapes of the molecules with low bending frequencies might be deformed by crystal forces. The vibrational spectrum of  $(\text{SiCl}_3)_2\text{O}$ , for instance, is much simpler for the crystal than for the vapor, and it has been interpreted as showing that the skeleton is linear in the crystal, though bent in the vapor.<sup>19</sup> The amine  $\text{SiH}_3\text{NMe}_2$ , which is pyramidal at N, is unusual in melting<sup>5</sup> at 276 K, though  $(\text{SiH}_3)_3\text{N}$  and  $(\text{SiH}_3)_2\text{NMe}$  both melt well below 170 K. In keeping with its high melting point,  $\text{SiH}_3\text{NMe}_2$  has been shown to be pentameric in the crystal (see Figure 1):<sup>20</sup> the molecular unit is a ten-membered ring, with 5-coordinated Si equivalently bound to two tetrahedral N atoms. We have therefore embarked on the difficult task of determining the crystal structures of a range of simple silyl compounds.

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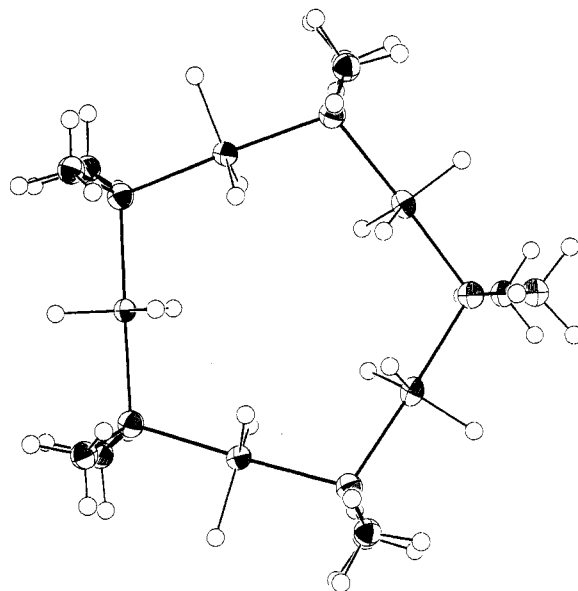
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**Figure 1.** The dimethylsilylamine pentamer, with thermal ellipsoids drawn at the 50% electron probability level, except for H atoms, which have an artificial radius of 10 pm for clarity. Taken from ref 20.

The crystallography is usually reasonably straightforward; the problem lies in growing and handling suitable crystals. Compounds that are both air-sensitive and low-melting must of course be handled in sealed tubes, and these constraints make it impossible to use most of the tricks used by crystallographers to grow crystals. It may take several weeks to grow a crystal that is suitable. This cannot be done on a diffractometer, which is too expensive to remain idle for such long periods. On the other hand, transferring a crystal that melts at, say, 170 K is difficult and unreliable. Moreover, many low-melting compounds show phase changes at low temperatures. A crystal will usually be grown near the melting point of the compound under study, but it is normally cooled in liquid nitrogen for transfer to a diffractometer; if there is a phase change between 77 K and the melting point, the crystal may shatter during transfer.

Sometimes a phase change leads to a less obvious alteration. We grew a crystal of  $\text{PO}(\text{OPF}_2)_3$  on our photographic equipment and determined the unit cell. The crystal was then transferred to the diffractometer, where the crystal habit was found to be the same but the dimensions of the unit cell were different. Closer investigation showed that there is a phase change at 77 K that is subtle enough to preserve the crystal but substantial enough to change the space group of the molecules in the crystal and the dimensions of the unit cell<sup>21</sup> and, presumably, the geometry and packing of the molecules. Some compounds have proved impossible to crystallize under the conditions of our experiments, and so our series of structures has some tantalizing gaps in it. However, patterns are beginning to emerge in the relationships between molecular geometries in the gas and in the crystal.

**Crystal Structures of  $\text{SiH}_3\text{NCO}$  and  $(\text{SiH}_3)_2\text{O}$ .** Rather unexpectedly, the intramolecular geometry for

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Table I.  
Some van der Waals Radii (in pm)<sup>a</sup>

Si	210	N	155	O	152	F	147
Ge	195	P	180	S	180	Cl	175
Sn	210	As	185	Se	190	Br	185
		Sb	205	Te	206	I	198

<sup>a</sup> Values from ref 2.

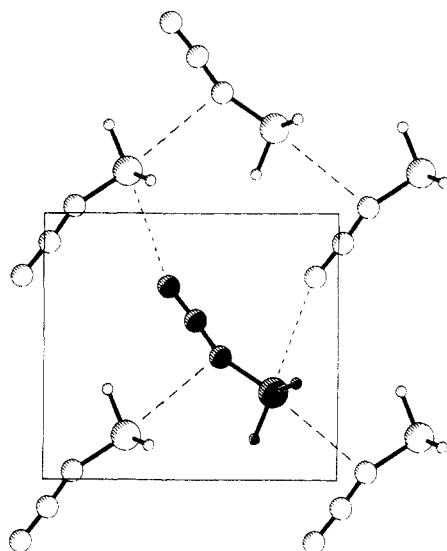


Figure 2. Arrangement of molecules on the mirror plane in crystalline  $\text{SiH}_3\text{NCO}$ , showing intermolecular interactions ( $T = 140 \text{ K}$ ). Taken from ref 22.

$\text{SiH}_3\text{NCO}$  is very much the same in the crystal as it is as determined by electron diffraction for the gas phase.<sup>22</sup> In particular, the angle at N is less than  $160^\circ$ . The similarity is surprising, since in the gas phase the deviation in the apparent angle from  $180^\circ$  is due to vibrational shrinkage. However, the bending at N in the crystal seems to be associated with a weak but stereochemically well-defined intermolecular interaction between the N atom of one molecule and the Si atom of another; the  $\text{Si}\cdots\text{N}$  distance is 331 pm vs. the sum of the van der Waals radii for Si and N of 365 pm (see Table I), and the  $\text{N}\cdots\text{Si}-\text{N}$  angle is very close to  $180^\circ$ , giving the silicon atom incipient 5-coordination<sup>23</sup> (see Figure 2).

The results with  $(\text{SiH}_3)_2\text{O}$  are very similar.<sup>24</sup> The angle at O in the molecule in the crystal is  $142^\circ$  vs. the angle determined by electron diffraction for the vapor of  $144^\circ$ , and there is a nonbonded  $\text{Si}\cdots\text{O}$  contact of 305 pm, with the O atom, the nonbonded Si atom, and both bound Si atoms in the same plane and the  $\text{O}\cdots\text{Si}-\text{O}$  angle very close to  $180^\circ$  (see Figure 3). The shortness of the nonbonded contact in comparison with the sum of the van der Waals radii (362 pm) and the planarity of the  $\text{Si}_2\text{O}$  skeleton and the nonbonded Si atom emphasize the stereochemical significance of the nonbonded interaction.

These two crystal structures, taken with that of  $(\text{SiH}_3\text{NMe}_2)_5$ , suggested to us that stereochemically significant but energetically weak intermolecular interactions, involving incipiently 5-coordinated silicon,

(23) Note that there is also a short nonbonded  $\text{Si}\cdots\text{O}$  contact; however, in crystalline  $\text{GeH}_3\text{NCO}$  (which has the same structure) the  $\text{Ge}\cdots\text{N}$  contact is shorter than in  $\text{SiH}_3\text{NCO}$  whereas the  $\text{Ge}\cdots\text{O}$  contact is longer, so we attach more significance to the former.

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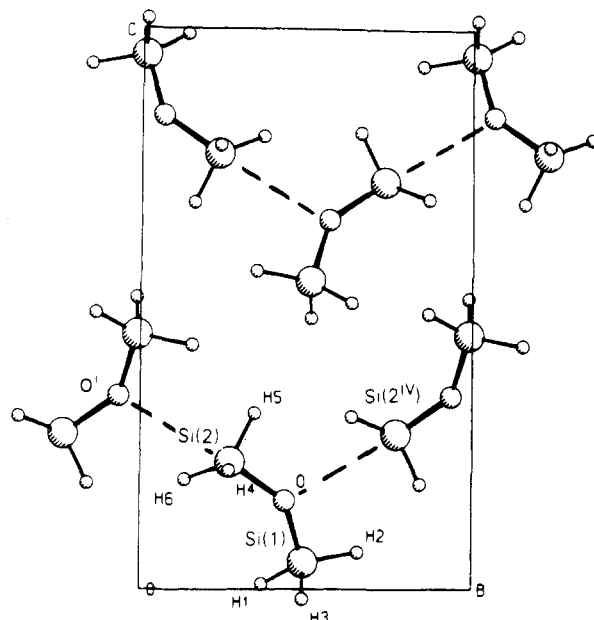


Figure 3. Nonbonded  $\text{O}\cdots\text{Si}$  contacts in the unit cell of crystalline  $(\text{SiH}_3)_2\text{O}$ , seen down the  $a$  axis. Taken from ref 24.

might be found in other systems. Moreover, it might be possible to learn from the geometry of the intermolecular contacts about the stereochemical behavior of lone pairs at atoms such as N, O, or S. The intermolecular crystal geometry of  $(\text{SiH}_3)_2\text{O}$ , for instance, has interesting implications for the electronic structure of the molecule. One of the lone pairs at oxygen could be regarded as in a pure p orbital with a node in the  $\text{Si}_2\text{O}$  plane; this lone pair might then be involved in intramolecular donor  $\pi$ -bonding through  $\pi$ -type d orbitals at Si. The other lone pair would lie in the  $\text{Si}_2\text{O}$  plane and along the  $\text{O}\cdots\text{Si}$  vector.

We may therefore be able to find out something about the directional properties of lone pairs from the stereochemistry of the secondary interactions. Some of our results with a range of silyl halides, oxygen, sulfur, and nitrogen derivatives are summarized below.

**Silyl Halides.** We have been able to grow single crystals of  $\text{SiH}_3\text{F}$  and  $\text{SiH}_3\text{I}$ . Unfortunately, our efforts with  $\text{SiH}_3\text{Cl}$  and  $\text{SiH}_3\text{Br}$  have been frustrated by phase changes or other unhelpful crystallization behavior. Both  $\text{SiH}_3\text{F}$  and  $\text{SiH}_3\text{I}$  show well-defined intermolecular interactions. In  $\text{SiH}_3\text{F}$ , the  $\text{Si}\cdots\text{F}$  nonbonded distance (289 pm) is much shorter than the sum of the van der Waals radii (357 pm), and the  $\text{Si}-\text{F}$  bond is slightly longer in the crystal than it is in the gas phase. The  $\text{F}\cdots\text{Si}-\text{F}$  angle is close to  $180^\circ$ , and the incipient 5-coordination at Si is well-defined.<sup>25</sup> The  $\text{Si}-\text{F}\cdots\text{Si}$  angle ( $146^\circ$ ) is also wide. In the crystal of  $\text{SiH}_3\text{I}$  the  $\text{Si}\cdots\text{I}$  contact distance (380 pm) is much closer to the sum of the van der Waals radii (408 pm), though still significantly shorter;<sup>25</sup> the  $\text{I}\cdots\text{Si}-\text{I}$  angle is again near  $180^\circ$ , but the angle at I is  $84^\circ$  (see Figure 4). The contrast between the angles at F and at I is striking and may tell us something about the directional properties of lone-pair orbitals at the halogen atoms.

**Silyl Cyanide.** Though silyl cyanide is not a halide, it is best considered with them. It is remarkable for its

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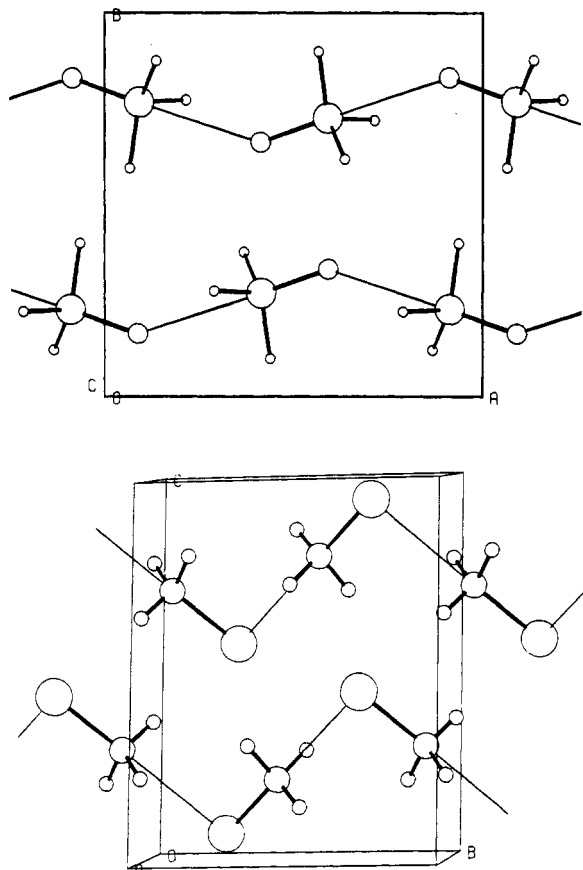


Figure 4. Nonbonded silicon-halogen contacts in  $\text{SiH}_3\text{F}$  (above) and  $\text{SiH}_3\text{I}$  (below). Taken from ref 25 and 26.

high melting point (307 K); in keeping with this, the intermolecular interactions are well marked in the crystal, which contains  $\text{Si-CN}\cdots\text{Si}$  chains; the  $\text{N}\cdots\text{Si}$  contact distance (280 pm) is much less than the sum of the van der Waals radii (365 pm). This short contact distance, however, does not noticeably affect the  $\text{Si-C}$  bond length, which is not significantly different in the crystalline and gaseous phases.<sup>27</sup> There is no sign of such a chain structure in any of the forms of acetonitrile that have been studied.<sup>28</sup> If we regard the  $\text{N}\cdots\text{Si}$  contacts as associated with a donor-acceptor interaction, the lone pair at N must be in a  $\sigma$ -orbital with essentially  $sp$  character. The acceptor properties of the silicon atom, however, are greatly modified by methylation. The structure of  $\text{Me}_3\text{SiCN}$  is disordered in some respects, so that we have not been able to determine all the details. However, the molecules are stacked in chains, as in silyl cyanide, and we have been able to determine the total  $\text{Si}\cdots\text{Si}$  distance. This is so great that if we allow reasonable values for the lengths of the  $\text{Si-C}$  and the  $\text{CN}$  bonds, the  $\text{Si}\cdots\text{N}$  nonbonded distance cannot be much less than the sum of the van der Waals radii.<sup>29</sup> Any nonbonded interaction has been essentially eliminated by methylation at silicon.

**Silyl Esters.** The case of disiloxane has already been discussed. In the crystal, the angle at O in  $(\text{Me}_3\text{Si})_2\text{O}$  is very close to that in  $(\text{SiH}_3)_2\text{O}$ , but there is no sign of significant  $\text{Si}\cdots\text{O}$  nonbonded interactions.<sup>24</sup> We have also determined the geometry of silyl acetate in the gas

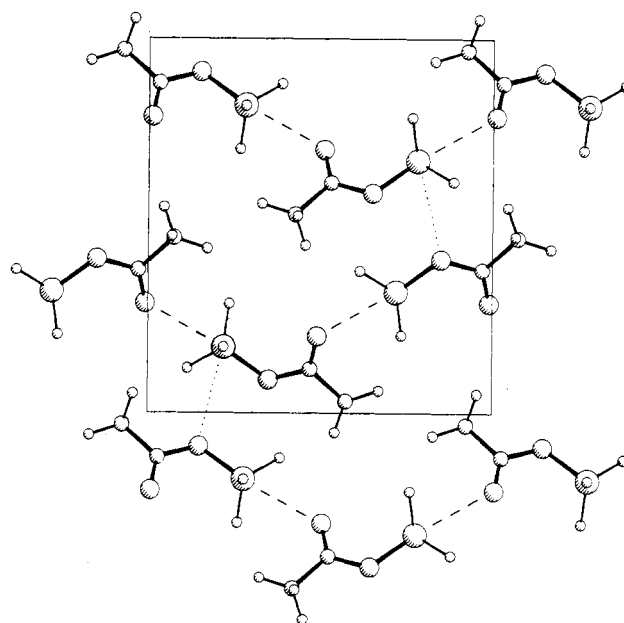


Figure 5. Nonbonded contacts in crystalline  $\text{CH}_3\text{COOSiH}_3$ . Taken from ref 30.

phase and in the crystal (see Figure 5). In the gas phase, silyl acetate adopts the same form as do silyl formate and methyl acetate: the silyl group is *cis* to the carbonyl oxygen, and the  $\text{O}\cdots\text{Si}$  distance (280 pm) is very much less than the sum of the van der Waals radii (362 pm). In the crystal,<sup>30</sup> the overall intramolecular geometry is maintained, though there are significant changes in some bond length and angles. The most interesting feature is that there is an intermolecular  $\text{Si}\cdots\text{O}$  nonbonded contact that is even shorter (272 pm) than the intramolecular contact. The  $\text{O-Si}\cdots\text{O}$  angle is near  $180^\circ$ , and there is a zigzag chain structure running through the crystal.<sup>31</sup> In the crystal of silyl mono-thioacetate we find a similar pattern.<sup>32</sup> The molecule is O bound, and the  $\text{Si}\cdots\text{S}$  nonbonded distance (338 pm) is somewhat shorter than the sum of the van der Waals radii (390 pm). We have determined the crystal structure of methyl acetate for comparison; the molecules are stacked quite differently, and there are no short nonbonded  $\text{C}\cdots\text{O}$  contacts.

**Silyl-Sulfur and Silyl-Selenium Compounds.** The only  $\text{Si-S}$  and  $\text{Si-Se}$  compounds whose crystal structures we have determined are  $(\text{SiH}_3)_2\text{S}$  and  $(\text{SiH}_3)_2\text{Se}$ . In each, the intramolecular geometry changes little from gas to crystal, but the intermolecular geometry is interesting.<sup>33</sup> The  $\text{Si}\cdots\text{S}$  or  $\text{Si}\cdots\text{Se}$  intermolecular contacts are about 10% shorter than the sum of the van der Waals radii, implying defined but relatively weak interactions. Each S or Se atom in the crystal is *tetrahedrally* coordinated, with two bound and two nonbonded silicon atoms. This suggests that there are two stereochemically directed lone pairs at S and Se, in contrast to the apparent 3-coordination at O in the crystal of  $(\text{SiH}_3)_2\text{O}$ .

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(31) There is another short lateral  $\text{Si}\cdots\text{O}$  contact, but it is not as short as the axial contact.

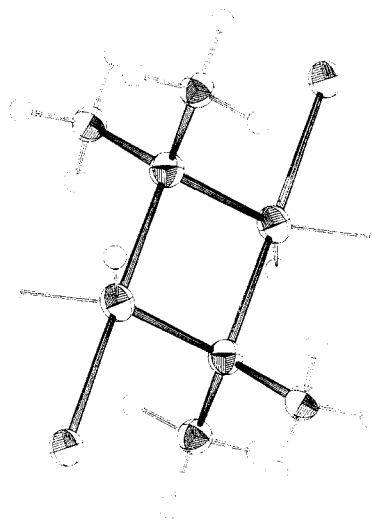
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**Figure 6.** The four-membered ring dimeric units in crystalline chlorosilyldimethylamine taken from ref 36.

**Other Silyl-Nitrogen Compounds.** Trisilylamine with its planar skeleton retains the same molecular structure in the crystal.<sup>34</sup> Here too, though, the molecular packing gives us a clue as to the electron distribution in the molecule itself. The trigonal-planar units stack in columns with each nitrogen atom over the one below. This form of packing implies that the nitrogen atoms do not bear significant charge; if they did, there would surely be some departure from exact stacking. The N...N contact distance is over 400 pm, and there are no short nonbonded contacts. We have so far been unable to determine the crystal structure of MeN(SiH<sub>3</sub>)<sub>2</sub>, despite repeated attempts. The remarkable change in structure of SiH<sub>3</sub>NMe<sub>2</sub> on crystallization has already been mentioned; it led us to explore the effect of substitution at Si on the structure of Me<sub>2</sub>NSi derivatives in the crystal.

We have been unable to obtain any crystals at all of MeSiH<sub>2</sub>NMe<sub>2</sub>; the compound always solidifies as a glass which softens at extremely low temperatures (ca. 110 K). It has proved easy to grow crystals of Me<sub>2</sub>NSiMe<sub>3</sub>. In this molecule the coordination around N is almost exactly planar in the gas phase, and the molecular structure is not significantly changed in the crystal, where there are no significant intermolecular contacts.<sup>35</sup>

The behavior of SiH<sub>2</sub>ClNMe<sub>2</sub> on crystallization is much more remarkable.<sup>36</sup> In the gas phase the molecular geometry is as expected, with almost planar N and normal Si-N and Si-Cl bond lengths. The melting point (200 K) is low, though higher than that of trisilylamine and many other simple silyl compounds. In the crystal, however, the compound forms dimeric units, containing unsymmetrical four-membered Si<sub>2</sub>N<sub>2</sub> rings (see Figure 6). Each N is tetrahedral, with one short (181 pm) and one long (205 pm) Si-N bond; each silicon is trigonal-bipyramidal, with the equatorial positions occupied by two hydrogens and the short-bound N and the apical positions occupied by chlorine and the long Si-N.

At first sight this seems a structure totally different from that of (SiH<sub>3</sub>NMe<sub>2</sub>)<sub>5</sub>, but the two can be related in terms of the apicophilicity of the groups bound to silicon. In the associated forms of both compounds the silicon atoms are 5-coordinated. In (SiH<sub>3</sub>NMe<sub>2</sub>)<sub>5</sub>, each silicon is bound to three hydrogen and two nitrogen atoms; the nitrogen atoms occupy the apical positions in the trigonal-bipyramidal around Si, and this leads to the pentameric structure observed. In (SiH<sub>2</sub>ClNMe<sub>2</sub>)<sub>2</sub>, one of the apical-positions around each silicon atom is occupied by Cl, which has a higher apicophilicity than N; thus, only one other apical position remains, while there are two N ligands. One of the N ligands must therefore become equatorial, and the distorted four-membered ring results.

So far, all the secondary interactions we have observed in crystals of SiH<sub>3</sub> compounds have involved axial donor atoms. We hoped that we might be able to force both N ligands into equatorial positions in SiHCl<sub>2</sub>NMe<sub>2</sub>, which might therefore have been expected to take up a trimeric six-membered ring form in the crystal; unfortunately, the geometry in the crystal is the same as it is in the vapor, there are no close nonbonded contacts, and our hopes were not realized. Perhaps the groups around Si are too bulky; perhaps two Cl substituents reduce the donor properties of N so much that the donor-acceptor links to Si cannot be formed. By suitable choice of ligand it may still prove possible to make a compound of the type SiHX<sub>2</sub>NMe<sub>2</sub> in which association occurs in the crystal and both N atoms are equatorial.

## Conclusions

This brief account of a limited study serves to show that there are some extremely interesting crystal effects to be found by studying the structures of low-melting and simple compounds of heavy nonmetallic elements. In almost all SiH<sub>3</sub> derivatives of groups containing potential donor atoms, there is evidence for secondary bonding in the crystal through incipient trigonal-bipyramidal coordination at silicon; this secondary bonding, however, may have little effect on the internal geometry of the molecule, apart from a slight lengthening of the Si-X bond trans to the donor in the secondary interaction. Where there is a significant effect, it is usually very large; we have so far only found such effects in molecules with strong donor substituents, such as Me<sub>2</sub>N. We have observed no short intermolecular contacts that we can ascribe to secondary bonding involving carbon as the acceptor atom; this is consistent with models in which secondary interactions use valence shell d orbitals of silicon as the acceptor levels. Finally, the acceptor properties of silicon in the crystal are very easily swamped if H bound to Si is replaced by CH<sub>3</sub>.

Much work remains to be done with silicon, where the influence of fluorine substituents is almost unexplored; comparison with germanium derivatives is only beginning. The exploration of the intermolecular interactions in the crystals in relation to reaction pathways is similarly in its earliest stages. The geometry of simple silyl

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compounds has already proved a challenging field for both experiment and theory; the additional dimension of the crystal lends further challenges in both respects.

*This work would have been impossible without the collabo-*

*ration of some exceptionally able colleagues, many of whose names appear in the references cited. I must give special thanks to Drs. S. Craddock, D. W. H. Rankin, M. J. Barrow, and A. J. Blake for all they have done to define important problems and then to solve them.*

## Intrinsic Barriers of Reactions and the Principle of Nonperfect Synchronization

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*Received January 15, 1987 (Revised Manuscript Received May 5, 1987)*

### Introduction

When discussing chemical reactivity, one needs to distinguish between the thermodynamic driving force of the reaction ( $\Delta G^\circ$ ) and a purely kinetic factor known as the intrinsic barrier ( $\Delta G_0^*$ ). For a reaction with forward and reverse rate constants  $k_1$  and  $k_{-1}$ , the intrinsic barrier is generally defined as  $\Delta G_0^* = \Delta G_1^* = \Delta G_{-1}^*$  (the intrinsic rate constant as  $k_0 = k_1 = k_{-1}$ ) for  $\Delta G^\circ = 0$  ( $K_1 = 1$ ). The theoretical as well as practical significance of  $\Delta G_0^*$  or  $k_0$  is that, at least in principle, they are representative of a whole reaction series and independent of the thermodynamics of a particular member within that series. Hence, understanding the factors that affect intrinsic barriers is to understand a great deal about chemical reactivity. This Account deals with some of these factors in carbanion-forming reactions, but the principles to be discussed are quite general. *A recurrent theme will be that high intrinsic barriers are typically associated with a lack of synchronization between concurrent reaction events such as bond formation/cleavage, solvation/desolvation, development (loss) of resonance, etc.*

The concept of the "intrinsic barrier" was introduced by Marcus<sup>1,2</sup> when he developed his theory of electron-transfer reactions. Marcus theory was later also applied to proton,<sup>3</sup> hydride,<sup>4</sup> and methyl transfers,<sup>2,5</sup> as well as some other processes.<sup>6</sup> Equations 1 and 2 express the two main facets of Marcus theory. Equation 1 describes how a reaction barrier ( $\Delta G^*$ ) depends on the intrinsic barrier ( $\Delta G_0^*$ ), the exothermicity (endothermicity) ( $\Delta G^\circ$ ) of the reaction, and the energy of bringing the reactants ( $w_R$ ) and products ( $w_P$ ) together; for reactions with high intrinsic barriers these latter "work terms" are usually neglected, though.

$$\Delta G^* = w_R + \Delta G_0^* \left\{ 1 + \frac{\Delta G^\circ - w_R + w_P}{4\Delta G_0^*} \right\}^2 \quad (1)$$

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$$\Delta G_0^*(A/B) = \frac{1}{2} \{ \Delta G_0^*(A/A) + \Delta G_0^*(B/B) \} \quad (2)$$

Equation 2 relates the intrinsic barrier of a reaction (e.g.,  $AH + B^- \rightleftharpoons A^- + HB$ ) to the intrinsic barrier of the corresponding exchange reactions ( $AH + A^- \rightleftharpoons A^- + HA$  and  $BH + B^- \rightleftharpoons B^- + HB$ ). For electron-transfer reactions Marcus theory also relates  $\Delta G_0^*$  to molecular size, charge, and solvent polarity,<sup>1</sup> but no such relationships have been proposed for the other reactions treated by the Marcus formalism. In other words, even though eq 2 is quite successful in correlating or predicting intrinsic barriers in terms of other intrinsic barriers, it does not provide a molecular understanding of what determines the height of intrinsic barriers.

Our aim has been to seek such understanding without necessarily adhering to the Marcus formalism. Our starting point is the growing realization by many workers that most elementary reactions in chemistry are not adequately described by the traditional free energy vs. reaction coordinate profile. Usually more than one concurrent process such as bond formation/cleavage, solvation/desolvation, delocalization/localization of charge, etc., is involved, and typically these processes have made unequal progress at the transition state ("imbalanced" transition state).<sup>7-13</sup> "Reaction progress" at the transition state then becomes an ambiguous concept that depends on which process is chosen as the reaction coordinate.

Energy surfaces based on two progress variables (More O'Ferrall<sup>7</sup>-Jencks<sup>8</sup> diagrams) deal qualitatively with this problem.<sup>7-15</sup> Such a diagram is shown in

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