

To date we are not aware of any unsaturated aromatic polysilacycles, but the cyclic anion radicals appear to resemble traditional aromatics in certain respects. Whether the SOMO is of the  $\pi^*$  or  $\sigma^*$  type, the electron is found to be completely delocalized around the ring and both are quite stable. Indeed, they can be formed readily from straight-chain silicon polymers through addition of naphthalide radical anion<sup>49</sup> and thus appear to be "unusually stable" with respect to straight-chain anion radicals. Unfortunately, no experimental or theoretical thermochemical data are available that would allow us to assess any measure of this stability.

### Conclusion

While the cyclopolysilanes are structural analogues of cycloalkanes, the strain energy of cyclotrisilane is 10 kcal/mol more than that of cyclopropane, and cyclotetrasilane is 10 kcal/mol less strained than cyclobutane. The strain energies can be rationalized by consideration of angle and torsional strain components, and substituent effects. We suggest that substituent effects (i.e., the peculiar role of hydrogen) may also be partially responsible for the nearly identical strain energies in  $C_3H_6$  and  $C_4H_8$ . That is, if we replace the hydrogens with other substituent the strain energies may be, and in the case of fluorine it is, quite different for the three- and four-membered rings. The arguments which conclude that cyclopropane has unusual stability, i.e., is  $\sigma$  aromatic, may be based on a questionable assumption about

the ability of force constants at one geometry to predict strain in a different molecule at a vastly different geometry.

For each of the neutral planar silicon hydride rings investigated here, the LUMO was of the same type, totally  $\pi$ -bonding between the silicon ring atoms and silicon-substituent antibonding. If we assume the SOMO of the substituted rings is of the same type, as our results for hexamethylcyclotrisilane suggest, then the available ESR and long-wavelength UV intensity data may be explained by reasons of symmetry alone. Alternative explanations for recent <sup>29</sup>Si ENDOR data, which seems inconsistent with this  $\pi^*$  model, are not apparent at this time. On the other hand, the  $\sigma^*$  model, which accounts for the small hyperfine anisotropy for <sup>29</sup>Si in the ENDOR studies by assuming equal participation of  $p_x$ ,  $p_y$ , and  $p_z$  orbitals in the SOMO of the radical anions, does not rigorously exclude s-orbital participation in the SOMO as ESR studies suggest. In addition, the small extinction coefficients observed for the longest wavelength transitions of cyclopolysilanes are not easily explained by the  $\sigma^*$  model. While the  $\pi^*$  model seems to rest on firmer ground, we are not in a position to decide which, if either, of these models is correct.

**Acknowledgment.** We wish to thank Professor Robert West for many helpful discussions. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

**Registry No.**  $Si_3H_6$ , 18548-76-0;  $Si_4H_8$ , 287-69-4;  $Si_5H_{10}$ , 289-22-5;  $Si_3H_6^-$ , 110174-36-2;  $Si_4H_8^-$ , 110174-37-3;  $Si_5H_{10}^-$ , 110174-38-4.

(49) Carberry, E.; West, R. *J. Am. Chem. Soc.* **1969**, *91*, 5440.

## Hetero-Substituted Cyclopolysilanes: Unusual Structures and a New Model of Bonding in 1,3-Disubstituted Four-Membered Rings

Roger S. Grev\* and Henry F. Schaefer III

Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. Received December 8, 1986

**Abstract:** The monosubstituted cyclopolysilanes  $(SiH_2)_nX$  ( $X = CH_2, NH, O, PH, \text{ and } S; n = 2 \text{ and } 3$ ) are investigated with ab initio quantum mechanical techniques. The monosubstituted four-membered rings do not exhibit any remarkable structural features, while all the monosubstituted three-membered rings have unusually short Si-Si bond distances and nearly planar Si-Si-H<sub>2</sub> units, which can be explained via Dewar's model of metal-olefin bonding. A simple extension of this model to the case of 1,3-disubstituted four-membered rings readily explains the unusual geometries found in many of these systems. This model is quite general and focuses on the ring orbitals themselves, unlike previous models which often invoked large lone pair-lone pair interactions to explain observed deviations from ideal square-planar geometries. Thus, it is applicable to both three- and four-membered substituted and unsubstituted rings alike. The bonding in cyclodisiloxane is described as that of a "dibridged  $\pi$ -complex", and the bond between the silicons, if it exists, is most likely that of an "unsupported  $\pi$ -bond".

Saturated silicon ring systems  $(SiR_2)_n$  are structural analogues of cycloalkanes yet they exhibit many unusual features not observed in saturated cyclic hydrocarbons. Unsubstituted cyclopolysilanes, for example, show strong absorptions in the ultraviolet, give charge-transfer complexes with  $\pi$  acceptors, and form cation and anion radicals in which the unpaired electron is completely delocalized around the ring. In addition, their photoionization and UV spectra can be interpreted by assuming that the Si-Si  $\sigma$  electrons are completely delocalized. Thus, despite their structural similarity to cycloalkanes, the cyclopolysilanes behave in many ways like typical unsaturated aromatic hydrocarbons.<sup>1</sup>

In contrast substituted cyclopolysilanes, in which one or more  $SiR_2$  units are replaced by isovalent units such as O, S,  $CH_2$ , etc.,

exhibit unusual structural features. For example, the S- and  $CH_2$ -substituted three-membered rings (3MRs) 1,1,2,2-tetramethyl-1,2-disilathirane<sup>2</sup> and 1,1,2,2-tetrakis(2,6-dimethylphenyl)-1,2-disilacyclopropane<sup>3a</sup> have Si-Si bond distances at least 0.1 Å shorter than trisilacyclopropane rings with similar functional groups attached to silicon.<sup>4-6</sup> These molecules are also unusual

(2) West, R.; DeYoung, D. J.; Haller, K. *J. Am. Chem. Soc.* **1985**, *107*, 4942.

(3) (a) Masamune, S.; Murakami, S.; Tobita, H.; Williams, D. *J. Am. Chem. Soc.* **1983**, *105*, 7776. (b) Ishikawa, M.; Sugisawa, H.; Kumada, M.; Higuchi, T.; Matsui, K.; Hirotsa, K.; Iyoda, J. *Organometallics* **1983**, *2*, 174.

(4) Masamune, S.; Hunzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *104*, 1150.

(5) Schafer, A.; Weiberbruch, M.; Peters, K.; von Schnering, H.-G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 302.

(1) West, R. *Pure Appl. Chem.* **1982**, *54*, 1041.

in that the Si-Si-R<sub>2</sub> units are nearly coplanar about the silicon atom. These results have been interpreted by assuming partial  $\pi$ -bonding between the silicons, but the presence of several close contacts between carbon atoms in the structures may contribute to the observed near-planarity at the silicon centers.<sup>2</sup>

Another seemingly unrelated observation is that the silicon atoms in 1,3-cyclodisiloxanes (R<sub>2</sub>SiO)<sub>2</sub> are separated by distances characteristic of singly bonded silicons.<sup>7,8</sup> This has stirred up considerable theoretical interest in these compounds,<sup>9-13</sup> much of it centered around the question of whether the two silicons are actually bonded to one another. To date, all these studies have concluded that a silicon-silicon bond does not exist, but the reason for the unusual structures is a more contentious matter. Most authors point to large oxygen-oxygen lone pair repulsions,<sup>10,11</sup> but others explain it in terms of the strength of Si-O bonds and less severe exchange repulsions between silicon atoms.<sup>12</sup> Many other 1,3-disubstituted cyclotrasilanes (R<sub>2</sub>Si-X)<sub>2</sub> are known, e.g., X = P-R,<sup>14</sup> N-R,<sup>15-18</sup> S,<sup>19-21</sup> CR<sub>2</sub>,<sup>22</sup> and these have widely varying nonbonded Si...Si distances, but all of them are significantly longer than normal single bond ranges (with the possible exception of X = NR).

In a recent study<sup>23</sup> we investigated the unsubstituted rings cyclotrisilane, cyclotrasilane, and cyclopentasilane using ab initio quantum mechanical methods.<sup>24</sup> The main goal of that research was to determine the structures and strain energies of the parent cyclopolysilanes and compare them to the analogous hydrocarbons. Here we investigate the parent monosubstituted three- and four-membered rings (H<sub>2</sub>Si)<sub>n</sub>X (n = 2, 3) with X = O, S, NH, PH, and CH<sub>2</sub>. As mentioned earlier, methylene<sup>2,24</sup> and sulfur<sup>2</sup> substituted cyclotrasilanes are known, albeit with hydrogens replaced by bulky functional groups, and oxygen substituted 3MRs have been synthesized,<sup>25</sup> but their crystal structures have not been determined. On the other hand, we are not aware of any previously identified monosubstituted cyclotrasilanes. The main goal of the present research is to determine the structures of the monosubstituted cyclopolysilane rings and to develop a consistent model to explain the structural trends.

The model we will employ is the familiar metal-olefin bonding model developed by Dewar<sup>26</sup> and later verified by Chatt and Duncanson.<sup>27</sup> In addition to metal-olefin systems, this model

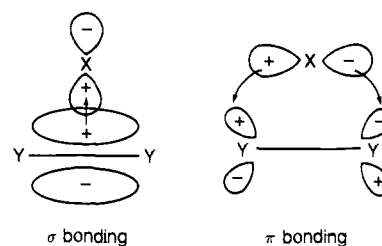


Figure 1. Dewar's model of monosubstituted three-membered ring bonding.

also provides a reasonable explanation for the interaction of transition metals and strained ring systems that are responsible for facile and unexpected rearrangements of the organic molecules.<sup>28</sup> More recently, Cremer and Kraka<sup>29</sup> have used this model to interpret the results of their Bader-type analysis of electron densities in a variety of three-membered monosubstituted hydrocarbon rings, ranging from the normal exocyclic bonding in cyclopropane to  $\pi$ -complexes, in essential agreement with the original suggestions of Dewar.<sup>26</sup> Basically, this model describes the bonding in terms of two components; first, a  $\sigma$ -bond is created between the metal and olefin by donation of  $\pi$ -electron density from the olefin into an orbital of the appropriate symmetry on the metal; second, the  $\pi^*$  orbital of the olefin is the recipient of electron density from a filled metal orbital of the same symmetry thus creating a  $\pi$ -bond with electron density in the exterior of the ring. For transition-metal bonding to olefins or strained hydrocarbons the donating metal orbital is usually a d-orbital, but p-orbitals can also be used as they, too, are of the appropriate symmetry for donation into  $\pi^*$  orbitals. A pictorial representation of this model is shown in Figure 1.

The structures that result from these interactions span the range from normal three-membered rings to  $\pi$ -complexes, or T-structures, depending on the accepting and donating capacity of the metals and olefins. If the  $\pi^*$  orbitals of the olefin are low lying, and the donor orbitals of the metal are high lying, one can expect to find a 3MR-type structure. If, on the other hand, the  $\pi^*$  orbitals are high lying and the metal donor orbitals are low lying, little electron density will accumulate in the exterior of the ring, and structures with short C-C, or in our case Si-Si, bonds will be found, reminiscent of  $\pi$ -complexes. Substituted cyclopolysilanes fit into the latter case, especially with the substituents considered here, because they are all much more electronegative than silicon, which has an anomalously low electronegativity to begin with. Thus we can expect that the O, S, NH, PH, and CH<sub>2</sub> substituted three-membered cyclopolysilane rings will have short Si-Si bonds as in a  $\pi$ -complex or a T-structure. Indeed, as we will show, this is the case.

Most of the 1,3-substituted cyclotrasilanes have been studied by previous workers using similar ab initio methods, and all of them have experimentally known derivatives; thus we have not carried out an extensive study of those compounds here. We will, however, suggest a very simple model for explaining the wide variation in nonbonded Si...Si distances observed in these compounds. Essentially, by considering the 1,3-disubstituted rings as dibridged olefin-type complexes, one can use the very same model Dewar proposed<sup>26</sup> to describe the 3MR structures in order to understand the disubstituted rings. We will emphasize that it is the lack of donation from electronegative substituents into the  $\pi^*$  orbital of the original olefin-like compound that leads to the unusually short nonbonded Si...Si distances found, e.g., in the cyclodisiloxanes. These rings will be called "dibridged  $\pi$ -complexes", and the bonding between the silicons, if it exists, may be like that of an "unsupported  $\pi$ -bond".

#### Theoretical Methods

All of the molecules investigated here have been optimized at the self-consistent-field (SCF) level of theory. The basis set used

(6) Dewan, J. C.; Murakami, S.; Snow, J. T.; Collins, S.; Masamune, S. *J. Chem. Soc., Chem. Commun.* **1985**, 892.

(7) Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, 106, 822.

(8) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, 5, 531.

(9) O'Keefe, M.; Gibbs, G. V. *J. Chem. Phys.* **1984**, 81, 876.

(10) O'Keefe, M.; Gibbs, G. V. *J. Phys. Chem.* **1985**, 89, 4574.

(11) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, 107, 1186.

(12) Kudo T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, 107, 2589

(13) Brenstein, R. J.; Scheiner, S. *Int. J. Quantum Chem.* **1986**, 29, 1191.

(14) Clegg, W.; Haase, M.; Klingebiel, U.; Sheldrick, G. M. *Chem. Ber.* **1983**, 116, 146.

(15) Wheatley, P. J. *J. Chem. Soc.* **1962**, 1721.

(16) Parkanyi, L.; Argay, Gy.; Hencsei, P.; Nagy, J. *J. Organomet. Chem.* **1976**, 116, 299.

(17) Clegg, W.; Klingebiel, U.; Sheldrick, G. M.; Vater, N. *Z. Anorg. Allg. Chem.* **1980**, 462, 207.

(18) Clegg, W.; Haase, M.; Klingebiel, U.; Neeman, J.; Sheldrick, G. M. *J. Organomet. Chem.* **1983**, 251, 281.

(19) Schklower, W. E.; Strutschkow, Yu. T.; Gusevnikov, L. E.; Wolkowa, W. W.; Awakyan, W. G. *Z. Anorg. Allg. Chem.* **1983**, 501, 153.

(20) Wojnowski, W.; Peters, K.; Weber, D.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1984**, 519, 134.

(21) Peters, J.; Krebs, B. *Acta Crystallogr.* **1982**, B38, 1270.

(22) Peters, K.; Peters, E.-M.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1983**, 502, 61.

(23) Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.*, submitted for publication.

(24) Schaefer, H. F. *The Electronic Structure of Atoms and Molecules* (Addison-Wesley; Reading, MA, 1972).

(25) Michalczyk, M. J.; West, R.; Michl, J. *J. Chem. Soc. Chem. Commun.* **1984**, 1525.

(26) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, 18, C71.

(27) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(28) Bishop, K. C. *Chem. Rev.* **1976**, 76, 461.

(29) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, 107, 3800.

Table I. Optimized Geometries of Monosubstituted Three-Membered Rings (H<sub>2</sub>Si)<sub>2</sub>X<sup>a</sup>

| parameter             | PH             |                          | NH    | S     | O     | SiH <sub>2</sub> <sup>j</sup> | CH <sub>2</sub> |
|-----------------------|----------------|--------------------------|-------|-------|-------|-------------------------------|-----------------|
|                       | C <sub>s</sub> | C <sub>2v</sub> (planar) |       |       |       |                               |                 |
| r(Si-Si)              | 2.270          | 2.344                    | 2.232 | 2.249 | 2.195 | 2.330                         | 2.251           |
| r(Si-H) <sup>b</sup>  | 1.4624         | 1.466                    | 1.467 | 1.461 | 1.462 | 1.466                         | 1.464           |
| r(Si-H) <sup>c</sup>  | 1.4618         |                          |       |       |       |                               |                 |
| r(Si-X) <sup>d</sup>  | 2.281          | 2.155                    | 1.724 | 2.156 | 1.674 |                               | 1.901           |
| r(X-H)                | 1.406          | 1.389                    | 0.999 |       |       |                               | 1.084           |
| ∠HSiH, deg            | 113.3          | 108.0                    | 108.8 | 111.6 | 110.2 | 113.1                         | 112.6           |
| θ,° deg               | 22.8           | 27.2                     | 12.7  | 19.1  | 6.7   | 30                            | 17.5            |
| ∠SiXSi, deg           | 59.7           | 65.9                     | 80.7  | 62.9  | 81.9  | 60                            | 72.6            |
| ε,° deg               | 7.3            | 1.3                      | 12.1  | 10.2  | 17.8  | 0                             | 9.4             |
| φ <sub>r</sub> ,° deg | 0.8            |                          |       |       |       |                               |                 |
| φ <sub>t</sub> ,° deg | 3.5            |                          |       |       |       |                               |                 |
| β,° deg               | 83.6           |                          |       |       |       |                               | 55.3            |

<sup>a</sup> Bond distances in Å. <sup>b</sup> SiH on same side of ring plane as PH. <sup>c</sup> SiH on opposite side of plane as PH. <sup>d</sup> X = PH, NH, S, O, SiH<sub>2</sub>, CH<sub>2</sub>. <sup>e</sup> θ = angle between H<sub>2</sub>Si plane and Si-Si bond. <sup>f</sup> Wagging angle: ε = 1/2(∠XSiSi) - θ. <sup>g</sup> Rocking angle: φ<sub>r</sub> = (α<sub>41</sub> + α<sub>43</sub>) - (α<sub>51</sub> + α<sub>53</sub>). For definition of α<sub>ij</sub> see Figure 2. <sup>h</sup> Twisting angle: φ<sub>t</sub> = (α<sub>41</sub> - α<sub>43</sub>) - (α<sub>51</sub> - α<sub>53</sub>). <sup>i</sup> β = angle between ring plane and X-H bond. <sup>j</sup> Reference 23. D<sub>3h</sub> symmetry.

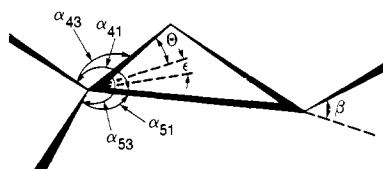


Figure 2. Definition of angles used to describe the SiH<sub>2</sub> group orientations in monosubstituted three-membered rings.

was the standard Huzinaga-Dunning<sup>30,31</sup> double- $\zeta$  (DZ) basis set of contracted gaussians with a single set of cartesian d-like functions appended to the heavy atoms (DZ+d). The uncontracted basis sets for the first row atoms C, N, and O was the 9s 5p set, and for the second row atoms Si, P, and S we used the 11s 7p set. The technical designation of these basis sets is thus (9s5p1d/4s2p1d) and (11s7p1d/6s4p1d) and the hydrogen basis set is (4s/2s) with use of the standard scaling factor 1.2. The polarization function exponents were  $\alpha_d(\text{Si}) = \alpha_d(\text{P}) = \alpha_d(\text{S}) = 0.5$ ,  $\alpha_d(\text{C}) = 0.75$ ,  $\alpha_d(\text{N}) = 0.8$ , and  $\alpha_d(\text{O}) = 0.85$ .

Analytical SCF gradient techniques<sup>32,33</sup> were used to determine the geometrical structure of all the molecules studied. The optimization of the 3- and 4-membered rings was initially carried out within the confines of C<sub>2v</sub> symmetry. The nature of these symmetry-constrained structures was then tested via the determination, using analytic SCF second derivative techniques,<sup>34</sup> of all quadratic force constants and the resulting harmonic vibrational frequencies. All of the 3MRs except the phosphorus-substituted rings are minima in C<sub>2v</sub> symmetry. The phosphorus 3MR minimum was located in C<sub>s</sub> symmetry. Of the 4MRs, for all except the PH- and CH<sub>2</sub>-substituted species, the planar structures were stationary points, and these each had a single imaginary vibrational frequency leading, presumably, to C<sub>s</sub> symmetry equilibrium geometries. We did not attempt to locate the actual minimum energy structures for these rings.

## Structural Predictions

**I. Three-Membered Rings.** The optimized geometries of the monosubstituted 3MRs are shown in Table I, along with the values obtained for the parent compound Si<sub>3</sub>H<sub>6</sub> obtained in our previous study.<sup>23</sup> The parameters used to describe the SiH<sub>2</sub> group orientations are shown in Figure 2 and are the same as those used by Skancke, Forgarasi, and Boggs (SFB) in their study of monosubstituted cyclopropanes.<sup>35</sup> As can be seen from Table I, the

internal coordinates of the SiH<sub>2</sub> group, i.e., the SiH bond distances and H-Si-H angles, do not vary to a significant degree. In addition, the Si-X bond lengths in the 3MRs are largely unremarkable, falling in the general vicinity of those found experimentally for other compounds with Si-C,<sup>36,37</sup> Si-N,<sup>38,39</sup> Si-P,<sup>40</sup> Si-O,<sup>41</sup> and Si-S<sup>42</sup> single bonds. Thus our discussion will focus on the Si-Si bond lengths and the orientation of the SiH<sub>2</sub> groups relative to the ring. The latter will be discussed in terms of the angles  $\theta$  and  $\epsilon$ ,  $\theta$  being the angle between the H<sub>2</sub>Si plane and the Si-Si bond, while  $\epsilon$  (the wagging angle) is the deviation of the H<sub>2</sub>Si plane from the X-Si-Si angle bisector. For the PH-substituted ring in C<sub>s</sub> symmetry, the SiH<sub>2</sub> groups may also undergo rocking and twisting motions. These are defined in the footnote to Table I.

The most striking feature of the substituted 3MR geometries is the unusually short Si-Si distance found in all the minimum energy structures. The values range from 2.195 Å in (H<sub>2</sub>Si)<sub>2</sub>O to 2.270 Å in C<sub>s</sub> symmetry (H<sub>2</sub>Si)<sub>2</sub>PH and are all significantly shorter than that found in Si<sub>3</sub>H<sub>6</sub> (2.330 Å), which is itself ~ 0.01–0.02 Å shorter than a normal Si-Si bond found, e.g., in disilane.<sup>23</sup> The oxygen-substituted ring is unique in that the Si-Si distance in it is much closer to the prototypical double bond value of 2.125 Å found in *trans*-disilene than it is to disilane (2.345 Å) or in trisilacyclopropane with use of identical methods. The NH-substituted ring has an Si-Si distance about half-way between the single and double bond lengths, and the others are all closer to the single bond value. The longest, however, in the case of PH, is still 0.06 Å shorter than that in Si<sub>3</sub>H<sub>6</sub>. The Si-Si bond lengths correlate well with the electronegativity of the heavy-atom substituent. That is, the Si-Si bond lengths decrease with increasing electronegativity of X. The CH<sub>2</sub> and S substituted rings have nearly identical Si-Si bond lengths, just as their electronegativities are close to another (even their relative electronegativities depend on the method used: Pauling, Sanderson, or Allred-Rochow<sup>43</sup>). We should note that similar C-C bond shortening has been observed for O, NH, and S substituted cyclopropanes,<sup>35</sup> but the effect is much smaller ( $\leq 0.05$  Å).

As shown in Table I, the angle  $\epsilon$ , which measures the wagging of the SiH<sub>2</sub> groups with respect to the Si-Si-X angle bisector, also increases with increasing electronegativity. In each case the

(36) Almenningen, A.; Fjeldberg, T.; Hengge, E. J. *Mol. Struct.* **1984**, *112*, 239.

(37) See, e.g.; Hummel, J. P.; Stackhouse J.; Mislow, K. *Tetrahedron* **1972**, *33*, 1925.

(38) Beagley, B.; Conrad, A. R. *Trans. Faraday Soc.* **1970**, *66*, 2740.

(39) Robiette, A. G.; Sheldrick, G. M.; Sheldrick, W. S. *J. Mol. Struct.* **1970**, *5*, 423.

(40) Glidewell, C.; Pinder, P. M.; Robiette, A. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1972**, 1402.

(41) Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M.; Beagley, B.; Freeman, J. M. *J. Mol. Struct.* **1970**, *5*, 417.

(42) Pazdernick, L.; Brisse, F.; Rivest, R. *Acta Crystallogr.* **1977**, *B33*, 1780.

(43) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper and Row: New York, 1978; pp 162–164.

(30) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(31) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 3, pp 1–27.

(32) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 4, pp 153–185.

(33) Dupuis, M.; King, H. F. *J. Chem. Phys.* **1978**, *68*, 3998.

(34) Saxe, P.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1982**, *77*, 5647.

(35) Skancke, P. N.; Forgarasi, G.; Boggs, J. E. *J. Mol. Struct.* **1980**, *62*, 259.

**Table II.** Optimized Geometries of  $C_{2v}$  Symmetry Monosubstituted Four-Membered Rings  $(H_2Si)_3X^a$ 

| parameter                  | CH <sub>2</sub> | PH    | NH    | S     | O     | SiH <sub>2</sub> <sup>d</sup> |
|----------------------------|-----------------|-------|-------|-------|-------|-------------------------------|
| $r(Si_1-Si_2)$             | 2.364           | 2.366 | 2.354 | 2.352 | 2.362 | 2.376                         |
| $r(Si_1-X)^b$              | 1.914           | 2.206 | 1.742 | 2.175 | 1.661 |                               |
| $\angle Si_1-X-Si_1$ , deg | 101.4           | 99.5  | 111.1 | 91.6  | 112.1 | 90                            |
| $r(Si_1-H)$                | 1.472           | 1.468 | 1.471 | 1.466 | 1.466 | 1.471                         |
| $r(Si_2-H)$                | 1.471           | 1.470 | 1.469 | 1.469 | 1.469 |                               |
| $\angle H-Si_1-H$ , deg    | 108.3           | 107.6 | 106.8 | 108.4 | 108.8 | 108.8                         |
| $\angle H-Si_2-H$ , deg    | 109.1           | 109.0 | 109.6 | 109.5 | 109.9 |                               |
| $\phi_{wag}^c$ , deg       | -5.7            | -0.6  | -7.1  | -9.2  | -12.1 | 0                             |
| $r(X-H)$                   | 1.088           | 1.388 | 1.002 |       |       |                               |
| $\angle H-X-H$ , deg       | 106.3           |       |       |       |       |                               |

<sup>a</sup> Bond distances in Å. For definitions of atom subscripts see Figure 3. <sup>b</sup> X = CH<sub>2</sub>, PH, NH, S, O, SiH<sub>2</sub>. <sup>c</sup> Wagging angle:  $\phi_{wag} = 2(\alpha_1 - \alpha_2)$ . For definition of  $\alpha_1$  see Figure 3. <sup>d</sup> Reference 23. Planar structure ( $D_{4h}$  symmetry).

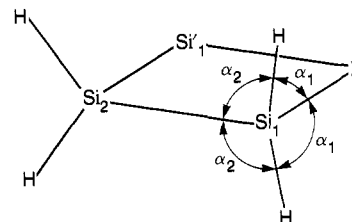
SiH<sub>2</sub> group is bent in such a way as to make the H<sub>2</sub>-Si-Si moiety more nearly planar. This is best exhibited by consideration of the angle  $\theta$ , the angle between the H<sub>2</sub>Si plane and the Si-Si bond. Inspection of Table I shows that, in each case, the bonding is more nearly planar about silicon than in Si<sub>3</sub>H<sub>6</sub>, and in particular, for the oxygen ring the Si-Si-R<sub>2</sub> fragment deviates only 6.7° from planarity: Monosubstituted cyclopropanes exhibit the same qualitative feature but, once again, on a much smaller scale. For example (H<sub>2</sub>C)<sub>2</sub>O has  $\theta \sim 22^\circ$ , and  $\theta$  for (H<sub>2</sub>C)<sub>2</sub>NH and (H<sub>2</sub>C)<sub>2</sub>S are even larger,  $\sim 26^\circ$  and  $28^\circ$ , respectively.<sup>35</sup>

While all of the molecules studied here have shown qualitatively similar distortions, i.e., shorter Si-Si bonds and Si-Si-R<sub>2</sub> frameworks closer to planarity, and the substituted cyclopropanes studied by SFB showed these distortions too, we must point out that this is not inevitable. For example, Gordon<sup>44</sup> has studied silacyclopropane [(H<sub>2</sub>C)<sub>2</sub>SiH<sub>2</sub>], in which one CH<sub>2</sub> group is replaced by the relatively electropositive SiH<sub>2</sub> unit, and there the distortions are just the opposite to those found here. That is the C-C bond distance increases and the C-C-H<sub>2</sub> framework becomes less nearly planar. Thus, the relative electronegativity of the substituent seems to play a crucial role.

Of all the rings, crystal structures of only the CH<sub>2</sub>- and S-substituted compounds are known. These both have large functional groups attached to the silicons so a direct comparison is not possible, but the results agree quite well nonetheless. For example, Masamune et al.<sup>3a</sup> found  $r(Si-Si) = 2.272$  Å,  $r(Si-C) = 1.887$  Å, and  $\theta(Si-C-Si) = 74.1^\circ$  in their CH<sub>2</sub>-substituted ring, which differs by less than 0.02 Å in the bond distances and 1.5° in the angle from our results for the parent molecule (H<sub>2</sub>Si)<sub>2</sub>CH<sub>2</sub>. One other carbon-substituted ring is known,<sup>3b</sup> but the carbon is doubly bonded to another CR<sub>2</sub> group and the Si-Si bond distance is significantly longer at 2.327 Å. Both molecules exhibit a striking degree of planarity about the silicon atoms. The only known sulfur-substituted 3MR is that of West and co-workers,<sup>2</sup> and it has  $r(Si-Si) = 2.289$  Å,  $r(S-Si) = 2.261$  Å, and  $\theta(Si-S-Si) = 64^\circ$ . Our value for the Si-Si distance is 0.04 Å shorter, but the Si-S distance and bond angles agree well. This molecule, too, was observed to be unusually near-planar about the silicon atoms.

The NH-substituted ring is planar about nitrogen, as are most silyl-substituted nitrogen compounds,<sup>38,39</sup> but the PH-substituted ring is decidedly nonplanar at the phosphorus center with the hydrogen lying out of the ring plane by 84°. The energy differences between the  $C_{2v}$  and  $C_s$  symmetry structures gives a barrier to planarity of 26 kcal/mol which is  $\sim 10$  kcal/mol less than that found for PH<sub>3</sub>.<sup>45,46</sup> The SiH<sub>2</sub> groups exhibit only slight rocking and twisting distortions, nearly identical in magnitude and sign to those found in (H<sub>2</sub>C)<sub>2</sub>NH by SFB.

**II. Four-Membered Rings.** The monosubstituted four-membered rings (4MRs) have been optimized in  $C_{2v}$  symmetry only. The optimized geometries are shown in Table II. Since these molecules have been restricted to planarity the SiH<sub>2</sub> group distortions are limited to wagging of the groups adjacent to the substituent. This distortion is defined in Table II, based on the

**Figure 3.** Definition of coordinates used to describe the monosubstituted four-membered rings in  $C_{2v}$  symmetry.**Table III.** Vibrational Frequencies and Normal Mode Assignments of  $C_{2v}$  Symmetry  $(H_2Si)_2S$  and  $(H_2Si)_2O^a$ 

| symmetry       | S    | assignment              | O    | assignment              |
|----------------|------|-------------------------|------|-------------------------|
| a <sub>1</sub> | 2434 | SiH str (100)           | 2433 | SiH str (100)           |
|                | 1055 | bend (96)               | 1083 | bend (89)               |
|                | 846  | wag (93)                | 1014 | wag (54) + OSi str (45) |
|                | 624  | ring breathe (100)      | 844  | OSi str (43) + wag (36) |
|                | 469  | ring deformation (97)   | 527  | SiSi str (92)           |
| a <sub>2</sub> | 2432 | SiH str (100)           | 2423 | SiH str (100)           |
|                | 645  | twist (91)              | 689  | rock (94)               |
|                | 613  | rock (86) + twist (14)  | 585  | twist (85) + rock (15)  |
| b <sub>1</sub> | 2438 | SiH str (100)           | 2430 | SiH str (100)           |
|                | 658  | rock (64) + twist (36)  | 740  | rock (76) + twist (24)  |
|                | 449  | twist (58) + rock (42)  | 434  | twist (63) + rock (37)  |
| b <sub>2</sub> | 2426 | SiH str (100)           | 2421 | SiH str, (100)          |
|                | 1048 | bend (99)               | 1074 | bend (98)               |
|                | 684  | wag (95)                | 871  | wag (54) + OSi str (43) |
|                | 417  | SSi str (82) + wag (17) | 591  | OSi str (49) + wag (44) |

<sup>a</sup> The assignments are based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix, given in parentheses as a percent. See text for a discussion of assignment notation.

angles shown in Figure 3. As in the 3MRs, increasing electronegativity of the substituent leads to increased wagging angles, always in the direction of the substituent. Only small differences in the Si-H distances and H-Si-H angles are observed for the groups adjacent and opposite to the substituted position, labeled Si<sub>1</sub> and Si<sub>2</sub>, respectively.

Of the five substituted 4MRs, three of them (O, S, and NH) have  $C_{2v}$  symmetry stationary points. The PH and CH<sub>2</sub> rings both prefer nonplanar geometries, as does the parent cyclohexane,<sup>23</sup> Si<sub>4</sub>H<sub>8</sub>. The largest geometrical difference between the 3- and 4MRs is that the planar PH-substituted 4MR has a P-Si distance that is 0.05 Å longer than the planar P-H substituted 3MR. It is not obvious, however, that this distance would be significantly different between the actual minimum energy structures of the 3- and 4MR. The Si<sub>1</sub>-Si<sub>2</sub> bond distance of the substituted rings is slightly shorter than that in planar Si<sub>4</sub>H<sub>8</sub> (2.376 Å) or in the minimum-energy  $D_{2d}$  structure (2.368 Å).

All of the above observations, except for the planarity of the NH- and S-substituted rings, is in general agreement with the

(44) Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7419.(45) Lehn, J. M.; Munsch, B. *Mol. Phys.* **1972**, *23*, 91.(46) Alrichs, R.; Keil, F.; Lischka, H.; Kutzelnigg, W.; Staemmler, V. *J. Chem. Phys.* **1975**, *63*, 455.

**Table IV.** Vibrational Frequencies and Normal Mode Assignments of  $C_{2v}$  Symmetry  $(H_2Si)_2CH_2^a$ 

| symmetry       | frequency | assignment   |
|----------------|-----------|--|
| a <sub>1</sub> | 3251      | CH str (100)   |
|                | 2414      | SiH str (100)  |
|                | 1525      | CH <sub>2</sub> bend (97)  |
|                | 1023      | SiH <sub>2</sub> bend (94)   |
|                | 874       | SiH <sub>2</sub> wag (63) + CSi str (36)   |
|                | 757       | CSi str (53) + SiH <sub>2</sub> wag (32)   |
| a <sub>2</sub> | 500       | SiSi str (93)  |
|                | 2415      | SiH str (100)  |
|                | 1011      | CH <sub>2</sub> twist (91)   |
|                | 668       | SiH <sub>2</sub> twist (89)  |
|                | 452       | SiH <sub>2</sub> rock (64) + CH <sub>2</sub> twist (33)                              |
| b <sub>1</sub> | 3327      | CH str (100)   |
|                | 2421      | SiH str (100)  |
|                | 856       | SiH <sub>2</sub> twist (42) + CH <sub>2</sub> rock (41) + SiH <sub>2</sub> rock (17) |
|                | 525       | CH <sub>2</sub> rock (56) + SiH <sub>2</sub> rock (41)                               |
|                | 335       | SiH <sub>2</sub> twist (52) + SiH <sub>2</sub> rock (32) + CH <sub>2</sub> rock (16) |
| b <sub>2</sub> | 2405      | SiH str (100)  |
|                | 1034      | CH <sub>2</sub> wag (83) + SiH <sub>2</sub> bend (14)                                |
|                | 1010      | SiH <sub>2</sub> bend (82) + CH <sub>2</sub> wag (16)                                |
|                | 684       | SiH <sub>2</sub> wag (75) + CSi str (22)   |
|                | 551       | CSi str (68) + SiH <sub>2</sub> wag (31)   |

<sup>a</sup>The assignments are based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix, given in parentheses as a percent. See text for a discussion of assignment notation.

hydrocarbon results of SFB. Thus the monosubstituted four-membered silicon rings do not appear to be exceptional in any way.

**III. Vibrational Frequencies.** Tables III–IX list the harmonic vibrational frequencies and normal mode assignments of the molecules studied here. The assignments have been determined on the basis of the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix, on a percentage scale. These are given in parentheses in the tables. The simple internal coordinates used are those recommended by Fogarasi and Pulay,<sup>47</sup> with only minor modification. For the three-membered S- and PH-substituted rings, the minimum energy structure ring modes are best described in pseudo- $D_{3h}$  fashion. Thus, we label these motions as ring breathe and deformation instead of SSi, PSi, or SiSi stretches. Since a large percentage of the modes refer to motions of the SiH<sub>2</sub> groups, the notation has been simplified to a considerable extent. Thus bend, wag, twist, and rock are understood to refer to the SiH<sub>2</sub> motions unless explicitly stated otherwise. Stretching motions are abbreviated str and the individual atoms are always listed. Thus, e.g., SSi str corresponds to an S–Si stretch. For the four-membered rings we have further abbreviated the notation to differentiate between motions of the SiH<sub>2</sub> groups adjacent to the substituent, labeled 1, and those trans to the substituent, labeled 2, as in Figure 3. Furthermore, bending, wagging, twisting, and rocking motions are abbreviated b, w, t, and r, respectively. Thus, for instance, 1b refers to a bending of the SiH<sub>2</sub> groups adjacent to the substituent and 2w represents a wagging of the *trans*-SiH<sub>2</sub> group. Finally, the notations oop and ip refer to out-of-plane bending and in-plane bending of NH and PH groups. For consistency, the results are compared with previous theoretical results for the unsubstituted polysilanes with use of identical basis sets.<sup>23</sup>

The first row substituted (X = O, NH, CH<sub>2</sub>) three-membered rings and all of the four-membered rings have clearly identifiable Si–Si stretches. The O, NH, and CH<sub>2</sub> substituted 3MR Si–Si stretches are all significantly higher (by 61, 45, and 34  $cm^{-1}$ , respectively) than that found in disilane (466  $cm^{-1}$ ) but much smaller than that for disilene (640  $cm^{-1}$ ), and they increase with decreasing Si–Si bond length as one would expect. On the other

hand, the Si–Si stretches of the substituted 4MRs all fall within the range 411–490  $cm^{-1}$ . The first row substituted 4MR Si–Si stretches resemble those found in trisilane (415 and 486  $cm^{-1}$ ), in that they occur in pairs split by at least 50  $cm^{-1}$ . The second row (S, PH) substituted rings, however, are more indicative of cyclotrasilane itself which has a much smaller range of Si–Si frequencies (430–463  $cm^{-1}$  for the  $D_{2d}$  minimum, 437–454  $cm^{-1}$  for the  $D_{4h}$  planar structure). As we mentioned, the S- and PH-substituted 3MRs do not have a clearly identifiable Si–Si stretching mode (due to the fact that the masses of S and P are close to that of Si), and a description in terms of breathing and deformation modes, as in a  $D_{3h}$  symmetry molecule, is much more accurate. As befits a more strongly bound ring, these frequencies are higher (624 and 469  $cm^{-1}$  for S, 572 and 455  $cm^{-1}$  for PH) than those in Si<sub>3</sub>H<sub>6</sub> (548 and 410  $cm^{-1}$ ).

In an extensive study of substituted disilanes, Hengge<sup>48</sup> has observed a strong correlation between Si–Si stretching force constants and Si–H force constants and, indeed, determination of the Si–H force constants can often be used to accurately predict associated Si–Si force constants. Thus, in light of the above observation of high Si–Si stretching frequencies is substituted 3MRs, it is not surprising that the Si–H stretching frequencies are also generally higher in these compounds. The only case in which the Si–H frequencies of the substituted 3MRs span a lower range than those in Si<sub>3</sub>H<sub>6</sub> (2392–2416  $cm^{-1}$ ) is for NH (2385–404  $cm^{-1}$ ). The reason for this is not clear, but it is worth noting that the Si–H frequencies of the  $C_{2v}$  symmetry PH-substituted 3MR (2393–2405  $cm^{-1}$ ) are considerably lower than they are at the  $C_s$  symmetry minimum (2415–2435  $cm^{-1}$ ). Thus the position of the lone pair seems to play an important role.

As in the 3MRs, the S- and O-substituted 4MR Si–H frequencies are ~20  $cm^{-1}$  higher than those of  $D_{2d}$  symmetry Si<sub>4</sub>H<sub>8</sub> (2364–2389  $cm^{-1}$ ) and the planar PH ring has Si–H frequencies that are also higher. Without fail, the highest frequencies correspond to stretches of the SiH<sub>2</sub> groups adjacent to the substituent and the two lowest to the *trans*-SiH<sub>2</sub> group. In direct contrast, the CH<sub>2</sub>- and NH-substituted 4MRs have SiH frequencies comparable to those of Si<sub>4</sub>H<sub>8</sub> and now the highest frequency motions are predominantly from the *trans*-SiH<sub>2</sub> groups. Once again, the reason for this is not obvious.

The only other motions that are relatively pure (in the sense that they are not mixtures of various motions) are the H–Si–H bends. The bending modes of the substituted 3- and 4MRs are invariably at higher frequency than in Si<sub>3</sub>H<sub>6</sub> (981–992  $cm^{-1}$ ) or Si<sub>4</sub>H<sub>8</sub> (1004–1036  $cm^{-1}$ ), and in the 4MRs the adjacent SiH<sub>2</sub> bending modes are at higher frequency than the *trans*.

Finally, we should comment on the planarity of the 4MRs. Inspection of Tables VII–IX shows that the planar rings all have ring pucker frequencies ~120  $cm^{-1}$  or less. The imaginary frequency for ring puckering in the CH<sub>2</sub>-substituted 4MR is only 75i  $cm^{-1}$ , and it is strongly coupled with rocking motions. This is very similar to the result found in planar Si<sub>4</sub>H<sub>8</sub>, which has a 60- $cm^{-1}$  imaginary frequency strongly coupled to rocking motions of the SiH<sub>2</sub> group.<sup>23</sup> The PH-substituted 4MR has a vibrational frequency of 407i  $cm^{-1}$ , less in magnitude than that found for the 3MR (633i  $cm^{-1}$ ), that mainly corresponds to out-of-plane bending of the P–H group. That ring puckering contributes so little to this mode may suggest that the optimum geometry has a nearly planar ring.

#### Discussion

Our primary goal in this research is to explain the unusual geometries of hetero-substituted cyclopolysilanes, and since the monosubstituted four-membered rings do not appear to be abnormal in any way, we will confine ourselves to a discussion of the monosubstituted three-membered rings. As mentioned in the introduction, the model we will employ is that of Dewar,<sup>26</sup> shown in Figure 1. Furthermore, we will show that this model, with only minor modification, can also explain the unusual geometries of

(47) Fogarasi, G.; Pulay, P. In *Vibrational Spectra and Structure*; Durig, J. R., Ed. Elsevier: Amsterdam, 1985; Vol. 14, pp 125–219. We have used, in their notation, the sum  $\beta_1 + \beta_2 + \beta_3 + \beta_4$  to describe the XH<sub>2</sub> bends.

(48) Hengge, E. In *Homoatomic Rings, Chains and Macromolecules of Main-Group Elements*; Rheingold, A. L., ed.; Elsevier: New York, 1977; pp 235–259.

**Table V.** Vibrational Frequencies and Normal Mode Assignments of  $C_{2v}$  Symmetry  $(H_2Si)_2PH$  and  $(H_2Si)_2NH^a$ 

| symmetry       | PH   | assignment                           | NH   | assignment                           |
|----------------|------|--------------------------------------|------|--------------------------------------|
| a <sub>1</sub> | 2682 | PH str (100)                         | 3867 | NH str (100)                         |
|                | 2405 | SiH str (100)                        | 2404 | SiH str (100)                        |
|                | 1080 | bend (98)                            | 1107 | bend (85) + NSi str (13)             |
|                | 827  | wag (97)                             | 1008 | NSi str (55) + wag (39)              |
|                | 611  | P-Si str (80) + Si-Si str (19)       | 847  | wag (53) + NSi str (34)              |
| a <sub>2</sub> | 415  | Si-Si str (82) + P-Si str (15)       | 511  | Si-Si str (94)                       |
|                | 2393 | SiH str (100)                        | 2385 | SiH str (100)                        |
|                | 625  | rock (53) + twist (47)               | 694  | rock (92)                            |
| b <sub>1</sub> | 585  | twist (52) + rock (48)               | 578  | twist (82) + rock (18)               |
|                | 2400 | SiH str (100)                        | 2392 | SiH str (100)                        |
|                | 646  | rock (49) + twist (47)               | 739  | rock (76) + twist (22)               |
|                | 520  | rock (60) + twist (35)               | 552  | twist (53) + NH oop (31) + rock (16) |
| b <sub>2</sub> | 6331 | PH oop (89) + twist (11)             | 309  | NH oop (45) + twist (36) + rock (19) |
|                | 2397 | SiH str (100)                        | 2391 | SiH str (100)                        |
|                | 1076 | bend (99)                            | 1127 | NH ip (66) + bend (29)               |
|                | 767  | wag (51) + PH ip (45)                | 1074 | bend (65) + NH ip (30)               |
|                | 620  | wag (44) + PH ip (38) + PSi str (19) | 838  | NSi str (50) + wag (44)              |
|                | 447  | PSi str (55) + PH ip (24) + wag (21) | 631  | wag (51) + NSi str (45)              |

<sup>a</sup>The assignments are based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix, given in the parentheses as a percent. See text for a discussion of assignment notation.

**Table VI.** Vibrational Frequencies and Normal Coordinate Assignments of  $C_s$  Symmetry  $(H_2Si)_2PH^a$ 

| symmetry | frequency             | assignment                           |              |
|----------|-----------------------|--------------------------------------|--------------|
| a'       | 2571                  | PH str (100)                         |              |
|          | 2435                  | SiH str (98)                         |              |
|          | 2422                  | SiH str (98)                         |              |
|          | 1012                  | bend (97)                            |              |
|          | 798                   | PH oop (75) + twist (20)             |              |
|          | 784                   | wag (94)                             |              |
|          | 572                   | ring breathe (97)                    |              |
|          | 544                   | PH oop (42) + rock (35) + twist (22) |              |
|          | 435                   | ring deformation (91)                |              |
|          | 369                   | twist (50) + rock (37) + PH oop (11) |              |
|          | a''                   | 2429                                 | SiH str (99) |
|          |                       | 2415                                 | SiH str (99) |
|          |                       | 1001                                 | bend (99)    |
| 826      |                       | PH ip (78) + twist (13)              |              |
| 676      |                       | twist (81) + rock (11)               |              |
| 610      |                       | wag (93)                             |              |
| 433      |                       | rock (58) + PH ip (34)               |              |
| 397      | ring deformation (93) |                                      |              |

<sup>a</sup>The assignments are based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix, given in parentheses as a percent. See text for a discussion of assignment notation.

1,3-disubstituted cyclotetrasilane, and in particular cyclodisiloxane. In fact the model of 1,3-disubstituted 4MRs we will develop appears to be quite general and can explain the distortions from ideal square-planar geometries observed in many types of rings such as  $(R_2CO)_2$  and the diazadiboretidines  $(RBNR')_2$ .

While Dewar's model was originally developed to describe metal-olefin bonding, it has recently been used by Cremer and Kraka<sup>29</sup> to describe main-group monosubstituted three-membered hydrocarbon rings. The molecules they investigated ranged from normal 3MRs, with exocyclic bonding, to  $\pi$ -complexes and T-structures, in which electronic density is concentrated in the interior of the ring. As it applies to the substituted cyclopolysilanes studied here, the following observations are in order. First, silicon is abnormally electropositive, and its bonding orbitals are quite high lying. This is even true of saturated straight-chain polysilanes. For example, while polysilanes are known to form charge-transfer complexes with tetracyanoethylene (TCNE),<sup>49,50</sup> saturated hydrocarbons at best form weak charge complexes and then only with strongly electron deficient halides. Second, formally antibonding orbitals of polysilanes are unusually low lying. This is evidenced by the fact that even saturated cyclopolysilanes form stable radical anions,<sup>1,23</sup> something that is observed for aromatic

hydrocarbons but never for saturated hydrocarbons. On the basis of these observations we can expect that, in terms of the model, the basal  $Si_2H_4$  unit will be both a better donor of  $\pi$ -electron density to the substituent and a better receiver of electron density through back-donation. On the other hand, the substituents considered here are all more electronegative than silicon and thus should act as better receivers of electron density but poor donors.

As far as the basal Si-Si bond distance is concerned, it seems clear that the dominating influence is the amount of back-donation into the  $Si_2H_4$   $\pi^*$  orbital. This is evidenced by the fact that the more electronegative substituents yield the shortest Si-Si distances. In principle, both increased donation to X and back-bonding from X should lead to longer basal distances. The observation that the most electronegative elements, which should be better receivers and poorer donors, actually have the shortest bond distances proves conclusively that back-donation is primarily responsible for basal bond lengthening. This is further supported by studies of the substituted cyclopropanes where, e.g., O and NH substitution lead to shorter C-C bond lengths,<sup>29,35</sup> but  $CH^{-29}$  and  $SiH_2^{44}$  substitution lead to longer bond lengths than in cyclopropane itself. We should note that this will not necessarily be the case in unsaturated molecules, because in these systems the basal unit may have unoccupied bonding orbitals that can accept electron density and lead to shorter bond distances with more electropositive substituents.<sup>29</sup>

It may seem somewhat surprising that the fragment donor-substituent acceptor mechanism does not lead to longer Si-Si distances in the rings with strongly electronegative substituents, but we must remember that the resulting multicenter MO, while it may be polarized toward the substituent, is still bonding between the basal fragment atoms. Thus, for example, bridge protonated ethylene  $(H_2C)_2H^+$ , which has a proton as a substituent and hence acts only as a receiver and not as a donor, has a C-C bond length of 1.371 Å, significantly closer to normal double bond distances than to single bond distances. Even the extremely electronegative substituent  $F^+$ , which should be a strong acceptor and a weak donor, produces a shorter C-C distance than substituents like O or NH.<sup>29</sup>

In terms of the model presented here, we can make the following statements about monosubstituted 3MRs. The unusual geometries of the substituted cyclotrisilanes observed experimentally and studied here are a direct result of decreased back-donation from the substituent into the  $\pi^*$  orbital of the  $Si_2H_4$  fragment. The electron densities of these molecules most likely show a significant buildup in the interior of the ring, as in  $\pi$ -complexes or T-structures, especially for the more electronegative substituents, and will not exhibit the standard exocyclic bonding of cyclopropane or cyclotrisilane. For a general saturated monosubstituted three-membered ring, it is the relative back-donating capacity of the substituent that determines whether the basal bond length is

(49) Traven, V. F.; West, R. *J. Am. Chem. Soc.* **1973**, *95*, 6824.(50) Sakurai, H.; Kira, M.; Uchida, T. *J. Am. Chem. Soc.* **1973**, *95*, 6826.

**Table VII.** Vibrational Frequencies and Normal Mode Assignments of  $C_{2v}$  symmetry  $(H_2Si)_3S$  and  $(H_2Si)_3O^a$ 

| symmetry       | S              | assignment                           | O                       | assignment                       |
|----------------|----------------|--------------------------------------|-------------------------|----------------------------------|
| a <sub>1</sub> | 2409           | 1 str (93)                           | 2414                    | 1 str (93)                       |
|                | 2382           | 2 str (93)                           | 2384                    | 2 str (92)                       |
|                | 1070           | 1b (96)                              | 1085                    | 1b (94)                          |
|                | 1015           | 2b (95)                              | 1027                    | 2b (58) + 1 w (31)               |
|                | 925            | 1 w (95)                             | 996                     | 1w (53) + 2b (36)                |
|                | 513            | SSi str (98)                         | 758                     | OSi str (82) + 1 w (12)          |
|                | 476            | SiSi str (96)                        | 482                     | SiSi str (92)                    |
|                | 297            | ring deform (85) + 1b (12)           | 396                     | ring deform (81) + 1b (14)       |
|                | a <sub>2</sub> | 2400                                 | 1 str (100)             | 2400                             |
| 744            |                | 1t (58) + 2t (58)                    | 760                     | 1t (77) + 1r (20)                |
| 685            |                | 2t (38) + 1r (36) + 1t (25)          | 703                     | 2t (70) + 1r (28)                |
| 431            |                | 1r (46) + 1t (27) + 2t (26)          | 409                     | 1r (41) + 1t (31) + 2t (27)      |
| b <sub>1</sub> |                | 2403                                 | 1 str (88) + 2 str (12) | 2404                             |
|                | 2386           | 2 str (88) + 1 str (12)              | 2388                    | 2 str (88) + 1 str (12)          |
|                | 698            | 1t (92)                              | 785                     | 1t (64) + 1r (35)                |
|                | 587            | 1r (78) + 2r (16)                    | 625                     | 1r (45) + 1t (38) + 2r (14)      |
|                | 367            | 2r (59) + 1r (21) + 1t (19)          | 368                     | 2r (57) + 1r (24) + 1t (19)      |
|                | 46             | ring pucker (65) + 2r (17) + 1t (13) | 123                     | ring pucker (72)                 |
|                | b <sub>2</sub> | 2401                                 | 1 str (100)             | 2403                             |
| 1053           |                | 1b (99)                              | 1063                    | 1b (98)                          |
| 835            |                | 1w (63) + 2w (32)                    | 1009                    | OSi str (74) + 1w (25)           |
| 727            |                | 2w (61) + 1w (37)                    | 839                     | 1w (52) + OSi str (25) + 2w (19) |
| 496            |                | SSi str (87)                         | 684                     | 2w (58) + 1w (25) + OSi str (15) |
| 450            |                | SiSi str (94)                        | 411                     | SiSi str (93)                    |

<sup>a</sup>The assignments are based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix, given in parentheses as a percent. See text for a discussion of assignment notation.

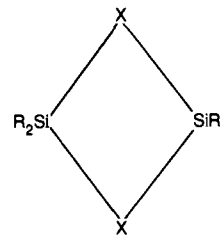
**Table VIII.** Vibrational Frequencies and Normal Mode Assignments of  $C_{2v}$  Symmetry  $(SiH_2)_3CH_2^a$ 

| symmetry       | frequency      | assignment  |
|----------------|----------------|---|
| a <sub>1</sub> | 3207           | CH str (100)  |
|                | 2381           | 2 str (54) + 1 str (46)                             |
|                | 2365           | 1 str (54) + 2 str (46)                             |
|                | 1542           | CH <sub>2</sub> bend (98)                           |
|                | 1044           | 1b (86) + 2b (12)                                   |
|                | 1016           | 2b (83) + 1b (13)                                   |
|                | 935            | 1w (84)   |
|                | 673            | CSi str (75)  |
|                | 475            | SiSi str (92)                                       |
|                | 354            | ring deform (75) + 1b (10)                          |
|                | a <sub>2</sub> | 2366  |
| 1093           |                | CH <sub>2</sub> t (45)                              |
| 745            |                | 1t (49) + 2t (44)                                   |
| 607            |                | 1t (39) + 2t (30) + CH <sub>2</sub> t (21)          |
| 344            |                | 1r (58) + 2t (23) + 1t (16)                         |
| b <sub>1</sub> | 3259           | CH str (100)  |
|                | 2378           | 2 str (78) + 1 str (22)                             |
|                | 2364           | 1 str (78) + 2 str (22)                             |
|                | 854            | 1t (63) + CH <sub>2</sub> r (25) + 1r (11)          |
|                | 647            | 1t (48) + CH <sub>2</sub> r (23) + 1r (18)          |
|                | 478            | CH <sub>2</sub> r (53) + 1r (18)                    |
|                | 342            | 2r (63) + 1r (18) + 1t (17)                         |
|                | 751            | 1r (36) + ring pucker (31) + CH <sub>2</sub> r (19) |
| b <sub>2</sub> | 2364           | 1 str (100)   |
|                | 1176           | CH <sub>2</sub> w (90)                              |
|                | 1025           | 1b (98)   |
|                | 824            | 1w (69) + 2w (25)                                   |
|                | 753            | CSi str (49) + 2w (40)                              |
|                | 686            | CSi str (40) + 2w (32) + 1w (26)                    |
|                | 425            | SiSi str (94)                                       |

<sup>a</sup>The assignments are based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix, given in parentheses as a percent. See text for a discussion of assignment notation.

shorter or longer than in the unsubstituted ring. More electronegative substituents will lead to shorter distances, as a result of decreased repulsions in the basal fragment, and electropositive substituents will have the opposite effect.

At this point we ask the questions "can the geometries of 1,3-disubstituted rings be explained by a similar mechanism?", or in other words, "is it the lack of *in-plane* 1,3-repulsions that leads to the distortions observed in many di-substituted rings?" Of course this is largely indistinguishable from asking if it is the



**Figure 4.** A 1,3-disubstituted cyclo-tetrasilane. X may be CH<sub>2</sub>, NH, O, PH, or S in the present research.

presence of 2,4 repulsions that leads to distortion, but we have asked the question in this way because the model presented above for the 3MRs explained the short basal distances in terms of unusually small repulsions, or little antibonding character, between the fragments. We would like to emphasize that we are speaking here in terms of the *in-plane ring orbitals* themselves. Previous workers have explained the distortions of 1,3-disubstituted 4MRs by discussing repulsions of *out-of-plane* lone pair orbitals as in, e.g., the diazadiboretidines (RBNR')<sub>2</sub>,<sup>51,52</sup> and cyclodisiloxanes (R<sub>2</sub>SiO)<sub>2</sub>.<sup>10,11</sup> Frankly, we find this unnecessary, and since lone pair repulsions cannot possibly explain the structures of the monosubstituted 3MRs or, for that matter, distortions of 1,3-disubstituted rings which have no lone pairs, the present analysis is more encompassing.

A general planar 1,3-disubstituted cyclo-tetrasilane is shown in Figure 4. The question, as it is usually asked, is whether the molecule will distort to a diamond shaped structure with elongated distances along one axis and furthermore along which axis will it distort? Unfortunately, analysis of these distortions is complicated by the fact that the sizes of the substituents are not the same. For example, cyclic diphosphazanes,<sup>53</sup> which contain an (N-P)<sub>2</sub> ring, invariably distort in such a way as to increase the P-N-P angle from the "ideal" 90° to 95–102°. But this seems mildly obvious when one considers that phosphorus is much larger than nitrogen, with a van der Waals radius ~1.80 Å compared to 1.55 Å for nitrogen. In fact Peterson and Wagner<sup>54</sup> have shown

(51) Hess, H. *Acta Crystallogr.* **1969**, *B25*, 2342.

(52) Paetzold, P.; Richter, A.; Thijssen, T.; Wurtenberg, S. *Chem. Ber.* **1979**, *112*, 3381.

(53) Grapov, A. F.; Razvodovskaya, L. V.; Mel'nikov, N. N. *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 606.

(54) Peterson, M. B.; Wagner, A. J. *J. Chem. Soc., Dalton Trans.* **1973**, 106.



**Table IX.** Vibrational Frequencies and Normal Coordinate Assignments of  $C_{2v}$  Symmetry  $(H_2Si)_3PH$  and  $(H_2Si)_3NH^a$ 

| symmetry       | PH             | assignment                               | NH                          | assignment                                |                             |
|----------------|----------------|--|-----------------------------|---|-----------------------------|
| a <sub>1</sub> | 2700           | PH str (100)                             | 3823                        | NH str (100)                              |                             |
|                | 2399           | 1 str (87) + 2 str (13)                  | 2391                        | 2 str (65) + 1 str (35)                   |                             |
|                | 2378           | 2 str (87) + 1 str (13)                  | 2374                        | 1 str (65) + 2 str (35)                   |                             |
|                | 1094           | 1b (97)                                  | 1105                        | 1b (95)                                   |                             |
|                | 1018           | 2b (97)                                  | 1031                        | 2b (73) + 1w (20)                         |                             |
|                | 876            | 1w (95)                                  | 993                         | 1w (56) + 2b (27) + NSi str (11)          |                             |
|                | 507            | PSi str (90)                             | 752                         | NSi str (73) + 1w (20)                    |                             |
|                | 448            | SiSi str (86)                            | 490                         | SiSi str (91)                             |                             |
|                | 299            | ring deform (88)                         | 396                         | ring deform (76) + 1b (11)                |                             |
|                | a <sub>2</sub> | 2383                                     | 1 str (100)                 | 2358                                      | 1 str (100)                 |
|                |                | 731                                      | 2t (69) + 1t (29)           | 749                                       | 1t (72) + 1r (26)           |
|                |                | 683                                      | 1r (47) + 1t (42) + 2t (11) | 709                                       | 2t (70) + 1r (26)           |
|                |                | 489                                      | 1r (42) + 1t (32) + 2t (26) | 438                                       | 1r (40) + 1t (33) + 2t (27) |
| b <sub>1</sub> | 2389           | 1 str (54) + 2 str (46)                  | 2387                        | 2 str (96)                                |                             |
|                | 2378           | 2 str (54) + 1 str (46)                  | 2358                        | 1 str (96)                                |                             |
|                | 647            | 1t (89)                                  | 788                         | 1t (47) + 1r (37) + NH oop (15)           |                             |
|                | 589            | 1r (73) + 2r (19)                        | 617                         | 1r (42) + 1t (39) + 2r (17)               |                             |
|                | 415            | 2r (57) + 1r (28) + 1t (13)              | 531                         | NH oop (78) + 1t (15)                     |                             |
|                | 118            | ring pucker (48) + 2r (36) + PH oop (13) | 369                         | 2r (49) + 1r (23) + 1t (14) + NH oop (13) |                             |
|                | 407i           | PH oop (76) + 1t (14) + ring pucker (5)  | 115                         | ring pucker (68) + NH oop (15)            |                             |
| b <sub>2</sub> | 2391           | 1 str (100)                              | 2370                        | 1 str (100)                               |                             |
|                | 1072           | 1b (99)                                  | 1294                        | NH ip (87) + NSi str (11)                 |                             |
|                | 859            | PH ip (58) + 2w (32)                     | 1082                        | 1b (99)                                   |                             |
|                | 779            | 1w (58) + PH ip (27) + 2w (13)           | 924                         | NSi str (69) + 1w (17) + NH ip (13)       |                             |
|                | 700            | 2w (52) + 1w (32) + PH ip (14)           | 826                         | 1w (51) + 2w (25) + NSi str (20)          |                             |
|                | 517            | PSi str (79)                             | 700                         | 2w (56) + 1w (29) + NSi str (13)          |                             |
|                | 447            | SiSi str (95)                            | 427                         | SiSi str (93)                             |                             |

<sup>a</sup>The assignments are based on the potential energy distribution (PED) among the diagonal elements of the symmetrized force constant matrix, given in parentheses as a percent. See text for a discussion of assignment notation.

**Table X.** Nonbonded Si...Si Distances (in Å) and Angles (in deg) in Planar 1,3-Disubstituted Four-Membered Rings  $(R_2SiS)_2$  and Si-Si Distances in the Monosubstituted Three-Membered Rings  $(H_2Si)_2X$  Studied Here

| X                | $(R_2SiX)_2$                  |                          |       | $(R_2Si)_2X$      |
|------------------|-------------------------------|--------------------------|-------|-------------------|
|                  | $r(\text{Si}\cdots\text{Si})$ | $\theta(\text{Si-X-Si})$ | ref   | $r(\text{Si-Si})$ |
| O                | 2.31-2.40                     | 86.2-91.1                | 7, 8  | 2.195             |
| NH               | 2.48-2.56                     | 91.7-94.3                | 15-18 | 2.232             |
| CH <sub>2</sub>  | 2.62                          | 85.9                     | 22    | 2.251             |
| S                | 2.81-2.84                     | 81.1-82.5                | 19-21 | 2.249             |
| PH               | 3.2                           | 89.2-92.9                | 14    | 2.270             |
| SiH <sub>2</sub> | 3.36                          | 90.0                     | 23    | 2.330             |

that the actual geometries of these rings have nonbonded P...N distances that are both about 70% of the sums of their van der Waals radii. Of course the difference between the nonbonded distance and the sum of the van der Waals radii is greater for phosphorus.

Despite often-times gross mismatches in atomic radii, many 1,3-disubstituted 4MRs distort surprisingly little from square-planar geometries and many distort in such a way as to actually decrease the distance between the bulkiest substituents. Such is the case in the cyclodisiloxanes<sup>7,8</sup> where the resulting nonbonded Si...Si distances are actually comparable to, and in one case significantly shorter than, normal Si-Si single bond distances. Similarly small or unexpected distortions are observed in other cyclopolysilanes. The nonbonded Si...Si distances and Si-X-Si angles of these are listed in Table X, along with the Si-Si bond distances found in the monosubstituted 3MRs studied here.

The first thing to notice in Table X is that the distortions from square-planar geometries are all quite small, this despite the fact that the van der Waals radius of silicon (2.10 Å) is significantly larger than any of the substituents: P (1.80 Å), S (1.80 Å), C (1.70 Å), N (1.55 Å), and O (1.42 Å).<sup>55</sup> Given this discrepancy in size it is surprising that any of the molecules would distort to yield Si-X-Si angles less than 90°, like the diphosphazanes mentioned earlier, but in fact at least one example of each of these types is known which distorts in just that way, except for nitro-

gen.<sup>15-18</sup> But even there the distortion is small and, indeed, it is smaller than that in the diphosphazanes where the size mismatch was considerably less. A second observation from Table X is that the nonbonded distances in the 1,3-disubstituted 4MRs almost exactly parallel the Si-Si bond distances in the monosubstituted 3MRs, the only exception being between CH<sub>2</sub> and S which had nearly identical distances in the 3MRs. Although this is by no means conclusive, it is highly suggestive that the causes may be identical. That is, if we consider the 1,3-disubstituted 4MRs to be bridged disilenes, then by analogy with the discussion of the 3MRs we might explain the 4MR geometries by saying that little back-donation into the  $\pi^*$  orbital is occurring, and hence the antibonding repulsions between the silicons are much less than they would be otherwise. Furthermore, these antibonding repulsions will be smaller as the electronegativity of X increases.

One way to check this hypothesis, in a qualitative way, is to determine the Mulliken overlap populations for the atoms across the ring. Thus we chose to optimize the cyclodisiloxane and cyclodisilathiane rings and compare the results of the overlap population analysis to other cases that have nonbonded silicons like planar cyclotetrasilane ( $Si_4H_8$ ) and trisilane ( $Si_3H_8$ ). The optimized geometries were the following for  $(H_2SiO)_2$ ,  $r(\text{Si-O}) = 1.661$  Å,  $r(\text{Si-H}) = 1.458$  Å,  $\theta(\text{H-Si-H}) = 110.7^\circ$ , and  $\theta(\text{Si-O-Si}) = 91.7^\circ$ ; and for  $(H_2SiS)_2$ ,  $r(\text{Si-S}) = 2.152$  Å,  $r(\text{Si-H}) = 1.459$  Å,  $\theta(\text{H-Si-H}) = 109.5^\circ$ , and  $\theta(\text{Si-S-Si}) = 83.4^\circ$ . These results are in general agreement with both previous theoretical results<sup>9-13</sup> and experiment.<sup>7,8,19-21</sup> The nonbonded Si...Si distances were 2.383 Å for  $(H_2SiO)_2$  and 2.865 Å for  $(H_2SiS)_2$ . Now one would usually expect that, as the nonbonded distance becomes smaller, the overlap population,  $n$ , will become more negative. Indeed, if one looks at the monosubstituted 4MRs, this is the case. For example,  $(H_2Si)_3PH$  has  $r(\text{Si}\cdots\text{Si}) = 3.367$  Å and  $n(\text{Si}\cdots\text{Si}) = 0.120$ ,  $(H_2Si)_3S$  has  $r = 3.117$  Å and  $n = -0.136$ ,  $(H_2Si)_3NH$  has  $r = 2.873$  Å and  $n = -0.177$ , and  $(H_2Si)_3O$  has  $r = 2.756$  Å and  $n = -0.195$ . However, for the 1,3-disubstituted rings just the opposite occurs, i.e., the overlap population becomes more positive (less negative) as  $r$  decreases. Thus in planar  $Si_4H_8$ ,  $r = 3.360$  Å and  $n = -0.152$ ; in  $(H_2SiS)_2$ ,  $r = 2.865$  Å and  $n = -0.068$ ; and for  $(H_2SiO)_2$ ,  $r = 2.383$  Å and  $n = -0.011$ ! In fact the overlap population in cyclodisiloxane is more positive than it is in trisilane,  $Si_3H_8$ , which has  $r = 3.896$  Å and  $n = -0.046$ ! Of course overlap populations are basis set dependent quantities



and should not be taken too seriously, but the trend here is obvious and, we are convinced, very real. Coincidentally, with two sets of polarization functions on both silicon and oxygen we find a positive overlap population,  $n = 0.017$ , further muddying the issue of whether there is an actual bond between the two silicons in cyclodisiloxane.

By analogy with the analysis of the substituted 3MRs, we can make some basic predictions about the bonding in the disubstituted 4MRs. For example, just as the lack of  $\pi^*$  contribution to the bonding in the 3MRs leads to electron densities concentrated in the interior of the three-membered ring (and a description in terms of  $\pi$ -complexes and T-structures), we can predict that in the disubstituted 4MRs there will be an unusual amount of electron density in the interior of the Si-X-Si ring. In fact theoretical evidence for this exists in the literature. In particular, Sax<sup>56</sup> has shown that valence electron density plots of cyclotetrasilane exhibit small distortions in the bond regions of the Si-Si bonds, showing slightly outward-bent bonds. On the other hand O'Keefe and Gibbs<sup>10</sup> have analyzed deformation density plots of  $(\text{H}_2\text{SiS})_2$  which clearly show separated bonding peaks between Si and S and for  $(\text{H}_2\text{SiO})_2$  which show bonding peaks between Si and O *joined by a ridge of high density in the interior of the ring*. Thus this analogy with the monosubstituted 3MRs also seems to hold true.

Finally we should turn to the hoary question of whether or not a bond exists between the two silicons in cyclodisiloxane. All of the researchers that have asked this question in the past have concluded that there is no bond,<sup>10-12</sup> but there is some chemical evidence to suggest that a bond may exist. In particular, while most of the reactions of the cyclodisiloxanes yield products with no Si-Si bond, reduction of tetramethylcyclodisiloxane with lithium naphthalide followed by quenching with water yields a disilanediol,<sup>7</sup> which does have an Si-Si bond. Now it may well be that no buildup of electron density (or anything resembling whatever it is that chemists think of as a bond) exists between the silicons, but the previous analysis suggests that at least a sort of  $\pi$ -bond (in the plane) may exist between the silicons, somewhat analogous to the multicenter bonding in, e.g.,  $\text{H}_3^+$ . In a sense then, by analogy with the monosubstituted 3MRs, we can call this a "dibridged  $\pi$ -complex", with the bonding between the silicons being not unlike that of a  $\pi$ -bond, unsupported by a  $\sigma$ -bond. Thus, for

lack of a better word, we could describe the bonding between the silicons as an "unsupported  $\pi$ -bond".

### Conclusions

While the  $\text{CH}_2$ , S, O, NH, and PH substituted four-membered cyclopolysilane ring appear to be fairly normal from a structural point of view, the monosubstituted three-membered rings have remarkable geometries. The Si-Si bond lengths are all considerably shorter than a normal single bond length, and in the case of oxygen substitution, the Si-Si distance is much closer to double bond lengths. In addition the bonding about the silicon atoms is nearly planar. These results are interpreted via Dewar's model of metal-olefin bonding, and the structures and electron densities are those of  $\pi$ -complexes, or even T-structures.

By a simple extension of Dewar's model to include dibridged compounds, we arrive at a model of bonding in saturated 1,3-disubstituted four-membered rings which seems to account for a vast array of data on these compounds. The model involves consideration of the ring orbitals themselves, and in its present form it makes no use of 1,3 lone pair repulsions. It is, in essence, a one-parameter model; only a knowledge of the relative electronegativities of the ring members is required, although the sizes of the atoms are obviously important as well. In cases of extreme electronegativity differences, such as in the cyclodisiloxanes, the bonding may be described as that of a "dibridged  $\pi$ -complex". The bonding between the silicon atoms in cyclodisiloxanes has been described as a multicenter bond very much  $\pi$ -like, and it may have no significant amount of electron density directly between the silicons. That is, there may be no  $\sigma$ -type bond to support the  $\pi$ -type multicenter bond. For this reason, we describe the bonding between the silicons as an "unsupported  $\pi$ -bond".

**Acknowledgment.** We thank Prof. Robert West for helpful discussions. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

**Registry No.**  $(\text{H}_2\text{Si})_2\text{PH}$ , 110205-55-5;  $(\text{H}_2\text{Si})_2\text{NH}$ , 157-32-4;  $(\text{H}_2\text{Si})_2\text{S}$ , 95912-91-7;  $(\text{H}_2\text{Si})_2\text{O}$ , 72926-93-3;  $(\text{H}_2\text{Si})_3$ , 18548-76-0;  $(\text{H}_2\text{Si})_2\text{CH}_2$ , 51130-21-3;  $(\text{H}_2\text{Si})_3\text{CH}_2$ , 79793-09-2;  $(\text{H}_2\text{Si})_3\text{PH}$ , 68492-56-8;  $(\text{H}_2\text{Si})_3\text{NH}$ , 110205-56-6;  $(\text{H}_2\text{Si})_3\text{S}$ , 87804-56-6;  $(\text{H}_2\text{Si})_3\text{O}$ , 87729-91-7;  $(\text{H}_2\text{Si})_4$ , 287-69-4;  $(\text{H}_2\text{SiO})_2$ , 34392-10-4;  $(\text{H}_2\text{SiS})_2$ , 287-67-2;  $\text{Si}_3\text{H}_8$ , 7783-26-8.

(56) Sax, A. F. *Chem. Phys. Lett.* **1986**, *127*, 163.