*Inorganica Chimica Acta*, *112* (1986) 159–165

# Why are Cyclodisilazane Rings more Stable than Cyclodisiloxanes? A Qualitative Molecular Orbital Approach to the Bonding in Cyclodisilazanes and Cyclodisiloxanes

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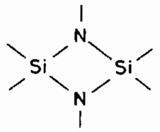
Received June 1, 1985

## Abstract

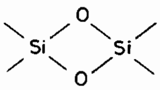
The approximate molecular orbitals of cyclic $Si_2E_2$ (E = nitrogen or oxygen) rings are discussed. It is shown that, due to high silicon $3p_z$ orbital contribution to the siloxane HOMO, the 3d orbitals can not strenghten the silicon–oxygen bond. In contrast, in the silazane ring considerable $Si(3d_\pi)$–$N(2p_\pi)$ bonding may occur. These additional $\pi$ bonds are responsible for the relative stability of cyclodisilazane rings as compared with the isoelectronic cyclodisiloxane rings.

## Introduction

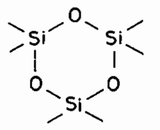
In the chemistry of inorganic heterocycles, small (e.g. four-membered) rings are quite frequent [1]. However, in the case of silicon, the great variety of disilazanes (**a**) and a paucity of cyclic disiloxanes (**b**) is intriguing. Geometric parameters suggest that both these rings are the subject of considerable strain, so questions arise as to why **a** should be more stable than **b**, and why the Si–O bonds are better accommodated in larger cyclic siloxanes like **c** or **d**. Another point of interest regarding these compounds is the variation of SiNSi and SiOSi angles with the substituents on the silicon and/or nitrogen atoms.



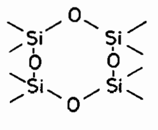
**a**



**b**



**c**

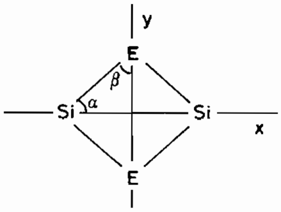


**d**

The aim of the present work is to link some of the experimental structural data on these compounds within a chemically reasonable model, on the basis of simple qualitative molecular orbital arguments*. Before going into any discussion of the results, we feel obliged to suggest that the reader take them no more seriously than we intend them to be taken. We are aware of the weaknesses of the methods we used, but at the same time one has to keep in mind that such models are still extremely useful for both experimental and theoretical chemists.

## Results and Discussion

Consider first a bare ring consisting of two silicon atoms alternating with two E atoms which possess only s and p type orbitals. For simplicity, we show these atoms at the corners of a square, as in **e**. Before combining the valence orbitals of Si and E (E = oxygen or nitrogen) to form the molecular orbitals**, it is useful to classify the atomic orbitals of the model, according to the symmetry species of the $D_{2h}$ point group. Table I contains the proper symmetry-adapted combinations of silicon and E orbitals. For simplicity, we dropped the principal quantum number, maintaining the symbol designating the atom to which a particular orbital belongs. For the technical aspects



**e**

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*For the principles of constructing qualitative MO diagrams of simple inorganic molecules see ref. 2.

**The valence orbitals of cyclobutane, a geometrically similar molecules are discussed in ref. 3.

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TABLE I. Symmetry-Adapted Combinations of $Si_2E_2$ Ring Orbitals

| Symmetry type | Ring atoms orbital combinations |
|---|---|
| $A_g$ | $s(Si_1) + s(Si_2)$; $s(E_3) + s(E_4)$; $p_x(Si_1) - p_x(Si_2)$; $p_y(E_3) - p_y(E_4)$; $d_{x^2-y^2}(Si_1) + d_{x^2-y^2}(Si_2)$; $d_{z^2}(Si_1) + d_{z^2}(Si_2)$ |
| $B_{1g}$ | $p_y(Si_1) - p_y(Si_2)$; $p_y(E_3) - p_y(E_4)$; $d_{xy}(Si_1) + d_{xy}(Si_2)$ |
| $B_{2g}$ | $p_z(Si_1) - p_z(Si_2)$; $d_{xz}(Si_1) + d_{xz}(Si_2)$ |
| $B_{3g}$ | $p_z(E_3) + p_z(E_4)$; $d_{yz}(Si_1) + d_{yz}(Si_2)$ |
| $A_u$ | $d_{yz}(Si_1) - d_{yz}(Si_2)$ |
| $B_{1u}$ | $p_z(Si_1) + p_z(Si_2)$; $p_z(E_3) + p_z(E_4)$; $d_{xz}(Si_1) - d_{xz}(Si_2)$ |
| $B_{2u}$ | $s(E_3) - s(E_4)$; $p_y(Si_1) + p_y(Si_2)$; $p_y(E_3) + p_y(E_4)$; $d_{xy}(Si_1) - d_{xy}(Si_2)$ |
| $B_{3u}$ | $s(Si_1) - s(Si_2)$; $p_x(Si_1) + p_x(Si_2)$; $p_x(E_3) + p_x(E_4)$; $d_{x^2-y^2}(Si_1) - d_{x^2-y^2}(Si_2)$; $d_{z^2}(Si_1) - d_{z^2}(Si_2)$ |

of producing such combinations, see, for example, ref. 4.

The overlap of silicon 3s and E 2s combinations belonging to $a_g$ representation will generate the lowest energy bonding molecular orbital $1a_g$ as shown in Fig. 1. The next two MOs $1b_{2u}$ and $1b_{3u}$ will have mainly nonbonding character localized at the silicon or E atoms. As we are talking about E as nitrogen or oxygen, the $1b_{2u}$ combination of $s(E_3) - s(E_4)$ should have lower energy than $1b_{3u}$ $(s(Si_1) - s(Si_2))$, since both nitrogen and oxygen are more electronegative than silicon. Both $1b_{2u}$ and $1b_{3u}$ may, however, be lowered in energy by the in-phase mixing with the proper $p_y$ and $p_x$ orbitals of silicon (f) (note that the $Si_2E_2$ rings are in the $x0y$ plane)

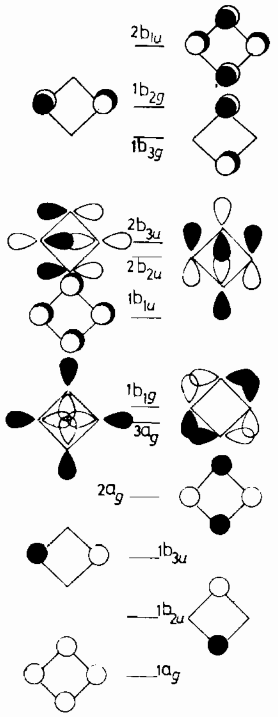
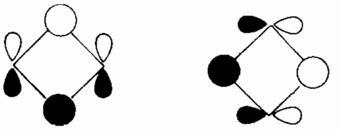
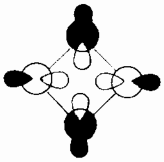


Fig. 1. Qualitative MO leveling in $Si_2A_2$ type rings.



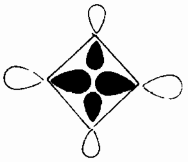
f

The next MO should be antibonding with respect to the Si–N bonds, and it is of $a_g$ symmetry ($2a_g$ of Fig. 1). Again $p_x(Si_1) - p_x(Si_2)$ and $p_y(E_3) - p_y(E_4)$ are allowed by symmetry to mix with $2a_g$ (g) and consequently $2a_g$ is somewhat stabilized.

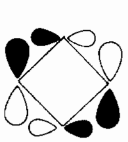


g

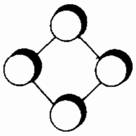
The next MOs are mainly combinations of p orbitals. Their in-phase overlap over the entire ring may proceed in the three ways shown by h, i and j:



h



i

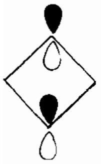


J

If we denote by $S_p^\sigma$ and $S_p^\pi$ the standard σ and π overlap integrals of p(Si) and p(E) orbitals, we find that $\int p_x(Si_1)\, p_y(E_4) d\nu = S_p^\sigma \cos\alpha \cos\beta + S_p^\pi \sin(\alpha +$

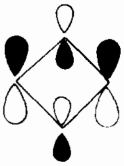
$2\beta)\sin(2\alpha + \beta)$ and $-\int p_y(Si_1)p_x(E_4)d\nu = S_p^{\sigma} \sin\alpha \sin\beta + S_p^{\pi} \cos\alpha \cos\beta$. Since in the chosen model $\alpha$ and $\beta$ have values of 45°, both of these integrals are approximately equal $0.5(S_p^{\sigma} + S_p^{\pi})$. Hence **h** and **i** should have about the same energy (**i** slightly higher), but lower energy than **j**, where only pure $\pi$ overlap occurs. These assumptions lead to the ordering shown in Fig. 1, *i.e.* $3a_g < 1b_g < 1b_{1u}$.

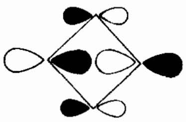
Next higher in energy should be the nonbonding MOs resulting from the out-of-phase combinations of $p_y(E_3)$ with $p_y(E_4)$, and $p_x(Si_1)$ with $p_x(Si_2)$, of $b_{2u}$ and $b_{3u}$ symmetry shown, respectively, as **h**′ and **j**′:


**h**′


**i**′

Since the overlap of $p_y$ orbitals of E atoms is rather small at the distance of *ca.* 2.30 Å (chosen to simulate real cases with E = nitrogen or oxygen), and the $p_y$ orbitals of E have lower energies than those of silicon, the energy of **h**′ should be lower than that of **i**′. However, both of them may be displaced to lower energies by the in-phase mixing with the $p_y$ combinations of silicon and $p_x$ combinations of E, giving $2b_{2u}$ and $2b_{3u}$, shown as **h**″ and **i**″ respectively.

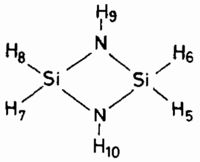

**h**″

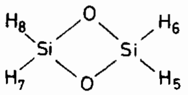

**i**″

So, the primary nonbonding (or slightly antibonding) character of **h**′ and **i**′ is diminished.

Now, besides the $1b_{1u}$ type interaction, the $p_z$ orbitals generate three more MOs, which clearly will be disposed in the following succession: $1b_{3g} < 1b_{2g} < 2b_{1u}$ (Fig. 1). Since the systems wer are dealing with contain no more than 24 electrons, higher MOs constructed with s and p atomic orbitals will not be considered in the present discussion.

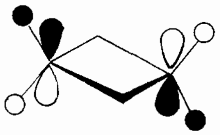
The nature of E atoms (nitrogen or oxygen) should play an important role in some properties of this type of ring. In order to improve the above qualitative picture of the MO succession, we carried out MO calculations at the extended Huckel level [5] on two basic model compounds, $H_4Si_2N_2H_2$ and $H_4Si_2O_2$, possessing only $\sigma$ type substituents on the ring



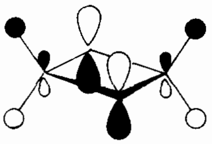


atoms (the orbitals on the ligands are designated by $s_5$ through $s_8$ on silicon and $s_9$, $s_{10}$ on nitrogen).

Let's take first the silazane ring. The computed energy levels show the same ordering of the first four occupied MOs, as predicted in Fig. 1, and no major influence of substituents on these MOs can be observed. It is $1b_{2g}$ of the higher MOs which is considerably affected by the mixing with $s_5 - s_6$ and $s_7 - s_8$ combinations of the ligand $\sigma$ type orbitals (**k**), so its energy drops enough to leave $2b_{1u}$ and $1b_{3g}$ as the highest occupied MOs.


**k**

The $1b_{3g}$ of Fig. 1 is not affected by the ligands attached to the ring because the overlap of $p_z(N_4) - p_z(N_3)$ (of $b_{3g}$ symmetry) gives zero overlap with the ligand's $\sigma$ orbitals. Actually, $2b_{1u}$ is altered (as a linear combination of ligand orbitals of $b_{1u}$ symmetry is possible) in the way illustrated in **k**′, but it still remains the occupied molecular orbital with the highest energy.


**k**′

What is remarkable about **k**′ is that the EH calculations reveal small coefficients of $p_z(Si_1)$ and $p_z(Si_2)$ relative to $p_z(N_3)$ and $p_z(N_4)$ (0.074 *vs.* 0.641). Recalling Table I, we see that the symmetry of HOMO is perfectly suited for overlapping with $3d_{xz}(Si_1) - 3d_{xz}(Si_2)$, a combination which is also of $b_{1u}$ symmetry, **l**:

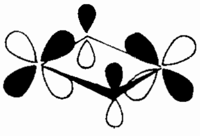
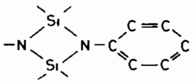
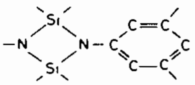
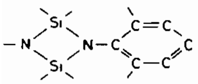
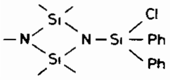
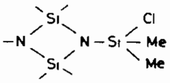
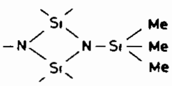
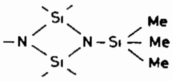

**l**

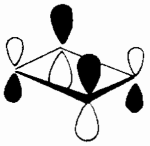
TABLE II Some Geometrical Parameters of Cyclodisilazane Rings

| Compound | | Si–N | N–R | SiNSi (°) | NSiN (°) | Reference |
|---|---|---|---|---|---|---|
|  | I | 1 74 | 1 38 | 94 3 | 85 7 | 8 |
|  | II | 1 74 | 1 41 | 94 | 85 | 11 |
|  | III | 1.73 | 1 45 | 92 9 | 87 1 | 11 |
|  | IV | 1 75 | 1 71 | 92 | 88 | 12 |
|  | V | 1 745 | 1 69 | 91 | 89 | 14 |
|  | VI | 1 72 | 1 71 | 92 | 88 | 13 |
|  | VII[a] | 1 72–1 75 | 1 71 | 89.1 | 90 1 | 15 |

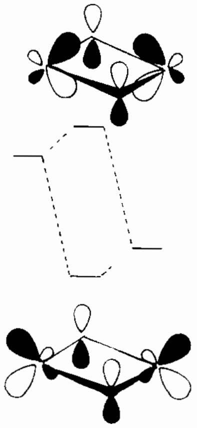
[a] This is the terminal fragment of (2b) from ref. 15

Note that the magnitude of $p_z(Si_1)$ and $p_z(Si_2)$ (these are the orbitals of silicon which could affect the angular distribution of d electron density around this atom) is negligible and too small to disturb the in-phase matching of $d_{xz}(Si_1) - d_{xz}(Si_2)$ with $p_z(N_3) + p_z(N_4)$. In other words, the electron pair of the HOMO is allowed by symmetry* to delocalize into the 3d orbitals of silicon, and in this way a better Si–N bonding is afforded. Another potential $d_\pi$–$p_\pi$ interaction could occur between $1b_{3g}$ of Fig. 1 and the $b_{3g}$ symmetry combination of silicon 3d orbitals ($d_{yz}(Si_1) + d_{yz}(Si_2)$). The Si–N bond lengths of about 1.72–1.75 Å found in most disilazane rings (see Table II) *vs.* 1.80 Å, the corrected sum of covalent radii [7], support these additional $d_\pi$–$p_\pi$ interactions. A $\pi$ bond order of 0.34 was also found by a PPP treatment of 1,3-diphenyl-2,2,4,4-tetramethylcyclodisilazane [8].

We now turn back to the disiloxane ring $H_4Si_2O_2$. Contrasting the silazanes, the HOMO $2b_{1u}$ has a higher $-p_z(Si_1) - p_z(Si_2)$ degree of mixing, along with a smaller $p_z(O_3) + p_z(O_4)$ contribution **m**, *i.e.* the antibonding character of this orbital is more pronounced than that of the silazane $2b_{1u}$ orbital. Let us again allow $d_{xz}(Si_1) - d_{xz}(Si_2)$ to mix into $2b_{1u}$ as above. Since the nodal pattern of the perturbed $2b_{1u}$ is of great importance in differentiating $Si_2O_2$ and $Si_2N_2$ rings, the interaction diagram is visualized in **n**.



**m**



**n**

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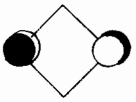
*This is a symmetry allowance Silicon 3d orbitals should be also energetically available, the case of trisilylamine is well known as an example of Si–N $d_\pi$–$p_\pi$ bonding [6]

Due to 3d(Si) – 3p(Si) hybridization, the out-of phase overlapping of $p_z(Si_1)$ and $p_z(Si_2)$ with $p_z(O_3)$ and $p_z(O_4)$ in $2b_{1u}$ is diminished; the new lobes of silicon orbitals in $2b_{1u}$ are directed outside the ring, rather than inside, and thus do not contribute to strengthening the ring bonds.

Hence, a major difference between the bonding in cyclic disiloxanes and disilazanes could be related to this behavior of the $2b_{1u}$ HOMO: in the silazane rings the Si–N bond is strengthened by the intervention of silicon 3d orbitals (as the $p_z$ contribution of silicon to $2b_{1u}$ is small and **l** is favored over **n**), as they are directed to the nitrogen $p_z$ orbitals; in the siloxane ring the interaction shown in **n**, where the silicon hybrid orbitals are oriented outside the ring bonding direction, is important.

This way, the ring strain in the cyclodisilazanes could be outweighted by the supplementary $d_\pi$–$p_\pi$ interactions, while in the cyclodisiloxanes these interactions are much smaller in magnitude. It should be mentioned here that CNDO/2 calculations [9] suggest direct silicon–silicon interactions, greater in silazane and lesser in siloxane four-membered rings. However, as k′ and n show, these are not pure Si–Si interactions as long as nitrogen or oxygen $p_z$ orbitals are also involved in these MOs.

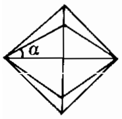
In order to preserve the strained ring of cyclodisiloxanes, bulky substituents on silicon with good spacial screening are needed. The fulfillment of this requirement recently made possible the first synthesis of a $Si_2O_2$ ring [10]. Another suggestion for stabilizing the $Si_2O_2$ ring emerges from the nodal properties of $1b_{2g}$ MO, o, which show that electron-withdrawing substituents like–$CF_3$ or, better, –$C(CF_3)_3$ should decrease the energy of this orbital.



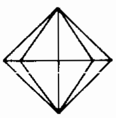
**o**

### *A Comment on the Ring Angles in Cyclodisilazanes and Cyclodisiloxanes*

The particular form of $2b_{1u}$ HOMO and the effect of silicon 3d orbitals have obvious consequences for the size of SiNSi bond angles. We mentioned the Si–N bond strengthening by the $3d_\pi$–$2p_\pi$ interactions. The Si–N bond may be shortened in the two ways shown below, **p** and **r**:

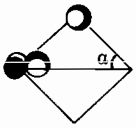


**p**



**r**

In the first case **p**, an opening of the SiNSi angle takes place; in the second (**r**), this angle is closed. We now show that the 3d(Si) – 2p(N) overlap is favored in the first case, (**p**). For this, consider the $d_{yz}$ orbital on silicon and the $p_z$ orbital on $N_4$ as in s:



s

The overlap integral of these orbitals in $S_{dp} = \int d_{yz}(Si)\, p_z(N)\, d\nu = S_{dp}{}^{\pi} \cos \alpha$, where $S_{dp}{}^{\pi}$ is the standard $\pi$ overlap integral of the two functions. As $\alpha$ decreases from 45° (the SiNSi angle increases), the nitrogen $p_z$ orbital comes into a more favorable position for overlapping with the $d_{yz}$ orbital of silicon. This way, SiNSi angles somewhat larger than 90° are expected for cyclodisilazanes. The extended Huckel calculated SiNSi angle falls around 92°, in good agreement with the experimentally determined structures of numerous $Si_2N_2$ cyclic derivatives. Table II includes some of the structural data on various cyclodisilazanes with different substituents on nitrogen or silicon. Although the observed differences are relatively small, they are still significant (the precision of the experimental data is within 0.2–0.4°). A quantitative ring angle/substituent relation can not be easily drawn; however, some tendencies in this variation can be made clearer on the basis of MO arguments.

Thus, in cyclodisilazanes, the $1b_{3g}$ level which lies immediately under $2b_{1u}$ can be regarded as the host of a nitrogen lone pair. If the nitrogen substituents are phenyl groups, this lone pair is disputed between the silicon 3d orbitals and the vacant $\pi^*$ orbitals of the phenyl groups. Since the latter have lower energy than those of silicon, they are preferred: consequently, the N–R bond is strenghtened* and the SiNSi angle increases as the antibonding interaction of $1b_{3g}$ is reduced. The observed SiNSi angles in this situation are around 94°. (**I** and **II** of Table II). If steric hindrance prevents or reduces the silicon–nitrogen $3d_\pi$–$2p_\pi$ bonding (as in **III** of Table III where the *ortho*-substituted phenyl group is rotated by *ca.* 67° relative to the silazane ring), the N–R bond shortening is much more moderate and the SiNSi angle is somewhat decreased. In examples **IV**–**VII** in Table II, the competition for the nitrogen lone pairs has approximately equal partners – the endocyclic and exocyclic silicon 3d orbitals. Hence, small variations in the SiNSi angles are noted for these compounds [22].

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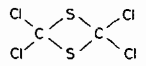
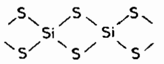
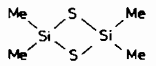
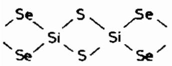
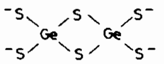
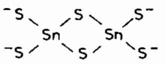
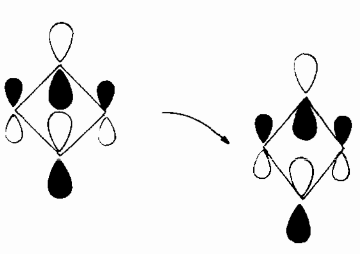
*For the single N–C bond a value of 1.45 Å is estimated on the basis of Shomaker-Stevenson approximation.

In the siloxane ring, the molecular orbital which by its nodal properties controls the SiOSi angle is $1b_{2g}$. Small SiOSi angles would create unfavorable overlap of the silicon $3p_z$ orbitals, so higher angles than in silazanes are expected. To verify this SiOSi angle opening in cyclodisiloxanes, the $E_2^{IV}E_2^{VI}$ homologs (E = an element of group IV, which may differ from silicon, and group VI, respectively) were examined (Table III).

TABLE III. The Values of $E^{IV}E^{VI}E^{IV}$ Angles in some $E_2^{IV}$-$E_2^{VI}$ Cyclic Compounds ($E^{IV}$ = C, Si, Ge, Sn; $E^{VI}$ = S, Se)

| Compound | $E^{IV}E^{VI}E^{IV}$ angle | Reference |
|---|---|---|
|  | 83.9 | 16 |
|  | 81. | 17, 18 |
|  | 82 | 19 |
|  | 81 | 20 |
|  | 86.1 | 21 |
|  | 86. | 21 |

The small $E^{IV}E^{VI}E^{IV}$ angles (81–86°) are really shocking. Krebs and Berger [16] suggest that the repulsion of the external lone pairs of $E^{VI}$ cause this angle to tighten, but at the same time, an internal orbital ring interaction might also be responsible for the small $E^{IV}E^{VI}E^{IV}$ angles observed. It is the $2b_{2u}$ MO consisting mainly or $E^{VI}$ $p_y$ orbitals (**t**) which influences the ring angle*, as the overlap across the ring of these $p_y$ orbitals is not negligible. Consequently, these systems deform in such a way as to bring the silicon (carbon, germanium, tin) atoms closer, thus reducing the unfavorable out-of-phase interaction of the sulfur (selenium) $p_y$ orbitals. Thus the effect of $2b_{2u}$ MOs, which reduces the bond angle at the chalcogen atom, compensates in part for the effect of the $1b_{2g}$ MO. The actual bond angle at the chalcogen and the transannular Si···Si distance will be the result of a compromise between the two opposite effects.



## Acknowledgement

We thank an unknown reviewer for calling our attention to a refined calculation on $(H_2SiO)_2$ which was published after this manuscript was submitted [23].

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*At this distance, the overlap of the oxygen $p_y$ orbitals is quite small and probably has little influence on the ring angle.

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