J. Phys. Chem. A **2000,** *104,* 8989−8994

Cyclic Delocalization of the Oxygen Lone Pair Electrons in the Unusual Structures of Disilaoxirane and 1,3-Cyclodisiloxane

Jing Ma and Satoshi Inagaki*

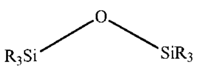
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

Received: April 13, 2000; In Final Form: July 13, 2000

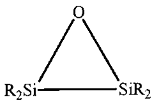
Significant interactions between the n orbitals of the oxygen lone pair electrons and the d-type polarization functions of the silicon atoms in disiloxane (**1**), disilaoxirane (**2**), and 1,3-cyclodisiloxane (**3**) were demonstrated by numerical evaluation of the bond interactions. The calculated Lewis index showed that the Si−O double bond model contributes more than the single bond and π-complex models. The oxygen atoms tend to form dative π bonds to the silicon atoms or be tetravalent. In the ring systems **2** and **3**, the lone pair electrons delocalize in a cyclic manner by the interaction of the p orbital of the oxygen lone pair and the d functions of the Si atoms. The cyclic delocalization is responsible for the short Si−Si bond in **2** and the short nonbonded Si···Si distance of **3**. The elongation of the distance between the silicon atoms in the protonated and cation radical species of **2** and **3** was predicted from the cyclic delocalization and confirmed by ab initio molecular orbital calculations.

1. Introduction

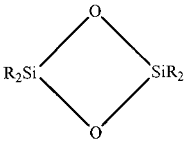
Some compounds containing silicon−oxygen bonds, such as **1**−**3**, have unusual geometry.[1−5] In disiloxane (**1**; R = H), the Si−O bond is short, and the Si−O−Si bond angle (144.1°)[3] is much wider than that in dimethyl ether **4** (111.5°).[6] The most striking feature of a three-membered ring (3MR) molecule, disilaoxirane **2** (R = H), is the extremely short Si−Si bond length. For example, the X-ray structure of 1,1,2,2-tetramesityldisilaoxirane (**2**; R = mesityl) exhibits a short Si−Si bond of 2.227 Å, which is much closer to that of a typical double bond length (ca. 2.16 Å) than to a normal Si−Si single bond (ca. 2.38 Å).[4] The strain energy was calculated to be very high, being almost 2.5 times higher than that of its carbon counterpart **5**.[7] The X-ray structure of a four-membered ring (4MR) molecule, 1,3-cyclodisiloxane **3** (R = mesityl) showed a remarkably short nonbonded Si···Si distance (2.31 Å),[5a] even shorter than the normal Si−Si single bond length. The Si···Si separation is also shorter than the nonbonded O···O distance (2.47 Å), although the van der Waals radius of Si atom is larger than that of O atom.



1



2



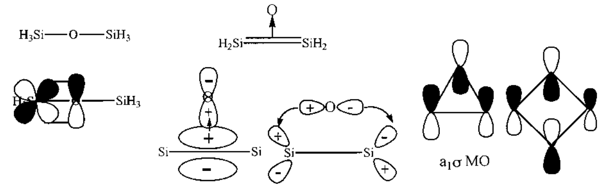
3

The unusual structures have raised some intriguing bonding models for such compounds containing silicon−oxygen bond.[8−20] The oldest chemical bonding model is the well-known but disputed (d−p) π-bonding, which still appears in some textbooks recently published by Cotton, Wilkinson, and Gaus.[21] Janes and Oldfield concluded, based on the analysis of oxygen-17 quadrupole coupling constants, that (d−p) π-bonding is important in silicates.[22] Grev and Schaefer applied the Dewar−Chatt−Duncanson model[11] for metal−olefin complexes to explain the structure of disilaoxirane (**2**).[12] They proposed that an electronegative atom X should shorten the basal Y−Y bond in the three-membered rings due to the decrease in the π back-donation from X to the Y═Y component. This explanation is, however, not necessarily convincing. The electronegative atom enhances the σ-donation, which is accompanied with the loss of the electron density from the π bonding orbital or with the elongation of the basal bond. Liang and Allen[13] employed the σ-bridged-π bonding model to draw a similar conclusion about the electronegative atom effects. The $a_1\sigma$ molecular orbital (MO) is identified as the σ-bridged-π orbital in the 3MRs. They concluded that an electronegative atom at the apex position of a triangle favors the σ-bridged-π bonding, leading to the short distance between the basal atoms and the relief in its strain energy. There is, however, a question about the preference of the $a_1\sigma$ MO to the $b_2\pi^*$ MO counterpart which exhibits the opposite effects.

There has long been controversy about the unusual Si···Si distance shorter than the normal single bond and the nonbonded O···O distance in 1,3-cyclodisiloxane (**3**). West, Michl, and coworkers[5a] proposed severe lone-pair−lone-pair repulsion between the oxygen atoms forcing contracted Si−O−Si bond angle, or a Si−Si bond with cyclic four-center six-electron delocalized bonding about the periphery. The deformation density map by O'Keeffe and Gibbs,[15] however, showed that there is no silicon−silicon σ bonding. By analogy with the analysis of the substituted 3MRs, based on the Dewar−Chatt−Duncanson model, Grev and Schaefer[12] proposed the "dibridged π-complex" model or the "unsupported π-bond" model where the π bonding between the silicon atoms in the molecular plane is not supported by a σ-bond. Liang and Allen[13] applied their own concept of the σ-bridged-π bonding to obtain similar conclusions. The electronegative atom, O makes the unsupported π-bond or σ-bridged-π bonding (Chart 1) more effective and brings the diagonal silicons closer in the 4MR **3**. Unfortunately, we cannot find any appreciable sign of the unsupported π-bond or σ-bridged-π bond in the deformation density on the molecular plane reported by O'Keeffe and Gibbs.[15] Kudo and Nagase[17] suggested that the short Si···Si distance is the result of very

10.1021/jp0014014 CCC: $19.00

CHART 1



p-d π bonding model in **1**

Dewar-Chatt-Duncanson model for **2**

σ-bridged-π bonding model in **2** and **3**

strong attraction between the silicon and oxygen atoms. Jemmis et al.[18] similarly concluded that the distance is predominantly determined by the short Si−O bond length.

In this paper, we investigated the interactions of the bonds including lone pairs and vacant atomic orbitals, and the relative weight of various bonding models, to give new insight into the unusual properties of **1**−**3**. A comprehensive understanding was obtained. The p−d bonding is important between the Si and O atoms. Numerical evaluation of the weight of the single bond, double bond, and π-complex models showed that double bond model contributes most, in agreement with the important p−d bonding. In the ring systems **2** and **3**, the lone pair electrons delocalize in a cyclic manner by the interaction of the p orbital of the oxygen lone pair and the d-type polarization functions on the silicon atoms. The cyclic (n, d, d) delocalization model was shown to be useful enough to predict the geometrical changes of disilaoxirane and 1,3-cyclodisiloxane with one electron removal and their protonated ions (**8**−**12**). The high ring strain of **2** was discussed in terms of the geminal bond interaction[25] as well as the n−d interaction.

2. Method of Calculations

We proposed and applied a bond model to analyze the electronic structures of molecules[24−28] and transition states.[26] The single Slater determinant of the Hartree−Fock wave function (Ψ) for the electronic structure of the molecule or the transition state is expanded into electron configurations:[27]

$$\Psi = C_G\Phi_G + \sum C_T\Phi_T + \sum C_E\Phi_E + ...$$

In the ground configuration (Φ_G), a pair of electrons occupies each bonding orbital of the bonds. A ground configuration corresponds to a Lewis structure for an electronic formula of molecules used to show the location of the valence electrons. The interactions between the bond orbitals are accompanied by electron delocalization and polarization. The delocalization is expressed by mixing an electron-transferred configuration (Φ_T), where an electron shifts from the bonding orbital of a bond to the antibonding orbital of another. The polarization is expressed by mixing a locally excited configuration (Φ_E) where an electron is promoted from the bonding orbital to the antibonding orbital of bond.

A set of bond orbitals, i.e., hybrid orbitals and bond polarities give the coefficients of the configurations, C_G, C_T, and C_E. The bonding and antibonding orbitals ϕ_i and ϕ_i* of the *i*th bond are expressed by a linear combination of hybrid atomic orbitals χ_{ia} and χ_{ib} on the bonded atoms a and b:

$$\phi_i = c_{ia}\chi_{ia} + c_{ib}\chi_{ib}$$

$$\phi_i^* = c_{ia}^*\chi_{ia} + c_{ib}^*\chi_{ib}$$

The bond (bonding and antibonding) orbitals of each bond are obtained by the diagonalization of the 2 × 2 Fock matrix on the basis of the hybrid orbitals.[26a] A set of bond orbitals are optimized to give the maximum value of the coefficient of the ground configuration.

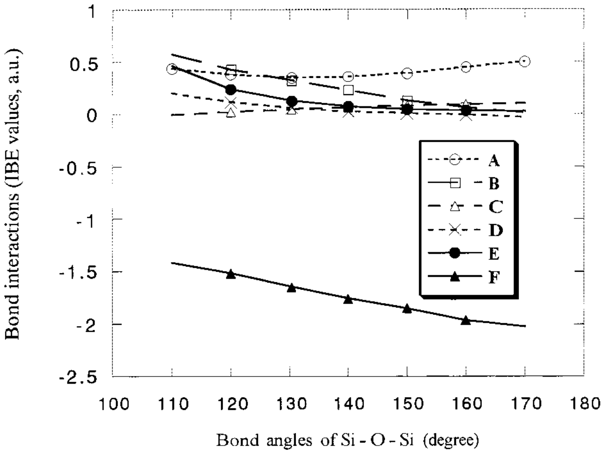


Figure 1. Variations in bond interactions: (A) (Si−O)−(Si−O); (B) n-(Si−O); (C) n-(Si−H); (D) (Si−O)−(Si−H); (E) (Si−H)−(Si−H); (F) n−d with the different Si−O−Si bond angles in molecule **1**.

A number of Lewis structures are generally conceivable for a molecule or a transition state. Which Lewis structure best represents the electron states is determined by the Lewis index[24] C_G, a measure of the contribution from the Lewis structure to the total electronic structure.

In order to estimate the interaction of the bond orbitals, ϕ_i and ϕ_j, we calculate the interbond energy IBE_{ij}[28]

$$\mathrm{IBE}_{ij} = P_{ij}(F_{ij} + H_{ij})$$

where P_{ij}, F_{ij}, and H_{ij} are the elements of the density, Fock, and core Hamiltonians, respectively.

The geometry optimization of molecules **1**−**5** and **8**−**12** has been carried out by the Hartree−Fock (HF) theory at the 6-31G* basis set, MP2/6-311G**, and B3LYP/6-311G** using Gaussian 98 program.[29] The 6-31G* basis set was used for the analysis of the bond interactions.

3. Results and Discussion

We employed the method introduced above to investigate the bond interactions in **1**−**3**. The Si−O−Si bond angle in **1** was shown to be widened by the significant interaction between the lone pairs on the oxygen atom and the vacant d-type polarization function on the silicon atoms, especially the in-plane (n_O)−(d_{Si}) interaction. On going to the ring systems **2** and **3**, the lone pair of oxygen was demonstrated to delocalize in a cyclic manner by the interaction of the p orbital of the oxygen lone pair and the d functions of the Si atoms. The cyclic (n, d, d) interactions in **2** and **3** accounted well for their unusually short distances between the Si atoms.

Disiloxane (1). In order to understand why the disiloxane **1** prefers the large Si−O−Si bond angle in contrast with its carbon counterpart, $H_3C{-}O{-}CH_3$, **4**, we investigated the bond interactions at the geometries optimized for the fixed bond angles ranging from 110° to 170°. Outstanding stabilization with the widening of the bond angle was found in the interaction between the lone pairs on the oxygen atom and the vacant d-type polarization function on the silicon atoms, as is illustrated in Figure 1, where the sum of the IBE values for all lone pairs and d-type polarization functions, (n_O)−(d_{Si}) is shown. Among all the bond interactions, the (n_O)−(d_{Si}) interaction changed most dramatically in the range of 110°−170°. The lack of such n−d

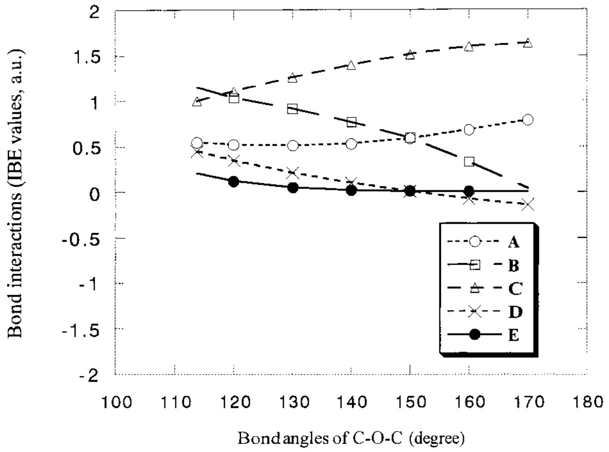
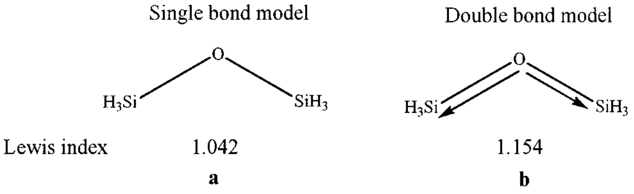


Figure 2. Variations in bond interactions: (A) (C−O)−(C−O); (B) n-(C−O); (C) n-(C−H); (D) (C−O)−(C−H); (E) (C−H)−(C−H) with the different C−O−C bond angles in molecule **4**.

CHART 2



interaction in the carbon counterpart **4** also implied that the (n_O)−(d_{Si}) interaction is one of the dominant factors of the special structure of **1**. In addition, the steric repulsion between the SiH_3 groups, reflected by the (Si−H)−(Si−H) interaction, decreases more than that between the CH_3 group in H_3C−O−CH_3 (Figure 2), especially at the narrow angles. This may be another factor favoring the wide bond angle in molecule **1**. This agrees with the experimental facts that the strictly linear SiOSi skeletons are observed in the disilyl ethers, $(R_3Si)_2O$ with the bulky substituents, e.g., $O(SiCH{=}CH_2)_2$, $O(SiPh_3)_2$, and $O[Si(CH_2Ph)_3]_2$.[1] The geminal interactions of the Si−O bonds with the lone pairs and the Si−H bonds also favor the wide Si−O−Si bond angle. However, the corresponding (n_O)−(C−O) and (C−O)−(C−H) interactions in **4** also prefer the linear geometry (Figure 2). So these interactions are not characteristic features of **1** responsible for the unusual geometry of disiloxane (**1**).

(n_O)−(d_{Si}) Interactions. The interaction between the nonbonding orbitals of the oxygen lone pair and the d-type polarization functions on the silicon atoms is the strongest one among various bond interactions. This suggests a dative π bond. It is interesting to see which Lewis structure (Chart 2) is more important, the single bond or double bond model. The calculated Lewis indices showed that the double bond model (1.154) should be a little more favorable than the single bond model (1.042). Figure 3 shows the contour map of the dative π bond. The π-bonding occurs between the p oxygen lone pair orbital and the d-type polarization basis of silicon, in agreement with the significant (n_O)−(d_{Si}) interaction.

The in-plane (n_σ) and out-of-plane (n_π) lone pairs of the oxygen atoms behave differently with the variations in the Si−O−Si bond angles. The bonding properties of the n_σ−d interactions increase dramatically from IBE = −0.4430 au at the bond angle of 110° to IBE = −0.9904 au at 170°, so that the in-plane n interaction favor the linear structure. On the other hand, the bonding properties of the n_π−d interactions increase much less (IBE = −0.9761 au at 110°; −1.0358 au at 170°).

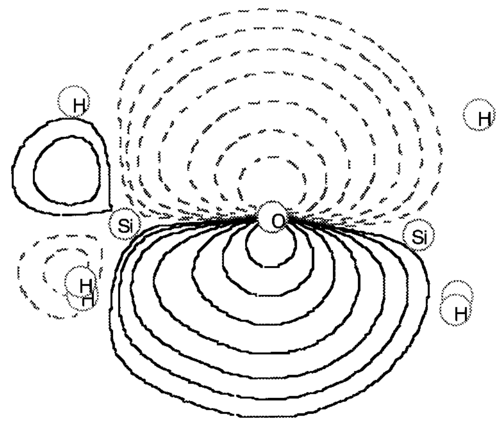
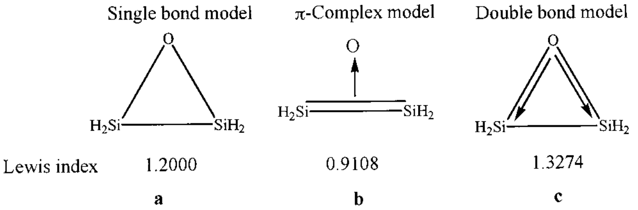


Figure 3. Contour map of the dative π_{SiO} bond orbital in **1**.

CHART 3



Our conclusion that the short Si−O bond length and the wide Si−O−Si bond angle should be due to the n_σ−d interaction and the steric repulsion agrees with the statement in the recent textbook.[21] The agreement strongly encouraged us to apply our method to the other molecules containing the Si−O bonds.

Disilaoxirane (2). The electronic structure of the three-membered ring molecule is usually represented by the single bond model (**a** in Chart 3). However, the extremely short Si−Si bond length close to that of a double bond suggests the π-complex model.[12] The significance of the n−d interaction disclosed in disiloxane leads to the double bond model. Here we show which bond model or Lewis structure better represents the electronic structure. We propose that the cyclic interaction of the oxygen lone pair orbitals and the d-type polarization function on the silicon atoms should contribute to the short Si−Si bond. The high strain is discussed in terms of the geminal bond interaction as well as the n−d interaction.

Lewis Structures. We calculated the Lewis indices of three bond models. The double bond model (1.327) was found to contribute the most, while the π-complex model is the least weighted (0.911). It is not surprising because the n−d interaction is still strongly bonding (the total IBE((n_O)−(d_{Si})) = −1.3963 au), the largest n−d interaction (−0.3984 au) occurs out of the molecular plane (Figure 4). The total in-plane n_σ−d interaction decreases dramatically from −0.9904 au in the open chain **1** to −0.1666 au in the 3MR **2**. The weakening of the n_σ-d interaction is in agreement with the longer Si−O bond in **2**.

Cyclic (n, d, d) Interaction. The considerable n−d interactions suggest the significance of the cyclic interaction among the nonbonding orbital on the oxygen and the two d-type polarization functions on the different silicon atoms (Figure 4). The cyclic orbital interactions are under the control of the orbital phase continuity−discontinuity properties.[30] The nonbonding orbital of the oxygen is a donating orbital, and the vacant d-type polarization functions of silicon atoms are accepting orbitals. The phase continuity requires that the n, d, and d orbitals should be in phase with one another. In fact, these requirements are satisfied in **2** (Figure 4). This implies that the cyclic electron

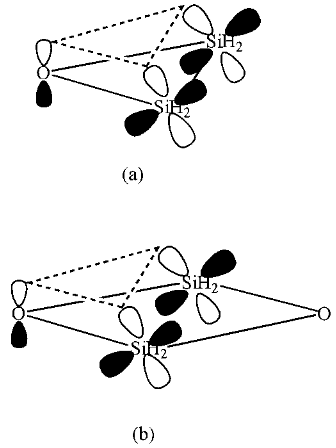


Figure 4. Cyclic (n, d, d) orbital interactions in (a) disilaoxirane and (b) 1,3-cyclodisiloxane.

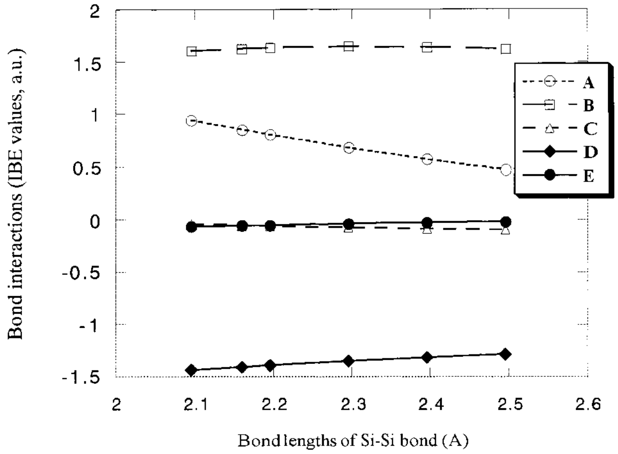


Figure 5. Variations in bond interactions: (A) (Si−Si)−(Si−O); (B) (Si−O)−(Si−O); (C) n-(Si−H); (D) n−d; (E) d−d with the different Si−Si bond lengths in molecule **2**.

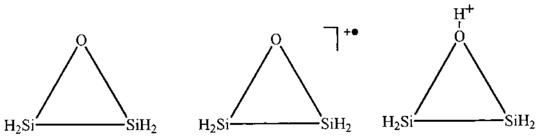
delocalization of the lone pair through the d-type polarization functions contributes to shortening the bond length of Si−Si.

The bond interactions at the different Si−Si bond distance were studied (Figure 5). The stabilizing n_O-d_{Si} and $d_{Si}-d_{Si}$ interactions increase as the Si−Si bond lengths decrease. The d−d interaction (IBE = −0.0408 au) is 16 times greater than that in the open chain molecule SiH_3SiH_2OH (**7**) (IBE = −0.0024 au). These results supported the important role of the cyclic delocalization of n electrons accompanied by the d−d bonding in **2**.

From the significant contribution of the d−d bonding by the cyclic delocalization of n electrons to the Si−Si bond shortening, we predicted that loss of the n electron delocalization should elongate the Si−Si distance. In fact, the calculated Si−Si bond lengths in the protonated disilaoxirane (**8**) and disilaoxirane radical cation (**9**)[31] are longer than that in **2** (Chart 4). These results argue against the predictions based on the π-complex model by Schaefer[12] and the σ-bridged-π bonding model[13] by Allen that the electronegative atom should shorten the Si−Si distance. The protonated oxygen and the oxygen atom in the cation radical are unequivocally more electronegative.

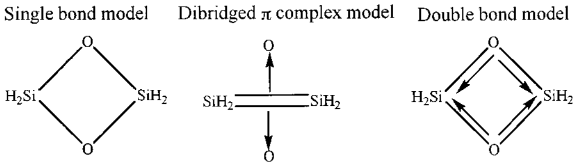
Ring Strain. The geminal bond interactions have been proposed to play an important role in the ring strains.[32] The geminal interaction between the Si−Si bond and the Si−O bond becomes about 1.4326 au more repulsive on going from the open chain reference molecule, SiH_3SiH_2OH (0.2026 au) to the three-membered ring **2** (1.6352 au). However, the C−O and C−C bond repulsion in oxirane **5** (1.0811 au) is only 0.7147 au greater than that in the open chain CH_3CH_2OH (**8**) (0.3664 au). That is why the calculated strain energy of disilaoxirane is 56.4 kcal/mol, almost 29 kcal/mol larger than that of the carbon counterpart. The geminal interaction between the Si−O and Si−O bonds does not change significantly from the open chain molecule **1** (0.5015 au) to the three-membered ring **2** (0.8051 au). Similarly, the bond interaction between the C−O and C−O bonds changes a little from 0.5460 au in dimethyl ether (**4**) to 0.7190 au in the oxirane (**5**). Therefore, the extremely large repulsion between the geminal Si−Si and Si−O bonds is an important factor of the high strain energy in the disilaoxirane (**2**). On the other hand, the large loss of the in-plane n−d, i.e., n_σ−d bonding interactions from the open chain molecule **1** (−0.9904 au) to the cyclic 3MR **2** (−0.1666 au) also increases the strain energy.

CHART 4: Calculated Bond Lengths (Å) of the Si−Si Bond at Various Levels



	2	8	9
R(O)HF/6-31G*	2.1963	2.4986	2.2501
(U)MP2/6-311G**	2.2003	2.4804	2.2649
(U)B3LYP/ 6-311G**	2.2135	2.5255	2.2777

CHART 5



	a	b	c
Lewis index	0.9215	0.9108	1.3274

1,3-Cyclodisiloxane (3). The unusual structures of the open chain molecule **1** and the three-membered ring molecule **2** have been shown to result from the n_σ−d interaction and the cyclic (n, d, d) interactions, respectively. We will show their importance in the four-membered ring molecule **3** by studying the Lewis structures and the bond interactions.

Lewis Structures. We calculated the Lewis indices of the single bond model, the double bond model, and the dibridged π-complex model (Chart 5). The double bond model was again found to have the largest Lewis index (1.3274). The Lewis index of the dibridged π-complex model (0.9108) is of the smallest weight. This shows the strong n_O-d_{Si} interaction in this molecule.

Cyclic (n, d, d) Interaction. Overlapping between the d-type polarization functions of the silicon atoms can be expected to take place to an appreciable degree even if there is no bond between the silicon atoms. The argument of the cyclic (n, d, d) interaction in the three-membered ring, disilaoxirane (**2**) can be reasonably extended to the four-membered ring system, 1,3-cyclodisiloxane (**3**). The cyclic orbital interactions (Figure 4b) are favored by the phase continuity. The d−d δ interaction involved contributes to the unusually short nonbonded Si···Si distance in **3**. In fact, the biggest n−d interaction was found to occur between the out-of-plane lone pair orbital of oxygen and

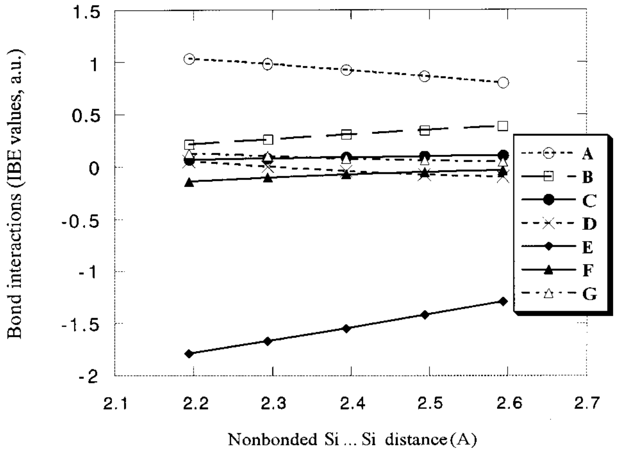
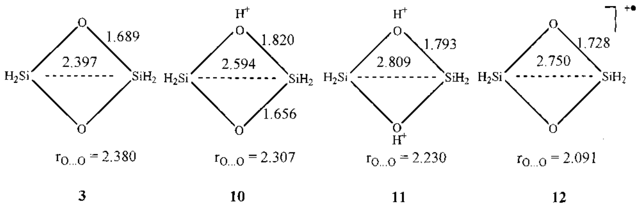


Figure 6. Variations in bond interactions: (A) (Si−O)−(Si−O)$_a$; (B) (Si−O)−(Si−O)$_b$; (C) n_O-n_O; (D) n-(Si−H); (E) n−d; (F) d−d; (G) (Si−H)−(Si−H)) with the different nonbonded Si···Si distances in molecule **3**.

CHART 6: Calculated Bond Lengths (Å) in the Four-Membered Rings at the (U)MP2/6-311G Level**



the d polarization function of the silicon atoms. The d−d δ-type interaction (−0.0600 au) is 24 times greater than that of the open chain molecule **7**. The variations in the bond interactions with the different nonbonded Si···Si distances (Figure 6) shows that the n_O-d_{Si} and $d_{Si}-d_{Si}$ interactions changed significantly with the nonbonded Si···Si distance. The closer the two silicon atoms approach each other, the larger the n_O-d_{Si} and $d_{Si}-d_{Si}$ bonding interactions become. These results are convincing evidence for the significance of the cyclic delocalization of the n electrons involving d−d interactions in the unusual shortening of the nonbonded Si···Si distance of **3**. The n−d interaction and the d−d interaction promote each other since both interactions are involved in the cyclic orbital interaction favored by the phase continuity. In fact, the Si−O bond distance decreases from 1.725 to 1.631 Å as the nonbonded Si···Si distance decreases from 2.594 to 2.194 Å. This is in agreement with the ideas of Nagase[17] and Jemmis[18] described in the Introduction. The cyclic (n, d, d) interaction plays an important role in the ring system **2** and **3**, where the silicons are close to each other under the constraints of the 3MR or 4MR σ-framework.

The finding of the cyclic (n, d, d) interaction leads to the prediction of the geometrical changes of **3** accompanied by one-electron oxidation and the protonation on the oxygen atoms. The cyclic delocalization of the n electrons is weakened. The nonbonded Si···Si distances were predicted to be longer. This was confirmed by the calculated 1,3-nonbonded Si···Si distances of the protonated species **10** (2.594 Å) and **11** (2.809 Å), and the cation radical **12** (2.750 Å) (Chart 6). The agreement of the calculated results with the predictions strongly supported the significance of the cyclic (n, d, d) interaction. The lengthening of the Si···Si distance argues against the conclusion based on the unsupported π bond model by Schaefer[12] and the σ-bridged-π bonding model by Allen[13] that electronegative atoms should shorten the distance. The oxygen atom in the protonated species and the cation radical is more electronegative. On the other hand, the lone pair−lone pair repulsion or the n_O-n_O interaction changes much less than the n−d interaction and even less than the d−d interaction. Furthermore, repulsion between the lone pairs is comparable to that between the nonbonded SiH_2 groups (cf. Figure 6). The present study produced no evidence for the predominance of the O···O repulsion over the short Si···Si distance.

4. Conclusions

The interactions of bonds including lone pairs and vacant atomic orbitals, and the relative weights of various bonding models, have been investigated to shed light on the unusual structures of disiloxane (**1**), disilaoxirane (**2**), and 1,3-cyclodisiloxane (**3**). A unified way of understanding has been established. The interaction between the p oxygen lone pair and the d-type polarization basis of silicon atom is important between the Si and O atoms. The calculations of the Lewis index showed that the Si−O double bond model contributes more than the single bond and π-complex models, supporting the important n_O-d_{Si} interactions in **1**−**3**. The oxygen atoms bonded to the silicon atoms show the tendency toward tetravalency in a sense. The cyclic delocalization of the n electrons involving the d−d bonding was shown to contribute to the unusually short distance between the silicon atoms in the ring systems **2** and **3**. The significance of the cyclic delocalization was substantiated by the geometries of the protonated and cation radical species of **2** and **3**. The optimized Si−Si bond or the nonbonded Si···Si distances in molecules **8**−**12** are elongated. In addition, the high strain of **2** results from both the repulsion between the geminal Si−Si and Si−O bonds and the loss of the in-plane n−d interactions.

Acknowledgment. This work was supported by a Grant-in-Aid from Japan Society for the Promotion of Science (JSPS) and partly from the Ministry of Education, Science, Sports and Culture, Japan for Scientific Research on Priority Areas (A) (No. 10146101). One of the authors (J.M., No. P98414) gratefully thanks JSPS for the award of the postdoctoral fellowship.

References and Notes

(1) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: London, 1989; p 57.

(2) Voronkov, M. G.; Mileshkevich, V. P.; Yuzhelevskii, Yu. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978.

(3) Almenningen, A.; Bastiansen, O.; Ewing, V.; Hedberg, K.; Traetteberg, M. *Acta Chem. Scand.* **1963**, *17*, 2455.

(4) Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865.

(5) (a) Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 822. (b) Michalczyk, M.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531. (c) Yokelson, H. B.; Millevolte, A. J.; Adams, B. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 4116.

(6) Kimura, K.; Kubo, M. *J. Chem. Phys.* **1959**, *30*, 151.

(7) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1988**, *92*, 3037.

(8) Ernst, C. A.; Allred, A. L.; Ratner, M. A.; Newton, M. D.; Gibbs, G. V.; Moskowitz, J. W.; Topiol, S. *Chem. Phys. Lett.* **1981**, *81*, 424.

(9) Raghavachari, K.; Chandrasekhar, J.; Frisch, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 3779.

(10) Durig, J. R.; Flanagan, M. J.; Kalasinsky, V. F. *J. Chem. Phys.* **1977**, *66*, 2775.

(11) Dewar−Chatt−Duncanson bonding model: (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(12) Grev, R. S.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 6577.

(13) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1991**, *113*, 1878.

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

(15) (a) O′Keeffe, M.; Gibbs, G. V. *J. Phys. Chem.* **1984**, *81*, 876. (b) O′Keeffe, M.; Gibbs, G. V. *J. Phys. Chem.* **1985**, *89*, 4574.

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

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

(18) Jemmis, E. D.; Kumar, P. N. V. P.; Kumar, N. R. S. *J. Chem. Soc., Dalton Trans.* **1987**, 271.

(19) Grigoras, S.; Lane, T. H. *J. Comput. Chem.* **1987**, *8*, 84.

(20) Oberhammer, H.; Boggs, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 7241.

(21) See, for example Cotton, F. A.; Wilkinson, G.; Gaus, P. L. *Basic Inorganic Chemistry*; John Wiley & Sons: New York, 1995; pp 383−385.

(22) Janes, N.; Oldfield, E. *J. Am. Chem. Soc.* **1986**, *108*, 5743.

(23) Roelandt, F. F.; Van de Vondel, D. F.; Van der Kelen, G. P. *J. Mol. Struct.* **1978**, *50*, 147.

(24) (a) The C_G value was previously[24b] introduced as the Kekulé index to indicate the weights of the Kekulé structures of polycyclic aromatic molecules. The C_G values can be used more generally to indicate the weights of the Lewis structures. The terminology was changed from the Kekulé index to the Lewis index in this paper. (b) Inagaki, S.; Hirabayashi, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2283.

(25) (a) Inagaki, S.; Kawata, H.; Hirabayashi, Y. *Bull. Chem. Soc. Jpn*. **1982**, *55*, 3724. (b) Inagaki, S.; Hirabayashi, Y. *Chem. Lett.* **1982**, 709. (c) Inagaki, S.; Kawata, H.; Hirabayashi, Y. *J. Org. Chem.* **1983**, *48*, 2928. (d) Inagaki, S. *Bull. Chem. Soc. Jpn*. **1984**, *57*, 3599. (e) Inagaki, S.; Iwase, K.; Kawata, H. *Bull. Chem. Soc. Jpn*. **1985**, *58*, 601. (f) Inagaki, S.; Iwase, K.; Goto, N. *J. Org. Chem.* **1986**, *51*, 362. (g) Sakai, S.; Inagaki, S. *J. Am. Chem. Soc*. **1990**, *112*, 7961. (h) Inagaki, S.; Yoshikawa, K.; Hayano, Y. *J. Am. Chem. Soc.* **1993**, *115*, 3706. (i) Inagaki, S.; Ishitani, Y.; Kakefu, T. *J. Am. Chem. Soc.* **1994**, *116*, 5954. (j) Inagaki, S.; Kakefu, T.; Yamamoto, T.; Wasada, H. *J. Phys. Chem.* **1996**, *100*, 9615. (k) Iwase, K.; Inagaki, S. *Chem. Lett*. **1993**, 1619. (l) Iwase, K.; Sakai, S.; Inagaki, S. *Chem. Lett*. **1994**, 1601. (m) Inagaki, S.; Ohashi, S.; Kawashima, T. *Org. Lett.* **1999**, 1145. (n) Inagaki, S.; Ohashi, S. *Theor. Chem. Acc.* **1999**, *102*, 65.

(26) (a) Inagaki, S.; Ikeda, H. *J. Org. Chem.* **1998**, *63*, 7820. (b) Ikeda, H.; Naruse, Y.; Inagaki, S. *Chem. Lett.* **1999**, 363. (c) Inagaki, S.; Ikeda, H.; Kawashima, T. *Tetrahedron Lett.* **1999**, *40*, 8893.

(27) Iwase, K.; Inagaki, S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2781.

(28) Inagaki, S.; Yamamoto, T.; Ohashi, S. *Chem. Lett.* **1997**, *977*, 5.

(29) *Gaussian 98* (Revision A.7); Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. A.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Reploge, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1998.

(30) (a) The orbital phase continuity requirements[30b] for the effective cyclic orbital interactions are as follows: the electron-donating orbitals are out of phase; the accepting orbitals are in phase; the donating and accepting orbitals are in phase. When the phase requirements are simultaneously satisfied, this system is stabilized. Otherwise, the system is less stable and the delocalization cannot effectively occur. *Cyclic orbital interaction was later disclosed to be involved even in acyclic conjugation*. The orbital phase theory then expanded its application to such acyclic conjugate systems as the regioselectivities of organic reactions,[25d] the abnormally acute L−M−L angles in ML_2[25g] and ML_3[25h] complexes, the relative stabilities of isomers of π-conjugated polyions[25e] and diradicals.[27] (b) Fukui, K.; Inagaki, S. *J. Am. Chem. Soc*. **1975**, *97*, 4445.

(31) ROHF/6-31G*, UMP2/6-311G**, and UB3LYP/6-311G** are adopted for this molecule.

(32) Inagaki, S.; Goto, N.; Yoshikawa, K. *J. Am. Chem. Soc.* **1991**, *113*, 7144.