

obtained at moderate theoretical levels, they should be correct qualitatively. More accurate calculations are underway to check the validity of these results.

(2) A simple model based on the second-order Jahn-Teller effect is shown to be able to explain double bond deformation observed in these long cumulenes as well as in group IV double bonds and cumulenes. Thus, a double bond will distort from its symmetric conformation when it possesses low-lying excited states (or high density of states) and vibrational modes with low intrinsic frequencies. The favored distortional mode for small molecules may be predicted from analysis based on orbital symmetry. This model, which is based on the second-order perturbation theory, should be universal, while Trinquier and Malrieu's model, though successful for a number of cases, failed to predict the geometries of long cumulenes. The reason is that in Trinquier and Malrieu's model, only the four electrons forming the double bond are considered. Therefore, the collective behavior of delo-

calized electrons, which leads to bending in long cumulenes as studied here and distortions of other large systems with extensive electron delocalization,<sup>38,39</sup> is not adequately accounted for.

**Acknowledgment.** We thank the U.S. Army, ARDEC, Dover, NJ, and Geo-Center for financial support. We also thank Dr. Ian Alberts (University of Georgia) for helping carrying out MP2 calculations using CADPAC.

**Registry No.** 1a, 463-49-0; 2a, 2873-50-9; 3a, 21986-03-8; 4a, 13703-38-3.

(39) It is known that large cyclic polyenes prefer bond alternation (see, for example: Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc.* **1959**, *A251*, 172. Paldus, J.; Chin, E. *Int. J. Quantum Chem.* **1983**, *24*, 373). This can be taken as a kind of distortion from more symmetric polyenes with equal or nearly equal ring bonds because the density of states would be too large if large polyenes assume extensively delocalized, bond equalized structures.

## $\sigma$ -Bridged- $\pi$ Bonding in Small-Ring Compounds

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**Abstract:**  $\sigma$ -Bridged- $\pi$  orbitals characterize the three-center bonds that often occur in electron-sufficient, small-ring compounds made of atoms such as C, N, O, Si, P, and S. This bonding pattern proves efficient in explaining bond length changes and strain energies in three-membered rings and the unusual geometries of some four-membered rings. It is also shown that explanations based on this type of orbital are compatible with a number of other theoretical models in the literature and that use of the  $\sigma$ -bridged- $\pi$ -bonding concept helps extend and unify them.

### I. Introduction

The term  $\sigma$ -bridged- $\pi$  (hitherto abbreviated as  $\sigma$ -b- $\pi$ ) and its use to characterize key features of the bonding in [1.1.1]propellane was proposed several years ago,<sup>1</sup> but its basic construct of three-center bonding orbitals (Chart I) in electron-sufficient and electron-excess species goes back as far as Dewar<sup>2</sup> and Chatt and Duncanson's  $\sigma$ -donation,  $\pi$ -back-donation model<sup>3</sup> and more specifically to Hoffmann et al.<sup>4</sup> and Rohmer and Roos<sup>5</sup> for the bonding in three-membered rings. It is also implicit in the more recent work of Cremer and Kraka,<sup>6</sup> West et al.,<sup>7</sup> and Grev and Schaefer.<sup>8</sup> The  $\sigma$ -b- $\pi$  bond can be taken as a manifestation of  $\sigma$ -electron delocalization.<sup>9,6b,c</sup> In the  $C_1$ - $C_3$  bond between bridgehead carbons in [1.1.1]propellane (A) this bond contributes



to the bonding of  $C_1$  to  $C_3$  as well as to the  $C_1$ - $C_2$  side bonds. This pattern of interaction is appealing in the sense that it offers an "economical" way of forming bonds out of limited valence electrons. This becomes more apparent when one compares [1.1.1]propellane to 1,3-diborabicyclo[1.1.1]pentane (B). Although the latter has two fewer valence electrons than the former, their bonding patterns are essentially the same.<sup>1</sup> In addition to six normal B-C bonds, B has a strong B-B bond<sup>1</sup> since the  $B_1$ - $B_3$  separation is only 1.61 Å as compared to 1.60-1.90 Å, a range for typical B-B bonding distances in carboranes and boron hydrides.<sup>10</sup> That is, structure B' is not unreasonable because of the  $\sigma$ -bridged- $\pi$  bonding in B.

### Chart I



In this paper, we explore this type of bonding by systematic ab initio calculations for 16 three-membered-ring (3MR) compounds. The results are employed to explain the strain energy of some 3MR compounds and also the unusual geometries of several four-membered-ring (4MR) molecules. In particular, recent developments in silicon chemistry have raised many interesting questions concerning the bonding in silicon ring compounds, and we offer an interpretation to these questions using  $\sigma$ -b- $\pi$  bonding.

The bonding in 3MR compounds has been extensively studied in the literature.<sup>2-9,11-15</sup> In the 1940s, Coulson and Moffitt<sup>11</sup>

- (1) Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591.
- (2) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79.
- (3) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.
- (4) Hoffmann, R.; Fujimoto, H.; Swenson, J. R.; Wan, C.-C. *J. Am. Chem. Soc.* **1973**, *95*, 7644.
- (5) Rohmer, M.-M.; Roos, B. *J. Am. Chem. Soc.* **1975**, *97*, 2025.
- (6) (a) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800, 3811. (b) Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467. (c) Cremer, D.; Kraka, E. In *Structure and Reactivity*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1988; Chapter 3.
- (7) Yokelson, H. B.; Millevalte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865.
- (8) Grev, R. S.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1987**, *109*, 6577.
- (9) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669 and references therein.
- (10) Beaudet, R. A. In *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH: New York, 1988; p 417.

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**Table I.** Comparison of Calculated (by Use of the Hartree-Fock Method) and Experimental Geometric Parameters<sup>a</sup>

method	oxirane <sup>c,d</sup>			azirane <sup>e</sup>			cyclopropane <sup>c,f</sup>	
	C—C	C—O	$\alpha^b$	C—C	C—N	$\alpha^b$	C—C	
3-21G	1.470	1.474	157.7	1.497	1.491	153.5	1.513	
6-31G*	1.453	1.402	158.5	1.468	1.456	154.4	1.498	
exptl	1.470	1.435	158.1	1.480	1.488	159.4	1.510	

method	cyclopropene <sup>c,g</sup>			oxirene <sup>c,h</sup>			dioxirane <sup>i</sup>	
	C=C	C—C	$\alpha^b$	C=C	C—O	$\alpha^b$	O—O	C—O
3-21G	1.282	1.523	149.6	1.249	1.556	161.3	1.522	1.427
6-31G*	1.276	1.495	150.2	1.244	1.467	162.8	1.447	1.359
exptl	1.300	1.515	149.9				1.516	1.388

<sup>a</sup> Bond lengths in angstroms, angles in degrees. <sup>b</sup>  $\alpha$  is the angle formed by the HCH plane and the C—C vector for oxirane, azirane, and cyclopropane and the HCC angle for cyclopropene and oxirene. <sup>c</sup> 6-31G\* data: Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Carnegie-Mellon University: Pittsburgh, 1983. <sup>d</sup> Experimental data: Turner, T. E.; Howe, J. A. *J. Chem. Phys.* **1956**, *24*, 924. <sup>e</sup> Experimental data: Turner, T. E.; Fiora, V. C.; Kendrick, W. M. *J. Chem. Phys.* **1955**, *23*, 1966. <sup>f</sup> Experimental data: Bastianson, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538.  $\alpha = 150^\circ$  by symmetry. <sup>g</sup> Experimental data: Kasai, P. H.; Myers, K. J.; Eggers, D. F., Jr.; Wiberg, K. B. *J. Chem. Phys.* **1959**, *30*, 512. <sup>h</sup> Experimental data not available since it has not been isolated yet (Lewars, E. G. *Chem. Rev.* **1983**, *83*, 519). <sup>i</sup> Experimental data: Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1978**, *100*, 5117.

**Table II.** HF/3-21G-Calculated Geometries of Molecules in Chart II<sup>a</sup>

	H <sub>2</sub> C—CH <sub>2</sub>				HC=CH			
	BH (1)	CH <sub>2</sub> (2)	NH (3)	O (4)	BH (5)	CH <sub>2</sub> (6)	NH (7)	O (8)
B—B	1.552	1.513	1.497	1.474	1.348	1.282	1.264	1.249
A—B	1.533	1.513	1.491	1.470	1.485	1.523	1.561	1.556
$\alpha$	145.5	150.0	153.5	157.8	139.2	149.6	155.7	161.3

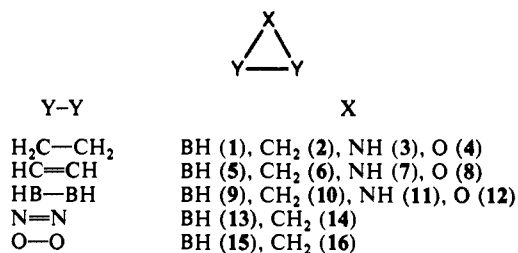
  

	HB—BH			N=N		O—O	
	BH (9)	CH <sub>2</sub> (10)	NH (11)	O (12)	BH (13)	CH <sub>2</sub> (14)	CH <sub>2</sub> (16)
B—B	1.732	1.670	1.621	1.594	1.328	1.218	1.599
A—B	1.732	1.569	1.421	1.409	1.437	1.522	1.380
$\alpha$	150.0	160.4	168.3	173.9			

<sup>a</sup> Bond length in angstroms, bond angle in degrees;  $\alpha$  is the angle formed by the HCH plane and the C—C vector when B is CH<sub>2</sub>, the HCC angle when B is CH, and the HBB angle when B is BH.

proposed a bent-bond model to explain the bonding in the cyclopropane ring. A competing explanation was provided by Walsh,<sup>12</sup> who hypothesized that three carbon sp<sup>2</sup> orbitals (occupied by two electrons) overlap in the center of the ring and three carbon p orbitals overlap at its periphery to form the ring bonds. These two models have been widely used in textbooks to explain the bonding in cyclopropane. In 1969, Kochanski and Lehn<sup>13</sup> carried out an ab initio study of cyclopropane, cyclopropene, and diazirine and interpreted the ring bonds as having pseudo- $\pi$  ( $\psi$ - $\pi$ ) character. In the 1970s, a  $\sigma$ -donation,  $\pi$ -back-donation model,<sup>4</sup> very similar to the one used by Dewar<sup>2</sup> and Chatt and Duncanson<sup>3</sup> in explaining the bonding in transition-metal olefin complexes, received much attention in understanding the bonding in hetero 3MRs.<sup>5,14,15</sup> Recently, Dewar<sup>9</sup> introduced the concept of  $\sigma$  aromaticity to explain the anomalous properties of cyclopropane. Likewise, an extensive study of the electron density pattern of 3MRs by use of catastrophe theory led to the idea of surface delocalization of electrons in 3MRs.<sup>6a</sup>

In contrast to the large number of studies on 3MRs, the bonding of four-membered-ring molecules containing first-row atoms has received little attention. However, recent developments in silicon chemistry have added a new frontier to the bonding of small-ring compounds. In particular, the bonding in 4MR silicon molecules has generated much theoretical interests.<sup>16–18</sup> In this paper, we give a unified explanation of the electronic structure in 3MRs and

**Chart II.** 3MR Compounds of First-Row Atoms

4MRs containing both first- and second-row atoms by using the concept of  $\sigma$ -bridged- $\pi$  bonding.

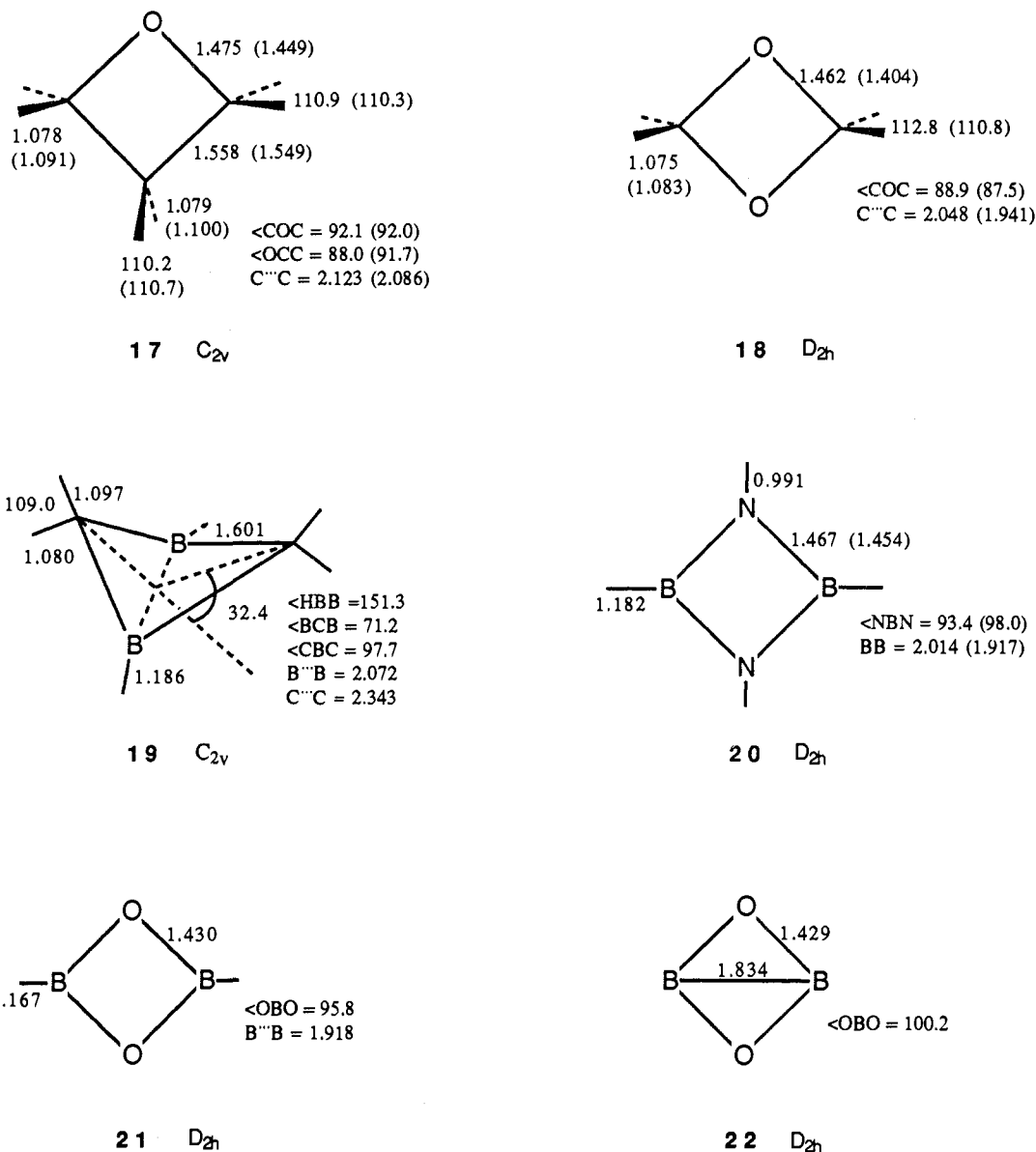
## II. Computational Methods

In order to explore the possibilities of forming strong  $\sigma$ -b- $\pi$  bonds, ab initio calculations were carried out on 16 3MR compounds. These compounds cover most of the stable and possibly stable 3MR molecules containing first-row atoms (Chart II). Several 4MR compounds (Chart III) containing first-row atoms were also studied to investigate the effect of  $\sigma$ -b- $\pi$  bonding on the geometry of 4MRs.

Ab initio electronic structure calculations within the framework of the Hartree-Fock (HF) approximation were carried out with the program GAUSSIAN82, and geometry optimizations were performed by use of the Berny method.<sup>19</sup> C<sub>2v</sub> symmetry was imposed on all of the 3MRs except azirane (for which C<sub>s</sub> symmetry was used). No symmetry was assumed in optimizing the geometries of 4MRs, although most of the molecules in Chart III have energy minima with high symmetry. A split-valence basis set (3-21G<sup>20</sup>) was employed for all calculations. Calculations were repeated with the 6-31G\*<sup>21</sup> basis in many cases, and electron-correlated wave functions at the MP2 level were also obtained where needed.

- (11) Coulson, C. A.; Moffitt, W. E. *Philos. Mag.* **1949**, *40*, 1.  
 (12) (a) Walsh, A. D. *Nature* **1947**, *159*, 165, 172; (b) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179.  
 (13) Kochanski, E.; Lehn, J. M. *Theoret. Chim. Acta* **1969**, *14*, 281.  
 (14) Delker, G. L.; Wang, Y.; Stucky, G. D.; Lambert, R. L., Jr.; Haas, C. K.; Seyferth, D. J. *Am. Chem. Soc.* **1976**, *98*, 1779.  
 (15) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978; pp 281–312.  
 (16) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531.  
 (17) Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589.  
 (18) Kumar, N. R. S. *J. Chem. Soc., Dalton Trans.* **1987**, 271.

- (19) Pople, J. A. Release H, GAUSSIAN82, Carnegie-Mellon University, GAUSSIAN82; Binkley, J. S.; Ragavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fluder, G.; Frish, M. J.; Seeger, R.; and Pople, J. A.  
 (20) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.  
 (21) Hariharan, P. C.; Pople, J. A. *Theoret. Chim. Acta* **1973**, *28*, 213.

Chart III. HF/3-21G-Calculated Structures of 4MRs<sup>a</sup>

<sup>a</sup>Data in parentheses are from experiment for 17,<sup>37</sup> from HF/631G\* calculation for 18,<sup>17</sup> and from experiment for 20.<sup>39</sup>

Jorgensen molecular orbital plots<sup>22</sup> were used to illustrate the shape of molecular orbitals.

As can be seen from Table I and Chart III, the Hartree-Fock approximation in conjunction with the relatively small 3-21G basis set is sufficient to reproduce experimental geometries of the small-ring compounds studied here. Our primary goal is to understand trends in geometries and relative energies, and broad experience has shown that the computational level employed here is adequate for this purpose.<sup>23</sup>

### III. Results and Discussion

**A.  $\sigma$ -Bridged- $\pi$  Bonding in 3MR Compounds.** Table I compares the HF/3-21G-calculated geometries for a few 3MR compounds with available experimental determinations and HF/6-31G\* predictions. The bond lengths calculated with the HF/3-21G method agree with experiments within 0.02 Å except for the C-O bond in oxirane, where theory overestimated its length by 0.039 Å. Bond angles were reproduced within 1.5° for most of the cases. The geometries obtained from the HF/6-31G\* method are also in satisfactory agreement with experiments. However, the HF/6-31G\* method is not better than HF/3-21G in reproducing the experimental geometries of 3MR compounds that are of in-

terest here, and thus, we chose the HF/3-21G method to optimize the geometries of the compounds shown in Chart II (results are collected in Table II).

Table II shows that when X is changed from BH to O, the X-Y (side-bond) bond length changes differently depending on whether the 3MR is saturated or unsaturated. It decreases if it is in a saturated 3MR such as 1-4 or 9-12 and increases in an unsaturated ring (5-8, 13-14, 15-16). The trend of the X-Y bond length change for 1-4 and 9-12 is understandable since the covalent radii<sup>24</sup> of X becomes smaller as it goes from BH to O. In fact, the X-Y bond length change in 1-4 (0.02 Å) is predictable from the differences of covalent radii of the heavy atoms (each change of covalent radii from B to C to N to O is also 0.02 Å<sup>24</sup>). The dramatic length change of the X-Y bond in 9-12 results from the delocalization of bond/lone-pair electrons of X into the empty p orbitals of HB-BH. But the trend of X-Y length change for unsaturated 3MRs suggests that the side bonds become weaker when X goes from BH to O (actually, 8 is so unstable that it has not been isolated<sup>15,25</sup>). Since the basal fragment in these molecules is electron rich, this trend can be explained in terms of electron

(22) Jorgensen, W. L. *QCPE*, 1977, 340.

(23) Hehre, W. J.; Radom, R.; Schelyer, P. v. R.; Pople, J. A. *ab initio Molecular Orbital Theory*; Wiley Interscience: New York, 1986.

(24) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983; p 258.

(25) Lewars, E. G. *Chem. Rev.* 1983, 83, 519.

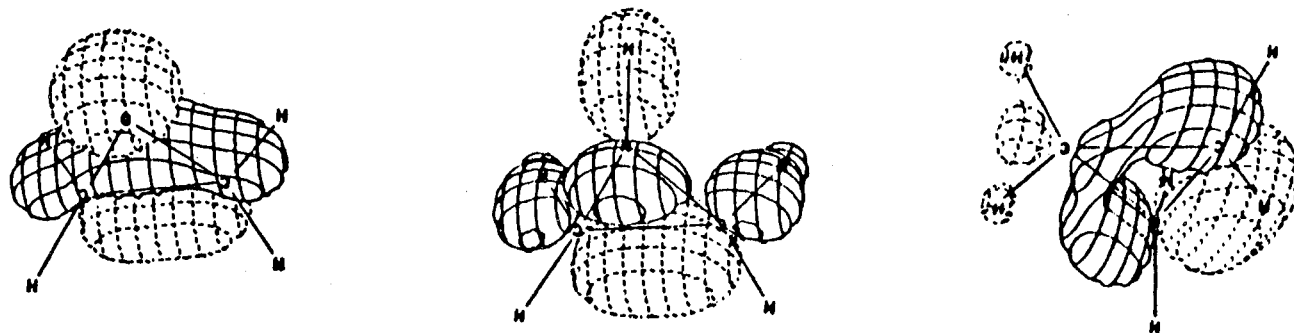


Figure 1. Comparison of the  $\sigma$ -bridged- $\pi$  orbital in cyclopropane, aziridine, and oxirane.

## Chart IV



repulsion: the electron density of X becomes denser from BH to O. (Electron-rich cyclic isomer of  $N_2O$  is not bonded according to HF/3-21G calculations.) The short-side bond length in **13** and **15** (X = BH in both cases) is explained by the double-bond character of B-N and B-O.

The change of Y-Y bond length and folding angle  $\alpha$ , defined as the angle formed by the HYH plane or the HY bond and the Y-Y vector, shows a simple trend (Table II). Changing X from BH to O always decreases the bond length of Y-Y and increases the folding angle  $\alpha$ . For unsaturated 3MRs (**5-8**, **13-16**) this trend may be explained by the increase in X-Y bond length, which, in turn, is caused by the increased electron repulsion between the X and Y-Y units. But for saturated rings it cannot be a simple consequence of the decreased covalent radii of X. For example, the shrinkage of the C-C bond in **1-4** cannot be taken as a result of the shortening C-X bond since the former changes more than the latter (the C-C bond length changes by 0.078 Å and the C-X bond by 0.063 Å). Neither can the folding angle change be explained by the change in covalent radii of X. In the literature,<sup>4,5,14,15</sup> this trend of Y-Y bond length and folding angle variation has been observed for heteroderivative cyclopropanes (including those containing heteroatoms from the second row<sup>14,15</sup>). Linear correlation was found between the Y-Y bond length change and the folding angle change.<sup>14,26</sup> The predominant explanation given is the  $\sigma$ -donation,  $\pi$ -back-donation model<sup>4,5,14,15</sup> similar to Dewar's model for the bonding in transition-metal olefin complexes.<sup>2</sup> But in the use of this model attention has only been focused on the back-donation of electron density to the basal  $\pi^*$  orbital through the  $b_2\pi^*$  molecular orbital (Chart IVa). Thus, for cyclopropane, azirane, and oxirane, as the electronegativity<sup>27</sup> of the heteroatom increases, the C-C bond becomes shorter as a result of less electron density in the C-C  $p_z \pi^*$  orbital.<sup>14,15</sup> The contribution of the  $a_1\sigma$  MO (Chart IVb) was largely ignored and sometimes considered destabilizing.<sup>14</sup> However, this explanation does not seem able to explain the stability of some 3MRs. For example, for the heteroderivative cyclopropanes, this explanation implies that the bonding interaction between the ethylene unit and the heteroatom becomes weaker as the electronegativity of the heteroatom increases. If that is the case, the 3MR would become less stable since it has a greater tendency to separate. But the following experimental observations disagree with this conclusion: (1) The heteroderivative cyclopropanes of the second-row atoms are much less stable than those of the first-row atoms. For example, phosphirane is much less stable than its nitrogen analogue<sup>28</sup> and silacyclopropane is less stable than cyclopropane.<sup>14,15</sup>

(That the strain energy of thiirane is smaller than that of oxirane<sup>15</sup> is understandable. Considering the similarity of electronegativity between carbon and sulfur and the small-angle strain around sulfur, thiirane would be expected to have a smaller strain energy than cyclopropane, but cyclopropane is known to have a strain energy similar to that of oxirane.) (2) The strain energies of azirane and oxirane are not larger than that of cyclopropane (see discussion in the next subsection).

Thus, we propose an alternative explanation to the above observations about bond length and bond angle variations. We focus on the  $a_1\sigma$  MO that we identify as the  $\sigma$ -bridged- $\pi$  orbital in 3MRs<sup>29</sup> (note the similarity between the  $\sigma$ -bridged- $\pi$  orbital of Chart I and the  $a_1\sigma$  MO in Chart IVb). Chart IVb shows that the relevant orbitals on the basal moiety must be parallel for favorable  $\sigma$ -bridged- $\pi$  bonding. The orientation of the  $\sigma$ -bridged- $\pi$  orbital will correlate with the folding angle if we assume that the orbitals on the heavy atom of Y are orthogonal (that is, for example, in **5-8** the C-H bond orbital is assumed to be orthogonal to the ring bond orbitals of Chart IV). Thus, a larger folding angle implies that the  $\sigma$ -bridged- $\pi$  bonding is more favorable since the relevant orbitals are in a better position to form a  $\sigma$ -bridged- $\pi$  bond. The fact that the Y-Y bonds become shorter as the electronegativity of the heavy atom in X increases can be consequently rationalized as a result of enhanced  $\sigma$ -bridged- $\pi$  bonding since the shrinkage of the Y-Y bond is accompanied by the increase of folding angle  $\alpha$  as noted above. Therefore, the data in Table II lead us to conclude that an electronegative atom at the apex of a 3MR will enhance the bonding of its opposite bond through more favorable  $\sigma$ -bridged- $\pi$  bonding and consequently make that bond shorter. Thus, the strongest  $\sigma$ -bridged- $\pi$  bonding among the molecules of Chart II is expected in **12** since the electronegativity difference between X and Y is the largest<sup>27</sup> (note that its folding angle is also the largest and the basal unit is close to linear).

This conclusion is supported by Jorgensen molecular orbital plots.<sup>22</sup> Figure 1 compares the  $\sigma$ -bridged- $\pi$  orbital of oxirane, azirane, and cyclopropane.<sup>30</sup> As can be seen, the  $\sigma$ -bridged- $\pi$  orbital in oxirane is the closest to the one shown in Chart I.

Although the above conclusion was drawn from 3MRs containing first-row atoms only, it can be generalized to 3MRs containing second-row atoms. The C-C bond length variation in thiirane, phosphiranes, and silacyclopropane<sup>15</sup> can be explained similarly. Recently, Grev and Schaefer<sup>8</sup> calculated the geometries of heteroderivative cyclotrisilanes,  $(H_2Si)_2X$  with X = SiH<sub>2</sub>, PH, CH<sub>2</sub>, S, NH, and O. They observed that the Si-Si bond lengths decrease with increasing electronegativity of the heavy heteroatom (this agrees with known experiments<sup>7</sup>). They also noted that the SiH<sub>2</sub> group bends up more toward the heteroatom X as the electronegativity of X increases. The explanation they employed is the  $\sigma$ -donation,  $\pi$ -back-donation model with emphasis on the  $\pi$ -back-donation of heteroatom into the  $\pi^*$  of the basal Si-Si unit.<sup>8</sup>

(26) Stalick, B. K.; Ibers, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3779.

(27) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.

(28) Wagner, R. I.; Freeman, L. D.; Goldwhite, H.; Rowsell, D. G. *J. Am. Chem. Soc.* **1967**, *89*, 1102.

(29) We think that  $b_2\pi^*$  and  $a_1\sigma$  are basically different because the former contributes to side bonds only while the latter contributes to all of the three-ring bonds. The degeneracy of these two orbitals in cyclopropane is merely a requirement of molecular symmetry.

(30) Jorgensen, W. I.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973.

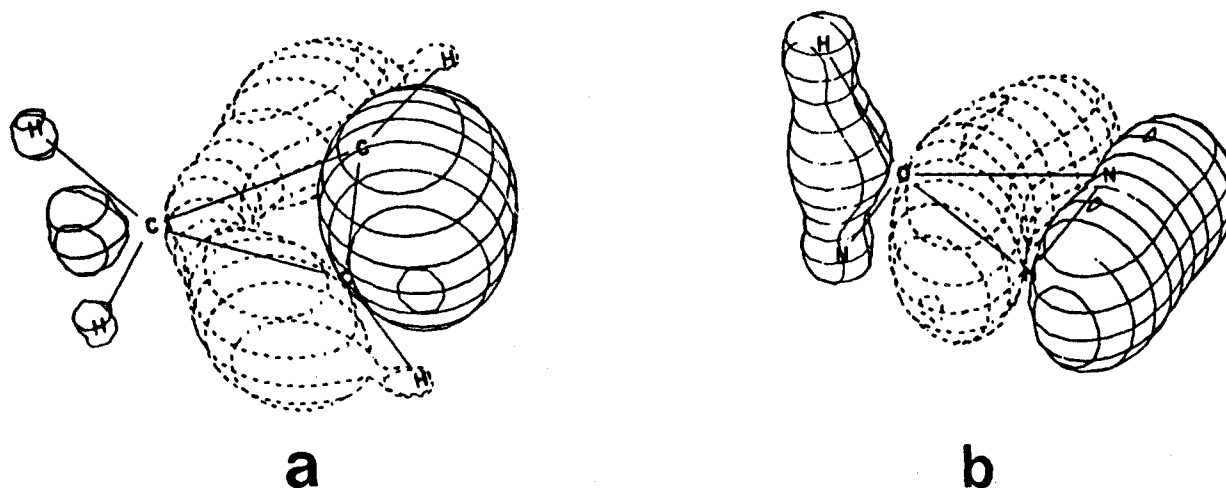


Figure 2.  $a_1\sigma$  orbital in cyclopropene (a) and diazirine (b).

Scheme I

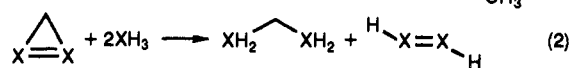
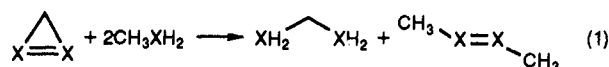


Table III. Strain Energies of Cyclopropene and Diazirane (in Kilocalories per Mole)

molecule	HSE		IBSE	
	3-21G	6-31G*	3-21G	6-31G*
cyclopropene	68.8	58.7	61.8	51.4
diazirine	55.7	31.6	41.2	17.0

However, this trend, which parallels the one observed in hetero-derivative cyclopropanes, can also be interpreted in terms of  $\sigma$ -bridged- $\pi$  bonding. As noted above, an electronegative atom in a 3MR will make its opposite bond shorter through more favorable  $\sigma$ -bridged- $\pi$  bonding. Thus, the shortening of the Si-Si bond in  $(\text{H}_2\text{Si})_2\text{X}$  as X becomes more electronegative is a consequence of more favorable  $\sigma$ -bridged- $\pi$  bonding.

The structure of disiloxirane is also very interesting. West and his collaborator<sup>7</sup> argued that significant double-bond character is retained in the basal unit since the Si-Si bond length is very close to a typical double-bond value and the four substituents on silicons are in essentially the same plane. This interpretation is supported by <sup>29</sup>Si NMR coupling constant.<sup>7</sup> Our  $\sigma$ -bridged- $\pi$  bond model also strongly supports this interpretation. Note that the electronegativity of silicon is similar to that of boron<sup>27</sup> and that strong  $\sigma$ -bridged- $\pi$  bonding between borons can be achieved through an electronegative, bridging oxygen as discussed previously. We hypothesize that a similar  $\sigma$ -bridged- $\pi$  bond also exists in disiloxirane and that the multiple bonding between the basal silicons, as evidenced from experimental data,<sup>7</sup> is a result of this bond.

The effect of a heteroatom on the length of its opposite bond also has a well-defined pattern in fused 3MRs. Extensive ab initio calculations of all of the cyclopropanes, bicyclobutanes, and propellanes containing carbon and/or silicon<sup>31</sup> show that bridging carbons shorten opposite silicon-silicon bonds and bridging silicons lengthen the opposite carbon-carbon bonds. In particular, when the bridging groups in [1.1.1]propellane are replaced by  $\text{SiH}_2$ , the  $\text{C}_1-\text{C}_3$  distance becomes 0.3 Å longer (1.904 Å as compared to 1.600 Å in [1.1.1]propellane), thereby transforming the bridgehead carbons from bonded to nonbonded. But when the bridging groups in pentasil[1.1.1]propellane are replaced by

methylens, the  $\text{Si}_1-\text{Si}_3$  distance (going from 2.729 to 2.283 Å) by so much that an actual Si-Si bond is formed since that Si-Si separation is shorter than the normal Si-Si bond distance (2.35 Å<sup>32</sup>). This change is understandable in terms of  $\sigma$ -bridged- $\pi$  bonding since carbon is more electronegative than silicon. Hence, bridging silylenes weaken the  $\text{C}_1-\text{C}_3$  bond and bridging methylens strengthen the  $\text{Si}_1-\text{Si}_3$  bond, as compared to their respective parent molecules.

**B. Strain Energy of 3MRs.** If one compares the  $\sigma$ -bridged- $\pi$  orbitals in Figure 1, it is clear that favorable  $\sigma$ -bridged- $\pi$  bonding brings electron density into the 3MR. This will enhance the bonding in the 3MR, making it more stable.

The strain energies of cyclopropane (2), azirane (3), and oxirane (4) have been discussed by Cremer and Kraka.<sup>6a</sup> They showed that their strain energies determined by homodesmic separation energies (HSE) and conventional strain energy (CSE) methods are essentially the same (this also agrees with other experimental measures<sup>33</sup>). In addition, they showed that the strain energy determined by isodesmic bond separation energies (IBSE) decreases from 2 to 3 and to 4. They argued that the angle strain for azirane and oxirane should be considerably larger than that for cyclopropane considering their differences in angle bending force constants and interpath angles. They attributed the observed strain energies to cancellation of changes in ring strain and surface delocalization. We note that this phenomenon can be simply explained in terms of  $\sigma$ -bridged- $\pi$  bonding. As noted above, the strength of the  $\sigma$ -bridged- $\pi$  bond increases from cyclopropane to azirane to oxirane and this will compensate the increase in angle strain. It should be noted that the increase of  $\sigma$ -bridged- $\pi$  bonding in 2, 3, and 4 is consistent with Cremer and Kraka's argument that the surface delocalization<sup>6a</sup> and/or  $\sigma$ -aromaticity<sup>6b</sup>, increases in the same order. While the other two-ring bonds of 2, 3, and 4 are essentially the same, their  $\sigma$ -bridged- $\pi$  orbitals (see Figure 1) are different in the extent of electron delocalization. Thus, the concept of  $\sigma$ -bridged- $\pi$  bonding provides an orbital origin for surface delocalization and/or  $\sigma$  aromaticity.

The strain energies of 3MRs containing silicon have recently been calculated by Kitchen, Jackson, and Allen<sup>31</sup> using homodesmic reactions. They found that the strain energies of cyclo-trisilane, silirane, and disilirane are larger (by about 10 kcal/mol) than that of cyclopropane.<sup>34</sup> This is surprising since the angle strain around Si should be smaller than that around C. However, it can be explained in terms of  $\sigma$ -bridged- $\pi$  bonding. Since the  $\pi$  bonding between silicons is much poorer than that between carbons, the  $\sigma$ -bridged- $\pi$  bonding between silicons is expected to be less effective.<sup>35</sup> In fact, the degree of delocalization decreases

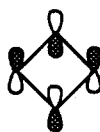
(31) Kitchen, D. B.; Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, *112*, 3408.

(32) Baxter, S. G.; Mislou, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605.

(33) Pihlaja, K.; Taskinen, E. In *Physical Methods in Heterocyclic Chemistry*; Kartritzky, A. R., Ed.; Academic Press: New York, 1974; Vol. 6, p 199.

(34) This may explain the instability of silacyclopropane noted in ref 14.

Chart V



as more silicon atoms are added to the 3MR.<sup>36</sup> (The weak  $\sigma$ -bridged- $\pi$  bonds formed by silicons are also responsible for the long Si<sub>1</sub>-Si<sub>3</sub> distance in pentasila[1.1.1]propellane.)

A comparison of the strain energy in diazirine to that of its isoelectronic species, cyclopropene, reveals another aspect of  $\sigma$ -bridged- $\pi$  bonding. We calculated their strain energies according to the HSE (1) and IBSE (2) reactions<sup>37</sup> (Scheme I) using 3-21G and 6-31G\*. It turns out that the strain energy of cyclopropene is higher than that of diazirine by both measures calculated with both basis sets (Table III). This is surprising since diazirine has more lone-pair electrons, and thus, the electronic repulsion should be greater. But it can be rationalized by use of the simple concept of  $\sigma$ -bridged- $\pi$  bonding. Figure 2 shows the relevant MOs of the two compounds,<sup>30</sup> and it is immediately clear that the  $a_{1\sigma}$  orbital in diazirine is almost a perfect  $\sigma$ -bridged- $\pi$  orbital (compare Figure 2b to Chart I). Thus, the smallness of strain energy of diazirine is a result of its strong  $\sigma$ -bridged- $\pi$  bond. (Diazirine is able to form a strong  $\sigma$ -bridged- $\pi$  bond because the lone pairs on the nitrogens can be bent up more easily in comparison to a bond pair.) The strain energy difference between cyclopropene and diazirine is reflected in their stabilities: while cyclopropene is very unstable, diazirine is remarkably stable toward organic and inorganic reagents.<sup>38</sup>

**C. Geometries of Some Square Molecules.** It is well-known that "square" molecules such as cyclobutane are nonplanar because of the repulsion among the eclipsing hydrogens and angle strain. But if a square molecule assumes a planar geometry, it would be in a perfect position to form a  $\sigma$ -bridged- $\pi$  bond. Chart V shows a schematic orbital diagram of one of the degenerate  $E_u$  molecular orbitals of planar cyclobutane,<sup>31</sup> and we identify it as the  $\sigma$ -bridged- $\pi$  orbital in planar square molecules. Since the bonding shown in Chart V is optimized in planar geometry, we expect that in cases where strong  $\sigma$ -bridged- $\pi$  bonding can be formed (e.g., when one of the methylene groups is replaced by a more electronegative atom or group) the molecule will assume planar geometry and the 1,3-nonbonded distance be shortened. This is indeed true.

Chart III shows the geometries of several four-membered-ring compounds containing first-row atoms, and our calculations agree well with the available experimental data or other theoretical predictions. It should be noted that molecules **20** and **21** are formally Huckel  $4\pi$  systems, and thus, the second-order Jahn-Teller effect might make two of the ring bonds longer than the other two (in analogy to cyclobutadiene). This effect, though very small, has manifested itself in the crystal structure of substituted **20**, where two of the ring N-B bonds are about 0.03 Å longer than the other two.<sup>39</sup> Geometry optimizations within the Hartree-Fock approximation (Chart III) show that the ring bonds are equivalent, and frequency calculations confirm that the geometries of **20** and **21** in Chart III are true energy minima at the HF/3-21G level of theory (that is, all HF/3-21G-predicted harmonic vibrational frequencies are positive). This is because partial double bonding between boron and nitrogen or oxygen is necessary for these molecules to have nearly degenerate states (thereby showing the second-order Jahn-Teller effect), and a single-determinant wave function is not adequate to describe this

(35) Cremer et al. reached the same conclusion using the concept of  $\sigma$  delocalization. See: Cremer, D.; Gauss, J.; Cremer, E. *THEOCHEM* **1988**, *169*, 531.

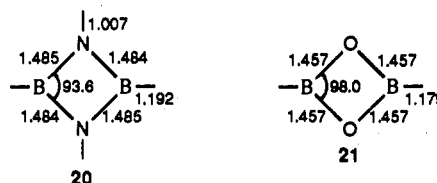
(36) See Jorgensen MO plots in: Kitchen, Douglas B. Ph.D. Dissertation, Department of Chemistry, Princeton University, 1987; p 114.

(37) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

(38) Liu, M. T. H. *Chem. Soc. Rev.* **1982**, *11*, 127.

(39) For the *N,N*-*tert*-butyl-B,B-pentafluorophenyl-substituted structure see: Hess, V. H. *Acta Crystallogr.* **1969**, *B25*, 2342.

Chart VI

Table IV. Si...Si Separations (Å) in (SiH<sub>2</sub>)<sub>3</sub>X<sup>a</sup>

X	Si...Si	X	Si...Si
SiH <sub>2</sub>	3.36	CH <sub>2</sub>	2.96
PH	3.37	NH	2.87
S	3.12	O	2.76

<sup>a</sup> Calculated from the planar geometries of (SiH<sub>2</sub>)<sub>3</sub>X reported in ref 8.

bonding. Thus, geometry optimizations were carried out for **20** and **21** with the 3-21G basis set and the second-order Møller-Plesset perturbation method (MP2) to incorporate electron correlation (structures are shown in Chart VI). As can be seen, **20** has little second-order Jahn-Teller effect since one pair of B-N bonds is only 0.001 Å longer than the other pair and the ring bonds in **21** are essentially identical. The smallness of the second-order Jahn-Teller effect for **20** is understandable since electron delocalization from nitrogen lone pairs to boron empty orbitals should be very small. For **21**, electron delocalization is even smaller because the electronegativity difference between oxygen and boron is larger than that between nitrogen and boron, and this explains why **21** has essentially no second-order Jahn-Teller effect. Since this small difference does not affect the geometrical trend we are interested in here, the following discussions are based on results from SCF calculations.

As can be seen from Chart III, when one of the CH<sub>2</sub> groups in cyclobutane is replaced by an oxygen, both *ab initio* calculation and the microwave spectroscopy determination<sup>40</sup> show that the resulting molecule, oxetane, is planar. The computed geometry of 1,3-dioxetane is planar, too (this agrees with other calculations<sup>17</sup>). In addition, the C...C nonbonded distance decreases significantly from cyclobutane to oxetane (2.123 Å) to 1,3-dioxetane (2.047 Å). The last C...C separation is 1.25 Å shorter than twice the van der Waals radius of carbon.<sup>24</sup>

Interestingly, when the CH<sub>2</sub> group in cyclobutane is replaced by a sulfur whose electronegativity is about the same as that of carbon,<sup>27</sup> the resulting molecule, thietane, is nonplanar as determined by microwave spectroscopy.<sup>41</sup> It is also experimentally known that selenium heteroderivative cyclobutane is nonplanar.<sup>42</sup> Moreover, the ring-puckering frequencies increase from oxetane<sup>43</sup> (35 cm<sup>-1</sup>) to thietane (274 cm<sup>-1</sup>) to trimethylene selenide (378 cm<sup>-1</sup>).<sup>40a</sup> All of these phenomena are understandable in terms of electronegativity-induced changes in  $\sigma$ -bridged- $\pi$  bonding.

Four square molecules containing borons are also shown in Chart III. As expected, the geometries of **19**-**22** vary according to the electronegativity of the heteroatom. Thus, while the CH<sub>2</sub> bridges are not able to bring the four-membered ring into planarity, NH and O bridges can. The B...B nonbonded separations in **20** (1.919 Å) and **21** (1.918 Å) are close to the upper bound of B-B distance (1.60-1.90 Å) in boron hydrides,<sup>10</sup> and they are only 0.05 Å longer than the B-B bond in **22**. This is because the electronegativity difference between boron and nitrogen or oxygen is so large that very effective  $\sigma$ -bridged- $\pi$  bonding can be achieved in the same way as in 3MR compounds (see Discussion in section III). (In **22**, electron repulsion and angle strain around oxygens

(40) (a) Moriarty, R. M. In *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Wiley: New York, 1974; Vol. 8, p 271. (b) Skuncke, P. N.; Fogarasi, G.; Boggs, J. E. *J. Mol. Struct.* **1980**, *62*, 259.

(41) White, M. S.; Beeson, E. C., Jr. *J. Chem. Phys.* **1965**, *43*, 1838.

(42) Harvey, A. B.; Durig, J. R.; Morrissey, A. C. *J. Chem. Phys.* **1969**, *50*, 4949.

(43) Although the puckered oxetane is slightly more stable than the planar one, the ground vibrational level is about 8 cm<sup>-1</sup> above the barrier. Thus, the molecule is actually planar.<sup>40a</sup>

prevent the borons from getting closer.)

The above trend likewise holds for silicon ring compounds. Ab initio calculations<sup>8</sup> show that while the O, S, and NH heteroderivative cyclotetrasilanes are planar, the CH and PH heteroderivative ones are puckered, as is the parent cyclotetrasilane. The ring-puckering frequencies for the planar species increase from S to NH to O heteroderivative cyclotetrasilanes,<sup>8</sup> and this correlates with the electronegativities of S, N, and O. It should be noted that the Si<sub>1</sub>...Si<sub>3</sub> nonbonded distances (Table IV) calculated from the geometries of planar (SiH<sub>2</sub>)<sub>3</sub>X (X = SiH<sub>2</sub>, PH, S, CH<sub>2</sub>, NH, and O)<sup>8</sup> decrease as the electronegativity of X increases.<sup>44</sup> The same trend has been observed for 1,3-disubstituted cyclotetrasilanes.<sup>8</sup> All of these phenomena can be accounted for with the concept of  $\sigma$ -bridged- $\pi$  bonding. Thus, an electronegative atom makes the bonding shown in Chart V more effective and brings the diagonal silicons closer.

Recently, the structure of 1,3-cyclodisiloxane has given rise to much theoretical interest.<sup>16-18,3,45-47</sup> In particular, different explanations have been given to rationalize the short Si...Si nonbonded distance (2.31–2.40 Å) in 1,3-disiladioxetanes.<sup>16</sup> These include the following: (1) severe lone pair–lone pair repulsions between the oxygen atoms;<sup>45,46</sup> (2) strong attraction between the silicon and oxygen atoms;<sup>17</sup> and (3) unsupported  $\pi$  bonding between the silicon atoms.<sup>8</sup> The view that there is a localized two-electron bond between the silicon atoms has been ruled out since the deformation density map of tetrahydroxycyclodisiloxane (which has a very short Si...Si distance, 2.375 Å) shows a shallow negative valley of density between the two silicon atoms.<sup>47</sup> Our explanation to this question is quite simple: the two electronegative bridging oxygen atoms create a strong  $\sigma$ -bridged- $\pi$  bond (Chart V). This  $\sigma$ -bridged- $\pi$  bond not only binds the oxygens and silicons but also binds the formally nonbonded silicon atoms through three-center orbital overlap. This argument strongly supports the “unsupported  $\pi$ -bonding” interpretation<sup>8</sup> and shows that the “unsupported  $\pi$ -bond” is supported by the  $\sigma$ -orbital of the bridging atoms (Chart V).

#### IV. Summary

Extensive ab initio electronic structure calculations of three-membered-ring compounds containing first-row atoms lead us to

propose that favorable  $\sigma$ -bridged- $\pi$  bonding is achieved when an electronegative atom is at the apex position of a triangle. This will do the following: (a) bring the basal atoms of the triangle closer and (b) relieve some of its strain energy, thereby making it more stable. It is shown that this simple bonding pattern, which has been largely ignored in the literature of small-ring compounds, is able to give an unified explanation to problems concerning bonding in both 3MRs and 4MRs containing first- and second-row atoms as summarized below:

(1) As the electronegativity of the heteroatom increases, the C–C bond length in heteroderivative cyclopropanes decreases as a result of enhanced  $\sigma$ -bridged- $\pi$  bonding.

(2) As the electronegativity of the heteroatom increases, the Si–Si bond length in monoheteroderivatived cyclotrisilanes decreases as a result of enhanced  $\sigma$ -bridged- $\pi$  bonding.

(3) The unusual properties of disilaoxirane are a consequence of the large electronegativity difference between oxygen and silicon, which makes effective  $\sigma$ -bridged- $\pi$  bonding between silicons possible.

(4) The dramatic geometrical change of heteroderivative carbon and silicon [1.1.1]propellanes is a result of the electronegativity difference between carbon and silicon.

(5) The similarity of strain energies of cyclopropane, azirane, and oxirane results from the cancellation of variations in angle strain energy and  $\sigma$ -bridging- $\pi$  bonding.

(6) The unusual geometry of some square molecules and the variation of 1,3-nonbonded distances can be explained using the  $\sigma$ -bridged- $\pi$  bonding model in planar square molecules.

This model agrees with other theories in many aspects. It offers an orbital explanation of the surface delocalization and/or  $\sigma$ -aromaticity concept<sup>6</sup> proposed for 3MRs. It supports the double-bonding hypothesis in explaining unusual properties of disilaoxirane.<sup>7</sup> It also supports the “unsupported  $\pi$ -bond” model proposed in explaining bonding in silicon ring compounds.<sup>8</sup>

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**Registry No.** 1, 39517-80-1; 2, 75-19-4; 3, 151-56-4; 4, 75-21-8; 5, 16488-40-7; 6, 2781-85-3; 7, 157-17-5; 8, 157-18-6; 9, 84837-52-5; 10, 60720-12-9; 11, 85302-95-0; 12, 130434-32-1; 13, 130434-33-2; 14, 157-22-2; 15, 130434-34-3; 16, 157-26-6; 17, 503-30-0; 18, 287-50-3; 19, 77385-69-4; 20, 18464-81-8; 21, 287-19-4; 22, 130434-35-4; (SiH<sub>2</sub>)<sub>4</sub>, 287-69-4; (SiH<sub>2</sub>)<sub>3</sub>PH, 68492-56-8; (SiH<sub>2</sub>)<sub>3</sub>S, 87804-56-6; (SiH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>, 79793-09-2; (SiH<sub>2</sub>)<sub>3</sub>NH, 110205-56-6; (SiH<sub>2</sub>)<sub>3</sub>O, 87729-91-7.

(44) The long C–S bond is responsible for the long Si...Si distance.

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

(46) Bachrach, S. M.; Streitwieser, A. *J. Am. Chem. Soc.* **1984**, *107*, 1186.

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