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σ and π Relaxation of Strain in Three-Membered Ring Molecules $(CH_2)_2X$, $(NH)_2X$, and $(SiH_2)_2X$ ($X = SiH_2$, PH, S)

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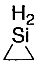
The σ and π relaxation of ring strain by electron delocalization from bonds to bonds was investigated to understand or predict the strains of $(CH_2)_2X$, $(NH)_2X$, and $(SiH_2)_2X$ ($X = SiH_2$, PH, S). The σ relaxation by the delocalization between the geminal ring bonds is found to be significant and general for these molecules as well as for the homoatomic molecules. Delocalization of the lone pair on the heteroatom to the neighboring σ bonds contributes to the π relaxation of ring strain in $(CH_2)_2X$ and $(SiH_2)_2X$ except for $X = SiH_2$ but contributes little to that of $(NH)_2X$. However, the cyclic delocalization of lone pairs is generally not significant except in $(SiH_2)_2S$.

Introduction

Three-membered ring molecules $(CH_2)_2X$ (**1**, $X = SiH_2$; **2**, $X = PH$; **3**, $X = S$)[1−8] have attracted considerable attention for a long time. There is an intriguing trend in the strains in these hetero three-membered ring molecules. Thiirane **3** has the lowest strain energy (SE) of 19.8 kcal mol^{-1}, as determined from the observed heat of formation.[1] Ab initio calculations[2] of the homodesmotic reaction energies[3] (eq 1) reproduced the strain of thiirane **3** (17.7 and 18.5 kcal mol^{-1}) at the RHF/6-31G(d)//RHF/6-31G(d) and MP2/6-31G(d)//RHF/6-31G(d) levels, respectively.[2] At the same levels of calculation,[2] phosphirane **2** is a little more strained (22.0 and 24.4 kcal mol^{-1}), whereas silirane **1** is much more strained (42.9 and 45.1 kcal mol^{-1}).[2] However, it is still not completely understood why the strain energies of $(CH_2)_2X$ ($X = SiH_2$, PH, S) decrease in the order of **1** > **2** > **3**.

We developed and successfully applied the geminal delocalization theory for ring strain to homoatomic molecules.[9−11] The delocalization of σ electrons between the geminal ring bonds was proposed to relax the ring strain (σ relaxation). On the other hand, π relaxation due to delocalization of the π electrons has been proposed for some unsaturated ring molecules (**10**−**13**).[12−15] We previously showed that the three-, four- and five-membered rings of unsaturated silicon compounds are less strained than the corresponding saturated molecules by the π relaxation.[12] In this paper, we evaluate the σ and π relaxation of the strains in **1**−**3.** The σ relaxation by geminal delocalization is also shown to be important in the hetero three-membered rings. We also predict the relative strains in $(NH)_2X$, siladiaziridine **4**, phosphadiaziridine **5**, and thiadiaziridine **6** and discuss those in $(SiH_2)_2X$ (cyclotrisilane **7**, disilaphosphirane **8**, and disilathiirane **9**) to examine the general applicability.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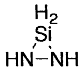
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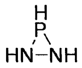
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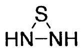
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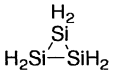
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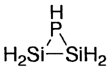
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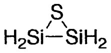
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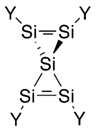
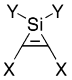
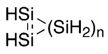
10 (Y = F, OH, Cl, NH_2, Br, I, CH_3)


12 (Y = $tBuMe_2Si$)


11a (X = H; Y = F, OH, Cl, NH_2, Br, I, CH_3)
11b (X = Me_3Si; Y = iPr_2N)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Theoretical Background

σ Relaxation.[9−11] σ electrons delocalize between the geminal σ bonds. The electrons in the doubly occupied σ bonding orbital of a bond shift into the vacant antibonding σ* orbital of another geminal bond. Geminal delocalization can be either bonding (Figure 1a) or antibonding (Figure 1b), depending on the nature of the bond.[16] The s character of the hybrid orbitals on the central atom has previously been shown to decrease the bonding property or to increase the antibonding property.[9]

Geminal delocalization between the C−C bonds is antibonding.[9] Electrons are repelled from the region where the σ and σ* orbitals overlap each other. The antibonding property of the geminal delocalization is attenuated or turns into the bonding property for acute bond angles. This has been proposed to account for the unexpectedly low strain energy of cyclopropane.[9] As the bond angle decreases, the antibonding property increases for Si−Si bonds and becomes a bonding property for P−P bonds.[10] These findings are in good agreement with the high

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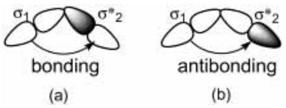


Figure 1. Bonding (a) and antibonding (b) geminal delocalization.

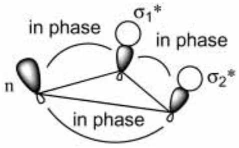


Figure 2. Cyclic (n, σ^*, σ^*) interaction and the phase continuity.

strain in cyclotrisilane and low strain in cyclotriphosphane. The bonding−antibonding properties have been used to predict the low strain of homoatomic three-membered rings consisting of oxygen, nitrogen, and sulfur relative to that of their four-membered analogues.[11]

The geminal delocalization relaxes the ring strain in $(CH_2)_2X$ with a change from X = SiH_2 to X = S. The s character of the hybrid orbital of the carbon for the C−X bond should decrease with the electronegativity of X. Delocalization from σ_{CC} to σ^*_{CX} gives rise to σ relaxation. For delocalization from σ_{CX} to σ^*_{XC}, the s character of the hybrid orbitals on X is important. The s character is enhanced as the electronegativity of X increases. However, the lone pair on X prefers strong s character, which keeps the s character of the ring bonds weak. Geminal $\sigma_{CX} \rightarrow \sigma^*_{XC}$ delocalizations can also relax strain. As a result, σ relaxation due to geminal delocalization is expected to reduce strain in the order of **1** > **2** > **3**.

***π* Relaxation.** We investigated the effects of the delocalization of a lone pair on the strain in **1**−**3**. Such delocalization can occur through the interaction of the nonbonding orbital(s) of the lone pair with σ^*_{CH} orbitals. When there is appreciable $\sigma^*-\sigma^*$ interaction, delocalization occurs in a cyclic manner (Figure 2).

Cyclic orbital interaction needs to meet the orbital phase continuity conditions:[17,18] (i) electron-donating orbitals are out of phase; (ii) electron-donating and electron-accepting orbitals are in phase; (iii) electron-accepting orbitals are in phase. The phase of the n, σ^*, and σ^* orbitals is found to be continuous (Figure 2). The lone pair is an electron donor. The σ^*_{CH} orbitals are electron-accepting orbitals. The n orbital is combined in phase with σ_1^* and σ_2^* orbitals. The σ_1^* and σ_2^* orbitals are in phase with each other. These relationships meet the orbital phase continuity conditions. Cyclic (n, σ^*, σ^*) interaction is favored by the phase continuity.

The n−σ^* interaction is enhanced as the energy gap between n and σ^* decreases. There is no lone pair but rather a σ bond in **1**. The σ bonding orbital lies lower in energy than the lone pair orbitals in **2** and **3**. The lone pair occupies an sp^n-hybridized orbital in **2** and a p orbital in **3**. The n orbital is higher in **3**. The delocalization of the lone pairs (σ electrons in **1**) or the π relaxation should be effective in the order of Si ≪ P < S and contributes to the ring strain in the order of **1** > **2** > **3**. The n → σ^* delocalization induces the cyclic delocalization involving the additional $\sigma^*-\sigma^*$ interaction. The effect of the n → σ^* delocalization is amplified by the cyclic delocalization.

Bond Model Analysis

The above qualitative theory for the σ and π relaxation of ring strain was examined by the bond model analysis previously developed[19] and successfully applied to various chemical phenomena.[20−23]

The single Slater determinant Ψ for the electronic structure is expanded into electron configurations (Scheme 1):

$$\Psi = C_G\Phi_G + \Sigma C_T\Phi_T + \cdots$$

In the ground configuration (Φ_G), a pair of electrons occupies a bonding orbital of a chemical bond (a nonbonding orbital of an unshared electron pair). Electron delocalization is expressed by mixing an electron-transferred configuration (Φ_T), where an electron shifts from a bonding orbital of one bond to an antibonding orbital of another.

The bonding and antibonding orbitals ϕi, and ϕi^* of the ith bond are linear combinations of hybrid atomic orbitals χ_{ia} and χ_{ib} on bonded atoms A and B:

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

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

We use the hybrid orbitals obtained by orthogonalizing the atomic basis functions on each atom. The bond orbitals are obtained by the diagonalization of the 2 × 2 Fock matrices of the basis of the hybrid orbitals. The hybrid atomic orbitals and therefore the bond orbitals are optimized to give the maximum value for the coefficient of the ground configuration (C_G). The bond orbitals of different bonds are not orthogonal to each other. To estimate the interactions between the bond orbitals i and j, we used the interbond energy IBE,[20] which was defined as

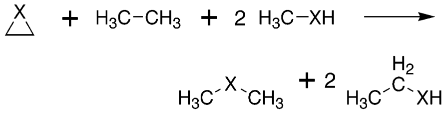
$$\mathrm{IBE}_{ij} = P_{ij}(H_{ij} + F_{ij})$$

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

We used the Gaussian 98 program to calculate the electronic structures,[24] which were used for the bond model analysis.

Results and Discussion

Strain in 1−3. The strain energies (SE) were calculated at the RHF/6-31G* level (with ZPE correction) from the homodesmotic reaction[3] (eq 1). The order (SE = 37.1 kcal mol^{-1} for **1**; 20.2 kcal mol^{-1} for **2**; 17.3 kcal mol^{-1} for **3**) is in good agreement with those calculated at the higher levels. The electronic structures obtained at the RHF/6-31G* level were subjected to the bond model analyses. The results are shown in Table 1.



(1)

The antibonding property of the geminal $\sigma_{CC}-\sigma^*_{CX}$ delocalization indicated by the positive IBE values decreases in the order of **1** (0.151 au) > **2** (0.085 au) > **3** (0.054 au), in agreement with the s character of the hybrid orbital on the carbon for the C−X bond ($sp^{2.8}$ for SiH_2; $sp^{3.3}$ for PH; $sp^{4.2}$ for S) as predicted. These results support the notion that geminal delocalization contributes to σ relaxation. However, the s character of the lone-pair orbitals on X in **2** ($sp^{0.58}$) is weaker than that in **3** ($sp^{0.19}$). The s character of the hybrid orbital on X for the C−X bond decreases in the order of **1** ($sp^{5.3}$) > **2** ($sp^{12.9}$) > **3** ($sp^{16.3}$) because of the lone-pair effects described above. Thus, the calculated IBE values showed that the antibonding property of geminal $\sigma_{CX} \rightarrow \sigma^*_{XC}$ delocalization decreased in the order of Si (0.125 au) > P (0.028 au) > S

SCHEME 1

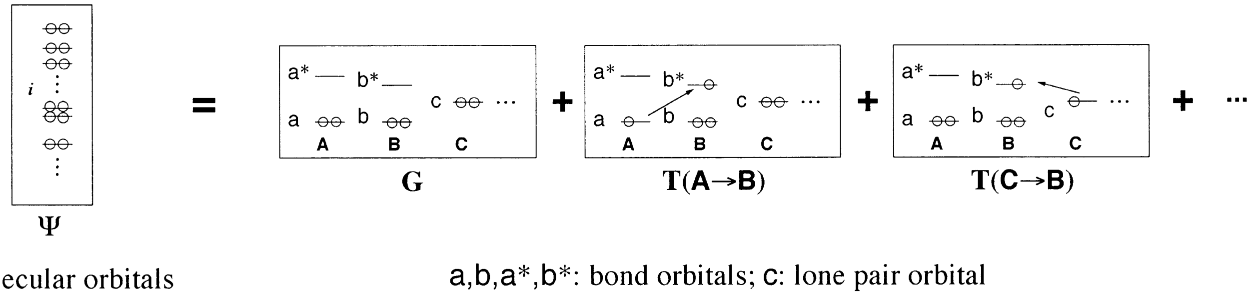


TABLE 1: Strain Energies (SE/kcal mol^{-1}), Hybridization, and Interbond Energies (IBE/au) of 1−3

		hybrid orbital			IBE					
									$\sigma^*_{CH} \leftrightarrow \sigma^*_{CH}$	
cmpd	SE^a	n_x	C in σ_{CX}	X in σ_{CX}	$\sigma_{CC} \rightarrow \sigma^*_{CX}$	$\sigma_{CX} \rightarrow \sigma^*_{XC}$	$\sigma_{XH} \rightarrow \sigma^*_{CH}$	$n_x \rightarrow \sigma^*_{CH}$	syn	anti
1	37.1		sp$^{2.8}$	sp$^{5.3}$	0.151	0.125	−0.005	0	0.004	−0.001
2	20.2	sp$^{0.58}$	sp$^{3.3}$	sp$^{12.9}$	0.085	0.028	−0.056	−0.029	0.004	−0.001
3	17.3	sp$^{0.19}$; p	sp$^{4.2}$	sp$^{16.3}$	0.054	−0.043		−0.117	−0.001	−0.003

[a] Strain energies calculated at RHF/6-31G* level (ZPE-corrected) by the homodesmotic reactions (eq 1).[3]

TABLE 2: Strain Energies (SE/kcal mol^{-1}), Hybridization, and Interbond Energies (IBE/au) of 4−6

		hybrid orbital			IBE					
								$\sigma_{XH} \rightarrow \sigma^*_{NH}$		
cmpd	SE^a	n_x	N in σ_{NX}	X in σ_{CX}	$\sigma_{NN} \rightarrow \sigma^*_{NX}$	$\sigma_{NX} \rightarrow \sigma^*_{XN}$	$n_x \rightarrow \sigma^*_{CH}$	syn	anti	$\sigma^*_{NH} \leftrightarrow \sigma^*_{NH}$
4	50.4		sp$^{4.0}$	sp$^{9.2}$	0.132	0.073		0.001	−0.006	0.000
5	35.4	sp$^{0.58}$	sp$^{5.2}$	sp$^{18.8}$	0.125; 0.111	0.013; 0.028	−0.002	−0.002	−0.036	0.001
6	33.1	sp$^{0.22}$; p	sp$^{4.9}$	sp$^{23.3}$	0.073	−0.089	−0.081			0.000

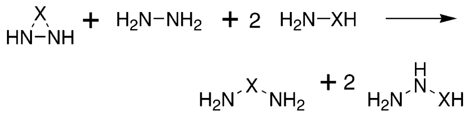
[a] Strain energies calculated at the RHF/6-31G* level (ZPE-corrected) by the homodesmotic reactions (eq 2).[3]

(−0.043 au). These results support the significance of the geminal CX → XC delocalization in the σ relaxation.

We now turn our attention to the π relaxation. The n−σ^* interaction is enhanced as the energy gap between n and σ^* decreases. The electron-donating entity in **1** is a σ_{SiH} bond. The σ bonding orbital lies at a lower level. The n orbital energy of **3** (−0.375 au) is higher than that of **2** (−0.543 au). The σ^*_{CH} orbital energies remain almost unchanged upon going from **1** to **3** (0.747 au for **1**; 0.750 au for **2**; 0.744 au for **3**). Thus, the stabilization due to interaction between σ_{XH}/n_X and σ^*_{CH} should increase in the order of Si < P < S. This was confirmed by the calculated IBE values (−0.005 au for $\sigma_{SiH} \rightarrow \sigma^*_{CH}$ in **1**; −0.056 au and −0.029 au for $\sigma_{PH} \rightarrow \sigma^*_{CH}$; and $n_P \rightarrow \sigma^*_{CH}$ in **2**, respectively; −0.117 au for $n_S \rightarrow \sigma^*_{CH}$ in **3**). The π relaxation due to n → σ^* delocalization is appreciable in **2** and outstanding in **3**. The σ^*−σ^* interaction is bonding between some pairs of bonds and antibonding between others (Table 1). The considerable bonding property of σ^*−σ^* interaction is indispensable for the cyclic delocalization. The π relaxation due to cyclic delocalization is not general in **1**−**3**.

The cyclic delocalization does not generally contribute to the π relaxation in **1**−**3**. This is in stark contrast to the situation in the silicon system **13**.[12] As the IBE values show, the σ^*−σ^* interaction in the cyclotetrasilene (−0.015 au) is strongly bonding (cf. 0.004 au in **1**; 0.004 au in **2**; −0.001 au in **3**). This can be understood in terms of the n(π) and σ^* orbital energies. The σ^*_{SiH} orbital energy (0.413 au in cyclotetrasilene) is lower than the σ^*_{CH} orbital energies (0.747 au in **1**; 0.750 au in **2**; 0.744 au in **3**). The π_{SiSi} orbital (−0.274 au in cyclotetrasilene) lies higher than the n orbital (−0.543 au in **2**; −0.375 au in **3**). The n → σ^* delocalization (−0.005 au in **1**; −0.056 and −0.029 au in **2**; −0.117 au in **3**) is less significant than the π → σ^* delocalization in cyclotetrasilene (IBE = −0.367 au).[12] The π relaxation due to cyclic delocalization, induced by the n → σ^* delocalization, is less significant in **1**−**3** than in the silicon system.

Strain in 4−6. The σ and π relaxations of the ring strains of **1**−**3** were substantiated by the results of the bond model analysis. The success led to a prediction that the strain in the diaza analogues $(NH)_2X$ should decrease in the order of **4** (X = SiH_2) > **5** (X = PH) > **6** (X = S). This was confirmed by the strain energies (SE = 50.4 kcal mol^{-1} for **4**; 35.4 kcal mol^{-1} for **5**; 33.1 kcal mol^{-1} for **6**) calculated from the homodesmotic reaction[3] (eq 2.).



(2)

The results of the bond model analysis (Table 2) show the significance of the σ relaxation. The geminal $\sigma_{NN} \rightarrow \sigma^*_{NX}$ delocalization is in agreement with the relative strains. The s character of the hybrid orbital on the nitrogen for the N−X bond of **4** (X = SiH_2, sp$^{4.0}$) is higher than that of **5** (X = PH, sp$^{5.2}$) and **6** (X = S, sp$^{4.9}$). The IBE values showed that the antibonding property of the $\sigma_{NN} \rightarrow \sigma^*_{NX}$ in **4** (0.132 au) is higher than that of **5** (0.125 and 0.111 au) and **6** (0.073 au). The geminal $\sigma_{NX} \rightarrow \sigma^*_{XN}$ delocalization is also in agreement with the relative strains. The s character of the lone-pair orbitals on X is rich in **5** (sp$^{0.58}$) and is rich compared to that in **6** (sp$^{0.22}$). The s character of the hybrid orbital on X for the N−X bond decreases in the order of **4** (sp$^{9.2}$) > **5** (sp$^{18.8}$) > **6** (sp$^{23.3}$) because of the lone-pair effects. Thus, the antibonding property of σ_{NX}

$\rightarrow \sigma^*_{XN}$ delocalization also decreased in the order of Si (0.073 au) > P (0.013 and 0.029 au) > S (−0.089 au).

The delocalization of lone pair(s) is not significant except in **6**, as is shown by the calculated IBE values (0.001 au for $\sigma_{SiH} \rightarrow \sigma^*_{NH}$ in **4**; −0.002 au and −0.002 au for $\sigma_{PH} \rightarrow \sigma^*_{NH}$ and $n_P \rightarrow \sigma^*_{NH}$ in **5**, respectively; −0.081 au for $n_S \rightarrow \sigma^*_{NH}$ in **6**). The $\sigma^*_{NH} \rightarrow \sigma^*_{NH}$ interactions do not stabilize the diaza analogues at all. Cyclic delocalization of the lone pair(s) has no effect on the strains. As a result, the π relaxation does not contribute to the change in strain in **4**−**6**.

Strain in 7−9. The strain energies of $(SiH_2)_2X$ were previously reported to be 38.9 kcal/mol for X = SiH_2, 30.7 kcal/mol for X = PH, and 28.1 kcal/mol for X = S.[7c] The dependence of relative strain on X is similar to that of $(CH_2)_2X$ and $(NH)_2X$. The general trend can be understood in terms of geminal delocalization. The IBE values show that the antibonding property decreases along the row of the periodic table both for the geminal delocalization from the Si−Si bond to the Si−X bond (1.264 au for X = SiH_2, 0.674 au for X = PH, and 0.509 au for X = S) and for the geminal delocalization between the Si−X bonds (1.264 au for X = SiH_2, 1.103 au for X = PH, and 0.694 au for X = S). These results support the general applicability of the σ relaxation of the ring strain by the geminal delocalization.

The π relaxation by the delocalization of a lone pair to the adjacent SiH bonds is appreciable in **8** and outstanding in **9**, as the IBE values (−0.080 au for **8** and −0.358 au for **9**) show. The cyclic delocalization is not general in **7**−**9** (appreciable only for **9**, X = S; the IBE values between the σ^*_{SiH} orbitals are −0.007 to ca. −0.012 au). The features are similar to those of $(CH_2)_2X$.

It is worthwhile to discuss a simple interpretation of the relative strain energies of **1**−**9** based on the Baeyer theory.[25] The bond angle around X in usual open-chain molecules is 109.5° for Si but much closer to 90° for P and S. The bond angles ∠C(N)XC(N) in three-membered rings deviate from the unstrained bond angles more for X = SiH_2 than for X = PH, S. However, there are many serious problems regarding this naïve theory. For example, the strain energies of cyclopropane and cyclobutane are close to each other.[26] Perfluorocyclopropane is more strained than cyclopropane,[27] whereas the unstrained bond angles are both 109.5°. The strain energy of cyclotrisilane is higher than that of cyclopropane by nearly 10 kcal/mol.[28] We previously proposed the geminal delocalization theory for the ring-strain relaxation to address these problems.[9−11] In this paper, we have confirmed the general applicability of the σ relaxation due to geminal delocalization and have demonstrated its importance in the hetero three-membered rings **1**−**9**.

Conclusions

The σ relaxation of the ring strain due to the delocalization of σ electrons between the geminal ring bonds has been demonstrated to be significant and general in the three-membered ring molecules with one third-row heteroatom (**1**−**9**) as well as in homoatomic molecules.[9−11] The π relaxation due to the delocalization of the lone pair on the heteroatom to the neighboring σ bonds is generally appreciable in $(CH_2)_2X$ and $(SiH_2)_2X$, except for X = SiH_2, but not in $(NH_2)_2X$. The cyclic delocalization of the lone pair does not contribute to the π relaxation except for $(SiH_2)_2S$ (**9**).

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Supporting Information Available: Optimized structures and energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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