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Relaxation of ring strain by introduction of a double bond

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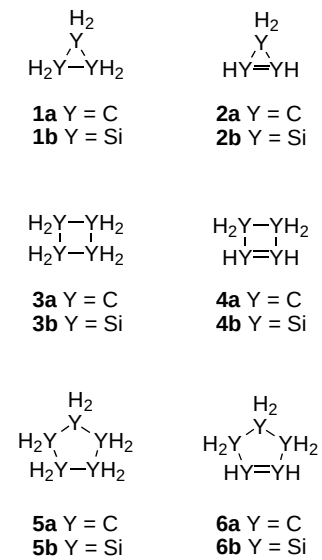
Abstract—Ring strains are relaxed by the cyclic orbital interaction between a π-bond and the σ-bonds on the saturated atoms in the rings. An effective relaxation by the π–σ* interaction occurs in the three-, four-, and five-membered silicon rings. Cyclotrisilene **2b**, cyclotetrasilene **4b**, and cyclopentasilene **6b** have lower strains than those of the parent saturated analogs. However, the stabilization is less significant for the hydrocarbons.

Cyclopropane (**1a**, Y = C) is well-known as a strained molecule (strain energy (SE) = 27.5 kcal mol^{-1}).[1] The ring strain is usually attributed to the acute bond angle of 60° in the three-membered ring, much deviated from the normal tetrahedral angle of 109.5°.[2] Since the normal sp^2-hybrid bond angle of 120° is much wider than the tetrahedral angle, introduction of a double bond into the saturated three-membered ring is intuitively considered to increase the ring strain. For example, the ring strain of **2a** (SE = 53.8 kcal mol^{-1}) increases by 16.7 kcal mol^{-1} upon dehydrogenation.[1] Here we apply the orbital phase theory to predict that the strain of small ring molecules could decrease or would not appreciably increase with introducing a double bond when π-electrons delocalize through σ-conjugation to a significant degree. In fact, the three-, four-, and five-membered ring molecules, cyclotrisilene **2b**, cyclotetrasilene **4b**, and cyclopentasilene **6b** are less strained than the corresponding saturated molecules, **1b**, **3b**, and **5b**, respectively.

π-Electrons in the unsaturated rings, **2**, **4**, **6** delocalize through σ_{YH} bonds in a cyclic manner due to the cyclic interaction of π and σ^*_{YH}(s) (Fig. 1). In the ground configuration **G**, the π is doubly occupied and the σ^*_{YH} orbitals are vacant (Fig. 2). An electron shifts from π to σ^*_1 of the adjacent Y–H bond, leading to the electron-transferred configurations $\mathbf{T}_1$. The transferred electron further shifts from σ^*_1 to σ^*_2 of the next Y–H bond, and finally to σ^*_n of the farthest Y–H bond. The electron shift occurs from π to σ^*_n through the other side chain. The cyclic interaction between π and σ^*_{YH} orbitals takes place in **2**, **4**, and **6**.



The cyclic orbital interactions are under the control of the orbital phase continuity–discontinuity properties.[3] The orbital phase continuity requirements for 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 does not effectively occur. The π-bonding orbital of the π_{YY} bond is a donating orbital, and the vacant antibonding orbital of the Y–H bond, σ^*_{YH}, is an accepting orbital. The phase continuity requires that the π-bonding orbitals should be in-phase with σ^*_{YH}, and the σ^*_{YH}'s should be in-phase with each other. In fact, this requirement is satisfied in **2**, **4**, and **6** (Fig. 1). The cyclic

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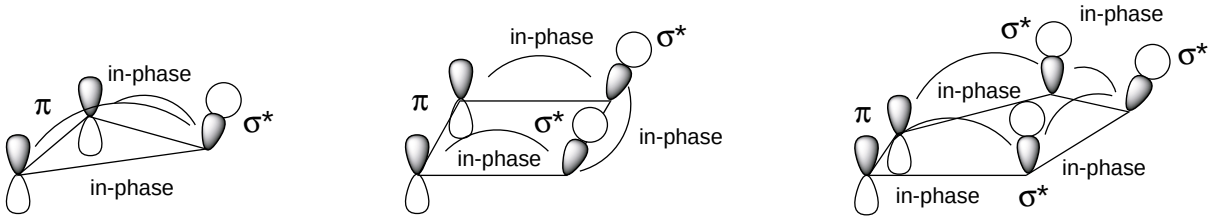

Figure 1. Cyclic orbital interaction in **2**, **4**, and **6**.

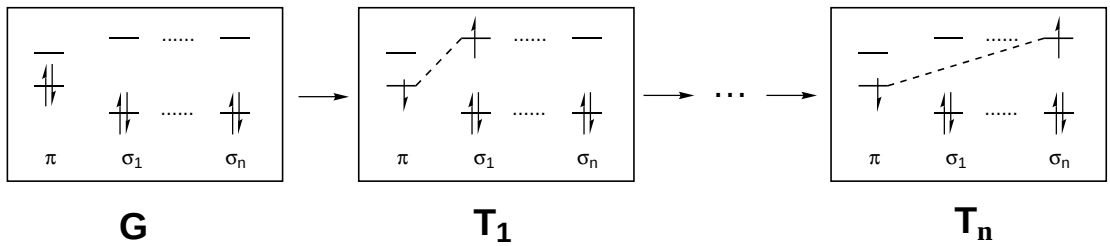

Figure 2. Cyclic delocalization of π electrons through the σ conjugation.

electron delocalization of the π-electrons through the σ-conjugation is expected to lower the strain energies of the unsaturated rings. Thus, in contrast to carbon rings, the unsaturated rings of silicon analogs might be less strained than the saturated ring, due to the π–σ* interaction enhanced by the high π-orbital energy and the low σ^*_{YH} orbital energy.

In fact, cyclosilenes **2b**,[4] **4b**, and **6b** (SE = 34.5, 9.1, and 0.9 kcal mol^{-1}, respectively)[1d,4] were confirmed by the heat of the homodesmotic reactions[5] calculated at B3LYP/6-311++G(3*df*,2*p*)//B3LYP/6-31G(d) level[6] to be less strained than the parent saturated analogs (SE = 35.5, 12.9, 3.0 kcal mol^{-1}),[1d,4] respectively (Table 1). The negative ΔSE, the difference in the strain energies between the unsaturated and the saturated rings, clearly reflects the relaxation in strain from the cyclic orbital interactions between π and σ bonds. The geometries around the unsaturated silicons are planar in cyclotrisilene **2b** and cyclotetrasilene **4b**, and almost planar in cyclopentasilene **6b** (Fig. 3), in contrast to the bent structure of the double bond in disilylene.[7]

We investigated the electronic structures by the bond model analyses[9] at RHF/6-31G* level using the B3LYP/6-31G(d) optimized structures to examine the bond interactions. To estimate the interactions between the bond orbitals *i* and *j*, we employed the interbond energy (IBE)[10] that is derived from the following equation:

$$IBE_{ij} = P_{ij}(H_{ij} + F_{ij})$$

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

The π–σ* interaction was found to stabilize **2b** ($IBE_{\pi SiSi-\sigma^*SiH} = -0.354$ a.u.) more than **2a** (–0.200 a.u.). This results from the higher π-orbital energy (–0.278 a.u.) and lower σ*-orbital energy (0.442 a.u.) than the corresponding energies in **2a** (–0.371 and 0.767 a.u.), respectively. The four-membered ring **4b** showed almost the same results as **2b**, which are summarized in Table 2. Delocalization between two σ^*_{SiH} at SiH_2 of **4b** is more bonding ($IBE_{\sigma^*SiH-\sigma^*SiH} = -0.015$ a.u.) than that of the corresponding orbitals of **4a** ($IBE_{\sigma^*CH-\sigma^*CH} = -0.007$ a.u.), confirming that the cyclic orbital interaction occurs more effectively in **4b**. The π–σ* interaction in **6b** is larger ($IBE_{\pi SiSi-\sigma^*SiH} = -0.357$ a.u.) than that of **6a** ($IBE_{\pi CC-\sigma^*CH} = -0.238$ a.u.). The σ*–σ* interactions including the distant σ_{Si-H} bond are bonding in **6b** ($IBE_{\sigma^*SiH-\sigma^*SiH} = -0.004$ a.u.), while they are antibonding in **6a** ($IBE_{\sigma^*CH-\sigma^*CH} = 0.002$ a.u.).

The significance of the π–σ* interaction was previously reported for some three-membered ring molecules.[4,11] Here we demonstrated that the cyclic interactions of π and one through three σ* orbitals are significant not only in three-membered ring molecules, but also in the four-, and five-membered ones.

Table 1. Calculated strain energies (in units of kcal mol^{-1})

Compounds		Strain energy (SE)/kcal mol^{-1}				ΔSE
		$H_2Y(YH_2)_{n-2}YH_2$		$HY(YH_2)_{n-2}YH$		
$n=3$	Y = C	**1a**	25.5[a]	**2a**	55.5[a]	20.0
	Y = Si	**1b**	35.5[a]	**2b**	34.5[a]	−1.0
$n=4$	Y = C	**3a**	22.6	**4a**	28.7	6.1
	Y = Si	**3b**	12.9	**4b**	9.1	−3.8
$n=5$	Y = C	**5a**	4.7	**6a**	4.5	−0.6
	Y = Si	**5b**	3.0	**6b**	0.9	−2.1

[a] From Ref. 4.

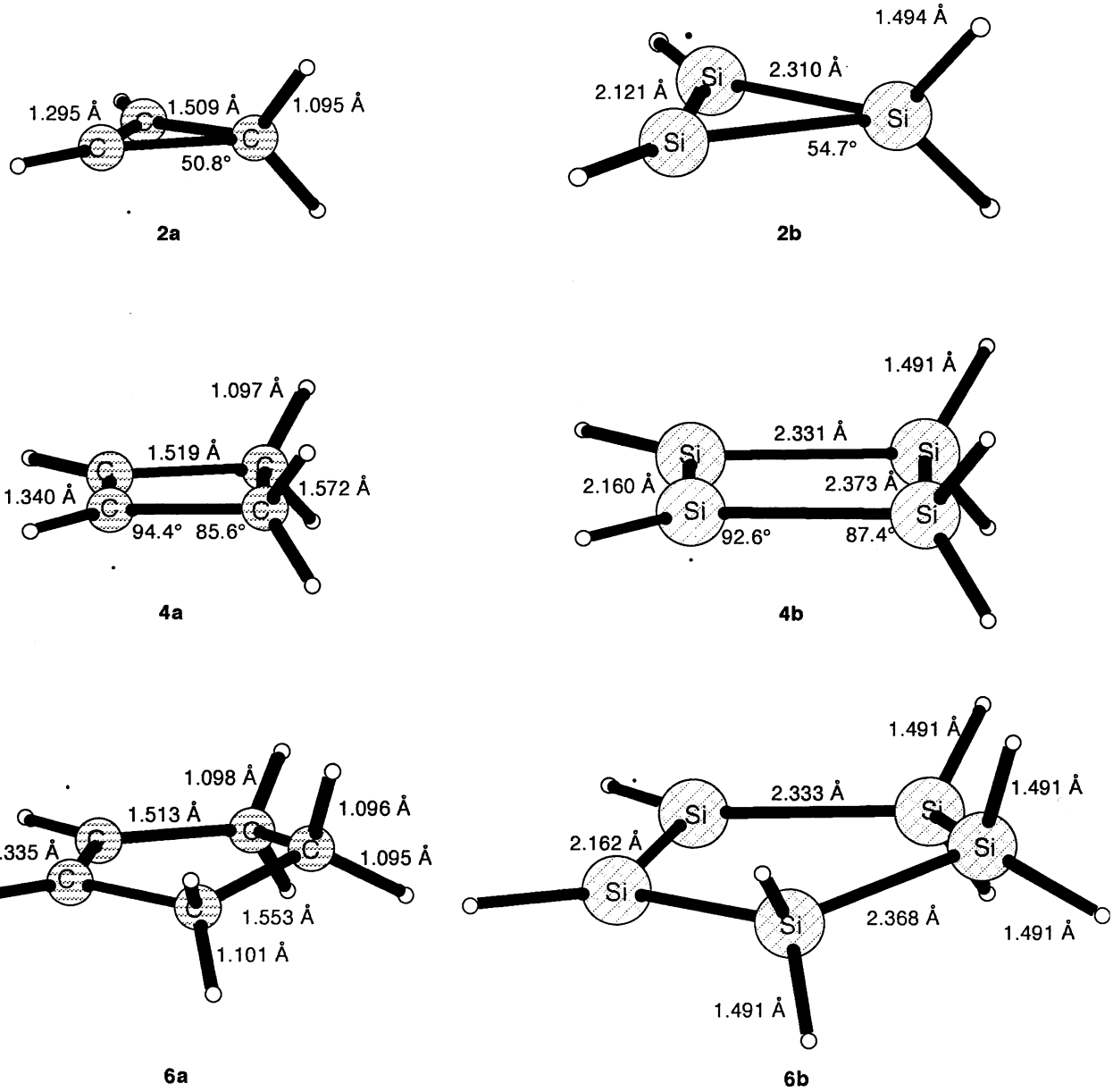

Figure 3. Optimized structures of molecules **1**–**6**.

Table 2. Bond interactions and bond orbital energies

		Bond interaction (a.u.)		Orbital energy (a.u.)	
		$IBE(_{\pi YY-\sigma^*YH})$	$IBE(_{\sigma^*YH-\sigma^*YH})$	$F_{ii}(_{\pi YY})$	$F_{ii}(_{\sigma^*YH})$
2a	Y=C	−0.200		−0.371	0.777
2b	Y=Si	−0.354		−0.278	0.442
4a	Y=C	−0.246	−0.007	−0.349	0.728
4b	Y=Si	−0.367	−0.015	−0.274	0.413
6a	Y=C	−0.238	0.002	−0.342	0.738
6b	Y=Si	−0.357	−0.004	−0.275	0.411

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5. (a) The strain energies were estimated by the homodesmotic reaction shown in Eqs. (1) and (2):[5b]

$$(YH_2)_n + n\,H_3Y\text{-}YH_3 \longrightarrow n\,H_3Y\text{-}YH_2\text{-}YH_3 \quad (1)$$

$$\begin{matrix} HY{=}YH \\ (YH_2)_n \end{matrix} + H_2Y{=}YH_2 + n\,H_3Y\text{-}YH_3 \longrightarrow 2\,H_2Y{=}YH\text{-}YH_3 + n\,H_3Y\text{-}YH_2\text{-}YH_3 \quad (2)$$

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