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Geminal Delocalization of σ-Electrons and Ring Strains

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Abstract: The delocalization of σ-electrons from bonds to bonds in three and four-membered ring molecules was studied in a theoretical manner. The antibonding property of the σ-electron delocalization between geminal C–C bonds increases in perfluorocyclopropane (**5**) and cyclopropene (**8**) while it decreases in cyclopropane (**2**). This accounts for the fact that the three-membered rings (**5** and **8**) are more strained than the four-membered rings (**6** and **9**) while the ring strains of **2** and cyclobutane (**3**) are comparable. The geminal delocalization between ring bonds is bonding in the three-membered ring molecules O_3 (**14**) and S_3 (**23**) and less antibonding in N_3H_3 (**11**). Ab initio molecular orbital calculations of the strain energies revealed that the three-membered rings (**11**, **14**, and **23**) should surprisingly be less strained than the four-membered rings (**12**, **15**, and **24**). The present findings contribute to establishing the geminal delocalization theory for ring strains.

There are some interesting problems about the strains of small ring molecules. von Baeyer[1] proposed that the deviation in bond angles from the normal tetrahedral value should be responsible for the instability of three- and four-membered ring compounds. However, measured heats of combustion showed that cyclopropane (**2**) and cyclobutane (**3**) have nearly the same strain energies (27.5 and 26.5 kcal/mol, respectively).[2] The bond angle is not an exclusive cause of the ring strains. There have appeared various ideas about components of the ring strains.[3,4] Torsional strains destabilize the small-ring molecules due to eclipsed or nearly so C–H bonds. 1,3-Nonbonded interaction was pointed out to contribute to the instability of **3**, while the repulsion is absent in **2**. The rehybridization caused by the acute bond angles should strengthen the C–H bonds due to high s characters to compensate to some extent for the weakening of the C–C bonds in **2**. The concepts of the σ-aromaticity[5] and the surface delocalization[6] were proposed to account for the stability of **2**.

The strain energies of perfluorocycloalkanes and cycloalkenes are remarkably different between the three- and four-membered rings. The strain energy of perfluorocyclopropane (**5**) was evaluated from the experimentally-determined enthalpy of formation (the heat of the homodesmotic reaction) to be 76.7 kcal/mol.[7] Perfluorocyclobutane (**6**) is much less strained (45.3 kcal/mol).[7] Cyclopropene (**8**) is highly strained (53.8 kcal/mol) relative to cyclobutene (**9**) (30.0 kcal/mol).[2] The perfluorination or the introduction of a double bond strains the three- more than the four-membered rings.

The strains of the small rings of the second row elements are intriguing. The three-membered ring cyclotrisilane (**17**) is more strained than the four-membered ring **18**. The calculated strain energies[4,8] are 36–41 kcal/mol for **17** and 13–19 kcal/mol for **18**. The strains of the small phosphorus rings are low. The strain energies of the permethyl derivatives of **20** and **21** were experimentally estimated by Baulder et al.[9] to be 7.8 and 6.0 kcal/mol, respectively. The theoretically calculated values of **20** and **21** are similarly small (6.7 and 4.3 kcal/mol).[10] The three-membered silicon ring has high strain relative to the four-membered ring while the phosphanes both have low strains.

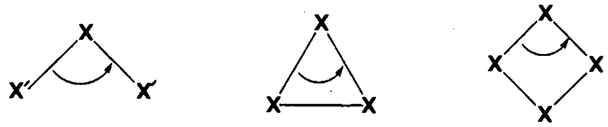

Figure 1. Geminal delocalization of σ-electrons.

We have been investigating the mechanism of the delocalization of σ-electrons from bonds to bonds.[11] The delocalization between geminal bonds (Figure 1) has been proposed to play an important role in angle strain.[12] The geminal delocalization between the C–C bonds is surprisingly antibonding. The antibonding property decreases as the bond angle is acute. The low antibonding property in **2** relative to **3** suggests the relaxation of the strain of **2**. Thus, the angle dependence of the antibonding property of the geminal delocalization has shed new light on the ring strain of the cycloalkanes. The strain theory has been applied to the silicon and phosphorus rings **17**, **18**, **20**, and **21**.[13] The antibonding property of the geminal delocalization increases in the silanes and decreases in the phosphanes for acute bond angles. The high strain of **17** and the low strain of **20** are attributable to the highly antibonding and bonding properties of the geminal delocalizations, respectively.

In this paper, we studied the bond-to-bond delocalization of σ-electrons in the perfluoroalkanes **4**–**6** and the unsaturated hydrocarbons **7**–**9**. The geminal delocalization theory for ring

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(1) von Baeyer, A. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2278.

(2) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

(3) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

(4) Schleyer, P. v. R. *NATO Adv. Study Inst. Ser., Ser. C* **1986**, *189*, 69.

(5) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.

(6) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800, 3811. Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467. Cremer, D.; Gauss, J.; Cremer, E. *J. Mol. Struct.* (THEOCHEM) **1988**, *169*, 531. Cremer, D. *Tetrahedron* **1988**, *44*, 7427. Cremer, D.; Kraka, E. In *Molecular Structure and Energetics, Structure and Reactivity*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1988; Vol. 7, p 65. Cremer, D.; Kraka, E. In *Theoretical Models of Chemical Bonding. The Concept of the Chemical Bond*; Maksic, Z. B., Ed.; Springer Verlag: Heidelberg, 1990, Vol. 2, p 453.

(7) Greenberg, A.; Liebman, J. F.; Dolbier, W. R., Jr.; Medinger, K. S.; Skancke, A. *Tetrahedron* **1983**, *39*, 1533.

(8) (a) Sax, A. F. *Chem. Phys. Lett.* **1986**, *127*, 163; *129*, 66. (b) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60. (c) Grev, R. S.; Shaefer, H. F., III *J. Am. Chem. Soc.* **1987**, *109*, 6569.

(9) Baudler, M.; Hahn, J.; Clef, E. *Z. Naturforsch.* **1984**, *39b*, 438.

(10) Schiffer, H.; Ahlrichs, R.; Haser, M. *Theor. Chim. Acta* **1989**, *75*, 1.

(11) Inagaki, S.; Iwase, K.; Mori, Y. *Chem. Lett.* **1986**, 417. Inagaki, S.; Mori, Y.; Goto, N. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1098. Inagaki, S.; Goto, N. *J. Am. Chem. Soc.* **1987**, *109*, 3234.

(12) Inagaki, S.; Goto, N.; Yoshikawa, K. *J. Am. Chem. Soc.* **1990**, *113*, 7144.

(13) Inagaki, S.; Yoshikawa, K.; Hayano, Y. *J. Am. Chem. Soc.* **1993**, *115*, 3706.

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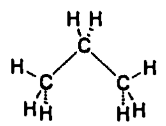
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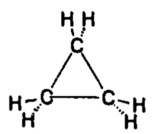
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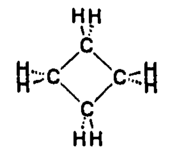
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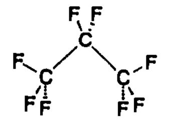
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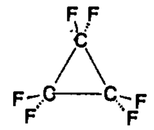
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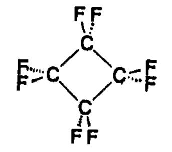
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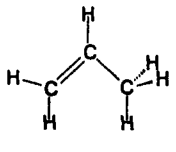
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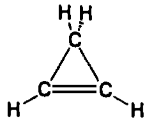
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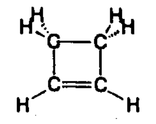
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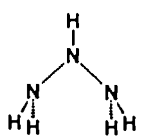
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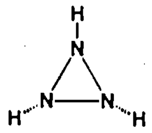
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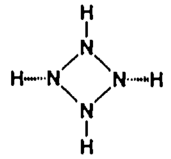
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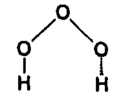
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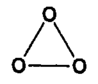
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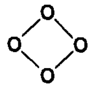
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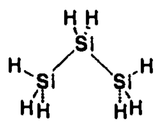
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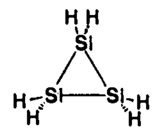
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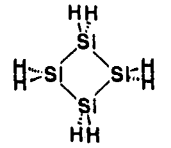
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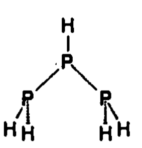
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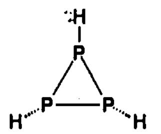
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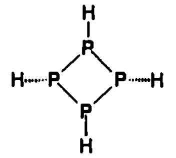
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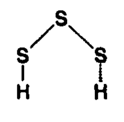
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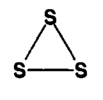
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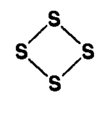
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strains was shown to be successfully applied to the substituent effects and to the striking difference in the strains between the saturated and unsaturated hydrocarbons. The study was extended to the other homocycles N_3H_3 (**11**),[14,15] N_4H_4 (**12**),[16] O_3 (**14**),[17,18] O_4 (**15**),[19] S_3 (**23**),[18,20] and S_4 (**24**)[21] to establish the theory. The calculations suggested unexpectedly low strain of the three- vs four-membered rings. The anomaly was proposed to result from the bonding or less antibonding properties of the geminal delocalization.

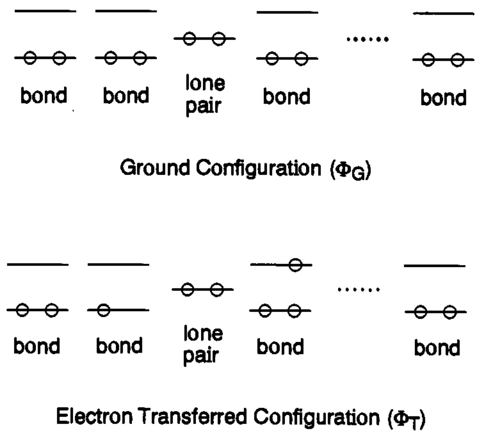

Figure 2. Electron configurations for analyzing bond-to-bond delocalization of σ-electrons.

Method of Calculation and Analysis

The method of analysis of electronic structures of molecules has been described in a previous paper.[12] The single Slater determinant Ψ was expanded into various electron configurations:[22]

$$\Psi = C_G\Phi_G + \sum\nolimits_T C_T\Phi_T \qquad (1)$$

In the ground configuration (Φ_G), a pair of electrons occupies a bonding orbital of a chemical bond or a nonbonding orbital of a lone pair (Figure 2). In an electron-transferred configuration (Φ_T), an electron shifts from a bonding orbital of a bond to an antibonding orbital of another. Bond orbitals were expressed by a linear combination of hybrid orbitals on bonded atoms. The hybrid orbitals were optimized to represent the electronic structure of molecules Ψ by a single configuration or the ground configuration Φ_G as much as possible.[12] The employment of the optimal hybrid orbitals then gives the maximum value of the coefficient C_G of Φ_G. The extent of electron delocalization from bonds to bonds was given by the coefficient ratio C_T/C_G.[23] The interbond population IBP_{ij}

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(14) Some derivatives of triaziridine (**11**) have been isolated and characterized: (a) Leuenberger, C.; Hoesch, L.; Dreiding, A. S. *J. Chem. Soc., Chem. Commun.* **1980**, *24*, 1197. (b) Hoesch, L.; Leuenberger, C.; Hilpert, H.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 2682. (c) Kaupp, G.; Dengler, O.; Burger, K.; Rottegger, S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 341. (d) Hilpert, H.; Hoesch, L.; Dreiding, A. *Helv. Chim. Acta* **1987**, *70*, 381. (e) Marterer, W.; Fritz, H.; Prinzbach, H. *Tetrahedron Lett.* **1987**, *28*, 5497. (f) Klingler, O.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 566.

(15) Theoretical calculations suggested that **11** should be less strained than **2** and that **11** should be fairly stable due to high energy barriers to the ring opening reactions: (a) Nguyen, M. T.; Kaneti, J.; Hoesch, L.; Dreiding, A. S. *Helv. Chim. Acta* **1984**, *67*, 1918. (b) Magers, D. H.; Salter, E. A.; Bartlett, R. J.; Salter, C.; Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 3435.

(16) Derivatives of tetrazetidine (**12**) were proposed to be transient species in the photoreaction of azobenzenophanes: Ritter, G.; Hafelinger, G.; Luddecke, E.; Rau, H. *J. Am. Chem. Soc.* **1989**, *111*, 4627.

(17) (a) Harding, L. B.; Goddard, W. A., III *J. Chem. Phys.* **1977**, *67*, 2377. (b) Wilson, C. W., Jr.; Hopper, D. G. *J. Chem. Phys.* **1981**, *74*, 595.

(18) Morin, M.; Foti, A. E.; Salahub, D. R. *Can. J. Chem.* **1985**, *63*, 1892.

(19) Feng, W. L.; Novaro, O. *Int. J. Quantum Chem.* **1984**, *26*, 521.

(20) (a) Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F., III *J. Chem. Phys.* **1986**, *85*, 963. (b) Patterson, C. H.; Messmer, R. P. *J. Am. Chem. Soc.* **1990**, *112*, 4138. (c) Hohl, D.; Jones, R. O.; Car, R.; Parrinello, M. *J. Chem. Phys.* **1988**, *89*, 6823. (d) Carlsen, N. R.; Schaefer, H. F., III *Chem. Phys. Lett.* **1977**, *48*, 30.

(21) Quelch, G. E.; Schaefer, H. F., III; Marsden, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 8719.

(22) For the original version of the configuration analysis for the interaction between two molecules, see: Baba; H.; Suzuki, S. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2457. Baba, H.; Suzuki, S.; Takemura, T. *J. Chem. Phys.* **1969**, *50*, 2078.

(23) Inagaki, S.; Kawata, H.; Hirabayashi, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3724.

Table 1. Strain Energies and Electronic Structures

	SE[a]	HO[b]	$IBP_{\sigma\sigma^*}$[c]		SE[a]	HO[b]	$IBP_{\sigma\sigma^*}$[c]		SE[a]	HO[b]	$IBP_{\sigma\sigma^*}$[c]
1		$sp^{2.9}$	−0.011	**10**		$sp^{3.3}$	−0.014	**13**		$sp^{6.7}$	−0.006
2	28.7 (26.5 ± 0.9)	$sp^{4.0}$	−0.003	**11**	31.8	$sp^{7.2}$	−0.004	**14**	38.7	$sp^{11.9}$	0.004
3	26.6 (25.1 ± 1.2)	$sp^{3.2}$	−0.017	**12**	33.4	$sp^{4.8}$	−0.022	**15**	57.0	$sp^{8.6}$	−0.011
4		$sp^{2.7}$	−0.015								
5	53.7 (83.3 ± 6.3[d])	$sp^{3.5}$	−0.026								
6	24.8 (53.3 ± 11.0)	$sp^{3.0}$	−0.025								
7		$sp^{1.7}$ (d) $sp^{2.1}$ (s)	−0.011 (a) −0.015 (b)								
8	55.1 (53.2 ± 1.4)	$sp^{2.1}$ (d) $sp^{2.9}$ (s)	−0.016 (a) −0.025 (b)								
9	28.9 (29.1 ± 1.4)	$sp^{2.0}$ (d) $sp^{2.3}$ (s)	−0.021 (a) −0.029 (b)								
16[e]		$sp^{2.9}$	−0.005	**19**[e]		$sp^{7.2}$	−0.004	**22**		$sp^{9.6}$	−0.003
17[e]	38.8	$sp^{3.6}$	−0.021	**20**[e]	11.2	$sp^{14.3}$	0.002	**23**	28.9	$sp^{16.3}$	0.002
18[e]	16.6	$sp^{3.4}$	−0.012	**21**[e]	9.5	$sp^{9.6}$	−0.007	**24**	39.6	$sp^{12.6}$	−0.006

[a] Strain energy (kcal/mol) as the heat of the homodesmotic reactions calculated by ab initio molecular orbital methods at the 6-31G* basis set. [The values in parentheses are based on the experimental thermochemical data (ref 2).] [b] Optimized hybrid orbitals for ring bonds. The characters s and d in parentheses denote the single (s) and double (d) bonds. [c] Interbond population between geminal bonding and antibonding orbitals. The characters, a and b, denote the direction of the electron delocalization (see Figure 3). [d] The standard heat of formation of 5 was taken from the following: Bomse, D. S.; Berman, D. W.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 3967. [e] Reference 13.

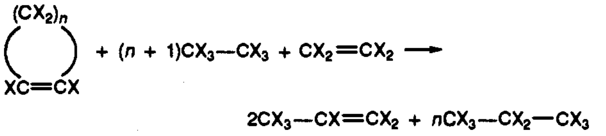
between the *i*th and *j*th bond orbitals was defined[12] by

$$IBP_{ij} = 2\sum_p n_p c_{pi} c_{pj} S_{ij} \qquad (2)$$

where n_p is the occupation number of the *p*th molecular orbital, c_{pi} being the expansion coefficient of the *i*th bond orbital for the *p*th MO. The bonding–antibonding property of the delocalization was evaluated by $IBP_{\sigma\sigma^*}$ between the bonding (σ) and antibonding (σ^*) orbitals involved. The overlap repulsion between the bonding orbitals was estimated by $IBP_{\sigma\sigma}$.

The geometries of the molecules studied here were optimized by ab initio molecular orbital calculations (GAUSSIAN86[24] program) at the Hartree–Fock level with the 6-31G* basis set. The strain energies of the three- and four-membered rings were calculated from the homodesmotic reactions (eqs 3 and 4).[25]

$$\text{c-}(CX_2)_n + nCX_3\text{–}CX_3 \rightarrow nCX_3\text{–}CX_2\text{–}CX_3 \qquad (3)$$



$$\text{c-}[(CX_2)_n\text{–}XC{=}CX] + (n+1)CX_3\text{—}CX_3 + CX_2{=}CX_2 \longrightarrow 2CX_3\text{—}CX{=}CX_2 + nCX_3\text{—}CX_2\text{—}CX_3 \qquad (4)$$

The STO-3G basis set[26] was used for clear chemical image of hybrid atomic orbitals to analyze the electronic structures of molecules or to investigate the bond-to-bond delocalization of electrons.

Results and Discussion

Perfluorocycloalkanes. The calculated strain energy of perfluorocyclopropane (**5**) (53.7 kcal/mol) is remarkably high relative to that of perfluorocyclobutane (**6**) (24.8 kcal/mol). The high strain of **5** relative to **6** was reproduced by the present calculations. The interbond populations between the bonding and antibonding orbitals of the geminal bonds are negative (Table 1). The antibonding property in the cyclic three-membered ring **5** (−0.026) is higher than that in perfluoropropane (**4**) (−0.015). The angle strain of **5** cannot be relaxed but is increased by the geminal delocalization. The effect is reserve to that on the parent cycloalkanes and accounts for the high strain of the perfluorinated three-membered ring. The antibonding property in the four-membered ring **6** is comparable to that of the three-membered ring **5**. The relative strains of **5** and **6** should not be influenced by the geminal delocalization but reflect the bond angle deformation. This is in accordance with the high strain of **5** relative to **6**. The antibonding property of the geminal delocalization was previously[12,13] proposed to increase with the s-character of the hybrid orbitals for the C–C bonds. The perfluoro derivatives have high s-characters (Table 1).

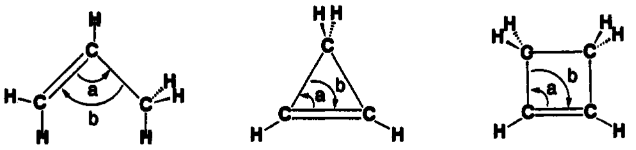


Figure 3. Notation of geminal delocalization of σ-electrons in the cycloalkenes.

Cycloalkenes. Cyclopropene (**8**) (55.1 kcal/mol) is much more strained than cyclobutene (**9**) (28.9 kcal/mol). The calculated strain energies are in good agreement with the experimental values.[2] The delocalization of σ-electrons between the geminal C—C and C═C bonds (Figure 3) is antibonding (Table 1). The antibonding property in the three-membered ring **8** (a, −0.016; b, −0.025) is greater than that in the open chain **7** (a, −0.011; b, −0.015). The geminal delocalization increases rather than relaxes the angle strain of **8**. Furthermore, the antibonding properties in the four-membered ring **9** (a, −0.021; b, −0.029) are similar to those in **8**. These features account for the high strain of **8** relative to **9**. The s-characters of the hybrid σ-orbitals for the double bonds do not decrease at acute bond angles as much as those for the single bonds in the cycloalkanes (Table 1).

N_nH_n. The relative strain energies of the three- vs four-membered nitrogen rings were found to be reversed. The three-membered ring **11** (31.8 kcal/mol) is less strained than the four-membered ring **12** (33.4 kcal/mol). The geminal delocalization between the N–N bonds is antibonding (Table 1). The antibonding property is reduced in the three-membered ring **11** (−0.004) compared with the acyclic structure **10** (−0.014). The relaxation of the angle strain is expected. The antibonding property of the four-membered ring **12** (−0.022) is enhanced. The strain is increased. The geminal delocalization contributes to the reversed strain energy ordering of the three- and four-membered rings. The low antibonding property in the three-membered ring results from the low s-characters of the hybrid orbitals (Table 1).

O_n and S_n. The cyclic structure of O_3 (**14**) (38.7 kcal/mol) has much lower strain energy than O_4 (**15**) (57.0 kcal/mol). The strain energy of S_3 (**23**) (28.9 kcal/mol) is similarly low relative to S_4 (**24**) (39.6 kcal/mol).

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[24] Frish, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, R. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. L.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *GAUSSIAN86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburg, PA, 1984.

[25] George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

[26] A reviewer pointed out that the minimal base set should overestimate the coefficients of electron-transferred configurations.

Table 2. Interbond Population ($\mathrm{IBP}_{\sigma\sigma}$) between Geminal Bonding Orbitals

molecule	$\mathrm{IBP}_{\sigma\sigma}$	molecule	$\mathrm{IBP}_{\sigma\sigma}$	molecule	$\mathrm{IBP}_{\sigma\sigma}$
1	–0.020	**10**	–0.010	**13**	–0.006
2	–0.132	**11**	–0.095	**14**	–0.061
3	–0.046	**12**	–0.033	**15**	–0.018
4	–0.026				
5	–0.151				
6	–0.053				
7	–0.029				
8	–0.136				
9	–0.061				
16[a]	–0.004	**19**[a]	–0.002	**22**	–0.002
17[a]	–0.087	**20**[a]	–0.058	**23**	–0.055
18[a]	–0.024	**21**[a]	–0.013	**24**	–0.013

[a] Reference 13.

The geminal delocalization is bonding (0.004) in the three-membered oxygen ring **14**, while it is antibonding (–0.006) in the acyclic molecule H_2O_3 (**13**). The angle strain is relaxed by the bonding property. The antibonding property (–0.011) in the four-membered ring **15** is comparable to that in the open chain **13**. The strain relaxation is not expected. These features are in agreement with the finding that the three-membered ring is less strained than the four-membered ring.

The geminal delocalization is bonding (0.002) in the three-membered sulfur ring **23**, while it is antibonding for the open chain molecule H_2S_3 (**22**) (–0.003). The bonding property of the geminal delocalization is responsible for the very low strain energy of **23**. The geminal delocalization in the four-membered sulfur ring **24** (–0.006) is as antibonding as that in the open structure **22**. The angle strain should not be relaxed. The results support the low strain of **23** relative to **24**.

The low strain energies of the three- relative to the four-membered oxygen and sulfur rings have been shown to be in agreement with the bonding–antibonding properties of the geminal delocalization. The bonding properties in the three-membered rings come from the low s-characters of the hybrid orbitals (Table 1).

Repulsion between Bonding Orbitals. The interaction between the bonding orbitals of the geminal bonds is repulsive since both orbitals are occupied by two electrons. This was confirmed by the negative $\mathrm{IBP}_{\sigma\sigma}$ values (Table 2). The antibonding property increases in the order of the open chains < the four-membered rings < the three-membered rings. The narrow angle implies that the bonding orbitals are close to each other. As the bond angle becomes acute, the orbital overlap and, consequently, the antibonding property between the geminal bonds increase. The overlap repulsion is one of the primary causes of the angle strain.

Lone Pair Effect. The strains of the three-membered rings relative to the four-membered rings are lowered with the increase in the atomic number of the elements. Cyclopropane is more strained than cyclobutane, though slightly. The three-membered N ring **11** is less strained than the four-membered ring **12**. The relative stability of the three-membered O ring **14** is notable. The relative strains of the second-row element ring molecules change similarly. The three-membered Si ring **17** is of high strain. The strains of the cyclophosphanes (**20** and **21**) are comparable. The relative stability of the three-membered S ring **23** is unambiguous.

The number of the lone pairs increases with the atomic number: none on C and Si; one on N and P; two on O and S. The hybrid orbitals for lone pairs may be more "flexible" than those for bonds. The flexibility allows the ring bonds to be of low s-character, as the small rings demand, leaving high s-characters for the lone pairs. The s-characters of the ring bond orbitals then decrease (C > N > O; Si > P > S) with the increase in the number of lone pairs. This agrees with the calculated ordering of the antibonding properties of the geminal delocalization or the relative three-membered ring strains.

Table 3. Electron Delocalization

molecule	$\lvert C_T/C_G \rvert$[a]	molecule	$\lvert C_T/C_G \rvert$[a]	molecule	$\lvert C_T/C_G \rvert$[a]
1	0.053	**10**	0.093	**13**	0.084
2	0.012	**11**	0.017	**14**	0.011
3	0.055	**12**	0.089	**15**	0.084
4	0.061				
5	0.036				
6	0.072				
7	0.053 (a)				
	0.048 (b)				
8	0.050 (a)				
	0.038 (b)				
9	0.068 (a)				
	0.053 (b)				
16[b]	0.108	**19**[b]	0.095	**22**	0.076
17[b]	0.079	**20**[b]	0.005	**23**	0.006
18[b]	0.106	**21**[b]	0.076	**24**	0.070

[a] Absolute value of the coefficient ratio of the electron-transferred configuration to the ground configuration, indicating the electron delocalizability. The characters, a and b, denote the direction of the electron delocalization (see Figure 3). [b] Reference 13.

σ-Aromaticity. The concept of the σ-aromaticity[5] has been proposed to explain the lower strain of cyclopropane than expected from the bond angle. The aromaticity is related to the delocalization of electrons. The absolute value of C_T/C_G, however, showed that the delocalization between the geminal C–C bonds is diminished in **2** (0.012), relative to **1** (0.053) and **3** (0.055).[12] The low degree of delocalization should be evidence against the σ-aromaticity of **2**.

The three-membered rings studied here were found to lower the geminal delocalization without any exceptions, as indicated by C_T/C_G (Table 3). However, the strains of the three- vs four-membered rings are high in the perfluorocycloalkanes, the cycloalkenes, and the cyclosilanes, while low in the cyclic hydronitrogens, the cyclophosphanes, O_n, and S_n. No correlation was found between the ring strains and the delocalizabilities of σ-electrons. If the stability due to electron delocalization is an attribute of the aromaticity as has been believed, then the σ-aromaticity is an inappropriate concept.

Coulson and Moffitt[27] first noted a plateau of relatively high negative charge inside the three-membered ring in cyclopropane. Other authors[28] have made similar observations. Cremer[6] based his argument for the σ-aromaticitiy or the surface delocalization of σ-electrons on this peculiar feature. The present approach provides an alternative explanation. The antibonding property of the geminal delocalization of σ-electrons between the C–C bonds is attenuated in cyclopropane.[12] Electron density is less reduced in the center of the three-membered ring, where the σ and σ* orbitals of the geminal bonds overlap with each other. Electrons remain inside the ring without being repelled outward.

We can point out another delocalization effect on the electron density inside the ring. The delocalization from the C_1–C_2 bond to the C_3–H bond is bonding and accumulates electrons between the C_1–C_2 and C_3–H bonds or inside the three-membered ring. The calculations showed an appreciable bonding property for **2** ($\mathrm{IBP}_{\sigma\sigma^*} = 0.008$). However, the delocalization is not necessarily the main source of the ring strain relaxation of **2**, since similar values were obtained for the highly strained three-membered rings, **5** (0.008) and **17** (0.007), and since the bonding property is low in the less strained ring **20** (0.001).

Ring Bond Strengths. Ring strains contain strengths of bonds as well as interactions of bonds. We evaluated the effects of the ring size on the bond strengths. The overlap integrals between the hybrid orbitals on the bonded atoms and the Mulliken's atomic

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(27) Coulson, C. A.; Moffitt, W. E. *Philos. Mag.* **1949**, *40*, 1.

(28) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985. Pan, D. K.; Gao, J. N.; Lin, H. L.; Huang, M. B.; Schwarz, W. H. E. *Int. J. Quantum Chem.* **1986**, *29*, 1154.

(29) Baghal-Vayjouee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838.

Table 4. Atomic Bond Population and Overlap of Hybrid Orbitals

X–X Bonds

	population	overlap		population	overlap		population	overlap
1	0.341	0.609	**10**	0.227	0.568	**13**	0.066	0.417
2	0.249	0.563	**11**	0.117	0.478	**14**	0.027	0.369
3	0.330	0.585	**12**	0.203	0.518	**15**	0.036	0.389
4	0.366	0.612						
5	0.051	0.570						
6	0.321	0.579						
16	0.364	0.478	**19**	0.276	0.413	**22**	0.110	0.396
17	0.152	0.437	**20**	0.133	0.360	**23**	0.020	0.356
18	0.357	0.454	**21**	0.265	0.394	**24**	0.051	0.366

X–H(F) Bonds

	population	overlap		population	overlap		population	overlap
1	0.392, 0.403	0.651, 0.652	**10**	0.331, 0.352	0.644, 0.637	**13**	0.253	0.564
2	0.399	0.668	**11**	0.318, 0.318	0.599, 0.633	**14**		
3	0.393, 0.395	0.655, 0.657	**12**	0.323	0.631	**15**		
4	0.216, 0.298	0.495, 0.510						
5	0.227	0.511						
6	0.227, 0.232	0.495, 0.495						
16	0.363, 0.381	0.582, 0.583	**19**	0.314, 0.337	0.564, 0.563	**22**	0.256	0.558
17	0.346	0.590	**20**	0.273, 0.277	0.562, 0.564	**23**		
18	0.357, 0.364	0.585, 0.587	**21**	0.304	0.562	**24**		

bond population showed that the ring bond strengths of the molecules examined here decrease in the order of open chains > 4-membered rings > 3-membered rings, without any exception (Table 4). The ordering is not completely satisfactory in explaining the ring strains.

Rehybridization. Rehybridization has been proposed as one of the main components of ring strains.[3,4] The high s-characters of the hybrid orbitals strengthen the C–H bonds in **2**, leading to the unexpectedly low strain. In fact, the rehybridization is more remarkable in **2** than in **1** and **3** (Table 1). The atomic bond population (Table 4) suggests that the C–H bonds of **2** are a little stronger than those of **3**. The rehybridization effects are not appreciable in the highly strained three-membered rings of the perfluoroalkanes and the silanes. The C–F bonds in the three-membered ring **5** are not strengthened relative to those in the four-membered ring **6**. The Si–H bonds are more weakened in the three-membered ring **17** than in the four-membered ring **18**. These results support the rehybridization effects on the ring strains. However, the general applicability does not seem convincing since the less or low strained three-membered rings **11** and **20** were suggested by the atomic bond population to have weaker X–H bonds than the four-membered rings.

Conclusion

We investigated the delocalization of σ-electrons from bonds to bonds in the small-ring molecules. The delocalizations between the geminal C–C bonds in the perfluorocycloalkanes (**5** and **6**) and the cycloalkenes (**8** and **9**) were found to be antibonding, as was previously reported for the cycloalkanes (**2** and **3**).[12] The antibonding property of the geminal delocalization was shown to increase in the three-membered rings **5** and **8**, in contrast to that in **2**. The three-membered ring strains cannot be relaxed. Thus the geminal delocalization accounts for the high strains of **5** and **8** relative to **6** and **9**. The three-membered N ring **11** is less strained than the four-membered ring **12** due to its low antibonding property of the geminal delocalization. The strain energies of O_3 and S_3 were calculated to be lower than those of O_4 and S_4, respectively. The relaxation of the three-membered ring strain was proposed to come from the bonding property of the geminal delocalization. The present work demonstrated the generality that the bonding–antibonding properties of the delocalization of σ-electrons between the geminal bonds were useful in understanding, interpreting, and, hopefully, predicting the strains of small-ring molecules.

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