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Antibonding Delocalization: Geminal Interaction of σ-Bonds and Angle Strain

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Abstract: Delocalization of σ-electrons between geminal bonds was found to give rise to the antibonding property between the bonds, in a striking contrast to the belief that delocalization accumulates bonding electrons in the interaction region. The antibonding delocalization and its dependence on the bond angle have given a new insight into angle strains of small ring molecules.

Geometrical structures of organic molecules are retained by σ-bonds. Organic reactions usually involve formation and/or cleavage of σ-bonds. Behaviors of σ-electrons should play important roles in the structures of the static states and in the mechanisms of dynamic processes. However, properties of σ-electrons have been much less understood than those of π-electrons. We have started systematic investigations of delocalization of σ-electrons from bonds to bonds[1] by the theoretical method previously presented and applied to the chemistry of π-electrons with fruitful results,[2-4] e.g., a new concept of cyclic orbital interaction in acyclic conjugation.[3-5] The first application to σ-electron systems[1] lead to a new insight into the antiperiplanar effects including the anomeric[6] and gauche[7] effects. The delocalization between the geminal bonds was surprisingly found[1] to be dependent on the conformation. The dihedral angle dependence of the delocalization between the vicinal bonds has also been examined there. In this paper, we describe the bond angle dependence of the geminal delocalization. Hopefully, we can disclose some fundamental properties of σ-electrons, or effects of the geminal interaction on angle strains.

The model compounds are propane (**1**) as an unstrained molecule, cyclopropane (**2**) as a highly strained molecule, and cyclobutane (**3**) of medium strain. Butadiene (**4**) and benzene (**5**) are also employed as acyclic and cyclic conjugated molecules, respectively, to compare σ- with π-electrons. In early attempts at understanding the strained molecules, Coulson and Moffitt,[8] Walsh,[9] and Hoffmann[10] have made significant contributions. Recent development of the analysis of the electron density by Bader[11] and its extensive application by Wiberg[12] have renewed the theoretical interest in these molecules.

In this paper, we focus our attention on one of some anomalies of the small ring hydrocarbons,[13] i.e., unexpectedly low angle strain of cyclopropane. The bond angle deviates from the sp^3 valence angle 2.5 times more in **2** (49.5°) than in **3** (19.5°). However, the strain energy of **2** (27.5 kcal/mol)[14] is only a little greater than that of **3** (26.5 kcal/mol). Dewar[15] proposed σ-aromaticity of **2**. Cremer and Kraka[16] proposed a similar view that strain is partially compensated by stabilizing surface delocalization of σ-electrons of the three-membered ring. Here, a serious question comes into our mind. The aromaticity has been believed to be related to the delocalization of electrons. This implies bond lengthening since the delocalization is accompanied by loss and gain of electrons in the bonding and antibonding orbitals, respectively. The σ-aromaticity appears in disagreement with the fact that the C–C bond lengths in **2** (1.509 Å)[17] are shorter than those in **1** (1.532 Å)[18] and **3** (1.568 Å).[19] The inconsistency between the low angle strain, the short bond lengths of cyclopropane, and the aromaticity theory is one of the most suitable subjects for investigating the bond angle dependence of the geminal interaction to explore fundamental properties of σ-electrons in terms of bond-to-bond delocalization.

Table I. Properties of Propane (**1**), Cyclopropane (**2**), Cyclobutane (**3**), Butadiene (**4**), and Benzene (**5**)

					IBP[f]		
	CSE[a]	BL[b]	C_T/C_G[c]	VA[d] (HO[e])	σ–σ*	σ–σ	σ*–σ*
1	0.0	1.532	–0.054	110 (sp$^{2.9}$)	–0.011	–0.022	–0.001
2	27.5	1.509	–0.011	104 (sp$^{4.1}$)	–0.002	–0.128	–0.002
3	26.5	1.568	–0.055	107 (sp$^{3.4}$)	–0.016	–0.044	–0.002
4			0.138		0.041	–0.034	–0.000
5			0.383		0.086	0.007	0.024

[a] The conventional strain energy (kcal/mol) estimated from heat of formation.[14] [b] Observed bond lengths (Å).[17-19] [c] The coefficient ratio ($S_{GT} > 0$) of the electron configurations (see eq 1) indicating the degree of the geminal delocalization. [d] The valence angle of the optimized hybrid orbital. [e] Hybrid orbital for C–C bond formation. [f] Interbond population (eq 2) between the geminal σ-bond orbitals in **1–3** and between the adjacent π-bonds in **4** and **5**.

Theoretical Background and Method of Calculation

Analysis of Bond-to-Bond Delocalization. The electronic structures are expressed by a linear combination of electron configurations:

$$\Psi = C_G\Phi_G + \sum C_T\Phi_T \tag{1}$$

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

(2) Inagaki, S.; Hirabayashi, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2283. Inagaki, S.; Hirabayashi, Y. *Inorg. Chem.* **1982**, *21*, 1798. Inagaki, S.; Iwase, K. *Nouv. J. Chim.* **1984**, *8*, 73.

(3) (a) Inagaki, S.; Hirabayashi, Y. *Chem. Lett.* **1982**, 709. (b) Inagaki, S.; Kawata, H.; Hirabayashi, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3724.

(4) Inagaki, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3599. Inagaki, S.; Iwase, K.; Goto, N. *J. Chem. Soc., Perkin Trans. 2* **1984**, 2019. Inagaki, S.; Iwase, K.; Kawata, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 601. Inagaki, S.; Iwase, K.; Goto, N. *J. Org. Chem.* **1986**, *51*, 362.

(5) The concept was shown to be applicable for the unusually acute C–M–C angle of metal (M) dicarbonyl complexes: Sakai, S.; Inagaki, S. *J. Am. Chem. Soc.* **1990**, *112*, 7961.

(6) Lemieux, R. U.; Koto, S. *Tetrahedron* **1974**, *30*, 1933. Szarek, W. A.; Horton, D. ACS Symp. Ser. **1979**, *No. 87*. Deslonchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: Oxford, 1983. Gorenstein, D. G. *Chem. Rev.* **1987**, *87*, 1047.

(7) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102 and references cited therein.

(8) Coulson, C. A.; Moffitt, W. E. *J. Chem. Phys.* **1947**, *15*, 151; *Philos. Mag.* **1949**, *40*, 1.

(9) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179.

(10) Hoffmann, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699.

(11) Bader, R. F. W.; Tang, T.-H.; Tal, Y.; Biegler-Konig, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 940, 946.

(12) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985, 1001.

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

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

(15) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669. Two hybrid orbitals on the CH_2 unit in **2** to be involved in the C–C σ-bond formation are seen to play the same role as two p-orbitals on the =C—C= unit in benzene.

(16) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800. Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467.

(17) Bastiansen, O.; Fritsch, F. N.; Hedberg, K. H. *Acta Crystallogr.* **1964**, *17*, 538.

(18) Iijima, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1291.

(19) Dunitz, J. D.; Schomaker, V. *J. Chem. Phys.* **1952**, *20*, 1703.

0002-7863/91/1513-7144$02.50/0

In the ground (G) configuration, a pair of electrons occupy a bonding orbital of a chemical bond (a nonbonding orbital in case of an unshared electron pair). Interactions between bonds accompany electron delocalization. This is expressed by mixing of electron-transferred (T) configuration where an electron shifts from a bonding orbital of a bond to an antibonding orbital of another. We are able to estimate the extent of the delocalization by the method of configuration analysis.[20] This gives the coefficients of electron configurations (C_G and C_T) by expanding the Slater determinant for the electronic structure of the whole system into those of various configurations. The coefficients provide us with detailed information of electronic structure. However, the coefficient ratio to the ground configuration, C_T/C_G, was previously[3b] proposed to be a preferable measure rather than C_T itself when we compare the corresponding parts of electronic structures in different molecules.

Interbond Population. In order to estimate effects of interactions between bonds on electron distribution, we calculated the interbond population between the bond orbitals i and j:

$$\mathrm{IBP}_{ij} = 2n\sum c_{pi}c_{pj}s_{ij} \tag{2}$$

where n is the occupation number of the pth molecular orbital, c_{pi} being the expansion coefficient of the ith bond orbital for the pth MO.

Optimal Hybrid Orbital. A bond orbital is assumed to be a linear combination of hybrid atomic orbitals on bonded atoms. It is desirable for the present purpose that the ground configuration represents the electronic structure of the molecule as much as possible. The optimal hybrid atomic orbital is then defined as giving the maximum value of the coefficient of the ground configuration (C_G).

Electronic structures of molecules were obtained by ab initio molecular orbital calculations on the experimentally determined geometries.[17-19] In this series of our investigation of bond-to-bond delocalization of σ-electrons, we have been attempting to found the theory on the intuitively understandable basis rather than quantitatively reproduce or predict chemical phenomena by sophisticated methods. We used the STO-3G basis set, which enables us to define the hybrid orbitals of clear image.

Results and Discussion

Bond-to-Bond Delocalization and Bond Lengths. The present calculations (Table I) show that σ-electrons localize well as expected. For example, the absolute value (0.054) of C_T/C_G for the delocalization between the geminal C–C bonds in **1** is much smaller than that (0.138) for the delocalization between the adjacent π-bonds in butadiene (**4**).

The geminal delocalization is remarkably depressed in **2** (0.011), relative to **1** (0.054) and **3** (0.055). The delocalization occurs from the bonding orbital to the antibonding orbital, leading to bond lengthening. The low degree of delocalization is compatible with the relatively short bond lengths of **2**.[21] This partially supports the validity of the present method. Here, it should be noted that the lesser extent of the delocalization[22] in **2** throws a doubt on the σ-aromaticity of **2**[15] and the surface delocalization.[16]

Valence Angle. In **2**, the optimized hybrid orbitals for the C–C bond formation are sp$^{4.1}$, completely in accordance with that obtained by Coulson and Moffitt[8] for the first time in an essentially different manner. This again lends support to the validity of the present method. In passing, the hybridization is sp$^{2.9}$ on the central carbon of **1** and sp$^{3.4}$ in **3**.

Baeyer originally supposed the deviation of the bond angle (geometry) from the valence angle (orbital) as a measure of angle strain. The deviations from the sp^3 valence angle are 49.5° in **2** and 19.5° in **3**. When the CCC bending force constant of **1** is utilized, the Baeyer strain of **2** (173 kcal/mol) is nearly 5 times greater than that (36 kcal/mol) of **3**.[16] The valence angles between the optimized hybrid orbitals are 104° in **2** and 107° in **3**. The deviation is appreciably reduced to 44° in **2** and much less to 17° in **3**. This indicates some extent of the strain relaxation of **2**. An unequivocal drawback of the arguments based solely on the valence angle is that interbond interactions are not taken into account.

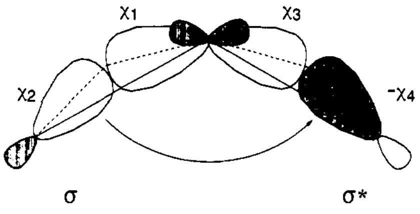

Figure 1. Orbital representation of the antibonding delocalization of σ-electrons between the geminal bonds.

Repulsion between Occupied (Bonding) Orbitals. The interactions between geminal bonds contribute to the angle strains. The interaction between the occupied (bonding) orbitals is repulsive and one of the main origins of the angle strains. The interbond population (Table I) indicates that the antibonding property increases in the order **1** < **3** < **2** with the overlap integral [**1** (0.093) < **3** (0.131) < **2** (0.199)]. The ordering is expected from the bond angle since the acute angle implies that the bonding orbitals are close to each other. The antibonding property due to the interactions between the geminal occupied (bonding) orbitals is remarkable in **2**.

Antibonding Delocalization and Angle Strain. The geminal delocalization of the present interest was surprisingly found to give rise to the antibonding property between the bonds (antibonding delocalization):

$$C_G C_T S_{GT} < 0 \tag{3}$$

as shown by the minus sign of C_T/C_G in case of the overlap integral $S_{GT} > 0$ (Table I). The delocalization has been believed to accumulate bonding electrons in the interaction region (bonding delocalization). For example, butadiene (**4**) and benzene (**5**) have positive values.

Figure 1 shows the orbital phase relation between the bonding (σ) and antibonding (σ*) orbitals. This is found when some occupied molecular orbitals for the C–C bonding in **1** are expanded on the basis of the bond orbitals. The bond orbital overlap is decomposed in terms of the hybrid orbital overlap: $s_{\sigma\sigma^*} = cc^*(s_{13} - s_{14} + s_{23} - s_{24})$, where c and c^* denote the coefficients of the hybrid orbitals in the σ- and σ*-orbitals, respectively. The hybrid orbitals on the same atom are orthogonal to each other ($s_{13} = 0$). The overlaps s_{14} and s_{23} are identical and cancel each other ($-s_{14} + s_{23} = 0$). The bond orbital overlap is then reduced to a sole hybrid orbital overlap: $s_{\sigma\sigma^*} = cc^*(-s_{24})$. The orbitals on the terminal carbons are out of phase. The geminal delocalization is antibonding. Electrons are repelled out of the overlap region.

The antibonding delocalization sheds new light on the angle strain. The C_T/C_G value showed that the antibonding delocalization occurs less in **2** than in **1**. The lesser extent of the antibonding property should relax the strain. The corresponding value of **3** is a little greater than that of **1**, suggesting that the geminal delocalization may impose slightly more strain on **3**. As a result, **2** enjoys the appreciable relaxation of the angle strain due to the lowered degree of the antibonding property.

The overlap integrals should be included for a more precise estimation of the antibonding property. We calculated the interbond population (eq 2) between the bonding and antibonding orbitals of the geminal bonds. The results confirmed that the antibonding property decreases in the order **3** > **1** > **2** (Table I).

Cyclic Delocalization. It is interesting to see cyclic delocalization of σ-electrons in **2** and to compare it with that of π-electrons in **5**. The donor–acceptor interaction between the adjacent bonds is indispensable for the cyclic delocalization.[23] As noted above,

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(20) Baba, H.; Suzuki, S. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2457. Baba, H.; Suzuki, S.; Takemura, T. *J. Chem. Phys.* **1969**, *50*, 2078.

(21) (a) Bader[21b] defined the bond path length that enables us to compare the "length" of the bent bonds. In **2**, the bond path length is 0.01 Å longer than the bond length.[12,21b] Even if this increment is taken into account, the "bond length" of **2** is still shorter. (b) Bader, R. F. W.; Tang, T. H.; Tal, Y.; Biegler-Konig, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 904, 946.

(22) The low degree of the geminal delocalization in **2** is possible to arise from the employment of the observed bond lengths, which are shorter in **2** than the others. The short bond length implies the low energy of the bonding orbital and the high energy of the antibonding orbital, depressing the delocalization. In order to examine the effects of the bond lengths, we analyzed the electronic structures of the molecules with the identical bond lengths (1.532 Å). The C_T/C_G values were found not to differ to an appreciable extent: **1** (0.054); **2** (0.010); **3** (0.054). The results ruled out the possibility that the low degree of the delocalization in **2** is primarily caused by the bond lengths.

(23) Fukui, K.; Inagaki, S. *J. Am. Chem. Soc.* **1975**, *97*, 4445. Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4693. Inagaki, S.; Hirabayashi, Y. *J. Am. Chem. Soc.* **1977**, *99*, 7418.

the geminal delocalization is antibonding, in contrast with the bonding delocalization between π-bonds. Furthermore, the delocalization in **2** has been pointed out to be depressed, compared with that of **1** (the antibonding property is reduced in **2**). In **5**, the delocalization and the resulting bonding degree are remarkably enhanced relative to **4** (see the C_T/C_G and IBP values in Table I). In these aspects, six electrons of the C—C σ-bonds in **2** and the C=C π-bonds in **5** behave in an opposite manner.

The delocalization described above occurs from a bond to a second, corresponding to the G–T configuration interactions or to the interaction between the occupied and unoccupied orbitals. A third bond is not explicitly involved. In this sense, the delocalization is not cyclic.[23] The T–T interaction is required for cyclic delocalization in addition to the G–T interaction.[23] The T–T interaction is approximated as the interaction between the occupied (bonding) orbitals or between the unoccupied (antibonding) orbitals.[23] In **2**, the interbond population is antibonding, both between the bonding orbitals (–0.128)[24,25] and between the antibonding orbitals (–0.002). The corresponding populations in **5** are bonding (0.024 and 0.006[24,26]). Cyclic delocalization of the six electrons gives rise to the opposite bonding properties in **2** and **5**.

Origin and Bond Angle Dependence of Antibonding Delocalization. The antibonding geminal delocalization has given a new insight into the angle strain. In order to see the origin of the antibonding property and its dependence on the bond angle, we employed the two-bond system (Figure 1) with the bonding and antibonding orbitals in each bond and the extended Hückel theory. The hybridization was fixed at sp^3, irrespective of the bond angle. The hybrid orbitals were directed in a way in which the deviations from the internuclear axis were identical.

The simple model and calculation reproduced the antibonding property ($C_G C_T S_{GT} > 0$) of the geminal delocalization in wide range of the bond angle (60–120°). This encouraged us to scrutinize the results in more detail. The off-diagonal matrix element for the σ–σ^* orbital interaction was found to be positive ($h_{\sigma\sigma^*} - s_{\sigma\sigma^*}h_{\sigma\sigma} > 0$) in case of $s_{\sigma\sigma^*} > 0$. This implies the antibonding delocalization. The anomaly arises from the predominance of $s_{\sigma\sigma^*}h_{\sigma\sigma}$ over $h_{\sigma\sigma^*}$. Usually, the off-diagonal element is negative in case of $s_{\sigma\sigma^*} > 0$ (bonding delocalization) since $h_{\sigma\sigma^*}$ is greater in the absolute value.

We can see the origin of the antibonding delocalization in a peculiar feature of the geminal interaction. The resonance integral between the bonding and antibonding orbitals is decomposed into the hybrid orbital terms: $h_{\sigma\sigma^*} = cc^*(h_{13} - h_{14} + h_{23} - h_{24})$ (see Figure 1). Since h_{14} and h_{23} are identical ($- h_{14} + h_{23} = 0$), $h_{\sigma\sigma^*} = cc^*(h_{13} - h_{24})$. For the overlap integral, $s_{\sigma\sigma^*} = cc^*(-s_{24})$ as described above. It should be noted that s_{13} is absent in $s_{\sigma\sigma^*}$ while h_{13} remains in $h_{\sigma\sigma^*}$. This breaks the parallerism between h and s presumably necessary for the bonding delocalization or for the predominance of $h_{\sigma\sigma^*}$ over $s_{\sigma\sigma^*}h_{\sigma\sigma}$ in the off-diagonal matrix element. The geminal delocalization should be bonding if $h_{13} = 0$ ($h_{24} - s_{24}h_{\sigma\sigma} < 0$ in case of $s_{24} > 0$). The additional term h_{13} reduces the absolute value of $h_{\sigma\sigma^*}$. The predominant term then switches from $h_{\sigma\sigma^*}$ to $s_{\sigma\sigma^*}h_{\sigma\sigma}$. The delocalization becomes antibonding. As a result, the antibonding property of the geminal delocalization comes from the peculiar feature of the geminal interactions that the hybrid orbitals on the same carbon are orthogonal ($s_{13} = 0$) but interact with each other ($h_{13} \neq 0$).

The antibonding property was shown by the simple model calculations to decrease as the bond angle is acute: $h_{\sigma\sigma^*} - s_{\sigma\sigma^*}h_{\sigma\sigma}$ (or $-C_T/C_G$) decreases. This is compatible with the result of the ab initio calculation that the degree of the antibonding delocalization is low in **2** of a small bond angle relative to **1** and **3**. The results suggest that the antibonding delocalization may depend primarily on the bond angle rather than on the number of the σ-electrons involved in the C–C bond ring formation.

The low antibonding property for the acute bond angle can also be understood in terms of the same peculiar feature of the geminal hybrid orbitals ($s_{13} = 0$; $h_{13} \neq 0$). As the bond angle is acute, h_{24} increases due to the spatial approach of the terminal carbons to each other. The geminal hybrid orbital interaction h_{13} remains constant in the present model, or decreases in a more realistic model where the s-character of the hybrid orbitals is low for acute bond angles. It follows that the relative weight of h_{13} in $h_{\sigma\sigma^*}$, responsible for the antibonding delocalization, decreases. The antibonding delocalization is then depressed.

Conclusion

In a series of theoretical studies of bond-to-bond delocalization of σ-electrons,[1] we have investigated the delocalization between the geminal bonds and its dependence on the bond angle. The geminal delocalization was found to give rise to the antibonding property between the bonds, in contrast to the belief that the delocalization is bonding. The antibonding delocalization comes from the effective interaction between the geminal hybrid orbitals orthogonal to each other.

The antibonding geminal delocalization has given a new insight into angle strains of the small ring compounds. As the bond angle is acute, the antibonding property is depressed, leading to the relaxation of the angle strain expected from the bond angle for **2**. The lesser extent of the delocalization in **2** also accounts for the short bond lengths.

Acknowledgment. The ab initio molecular orbital calculations with GAUSSIAN 80 programs were carried out on a HITAC M-680H computer at the Institute for Molecular Science and a FACOM M-782 computer at Nagoya University computer center. The electronic structure was analyzed on a FACOM M-360 computer at Gifu University computing center. This work was supported by a Grant-in-Aid from the Ministry of Education, Science, and Culture.

Registry No. 1, 74-98-6; **2**, 75-19-4; 3, 287-23-0; **4**, 106-99-0; **5**, 71-43-2.

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[24] The interbond population between the bonding orbitals includes the effects of the overlap repulsion as a major component and the T–T interaction as a minor one.

[25] The highly antibonding property between the bonding orbitals in **2** may arise from the overlap repulsion between the occupied orbitals included.

[26] The low bonding property between the bonding orbitals relative to that between the antibonding orbitals may be due to the overlap repulsion included in the former.