Highlight Review

Participation of Geminal Bonds in Organic Reactions

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Abstract

The σ-bonds geminal to the π-reacting center have been proposed to participate in the organic reactions via the cyclic transition states and to control the reactivity and the selectivity. An electron-donating geminal σ bond at the Z position enhances the reactivity of the olefins. An electron-donating σ bond prefers the Z position of the π bond in the products of the reverse reactions. The effects of the geminal bond participation come from the orbital phase properties of the cyclic interactions including the geminal σ bonds.

Interactions of π bonds with the vicinal σ bonds (Figure 1) are known as hyperconjugation, resonance, and so on.[1,2] The vicinal interactions have been proposed to participate and control the selectivity of some organic reactions: A nucleophile (electrophile) approaches the π bond in the direction opposite to an electron-withdrawing group X (an electron-donating group Y) (Figure 2).[3,4]

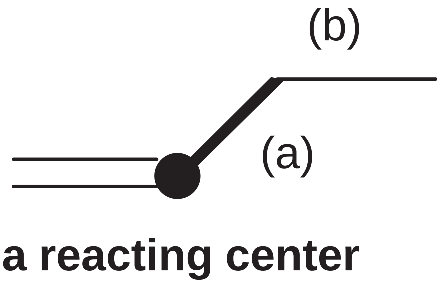
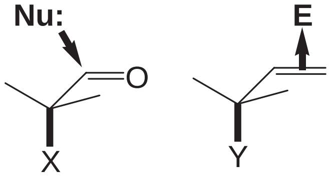


Figure 1. Bonds geminal (a) and vicinal (b) to the π bond.

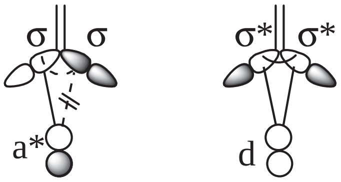


(a) (b)

Figure 2.

The *geminal σ-bonds take part in the interaction* with the reaction partners when the π bond reacts. We herein describe the origin of the geminal bond participation and its chemical consequences, i.e. the reactivity and the selectivity.

◆ Geminal Bond Participation



(a) (b)

Figure 3. The orbital phase properties in the interactions of the geminal σ bonds with an electron-acceptor and -donor: (a) the discontinuity in the cyclic (σ, σ, a*) interaction; (b) the continuity in the cyclic (σ*, σ*, d) interaction. The in-phase and out-of-phase relations are shown by the solid and dotted lines, respectively.

Cyclic orbital interactions occur among the two geminal σ bonds and the reaction partner (Figure 3). Cyclic orbital interactions are under the control of the orbital phase continuity conditions:[5] (i) Electron-donating orbitals are out of phase with each other; (ii) An electron-donating orbital is in phase with the electron-accepting orbitals; (iii) Electron-accepting orbitals are in phase with each other. When the conditions are simultaneously satisfied, the cyclic interaction promotes electron delocalization and leads to the stablization. The electron delocalization from the geminal σ bonds to an electron-accepting bond involves the cyclic orbital interaction among the two σ bonding orbitals and the accepting orbital (a*) (Figure 3a). The phase is discontinuous. The out-of-phase combined σ orbitals cannot be both in phase with a*. This suggests that stronger $\sigma \rightarrow$ a* delocalization or the delocalization from the geminal σ bond closer to the acceptor at the transition state shows a bonding character while the other is antibonding. When the delocalization from a donating reaction partner to the geminal σ bonds occurs, the important cyclic interaction occurs among the σ* antibonding orbitals of the geminal bonds and the donating orbital (d). The phase continuity requires that the d, σ*, σ* orbitals are combined in phase with one another (Figure 3b). The cyclic interaction satisfies these requirements. Both d $\rightarrow \sigma$* delocalizations should effectively occur in a bonding manner. Therefore, this interaction makes less difference between the effects of the geminal bonds at the Z and E positions, and less significantly affects the reactivity and the selectivity. In short, the bonding–antibonding properties of the delocalization from the geminal σ bonds are opposite to each other, while those to the geminal bonds are both bonding. Consequently, the delocalization from the geminal σ bonds should play a crucial role for both the reactivity and the selectivity rather than that to the geminal σ bonds.[6]

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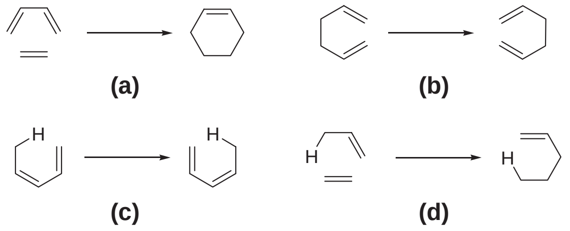

Scheme 1.

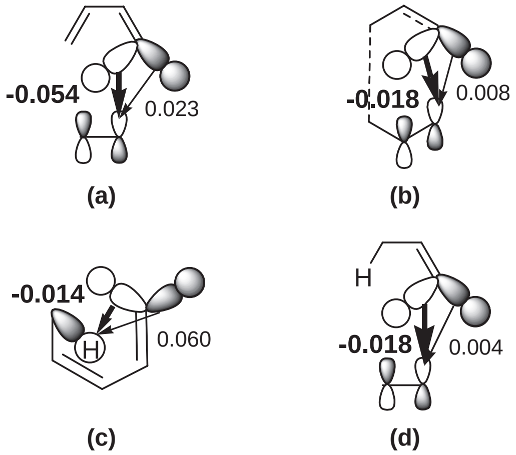

Figure 4. The IBE values (au) at the transition states of (a) the Diels–Alder reaction, (b) the Cope rearrangement, (c) the sigmatropic rearrangement, and (d) the Alder ene reaction.

♦ *Reactivity*

The bond model analysis[6,7] of the transition state[8] of the Diels–Alder reaction between butadiene and ethylene (Scheme 1a)[6] showed that the interbond energy IBE[9] between σ_{CH} of the geminal bond at the Z position of the diene and π^* orbital of the dienophile is negative (IBE $= -0.054$ au), while that between $\sigma_{C\text{–}H}$ at the E position and π^* is positive (IBE $= 0.023$ au) (Figure 4a). The transition states of the Cope rearrangement (Scheme 1b),[10] the sigmatropic rearrangement (Scheme 1c)[11] and the Alder ene reaction (Scheme 1d)[12] were also subjected to the bond model analysis. The results are shown in Figures 4b–4d.[10–12] In all cases, the interbond energies between σ_{CH} of the geminal bond at the Z position of the donating double bond and π^* of the acceptor are negative, while those between $\sigma_{C\text{–}H}$ at the E position and π^* are positive (Figure 4). These results suggested that the delocalization from σ bond at the Z position could stabilize the transition state. An electron-donating geminal σ bond at the Z position could enhance the reactivity (Figure 5).

We calculated the enthalpies of activation $\Delta H^\ddagger$ of the reactions of substituted molecules. The results are in a good agreement with our prediction as are illustrated by the representative reactions of the methyl silyl derivatives in Figure 6. The σ-bonding orbital energies calculated by the bond model analysis showed that the $\sigma_{C\text{–}Si}$ bond (Fii $= -0.709$ au) is more electron donating than the $\sigma_{C\text{–}C}$ bond (Fii $= -0.789$ au). A silyl group at the Z position enhances the reactivity.

Recently, we predicted significant geminal bond participation in other organic reaction than the pericyclic reactions. An electron-donating geminal σ bond at the Z position enhances the reactivity of the enolates in the aldol reaction (Figure 7).[13]

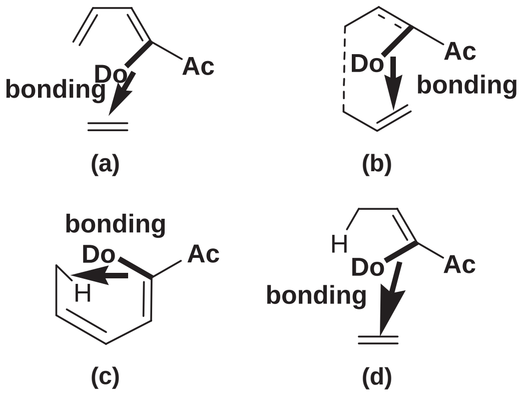

Figure 5. An electron-donating geminal σ bond (σ_{CR}) enhances the reactivities of (a) the Diels–Alder reaction, (b) the Cope rearrangement, (c) the sigmatropic rearrangement, and (d) the Alder ene reaction (C-Do: electron-donating σ bond; C-Ac: electron-accepting σ bond).

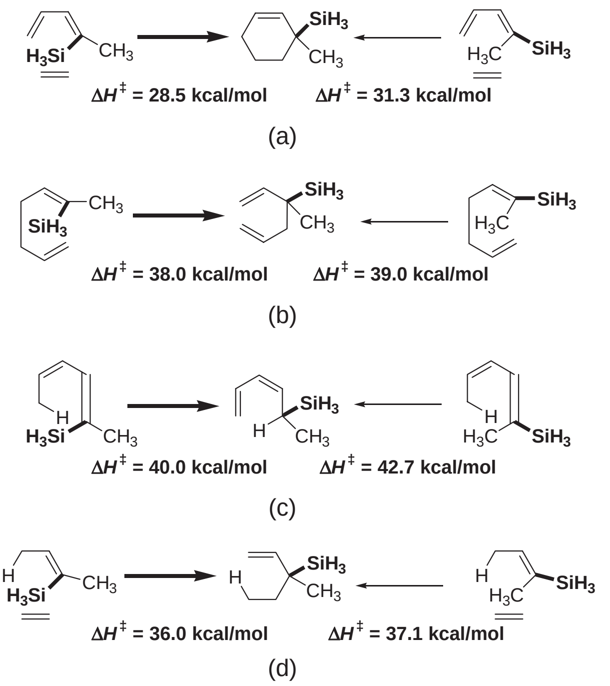

Figure 6. The reactivities in (a) the Diels–Alder reaction, (b) the Cope rearrangement, (c) the sigmatropic rearrangement, and (d) the Alder ene reaction.

♦ *Selectivity*

Ring opening of cyclobutenes were experimentally and theoretically known to proceed in the conrotatory fashion.[14,15] A new stereoselectivity, i.e., the torquoselectivity (Scheme 2a) has been reported. Houk et al.[16] reported the exclusive inward torquoselective rotation of a formyl group at the 3-position of cyclobutene whereas Dolbier et al. showed the (*E*)-fluorobutadiene is the sole product of the electrocyclic reaction of the 3-fluorocyclobutene (Scheme 3).[17] Rondan, Houk, and co-

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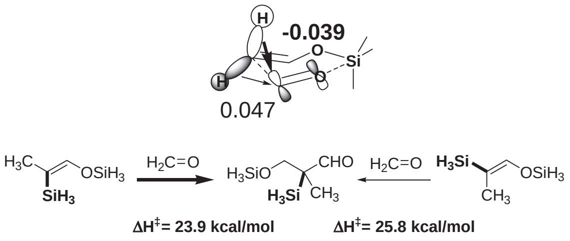
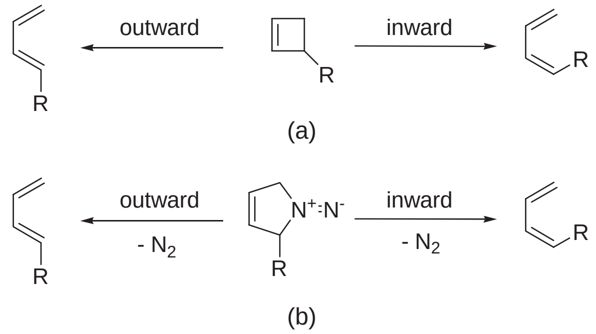
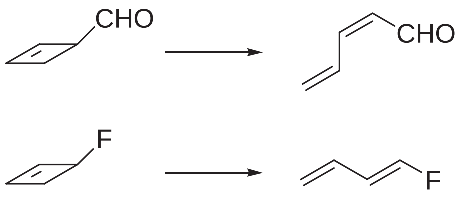


Figure 7. The IBE values (au) at the transition state and the reactivities of the E and Z isomers of the silyl enolate in the uncatalyzed Mukaiyama aldol reaction.



Scheme 2.



Scheme 3.

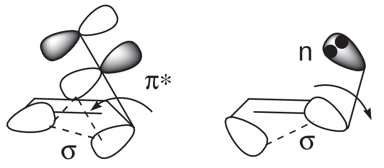


Figure 8. The vicinal π bond (lone pair) participations.

workers proposed the vicinal π bond (lone pair) participation (Figure 8):[18] electron-accepting unsaturated groups inwardly rotate due to the attraction between the breaking σ bond and the formyl π bond whereas the substituents with the lone pair(s) prefer the outward rotation due to the repulsion with the breaking σ bond.

We subjected the transition structure of the electrocyclic reaction of cyclobutene to butadiene to the bond model analysis.[7] When the product-like bond model was used, the IBE value between the inwardly rotating $\sigma_{C\text{–}H}$ and π^* is negative (IBE $= -0.121$ au), while that between the outwardly rotating $\sigma_{C\text{–}H}$ and π^* orbital is positive (IBE $= 0.016$ au). The σ bond at the Z position shows the bonding character with the incipient π bond (Figure 9a) while that at the E position is antibonding.[19]

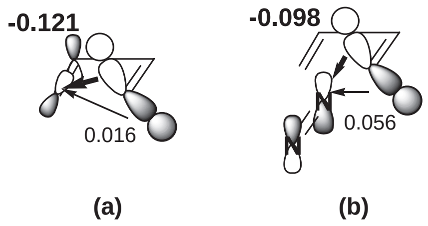


Figure 9. The IBE values (au) at the transition state of (a) the electrocyclic reaction and (b) the cheletropic reaction.

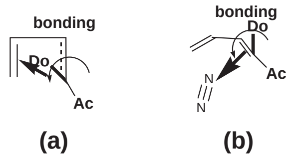


Figure 10. An electron-donating geminal σ bond (σ_{CR}) prefers the inward rotation in (a) the electrocyclic reaction and (b) the cheletropic reaction.

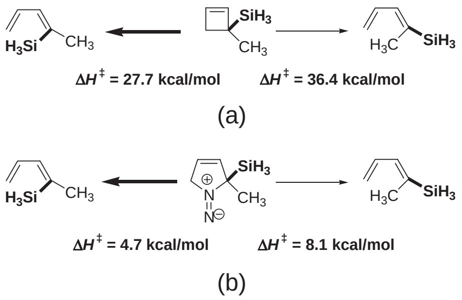


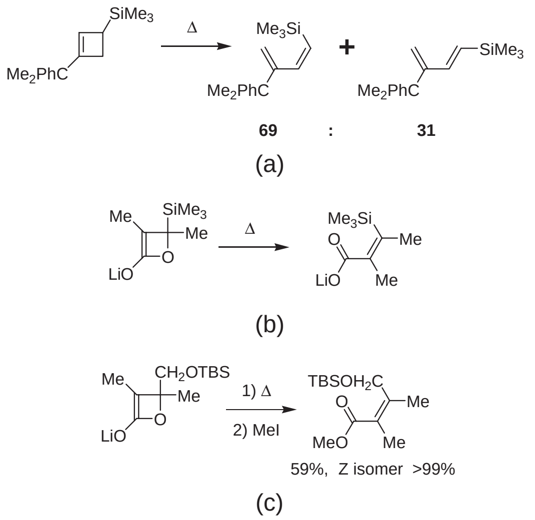
Figure 11. The torquoselectivities in (a) the electrocyclic reaction and (b) the cheletropic reaction.

The electron-donating geminal σ bond was predicted to rotate inwardly and to occupy the Z position in the product (Figure 10). The results of the calculations of substituted cyclobutenes are in a good agreement with our prediction. The result of the methyl silyl derivative is shown in Figure 11a.

The torquoselectivity of the cheletropic reaction (Scheme 2b) are also under the control of the geminal bond participations (Figure 9b).[20] The electron-donating geminal σ bond stabilizes the transition state when it rotates inwardly (Figure 10b). The silyl group prefers the inward rotation (Figure 11b). Yamabe and Minato[21] discussed the geminal bond participation in the cheletropic reaction of diazetines.

Murakami et al. independently reported experimental observation of the inward rotation of the silyl groups of 1-(1-methyl-1-phenylethyl)-3-trimethylsilylcyclobutene (Scheme 4a) and 1-octyl-3-(phenyldimethylsilyl)cyclobutene.[22] Shindo and co-workers also observed the preferential inward rotation of the silyl group in the ring opening of the β-lactone enolates (Scheme 4b).[23]

Murakami extended the Rondan–Houk's proposal of the vicinal bond participation to explain the torquoselectivity. The interaction of the breaking σ bond of the cyclobutene with $\sigma^*_{C\text{–}Si}$ determines the selectivity (Figure 12a).[22] Houk et al. agreed with the Murakami's proposal.[18e] Shindo, Mori, and co-workers initially assumed the applicability of the Murakami's proposal to their systems,[23a] and later proposed the importance



Scheme 4.

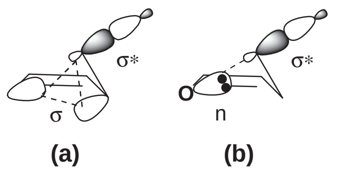


Figure 12. The vicinal σ bond participations.

of the interaction between the lone pair(s) on the oxygen and σ^* on the substituent (Figure 12b).[23b] Very recently, Shindo et al. again emphasized on the Murakami's proposal for the inward rotation of CH_2OR group (Scheme 4c).[23c]

♦ *Orbital Phase Theory*

We developed an orbital phase theory for the torquoselectivity and the theory strongly supported the geminal bond participation.[24]

The thermal ring opening of the electrocyclic reactions of cyclobutenes is caused by the interactions between $\sigma_{CC}{}^*$ and π_{CC} and between σ_{CC} and $\pi_{CC}{}^*$. The σ_{CR} bond geminal to the σ_{CC} bond can participate in the reactions through the interactions with the σ_{CC} and π_{CC} bonds. Cyclic orbital interactions occur between the σ_{CR}, π_{CC}, and σ_{CC} bonds. The torquoselectivities are under control of the orbital phase continuity conditions.[6]

The orbital phase theory shows that electron-donating σ_{CR} bonds rotate inwardly. The participation of the bonding (donating) σ_{CR} orbital in the σ_{CC}–$\pi^*{}_{CC}$ interaction is illustrated in Figure 13a. The σ_{CR} orbital is required by the phase continuity requirements to be out of phase with the σ_{CC} (donating) and in phase with $\pi^*{}_{CC}$ (accepting). The phase relations of σ_{CR}, σ_{CC}, and $\pi^*{}_{CC}$ are fixed. The electron-donating σ_{CC} and -accepting $\pi^*{}_{CC}$ orbitals are required to be in phase with each other. The requirement leads to the inward rotation of the σ_{CR} bond. The same torquoselectivity is deduced for the σ_{CR} participation in the $\sigma^*{}_{CC}$–π_{CC} interaction (Figure 13b).

The orbital phase theory shows that electron-withdrawing σ_{CR} bonds rotate outwardly (Figure 13c and Figure 13d). As the outward rotation proceeds, the σ_{CR} and π_{CC} bonds go farther from each other, and the interaction between the bonds weakens. The electron-withdrawing geminal bonds exhibit less direct effect on the torquoselectivity. However, the electron-withdrawing groups should rotate outwardly since the counterpart groups, e.g. hydrogen atom, preferentially rotate inwardly due to the σ_{CH} orbital energy high relatively to that of σ_{CR}.

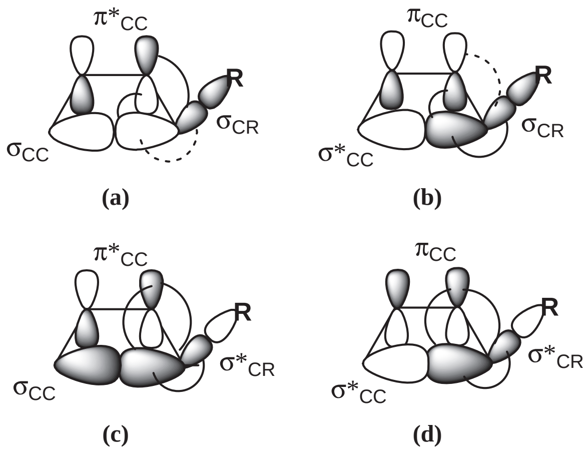


Figure 13. The orbital phase control of the inward rotation of electron-donating σ_{CR} bond (a and b) and the outward rotation of electron-accepting σ_{CR} bond (c and d). The in-phase and out-of-phase relations are shown by the solid and dotted lines, respectively.

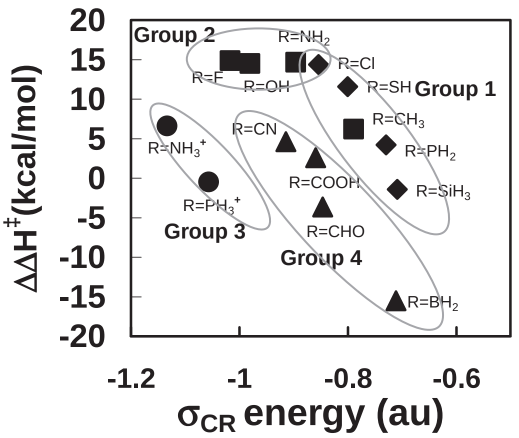


Figure 14. Dependence of the torquoselectivity (difference in the enthalpy of activation $\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}{}_{\mathrm{inward}} - \Delta H^{\ddagger}{}_{\mathrm{outward}}$, B3LYP/6-31G(d)) of the 3-R-cyclobutenes on the σ_{CR} orbital energy.

The geminal bond participation is supported by the calculations of the enthalpies of activation of the inward and outward rotations of 3-substituted cyclobutenes and the σ_{CR} orbital energy (Figure 14). The correlation of the torquoselectivity ($\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}{}_{\mathrm{inward}} - \Delta H^{\ddagger}{}_{\mathrm{outward}}$) with the σ_{CR} orbital energy shows that the inward rotation is enhanced with the electron-donating capability of the σ_{CR} bonds (See the Groups 1, 3, and 4 in Figure 14).

The torquoselectivity does not appreciably change for the electronegative substituents (See Group 2 in Figure 14.), in agreement with the prediction from the geminal bond participation. The σ_{CH} bond is more electron-donating than σ_{CR}. The σ_{CH} bond rather than σ_{CR} determines the selectivity.

For the inward rotations of the unsaturated substituents with low-lying vacant orbitals, a correlation is found between the torquoselectivity and the σ_{CR} energy (Group 4), supporting the geminal bond participation. However, the substituents in Group 4 were found to favor the inward rotation more than expected from the σ_{CR} energy (Compare with the saturated substituents in Group 1.). The additional preference of the inward rotations of Group 4 are expected from the effect of the interaction between the σ_{CC} orbital and the π^* orbital on the substituent proposed by Houk et al.[18]

The outward rotations preferred by 4.3 kcal/mol for 3-cyanocyclobutene ($\mathrm{R} = \mathrm{CN}$)[18c] and by 2.3 kcal/mol for cyclobutene-3-carboxylic acid ($\mathrm{R} = \mathrm{COOH}$)[18d] cannot be explained by the Houk's σ–π^* interaction, but by the geminal bond participation. The σ_{CR} energies of $\mathrm{R} = \mathrm{CN}$ and COOH are lower than those of $\mathrm{R} = \mathrm{CHO}$ and $\mathrm{BH_2}$ (See Group 4 in Figure 14). The geminal bond participation is too ineffective for $\mathrm{R} = \mathrm{CN}$ and COOH for the inward rotation.[25]

The $\mathrm{SiH_3}$ substituent is clearly not classified into the group of the unsaturated substituent (Group 4), but the group of the saturated substituents (Group 1). This suggests that geminal bond participation is more important for the inward rotation of the silyl groups than the σ_{CC}–σ^*_{CSi} interaction proposed by Murakami and Houk.

Conclusion

The bonds geminal to a reacting π bond significantly participate in the reaction and control the reactivity and the selectivity. The geminal bond participation is controlled by the orbital phase properties of the cyclic orbital interactions including the geminal σ bonds. The electron-donating geminal σ bond at the Z position enhances the reactivity in the Diels–Alder reaction, the Cope rearrangement, the sigmatropic rearrangement, and the Alder ene reaction. The aldol reaction is also under the control of the geminal bond participation, where the electron-donating geminal σ bond at the Z position of the enolate enhances the reactivity. The electron-donating σ bond rotates inwardly to occupy the Z position of the products of the electrocyclic reaction and the cheletropic reaction.

An orbital phase theory for the torquoselectivity of the ring-opening reaction of the cyclobutene was developed to demonstrate that the torquoselectivity is under the control of the σ energies of the substituents at the 3-position, which strongly supports the geminal bond participation.

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$$\mathrm{IBE}_{ij} = \mathrm{P}_{ij}(\mathrm{H}_{ij} + \mathrm{F}_{ij})$$

where P_{ij}, H_{ij}, and F_{ij} are the elements of the density, Fock and core Hamiltonian matrices of the bond orbitals, respectively. For its application, see: a) S. Inagaki, S. Ohashi, T. Kawashima, *Org. Lett.* **1999**, *1*, 1145. b) S. Inagaki, H. Ikeda, T. Kawashima, *Tetrahedron Lett.* **1999**, *40*, 8893. c) Y. Naruse, A. Hayashi, S. Sou, H. Ikeda, S. Inagaki, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 245. d) Y. Naruse, S. Inagaki, N. Kano, N. Nakagawa, T. Kawashima, *Tetrahedron Lett.* **2002**, *43*, 5759. e) Y. Naruse, M. Sugiura, S. Inagaki, *Phosphorus, Sulfur Silicon* **2003**, *178*, 2447. f) Y. Otani, O. Nagae, Y. Naruse, S. Inagaki, M. Ohno, K. Yamagichi, G. Yamamoto, M. Uchiyama, T. Ohwada, *J. Am. Chem. Soc.* **2003**, *125*, 15191. g) Y. Naruse, J. Ma, K. Takeuchi, T. Nohara, S. Inagaki, *Tetrahedron* **2006**, *62*, 4491. See also refs. 7, 10–13, 19–20 and 24.

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