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An Orbital Phase Theory for the Torquoselectivity of the Ring-Opening Reactions of 3-Substituted Cyclobutenes: Geminal Bond Participation

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We apply an orbital phase theory to the torquoselectivity of the electrocyclic reactions of 3-substituted (X) cyclobutenes. The torquoselectivity is shown to be controlled by the orbital-phase relation of the reacting π_{CC} and σ_{CC} bonds with the σ_{CX} bond geminal to the σ_{CC} bond to be cleaved. The inward rotation of electron-donating σ_{CX} bonds and outward rotation of electron-withdrawing σ_{CX} bonds have been deduced from the orbital-phase theory. Enhancement of the inward rotation by the electron-donating capability of the σ_{CX} bonds is confirmed by the correlation between the torquoselectivity and σ_{CX} orbital energy. The orbital overlaps between the geminal σ_{CX} (σ_{CH}) and σ_{CC}* bonds are found to be important as well. Unsaturated substituents with low-lying unoccupied π* orbitals also promote the inward rotation.

Introduction

We recently proposed a theory of geminal bond participation in the organic reactions. σ Bonds geminal to the reacting centers significantly control the reactivities of *Z*- and *E*-isomers of dienes in Diels−Alder reactions (A),[1] Cope rearrangements (B),[2] and sigmatropic reactions (C)[3] and the torquoselectivities of electrocyclic reactions (D)[4] and cheletropic reactions (E) (Scheme 1).[5] These pericyclic reactions are accelerated by electron-donating geminal σ bonds inside the ring structures of the transition states.

The torquoselectivity of electrocyclic reactions (Scheme 2)[6−8] has attracted chemists' interest during the past decades. We applied the theory of the geminal bond participation to the torquoselectivity of electrocyclic reactions of cyclobutenes with substituents (X) at the 3-position affording *Z*- and *E*-isomers of 1,3-butadienes.[3] Substituents with electropositive atoms were proposed to prefer the inward rotation. We predicted preferential inward rotation of silyl group and confirmed it by the theoretical calculations. Murakami et al.[9] independently reported experimental observation of the inward rotation of the silyl groups of 1-(1-methyl-1-phenylethyl)-3-trimethylsilylcyclobutene and 1-octyl-3-(phenyldimethylsilyl)cyclobutene. Shindo and co-workers[10] also observed the preferential inward rotation of a silyl group in the ring-opening of the β-lactone enolates. Houk and co-workers proposed that σ−π* interaction of the breaking σ bond with an electron-accepting π bond on the substituent (A in Scheme 3)[7] should rotate the substituent inwardly, while there are some exceptions, i.e., the outward rotation of CN and COOH groups.[8] Murakami and Shindo proposed the significance of the interaction of the σ orbital of the breaking bond with the σ_{SiR}* orbital on the silyl group (B in Scheme 3)[9] and with the vacant orbitals on the Si atom (C in Scheme 3).[10] Houk and co-workers[11] argued for the σ−$\sigma*_{SiR}$ interaction and against the geminal bond participation.

In this paper, we apply an orbital-phase theory[12] to the torquoselectivity of electrocyclic reactions. We demonstrated control of the torquoselectivity by the orbital phase properties and significant participation of the geminal bonds. The electron-donating σ_{CX} bond is deduced from the theory to rotate inwardly.

Method of Calculation

We developed[1,13] and applied[14] the bond model method to analyze the electronic structures of molecules and transition

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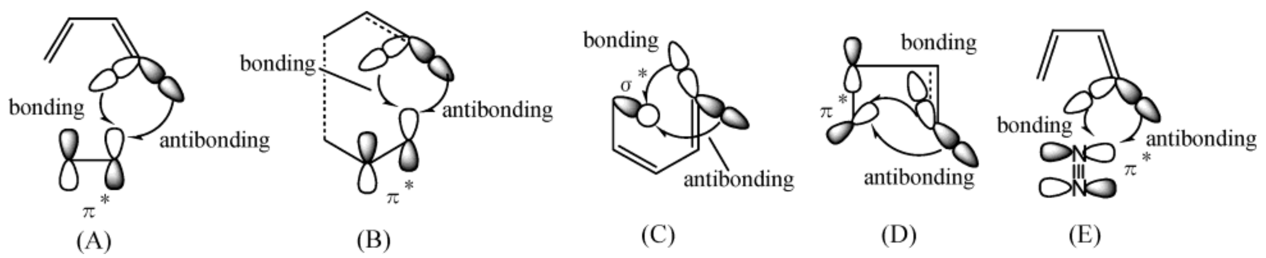
SCHEME 1



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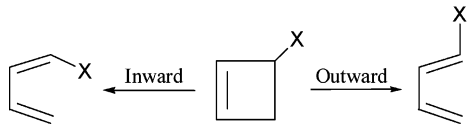
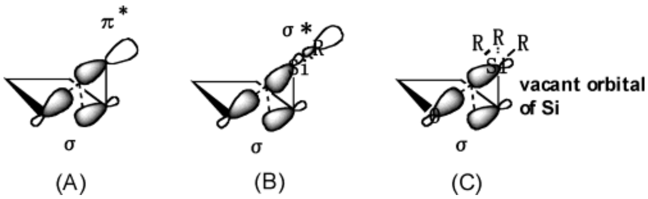


1 X= H
2 X= SH
3 X= CH_3
4 X= PH_2
5 X= SiH_3
6 X= F
7 X= OH
8 X= NH_2
9 X= Cl
10 X= NH_3^+
11 X= PH_3^+
12 X= CN
13 X= COOH
14 X= CHO
15 X= BH_2

SCHEME 3



states. Wave functions (Ψ) are expanded into electron configurations:

$$\Psi = C_G\Phi_G + \Sigma C_T\Phi_T + \Sigma C_E\Phi_E + ...$$

In the ground configuration (Φ_G), a pair of electrons occupies each bonding orbital of the bonds. A ground configuration corresponds to a Lewis structure for electronic formulas of molecules used to show the location of the paired valence electrons. Interactions between the bonds are accompanied by electron delocalization from bonds to bonds and polarization of bonds. The delocalization is expressed by mixing an electron-transferred configuration (Φ_T), where an electron shifts from the bonding orbital of a bond to the antibonding orbital of another. The polarization is expressed by mixing a locally excited configuration (Φ_E) where an electron is promoted from the bonding orbital to the antibonding orbital of a bond.

A set of bond orbitals, i.e., hybrid orbitals and their coefficients, give the coefficients C_G, C_T, and C_E of the configurations.[5] The bonding and antibonding orbitals ϕ_i and ϕ_i* of the *i*th bond are expressed by a linear combination of hybrid atomic orbitals χ_{ia} and χ_{ib} on the bonded atoms A and B:

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

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

The bond (bonding and antibonding) orbitals of each bond are obtained by the diagonalization of the 2 × 2 Fock matrix on the basis of the hybrid orbitals. A set of bond orbitals are optimized to give the maximum value of the coefficient of the ground configuration.

The geometry optimization was carried out by the B3LYP/6-31G(d) level using Gaussian 98 program.[15] For the bond model analysis, we employed the RHF/6-31G(d) wave functions of the B3LYP/6-31G(d)-optimized geometries.

Results and Discussion

Orbital Phase Theory for the Torquoselectivity. Electrocyclic reactions of cyclobutenes occur between the π bond and the σ bond to be cleaved. The stereochemical course is controlled by the interactions between σ_{CC}* and π_{CC} and between σ_{CC} and π_{CC}*.[16] The σ_{CX} bond geminal to the σ_{CC} bond can participate in the reactions through the interactions with the σ_{CC} and π_{CC} bonds. There are cyclic orbital interactions between the σ_{CX}, π_{CC}, and σ_{CC} bonds. Cyclic orbital interactions are controlled by the orbital phase continuity conditions:[12] (1) electron-donat-

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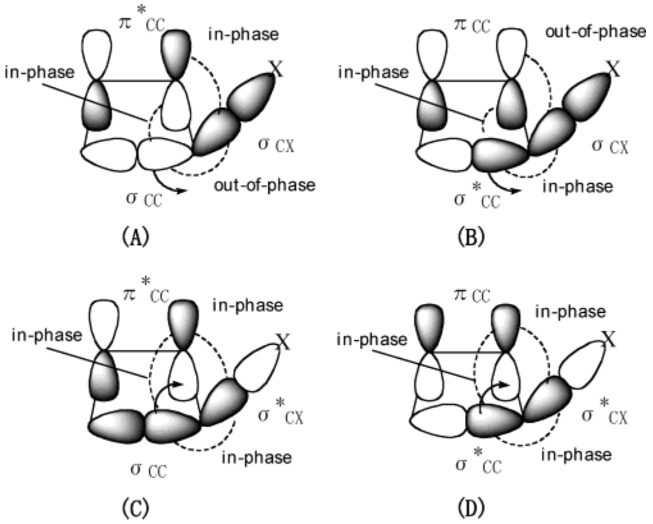

FIGURE 1. Inward rotation of electron-donating σ_{CX} bond (A and B) and outward rotation of electron-accepting σ_{CX} bond (C and D) deduced from the orbital phase theory.

ing orbitals out of phase, (2) electron-accepting orbitals in phase, and (3) donating and accepting orbitals in phase. The cyclic interaction that simultaneously satisfies the three requirements stabilizes the transition states.

The orbital phase theory shows that electron-donating σ_{CX} bonds rotate inwardly. The participation of the bonding (donating) σ_{CX} orbital in the $\sigma_{CC}-\pi^*_{CC}$ interaction is illustrated in Figure 1A. The σ_{CX} orbital is required from the phase continuity requirements to be out of phase with the σ_{CC} (donating) and in phase with π^*_{CC} (accepting). The phase relations of σ_{CX}, σ_{CC}, and π^*_{CC} are fixed. The electron-donating σ_{CC} and -accepting π^*_{CC} orbitals are required to be in phase with each other. The requirement leads to the inward rotation of the σ_{CX} bond. The same torquoselectivity is deduced for the σ_{CX} participation in the $\sigma^*_{CC}-\pi_{CC}$ interaction (Figure 1B). The phase continuity requires σ_{CX} in phase with σ^*_{CC} and out of phase with π_{CC}. The σ^*_{CC} and π_{CC} should be in phase. The σ_{CX} bond rotates inwardly.

Electron-withdrawing σ_{CX} bonds are similarly deduced from the orbital phase theory to rotate outwardly. Participation of σ^*_{CX} in the $\sigma_{CC}-\pi^*_{CC}$ interaction and the $\sigma^*_{CC}-\pi_{CC}$ interaction are illustrated in parts C and D of Figure 1, respectively. As the outward rotation weakens the interaction of the σ_{CX} and π_{CC} bonds, the electron-withdrawing geminal bonds exhibit less direct effect on the torquoselectivity. However, the electron-withdrawing groups rotate outwardly since the counterpart groups, e.g., hygrogen atom, preferentially rotate inwardly due to the σ_{CH} orbital energy relatively high to that of σ_{CX}.

Torquoselectivity vs σ_{CX} Orbital Energy. According to the geminal bond participation theory, the inward rotation should be enhanced with increase in the electron donating capability of the σ_{CX} bonds. We calculated the enthalpies of activation of both of the inward and outward rotations and the σ_{CX} orbital energy of 3-substituted cyclobutenes. The torquoselectivity ($\Delta\Delta H^\ddagger = \Delta H_{inward}{}^\ddagger - \Delta H_{outward}{}^\ddagger$; the difference in the enthalpy of activation between the outward and inward rotations) is compared with the σ_{CX} orbital energy (Figure 2).

The relation of the torquoselectivity to the σ_{CX} orbital energy suggested the classification of the substituents into the four groups: (1) substituents with high σ_{CX} energies (Group 1); (2) substituents with low σ_{CX} energies (Group 2); (3) positively charged substituents (Group 3); (4) subsituents with low lying vacant π or p orbitals (Group 4).

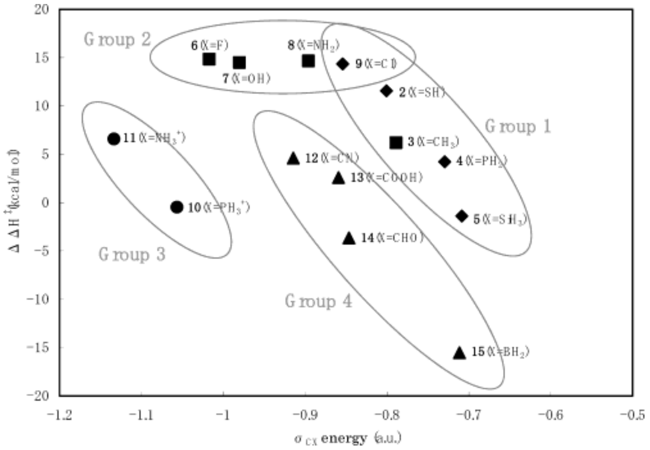

FIGURE 2. Relation between the σ_{CX} energies and the difference in the enthalpies of activation between the inward and outward rotations ($\Delta\Delta H^\ddagger = \Delta H_{inward}{}^\ddagger - \Delta H_{outward}{}^\ddagger$).

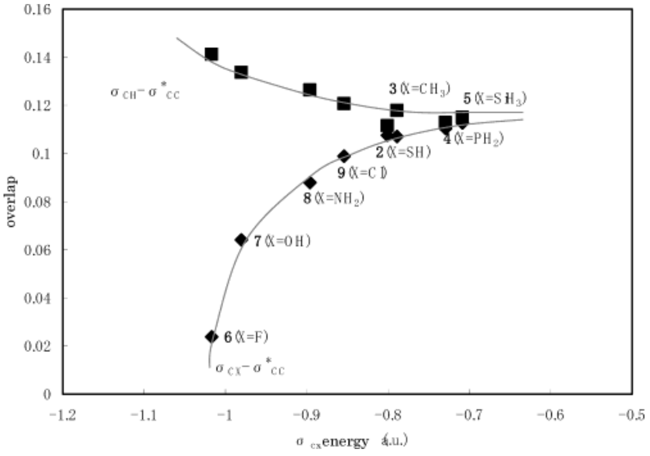

FIGURE 3. Orbital overlap of σ_{CX} and σ_{CH} with σ_{CC}*.

For the substituents of Group 1, the torquoselectivity is in a good correlation with the σ_{CX} orbital energy. The increase in the σ_{CX} energy reduces the outward selectivity or enhances the inward selectivity in the order X=Cl < SH < CH_3 < PH_2 < SiH_3. The correlation between the torquoselectivity and the σ_{CX} energy supports the orbital phase theory and the geminal bond participation.

The torquoselectivity do not appreciably change for the electronegative substituents F, OH, NH_2, Cl (see Group 2 in Figure 2). This is also expected from the prediction based on the geminal bond participation. The electron-withdrawing substitutents exhibit less direct effect on the degree of the torquoselectivity as discussed in the preceding section.

The orbital overlaps are as important as the σ_{CX} orbital energy in torquoselectivity. The σ_{CX} orbital overlaps with σ^*_{CC} as much as the counterpart σ_{CH} orbital for less electronegative atom substituents in Group 1 (Figure 3). The orbital overlap makes little difference. The σ_{CX} orbital energy determines the torquoselectivity. For the electronegative substituents in Group 2, however, the $\sigma_{CX}-\sigma^*_{CC}$

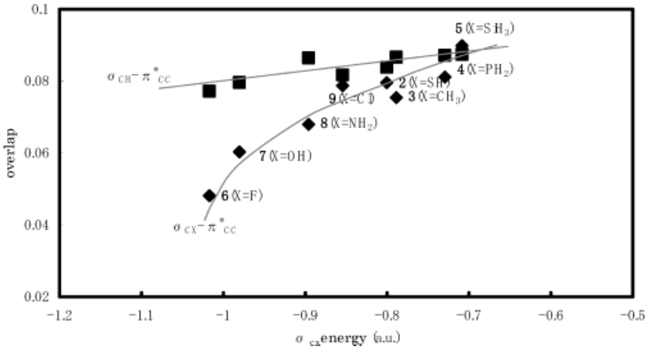

FIGURE 4. Orbital overlap of σ_{CX} and σ_{CH} with π_{CC}*.

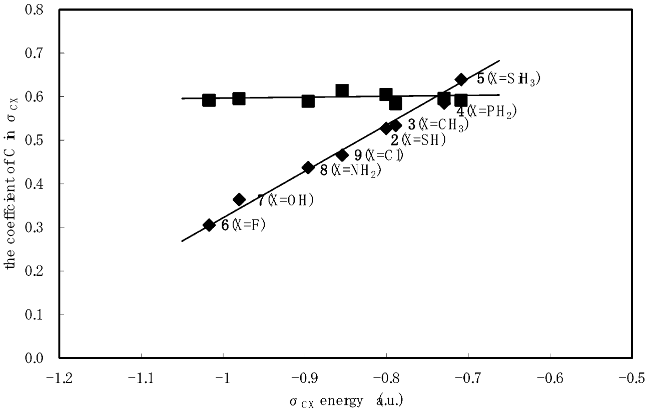

FIGURE 5. Bond polarization and σ_{CX} energy.

overlap is considerably smaller than the $\sigma_{CH}-\sigma^*_{CC}$ overlap. The $\sigma_{CH}-\sigma^*_{CC}$ interaction is more important. Similar features are found to be in the overlap integrals of the geminal σ_{CX} and σ_{CH} orbitals with π^*_{CC} (Figure 4). The σ_{CH} orbital is essential rather than σ_{CX} for determining the torquoselectivity. The C−H bond rotates inwardly, while the C−X bond rotates outwardly. The σ_{CH} energy and the overlap of σ_{CH} with σ^*_{CC} does not change with X to a considerable degree. The torquoselectivity remains almost unchanged in Group 2.

The change of the overlap of σ_{CX} with σ^*_{CC} and π^*_{CC} results from the polarization of the σ_{CX} and σ_{CH} orbitals. The coefficients of the hybrid orbitals on the carbon atoms in the σ_{CX} bond orbitals are shown in Figure 5. With the increase in the electronegativity of X, the coefficients decrease while those in σ_{CH} remain almost unchanged. The σ_{CX} and σ_{CH} orbitals overlap at the hybrid orbitals on the carbon atom rather than X. The overlaps of σ_{CX} with σ^*_{CC} and π^*_{CC} then decrease with the electronegativity of X while those of σ_{CH} remain almost unchanged.

Positively charged substituents, PH_3^+ and NH_3^+, are classified into a separate group (Group 3 in Figure 2). However, there is a similar tendency that the increase in the σ_{CX} energy enhances the inward rotation. This is in agreement with the orbital phase prediction and the importance of the geminal bond participation.

For the unsaturated substituents with low-lying vacant π or p orbitals (Group 4: X = CN, COOH, CHO, BH_2), a linear correlation is found between the torquoselectivity and the σ_{CX} energy, supporting the geminal bond participation. However, the substituents in Group 4 were found to favor the inward rotation more than expected from the σ_{CX} energy (compare with the saturated substituents in Group 1). The preferential 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.[7]

The outward rotation for **12** (X = CN) and **13** (X = COOH) cannot be explained by the Houk's $\sigma-\pi^*$ interaction but by the geminal bond participation. The σ_{CX} energies are lower for **12** and **13 (**X = CN, COOH) than those for **14** and **15 (**X = CHO, BH_2) (see group 4 in Figure 2). The σ_{CX} energy is too low in **12** and **13** for the inward rotation.

Furthermore, the SiH_3 substitutent (compound **5**) is clearly not classified into the group of the unsaturated substituent (Group 3), but the group of the saturated substituents (Group 1). This suggests that geminal bond participation is more important than the vacant orbitals on the silicon atom (Scheme 3B,C) for the inward rotation of the silyl groups.

Conclusion

The orbital phase theory was applied to the torquoselectivity of the ring opening in the electrocylic reactions of 3-substituted (X) cyclobutenes. The torquoselectivity is controlled by the orbital-phase relation of the σ_{CX} bond with the reacting σ and π bonds. The σ_{CX} bond is deduced from the orbital phase theory[12] to rotate inwardly as the electron-donating capability of σ_{CX} increases. The selectivities, i.e., the differences in the enthalpies of activation between the inward and the outward rotation, are confirmed by the calculations to correlate with the σ_{CX} orbital energy. Not only σ_{CX} or σ_{CH} energies but also the overlap of σ_{CX} (σ_{CH}) with σ_{CC}* and π_{CC}* are important for the torquoselectivity. The σ_{CX} bond is geminal to the σ_{CC} bond to be cleaved. The geminal bond participation is important in the electrocyclic reactions and general in the pericyclic reactions, including Diels−Alder reactions,[1] Cope rearrangements,[2] sigmatropic reactions,[4] and cheletropic reactions.[5]

Supporting Information Available: Optimized structures/TSs with energies and minimum (or one imaginary) vibrational frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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