Torquoselectivity of the Ring-Opening Reaction of 3,3-Dihalosubstituted Cyclobutenes: Lone Pair Repulsion and Cyclic Orbital Interaction

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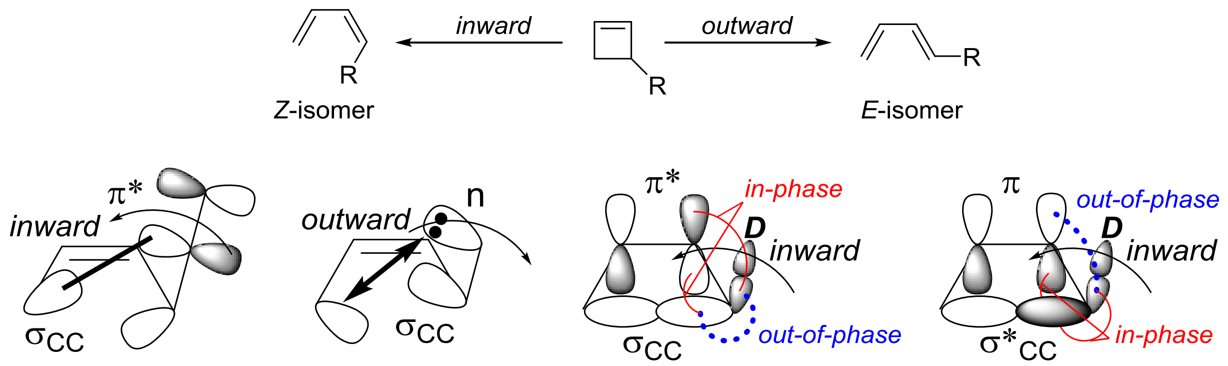
KEYWORDS: Torquoselectivity, Electrocyclic Ring-Opening Reaction, Geminal Bond Participation, Bond Model Analysis.

ABSTRACT. Three major factors determine torquoselectivity, which is the diastereoselectivity in electrocyclic ring-opening reactions to produce *E*/*Z*-double bond(s). One is the interaction between the decomposing σ_{CC} bond and low-lying vacant orbital(s), such as a π*- or σ*-orbital on the substituent, which promotes the reaction, resulting in inward rotation of the substituent. Second, for a substituent with a lone pair(s), repulsive interaction between the decomposing σ-bond and the lone pair(s) hinders inward rotation, so that the products of outward rotation should be preferred. Finally, a more strongly donating σ-electron-donating group (σEDG) rotates

inwardly due to stabilization by phase-continuous cyclic orbital interaction. We compared the latter two interactions, repulsion between the lone pairs on the substituent and stabilization from phase-continuous cyclic orbital interaction, to determine which has a greater effect on the diastereoselectivity. We considered a series of model reactions with halogen substituents, and concluded that the diastereoselectivity is mainly controlled by cyclic orbital interaction.

1. Introduction

Torquoselectivity is the diastereoselectivity in electrocyclic ring-opening reactions that produces *E*-/*Z*-isomers of the double bond.[1-4] Many reports have discussed this diastereoselectivity, especially with regard to the electrocyclic ring-opening reaction of 3-substituted cyclobutenes. However, the diastereoselectivity often does not seem to be guided by steric considerations, so that electronic effects need to be considered. Three major interactions of the electronic effect have been proposed to explain this torquoselectivity (Figure 1).



(a) π^*/σ^* attraction

(b) lone pair repulsion

(c) σ_{CC}-$\pi^*_{C=C}$-$\sigma_{C\text{-}\boldsymbol{D}}$-interaction

(d) σ^*_{CC}-$\pi_{C=C}$-$\sigma_{C\text{-}\boldsymbol{D}}$-interaction

Figure 1. Torquoselectivity of 3-substituted cyclobutenes and its proposed electronic effects.

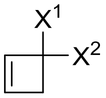
One is the interaction between the decomposing σ_{CC} bond and a low-lying vacant orbital, such as a π^*- or σ^*-orbital on the substituent, which promotes the reaction (Figure 1a).[3-6] Cyclobutene with an alkoxycarbonyl group at the 3-position was reported to show torquoselectivity with inward rotation of the alkoxycarbonyl group. This would be a donor-acceptor interaction, and hence an attractive interaction, and the TS should be considerably stabilized, resulting in inward rotation of the substituent. On the other hand, interaction between the decomposing σ_{CC} bond and the lone pair(s) on the substituent is a type of donor-donor interaction, which leads to repulsive destabilization. Substituent(s) with lone pairs should prefer outward rotation (Figure 1b).

In contrast, Inagaki proposed that phase-continuous cyclic orbital interaction[8] that includes geminal bond participation controls the diastereoselectivity (Figures 1c and 1d).[7b] The cyclic orbital interactions among $\pi^*_{C=C}$, decomposing σ_{CC} and $\sigma_{C\text{-}\boldsymbol{D}}$ of the σ-donating group (σEDG) $\boldsymbol{D}$ (Figure 1c) and among $\pi_{C=C}$, decomposing σ^*_{CC} and $\sigma_{C\text{-}\boldsymbol{D}}$ (Figure 1d) satisfy the phase continuity requirements, so that electron delocalization among them is enhanced to produce considerable stabilization at TSs.

We wondered which of these three effects controlled the diastereoselectivity most effectively. As a first step, we compared the effects of the latter two, i.e., the repulsive interaction between the decomposing σ_{CC} bond and the lone pair(s) on the substituent(s) and the cyclic orbital interaction including geminal bond participation.

2. Expected torquoselectivity

To compare these effects, we should choose a system that is free from bond interaction on the substituent(s). Thus, we chose 3,3-dihalocyclobutenes **1** as models. Halogens are monovalent, so that there no other bonds on the substituent(s) and no effects from the π^* or σ^*-orbital. The atomic radii of halogens are in the order F < Cl < Br and the bond lengths of carbon-halogen bonds are in the order $\sigma_{\mathrm{C-F}} < \sigma_{\mathrm{C-Cl}} < \sigma_{\mathrm{C-Br}}$. If repulsion with the decomposing σ_{CC} bond is the main contributor to diastereoselectivity, the preference for inward rotation should be in the order F > Cl > Br, considering the atomic radii. In contrast, if a longer bond length reduces repulsion, the order of preference should be reversed to F < Cl < Br.



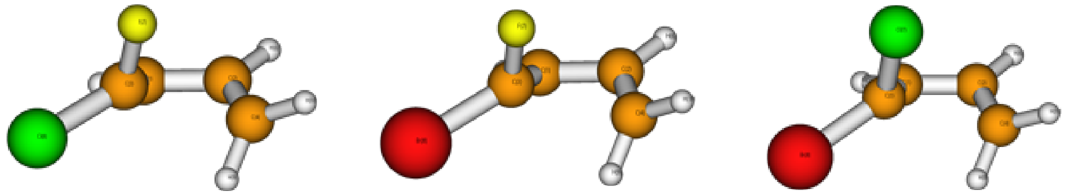
1a: X^1 = F; X^2 = Cl
1b: X^1 = F; X^2 = Br
1c: X^1 = Cl; X^2 = Br
1d: $X^1 = X^2$ = F
1e: $X^1 = X^2$ = Cl
1f: $X^1 = X^2$ = Br

Figure 2. 3,3-Dihalocyclobutenes considered.

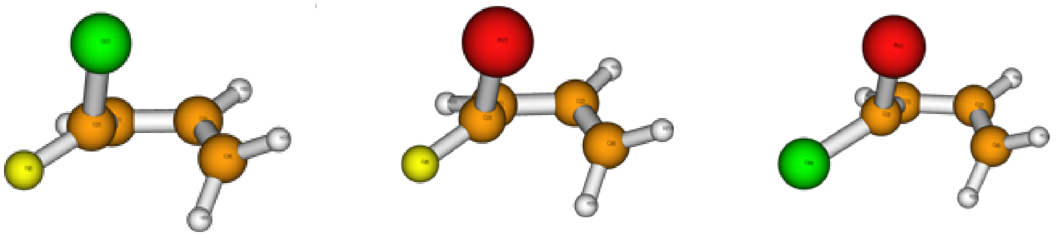
From the perspective of cyclic orbital interaction[7b,8], the energy level of $\sigma_{\mathrm{C-X}}$ is well correlated with electronegativity, so that the donating character is in the order $\sigma_{\mathrm{C-F}} < \sigma_{\mathrm{C-Cl}} < \sigma_{\mathrm{C-Br}}$, since fluorine is the most electronegative (4.0), followed by chlorine (2.8) and bromine (2.7). We previously confirmed this order by evaluating the energy levels of $\sigma_{\mathrm{C-X}}$ bond orbitals: $\sigma_{\mathrm{C-F}}$ (-1.068 a.u.) < $\sigma_{\mathrm{C-Cl}}$ (-0.882 a.u.) < $\sigma_{\mathrm{C-Br}}$ (-0.834 a.u.).[7b-d,9] Since the more strongly donating character of the geminal $\sigma_{\mathrm{C-X}}$ bond enhances the cyclic orbital interaction among $\pi^*_{\mathrm{C=C}}$, decomposing σ_{CC} and $\sigma_{\mathrm{C-}D}$ and among $\pi_{\mathrm{C=C}}$, decomposing σ^*_{CC} and $\sigma_{\mathrm{C-}D}$, we can expect that the preference for inward rotation should be in the order F < Cl < Br.

3. Theoretical calculations

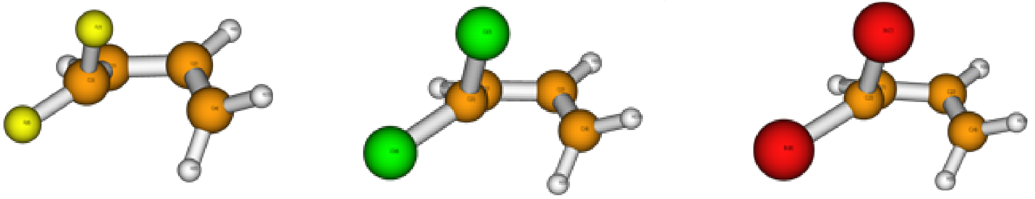
First, we performed theoretical calculations at the M06-2X/6-311++G** level (Figure 3).[10] The results are summarized in Table 1.



TS1ain: X^1 = F; X^2 = Cl **TS1bin: X^1 = F; X^2 = Br** **TS1cin: X^1 = Cl; X^2 = Br**



TS1aout: X^1 = Cl; X^2 = F **TS1bout: X^1 = Br; X^2 = F** **TS1cout: X^1 = Br; X^2 = Cl**



TS1d: X^1 = X^2 = F **TS1e: X^1 = X^2 = Cl** **TS1f: X^1 = X^2 = Br**

Figure 3. Optimized TS structures (M06-2X/6-311++G**).

Table 1. Torquoselectivity of 3,3-dihalocyclobutenes (kcal/mol, M06-2X/6-311++G**)

substrate	$\Delta E^{\ddagger}$(X^1 inward)	$\Delta E^{\ddagger}$(X^2 inward)	$\Delta\Delta E^{\ddagger}$
1a (X^1 = F; X^2 = Cl)	**TS1ain** 42.4	**TS1aout** 41.6	0.74
1b (X^1 = F; X^2 = Br)	**TS1bin** 42.4	**TS1bout** 41.2	1.2
1c (X^1 = Cl; X^2 = Br)	**TS1cin** 41.5	**TS1cout** 41.0	0.43
1d (X^1 = X^2 = F)	**TS1d** 42.7		] 1.3
1e (X^1 = X^2 =Cl)	**TS1e** 41.4		] 1.6
1f (X^1 = X^2 = Br)	**TS1f** 41.1		] 0.3

Apparently, the preference for inward rotation is in the order F < Cl < Br. The activation energies are in the order **TS1d** (difluoro, 42.7 kcal/mol) > **TS1e** (dichloro, 41.4 kcal/mol) > **TS1f** (41.1 kcal/mol, dibromo), and there is a preference for inward rotation of a chloro group in **TS1a** and a bromo group in **TS1b** and **TS1c.** There is some regularity in these values. The activation energies $E^{\ddagger}$ for fluoro-inward rotation of **TS1ain** (42.4 kcal/mol) and **TS1bin** (42.4 kcal/mol) are almost the same as that of difluoro **TS1d** (42.7 kcal/mol), the activation energies $E^{\ddagger}$ for chloro-inward rotation of **TS1aout** (41.6 kcal/mol) and **TS1cin** (41.5 kcal/mol) are almost the same as that of dichloro **1e** (41.4 kcal/mol), and finally, the activation energies $E^{\ddagger}$ for bromo-inward rotation of **TS1bout** (41.2 kcal/mol) and **TS1cout** (41.0 kcal/mol) are almost the same as that of dibromo **TS1e** (41.1 kcal/mol). These results clearly indicate that the activation energy heavily depends on the substituent that rotates inward.

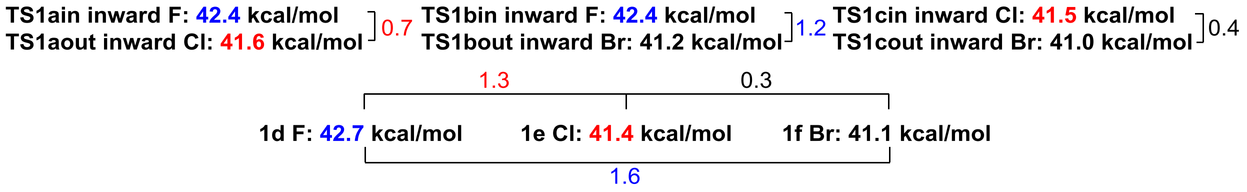


Figure 3. Relationship among the optimized activation energies.

Furthermore, the activation energy decreases with the outward-rotating substituent in the order ~~of~~ F > Cl > Br, e.g., **1d** (outward F: 42.7 kcal/mol) > **1a** (outward Cl: 42.4 kcal/mol) ~ **1b** (outward Br: 42.4 kcal/mol) in the inward-F series, and **1a** (outward F: 41.6 kcal/mol) > **1e** (outward Cl:41.4 kcal/mol) > **1c** (outward Br: 41.0 kcal/mol) in the inward-Cl series. For the inward Br series, there are no apparent differences of ca. 0.1 kcal/mol.

We can expect that these relationships can be attributed to the inductive effect. The stronger σ-electron-withdrawing group attracts electrons on other atoms in the neighborhood, so that the σ-bond energies of the other substituent bonds should be lowered. This inductive effect also affects the charge on the other substituents to reduce steric repulsion while the bond lengths are almost the same.

Thus, we can conclude that the obtained values are consistent with our expectation. Repulsion should be reduced with longer bond lengths, and only the σ-bond of the substituent C-X bond with inward rotation is involved in the cyclic orbital interaction. Thus, we can expect that one of these two effects should mainly control the torquoselectivity.

4. Bond model analysis

To determine which effect should contribute more to the torquoselectivity, we performed a bond model analysis[11] to evaluate the bond interactions. We used the interbond energy IBE[12] for this evaluation. Due to the difficulty of separating the lone pairs of the valence electrons and the core orbitals, we evaluated the sum ΣIBE(σ_{CC}-n_X) of the repulsive interactions between decomposing σ_{CC} and the lone pairs on the halogen atom that rotates inward. We summarize our analysis in Table 2.

Table 2. Charge and bond interactions (IBE in a.u., RHF/6-31G(d)//M06-2X/6-311++G**).

	Lone pair repulsion		Cyclic orbital interaction			
			Among σ_{CC}-$\pi^*_{C=C}$-$\sigma_{C\text{-}\boldsymbol{D}}$- orbitals		Among $\pi_{C=C}$-σ^*_{CC}-$\sigma_{C\text{-}\boldsymbol{D}}$- orbitals	
	Mulliken charge on X[a]	ΣIBE(σ_{CC}-n_X)/a.u.	IBE(σ_{CC}-$\pi^*_{C=C}$)/a.u.	IBE($\sigma_{C\text{-}\boldsymbol{D}}$-$\pi^*_{C=C}$)/a.u.	IBE($\pi_{C=C}$-σ^*_{CC})/a.u.	IBE($\sigma_{C\text{-}\boldsymbol{D}}$-$\sigma^*_{CC}$)/a.u.
1a F-inward	0.0457 (-0.3370)	0.7814	-2.2363	-0.0356	-1.0408	0.0798
1a Cl-inward	0.1492 (0.0126)	0.8466	-2.2637	-0.0601	-1.1634	0.3288
1b F-inward	0.0366 (-0.3898)	0.9466	-2.6783	-0.0406	-1.2335	0.0981
1b Br-inward	-0.0232	0.9495	-2.7379	-0.1082	-1.4206	0.4624

	(-0.1045)					
1c Cl-inward	0.1138 (0.0574)	1.1782	-2.6154	-0.0996	-1.5448	0.3961
1c Br-inward	-0.0571 (-0.0568)	1.1044	-2.6363	-0.1118	-1.6146	0.3358
1d difluoro	-0.0236 (-0.3360)	0.6758	-2.1999	-0.0263	-0.8872	0.0743
1e dichloro	0.1042 (0.0439)	1.0088	-2.2158	-0.0826	-1.1340	0.3229
1e dibromo	-0.0343 (-0.0517)	1.2536	-3.0452	-0.1619	-1.8195	0.5669

[a]M06-2X/6-311++G**; at the level of RHF/6-31G(d)//M06-2X/6-311++G** in parentheses.

First, the evaluated steric repulsion ΣIBE(σ_{CC}-n_X) is in the order F < Cl < Br, which is opposite the order we expected. From a charge perspective, there is no correlation with the changes in the activation energies. The steric repulsion should mostly depend on the atomic radii of the halogens. The only exception is the case of **1c**, where less steric repulsion is calculated for the inward rotation of Br. We suppose that the longer bond length of $\sigma_{C\text{-}Br}$ (1.957 Å, M06-2X/6-311++G**) compared to that of $\sigma_{C\text{-}Cl}$ (1.785 Å) would be the main contributor in this case. Considering these results, we conclude that steric repulsion does not control the torquoselectivity.

For the cyclic orbital interaction, stabilization due to the bond interactions between σ_{CC} and $\pi^*_{C=C}$ and between $\sigma_{C\text{-}\boldsymbol{D}}$ and $\pi^*_{C=C}$ in the cyclic orbital interaction among σ_{CC}-$\pi^*_{C=C}$-$\sigma_{C\text{-}\boldsymbol{D}}$- orbitals, and those between $\pi_{C=C}$ and σ^*_{CC} and between $\sigma_{C\text{-}\boldsymbol{D}}$-$\sigma^*_{CC}$ in the cyclic orbital interaction among $\pi_{C=C}$-σ^*_{CC}-$\sigma_{C\text{-}\boldsymbol{D}}$- orbitals are all enhanced in the order F < Cl < Br. For inward rotation of the same atom, repulsive interaction increased in the order F < Cl < Br. In contrast, the stabilization from the cyclic orbital interactions also increased. They should cancel each other so that the activation energies remained almost the same regardless of the substituent rotating outward. For example, in fluoro-inward rotation, repulsion between the decomposing σ_{CC} and lone pairs on the halogen ΣIBE(σ_{CC}-n_X) increases according to the outward-rotating substituent in the order F (**1d**, fluoro-outward: 0.6758 a.u.) < Cl (**1a**, Cl-outward: 0.7814 a.u.) < Br (**1b**, Br-outward: 0.9466 a.u.). On the other hand, stabilization from σ_{CC}-$\pi^*_{C=C}$ in the cyclic orbital interaction is in the order F (**1d**, -2.1999 a.u.) < Cl (**1a**, -2.2363 a.u.) < Br (**1b**, -2.6783 a.u.). Note that the geminal interaction between $\sigma_{C\text{-}\boldsymbol{D}}$-$\sigma^*_{CC}$ shows an antibonding character of IBE values. Inagaki explained this phenomenon in terms of the antibonding nature of geminal delocalization.[13] The geminal bond interaction was erroneously considered to mean that there was no interaction between the two geminal bonds. However, although the two hybrid orbitals on the center atom are orthogonal, the geminal bonds still interact mostly via the hybrid orbital at the terminal positions (Figure 4). The phase between the two geminal bonds is determined by the two hybrid orbitals on the center atom. Thus, the overlaps between the other three hybrids should often be out-of-phase combinations for the obtuse bond angle, which results in the antibonding nature. This characteristic of geminal delocalization leads to the positive values for IBEs. Thus, we can conclude that a more electron-donating character of σEDG prefers inward rotation by enhancing the cyclic orbital interaction, i.e., the order of electronegativity F > Cl > Br should result in the donating character of a C-X bond to be in the order $\sigma_{C\text{-}F} < \sigma_{C\text{-}Cl} < \sigma_{C\text{-}Br}$, so that the preference for inward rotation is in the order F < Cl < Br due to the stabilization from the cyclic orbital interaction at the TS. These results are in good agreement with our expectations.

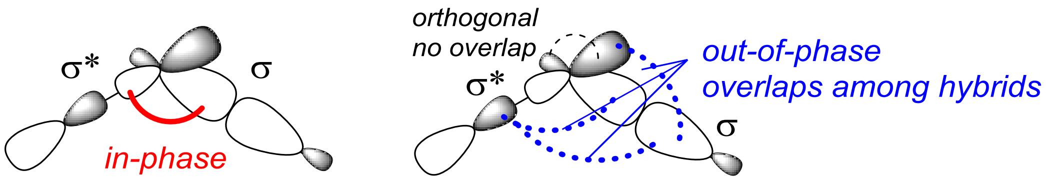


Figure 4. Phase relationship and overlaps in geminal delocalization

Conclusion

We evaluated the electronic effects that affect torquoselectivity in the electrocyclic ring-opening reaction of 3,3-dihalocyclobutenes. According to theoretical calculations, the change in activation energies is in the order F > Cl > Br. From the perspective of repulsion between the decomposing σ_{CC} and the lone pair(s) on the halogens, the order was assumed to result from longer bond lengths. On the other hand, from the perspective of cyclic orbital interaction, the order was believed to be due to phase-continuous cyclic orbital interactions, where the electron-donating ability of the $\sigma_{C\text{-}X}$ bond is essential. Electronegativity is in the order F > Cl > Br, and thus, the σ-bond orbital energy is in the order $\sigma_{C\text{-}F} < \sigma_{C\text{-}Cl} < \sigma_{C\text{-}Br}$. The cyclic orbital interaction is enhanced in the order F < Cl < Br. According to our bond model analysis, the change in cyclic orbital interaction is consistent with our expectation, while repulsive interaction between the decomposing σ_{CC} and the lone pair(s) on the halogens does not follow the change in the activation energies. Thus, we conclude that the cyclic orbital interaction controls torquoselectivity in the electrocyclic ring-opening reaction of 3,3-dihalocyclobutenes.

ASSOCIATED CONTENT

Supporting Information. Summary of the theoretical calculations. This material is available free of charge via the Internet.

Author Contributions

Both authors contributed to writing the manuscript and approved the final version of the manuscript.

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12. Interbond energy IBE is derived using the following equation:

$$IBEij = Pij(Hij + Fij)$$

where Pij, Hij, and Fij are the elements of the density, Fock and core Hamiltonian matrices of the bond orbitals, *i* and *j*, respectively.

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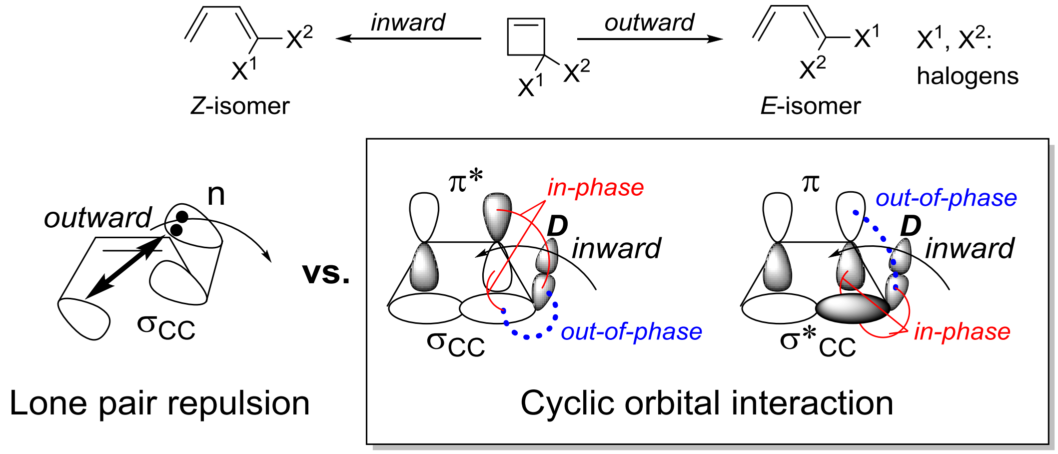

Cyclic orbital interaction controls the torquoselectivity.