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Geminal bond participation and torquoselectivity in cheletropic reactions

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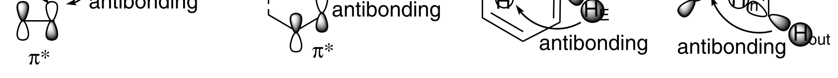
Abstract—We applied the geminal bond participation theory to cheletropic reactions. The interaction between σ-orbital of the inner bond and the π*-orbital of the N≡N bond was predicted to be bonding, while that involving the outer bond should be antibonding. The difference in the bonding/antibonding character of these interactions is due to the cyclic orbital interaction between the π*-orbital of the N≡N bond and the geminal bonds at the reaction center, which is influenced by the phase continuity between the $\underbrace{\pi^*–\sigma–\sigma}$ orbitals. This prediction was confirmed by the bond model analysis of model compound **1a**. These results suggest that reactivity could be enhanced by substituting the inwardly rotating σ-bond by a more electron-donating one, i.e. inward rotation of a substituent with a more electropositive atom. Theoretical calculations were performed for systematically substituted substrates. The prediction was confirmed except in the case of **1g**, which was affected by the inductive effect of oxygen. Silyl/methyl-substituted **1e** was subjected to the bond model analysis to confirm that the preferred inward rotation of the silyl group of **1e** results from the geminal bond participation and little affected by steric effects.

A theory for the participation of geminal bonds in organic reactions was developed and applied to the reactivity and selectivity in the Diels–Alder reaction,[1] Cope rearrangement,[2] sigmatropic [1,5]-hydrogen shifts[3] and electrocyclic reactions.[4] The main point of this theory is the participation of the σ-bond geminal to the reaction center (Fig. 1). For example, substitution of a more electron-donating σ-bond to the Z-position of the diene termini enhances the reactivity in the Diels–Alder reaction.[1] A lower activation energy is calculated when the inner σ-bond is more electron-donating in the Cope rearrangement[2] and sigmatropic [1,5]-hydrogen shifts.[3] A preference for inward rotation of the more σ-bond electron-donating group was predicted[4] and observed[5] in the ring-opening reaction of the cyclobutene.[6]

These results arise from the bonding nature of the geminal bond participation of the σ-bond (Fig. 1).[1–4] In the transition state, the delocalization from the inner σ-bond to the dienophile acceptor is bonding in the Diels–Alder reaction.[1] On the other hand, that from the outer σ-bond is antibonding. Furthermore, delocalization from the inner σ-bond of the terminal olefin is bonding in the Cope rearrangement, while that from the outer σ-bond is antibonding.[2] The same trends were observed for sigmatropic hydrogen shifts[3] and the electrocyclic reactions.[4] In summary, the reactivity is



(a) (b) (c) (d)

Figure 1. Geminal bond participation in (a) Diels–Alder reaction; (b) Cope rearrangement; (c) sigmatropic [1,5]-hydrogen shifts; (d) electrocyclic reaction.

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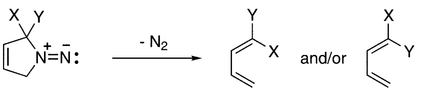
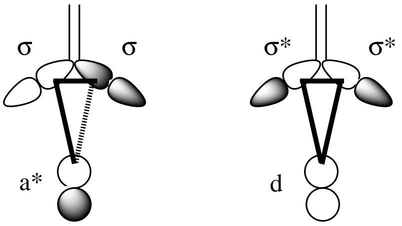
enhanced when the inner position is occupied by a more electron-donating σ-bond geminal to a reacting accepting bond.



1a-g **2a-g** **3a-g** (1)

a: X = Y = H
b: X = H, Y = CH_3
c: X = H, Y = NH_2
d: X = H, Y = OH
e: X = SiH_3, Y = CH_3
f: X = PH_2, Y = NH_2
g: X = SH, Y = OH

Cyclic orbital interactions are involved in electron delocalization from the σ-bonds geminal to a reacting donor π-bond to another accepting reacting bond and in the reverse delocalization to the geminal σ-bonds (Fig. 2). Cyclic orbital interactions are under the control of orbital phase continuity conditions:[8] (i) electron-donating orbitals are out-of-phase; (ii) electron-donating and electron-accepting orbitals are in-phase; and (iii) electron-accepting orbitals are in-phase. When these conditions are simultaneously satisfied, the cyclic interaction promotes electron delocalization.



(a) (b)

Figure 2. Orbital phase properties in the cyclic interactions of the geminal s bonds with an electron-accepting (A) and donating s bonds (D). (a) the discontinuity in the $\underline{\sigma\text{–}\sigma\text{–}a^*}$ interaction; (b) the continuity in the $\underline{\sigma^*\text{–}\sigma^*\text{–}d}$ interaction.

Electron delocalization from the geminal σ-bonds to an electron-accepting bond (A) involves the cyclic orbital interactions among the two σ bonding orbitals and the accepting orbital (a*) (Fig. 2(a)). Phase continuity requires the in-phase combination of the σ and a* orbitals and the out-of-phase combination of the σ orbitals. Cyclic interaction cannot satisfy these requirements simultaneously. This suggests that the stronger σ→a* delocalization is bonding while the other is antibonding. In contrast, the reverse delocalization from the donating bond (D) to the σ* orbitals of the geminal bonds satisfies the phase continuity requirement: the d and two σ* orbitals of the geminal bonds are all in-phase (Fig. 2(b)). Both d→σ* delocalizations should effectively occur in a bonding manner. The bonding-antibonding properties of the delocalization from the geminal σ-bonds are opposite to each other, while the delocalization to the geminal bonds are both bonding. Consequently, the delocalization **from** the geminal σ-bonds should differ greatly from that **to** the geminal σ-bonds.

After our successes,[1–4] we wondered whether these effects would be general and common in pericyclic reactions. Thus, we examined the applicability of this theory to torquoselectivity in cheletropic reactions.[9,10] To the best of our knowledge, there have been no previous reports on experimental results regarding torquoselectivity in cheletropic reactions.[10,11] We report here our theoretical study to identify the common features that control the reactivity and selectivity in pericyclic reactions.

We applied the geminal bond participation theory to cheletropic reactions. We chose a model reaction of 3-pyrroline diazene **1a**, which liberates nitrogen to give butadiene. For comparison with other reactions, let us use a product-like bond model of **1a**, shown in Figure 3(b). If we apply the geminal bond participation theory to this problem, the interaction from the σ-orbital of the inner bond to the π*-orbital of the N≡N bond should be bonding, while that from the outer bond should be antibonding. A more electron-donating inner σ-bond leads to enhanced reactivity, and a functional group with a more electron-donating σ-bond rotates inward to be located at the *Z*-position of the product.

(a) reactant-like model (b) product-like model

Figure 3. Bond models for the transition state.

We calculated the transition state for the release of nitrogen from model compound **1a**[12] at the B3LYP/6-31G* level.[13] The activation energy ($\Delta E^{\ddagger}$) for **1a** is 5.5 kcal/mol (ZPE corrected). The electronic structure at the RHF/6-31G* level using the located transition structure was subjected to the bond model analysis.[14] To estimate the interactions between the bond orbitals, we used the interbond energy IBE.[15] As expected, the delocalization from the inner σ-bond to the π* orbital of the N≡N bond shows a bonding nature ($\mathrm{IBE}(\sigma_{(\mathrm{CH})\mathrm{in}} \rightarrow \pi^*_{\mathrm{N=H}}) = -0.0976$ a.u.), while that from the outer σ-bond is antibonding ($\mathrm{IBE}(\sigma_{\mathrm{out(CH)}} \rightarrow \pi^*_{\mathrm{N=N}}) = 0.0559$ a.u.) (Fig. 4). On the other hand, both delocalization from $\pi_{(\mathrm{N\equiv N})}$ to the σ* orbitals of the inner σ-bond (IBE = –0.0153 a.u.) and outer σ-bond (IBE = –0.0420 a.u.) were bonding.

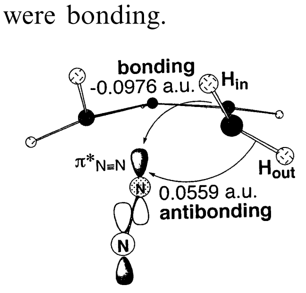


Figure 4. Geminal bond participation in the cheletropic reaction.

Based on these results, we can expect that a more electron-donating σ-bond substituent should prefer inward rotation in a cheletropic reaction. To test our

Table 1. Activation energies (in kcal mol^{-1} at B3LYP/6-31G*) in the cheletropic reaction

Subst.	X	Y	$\Delta E^{\ddagger}_{\text{X-in}}$	$\Delta E^{\ddagger}_{\text{X-out}}$	$\Delta\Delta E^{\ddagger a}$
1b	H	CH_3	**2b** 4.4	**3b** 8.6	−4.2
1c	H	NH_2	**2c** 2.9	**3c** 8.9	−6.0
1d	H	OH	**2d** 6.5	**3d** 10.7	−4.2
1e	SiH_3	CH_3	**2e** 4.7	**3e** 8.1	−3.4
1f	PH_2	NH_2	**2f** 3.0	**3f** 7.1	−4.1
1g	SH	OH	**2g** 8.5	**3g** 7.5	1.0

[a] $\Delta\Delta E^{\ddagger} = \Delta E^{\ddagger}_{\text{X-in}} - \Delta E^{\ddagger}_{\text{X-out}}$.

prediction, we calculated the transition states in the reactions of systematically substituted substrates **1b**–**g**. The Si atom (1.9) is less electronegative than carbon (2.6). Within the same group, a σ-bond with a heavier atom should be more electron-donating. Thus, the silyl group should occupy the *Z*-position in the product of **1e**. In an analogous fashion, the phosphino and mercapto groups in **1f** and **1g**, respectively, should rotate inward. The results are summarized in Table 1. We confirmed our prediction, except for **1g**. For hydroxyl- and mercapto-substituted **1g**, the C–S bond is less electron-donating than the C–O bond because of the inductive effect from the hydroxyl group, as is observed for other pericyclic reactions.[1–4]

We subjected the electronic structures at the transition states in the inward and outward rotation of **1e** to the bond model analysis. The total interaction of $\sigma_{\text{in(C–Si)}} \rightarrow \pi^*_{(\text{N}\equiv\text{N})}$ in the SiH_3-inward transition state is bonding (IBE = −0.1879 a.u.), while that of the outward-rotating σ-bond $\sigma_{\text{out(C–C)}} \rightarrow \pi^*_{(\text{N}\equiv\text{N})}$ (IBE = 0.0746 a.u.) is antibonding. Furthermore, the interaction of $\sigma_{\text{in(C–Si)}} \rightarrow \pi^*_{(\text{N}\equiv\text{N})}$ is more bonding than that of $\sigma_{\text{in(C–C)}} \rightarrow \pi^*_{(\text{N}\equiv\text{N})}$ at the CH_3-inward transition state (IBE = −0.1310 a.u.). These results suggest that, as expected, geminal bond participation is under the control of the phase continuity, and that more $\sigma_{\text{in}} \rightarrow \pi^*_{(\text{N}\equiv\text{N})}$ delocalization occurs with the more electron-donating C–Si bond in the transition state that prefers SiH_3-inward rotation.

Notably, the more sterically demanding silyl group[16] prefers inward rotation in the reaction of **1e**. The total IBE (0.1463 a.u.) at the transition state between the bonds of the inward rotating silyl group and the C–H bond on the other side is more repulsive than that (IBE = 0.1129 a.u.) between the bonds of the inward rotating methyl group and the C–H bond. The steric bulkiness of the substituents contributes less to the reaction of **1e** than geminal bond participation.

We have demonstrated that geminal bond participation is general and common for pericyclic reactions. Further application of this theory to other reactions is currently underway in our laboratory.

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