

Geminal Bond Participation and Reactivities of *Z*- vs *E*-1-Substituted Butadienes in the Diels–Alder Reactions

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A bond model for the transition states of organic reactions was proposed to investigate the interactions of bonds at the transition states. The application to the Diels–Alder reaction between butadiene and ethylene disclosed the significant participation of geminal σ bonds at the reacting centers of the diene. It was found that the electron delocalization from the geminal σ bonds at the *Z*-positions to the π bond in the dienophile is bonding while that from the σ bonds at the *E*-positions is antibonding. The finding led to the prediction that electron-donating σ bonds at the *Z*-positions should enhance the reactivity more than those at the *E*-positions. The prediction of the relative reactivities of *Z*- vs *E*-1-substituted butadienes was confirmed by the calculated activation energies of the reactions.

Introduction

Chemists have developed the concept of the chemical bond to understand and predict chemical phenomena. Recently, we proposed a bond model to analyze the electronic structures of molecules.^{1–5} This bond model for molecules has been successfully applied to shed new light on molecular properties. We disclosed cyclic interactions of the bond orbitals in acyclic conjugated molecules to advance the orbital phase theory.^{1,2} The delocalization of σ -electrons between the geminal bonds was proposed to play a significant role in relaxing the strain of small ring molecules.^{3–5} The geminal delocalization was suggested to contribute to the molecular conformations.⁶

The successful applications of the bond model to the molecules turned our attention to the transition states of chemical reactions. The electronic structure of the transition states is a key factor for understanding and designing chemical reactions. Both geometrical and electronic structures of the transition states are readily obtained by molecular orbital calculations. We can analyze the electronic structure of the transition states in terms of the bond interactions, on the assumption that the bonds to be broken and formed at the transition states are similarly treated. In this paper, we propose a bond model for the transition states, disclose the signifi-

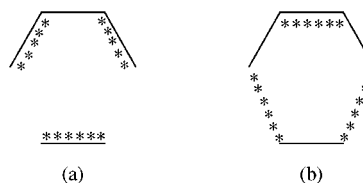
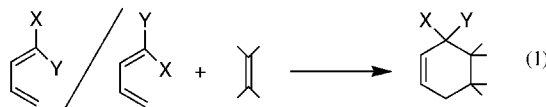


Figure 1. Bond models for the transition states of the Diels–Alder reactions: (a) reactant-like; (b) product-like.

cant participation of the geminal σ bonds at the reacting centers in the Diels–Alder reactions, and predict and confirm the relative reactivities of *Z*- vs *E*-1-substituted butadienes in the Diels–Alder reactions (eq 1).



Bond Model for Transition States

At the transition states, some bonds are being broken while some other bonds are being formed. Early transition states are modeled by the reactant-like bond structure where bonds are supposed to exist as in the reactant molecules. For the Diels–Alder reaction between butadiene and ethylene, there are supposed to be two π bonds in the diene and one π bond in the dienophile as is shown by the lined asterisks in Figure 1a. Late transition states are represented by the product-like bond model. There are supposed to be one π bond and two σ bonds as in cyclohexene (Figure 1b).

The wave function Ψ for the electronic structure of the transition state is expanded into electron configurations (Figure 2):^{2,3}

$$\Psi = C_G \Phi_G + \sum C_T \Phi_T + \sum C_E \Phi_E + \dots \quad (2)$$

In the ground configuration (Φ_G), a pair of electrons occupies each bonding orbital of the bonds (each non-bonding orbital of unshared electron pairs). The interactions between the bond orbitals are accompanied by electron delocalization and polarization. The delocaliza-

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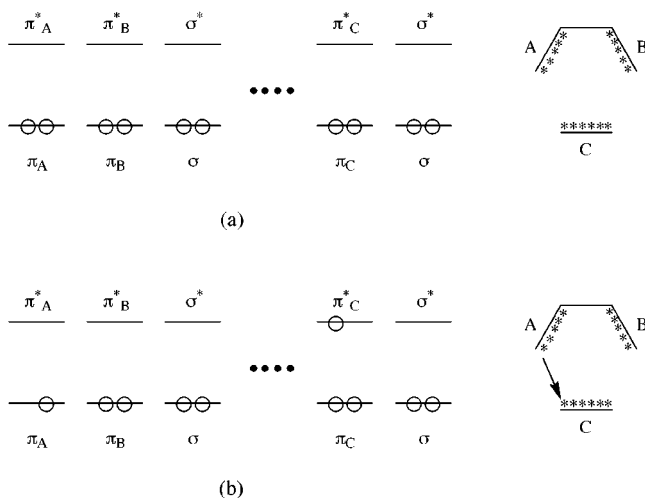


Figure 2. Bond model for the transition states: (a) the ground configuration; (b) electron-transferred configuration.

tion 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. The bonding and antibonding orbitals ϕ_i and ϕ_{i^*} of the i th bond are expressed by a linear combination of the hybrid atomic orbitals $\chi_{i\alpha}$ and $\chi_{i\beta}$ on the bonded atoms α and β :

$$\phi_i = c_{i\alpha} \chi_{i\alpha} + c_{i\beta} \chi_{i\beta} \quad (3)$$

$$\phi_{i^*} = c_{i\alpha}^* \chi_{i\alpha} + c_{i\beta}^* \chi_{i\beta} \quad (4)$$

A set of bond orbitals, i.e., hybrid orbitals and bond polarities $|c_{i\alpha}/c_{i\beta}|$ gives the coefficients of the configurations, C_G , C_T , and C_E . The bond orbitals (hybrid orbitals) were optimized⁷ to give the maximum value of the coefficient (C_G) of the ground configuration.

Whether the transition state is reactant-like (early) or product-like (late) is determined by the C_G^2 value, a measure of the contribution from the electronic structure Φ_G without any bond interactions. The transition state is early when the C_G^2 value of the reactant-like bond structure is greater than that of the product-like bond structure (*vice versa*). The bond interactions were investigated on the basis of the reactant-like bond structure for the early transition states or on the basis of the product-like bond structure for the late transition states.

(7) Schmidt orthogonalization of atomic basis functions on each atom gives a set of orthonormal atomic orbitals, $a_1, a_2, \dots, a_i, a_j, \dots, a_n$. A pair of the orthonormal orbitals, a_i and a_j on the atom is transformed (hybridized) by an 2×2 orthogonal matrix into a'_i and a'_j to give a new set of orthonormal atomic orbitals ($a_1, a_2, \dots, a'_i, a'_j, \dots, a_n$).

$$\begin{bmatrix} a'_i \\ a'_j \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} a_i \\ a_j \end{bmatrix}$$

The bond (bonding and antibonding) orbitals of each bond were obtained by the diagonalization of the 2×2 Fock matrix on the basis of the hybrid orbitals. Each lone pair orbital is represented by a hybrid orbital. The remaining hybrid orbitals are vacant orbitals. The successive rehybridizations by the 2×2 orthogonal matrix followed by the Fock matrix diagonalization for the bond orbitals were carried out to meet the condition (or to give the maximum value of C_G as described in the text).

Table 1. Interbond Energies (au) and Interbond Populations at the Transition State of the Diels–Alder Reaction between Butadiene and Ethylene

interactions	IBE _{ij}	IBP _{ij}
$\pi_{C_1-C_2}-\pi^*_{C_5-C_6}$	-0.7238	0.1007
$\pi_{C_5-C_6}-\pi^*_{C_1-C_2}$	-0.3861	0.0545
$\pi_{C_1-C_2}-\pi^*_{C_3-C_4}$	-0.6787	0.0998
$\sigma_{C_1-C_2}-\pi^*_{C_5-C_6}$	-0.0537	0.0075
$\sigma_{C_1-H_E}-\pi^*_{C_5-C_6}$	0.0227	-0.0034
$\pi_{C_5-C_6}-\sigma^*_{C_1-H_Z}$	-0.0125	0.0014
$\pi_{C_5-C_6}-\sigma^*_{C_1-H_E}$	-0.0015	0.0002

To estimate the interaction of the bond orbitals, ϕ_i and ϕ_j , we calculated the interbond population $IBP(i,j)$ ^{3,4} and the interbond energy $IBE(i,j)$.⁵

$$IBP(i,j) = 2P_{ij}S_{ij} \quad (5)$$

$$IBE(i,j) = P_{ij}(H_{ij} + F_{ij}) \quad (6)$$

where P_{ij} , F_{ij} , H_{ij} , and S_{ij} are the elements of the density, Fock, core Hamiltonian, and overlap matrixes, respectively.

Results and Discussion

Bond Interactions at the Transition State. We investigated the bond interactions at the transition state of the prototype of the Diels–Alder reaction between butadiene and ethylene.⁸ The C_G^2 values of the reactant- and product-like bond models are 2.189 and 1.380, respectively.¹² The transition state is close to the reactants rather than the product. The transition state is early. The reactant-like bond model was employed for the investigation of the bond interactions at the transition state.

The interbond energies and populations (Table 1) indicated that the interactions between the π orbitals of the diene and the π^* orbital of the dienophile (IBE =

(8) The bond interaction was analyzed at the 6-31G* level by our original program. The geometry of the transition state was optimized by *ab initio* molecular orbital calculation at the same level.⁹

(9) The geometries and energies were obtained by molecular orbital and density functional theory calculations at the RHF/6-31G¹⁰ and B3LYP/6-31G* levels of theory using GAUSSIAN 94¹¹ program. All geometries examined here were optimized by the gradient methods and checked by the frequency calculations using analytical second derivatives.

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(12) It may be surprising that the C_G values are greater than the unity. This results from some negative cross terms ($\int C_i C_j \phi_i \phi_j d\tau$) in $\int \Psi^2 d\tau$ of considerable magnitude. For methane, the sum of the cross terms of the ground configuration (Φ_G) with the electron-transferred configurations (Φ_T) for the electron delocalization between the C–H bonds is -0.389. The sum of the remaining cross terms with Φ_G is -0.278. In fact, The C_G^2 value of methane is 1.810.

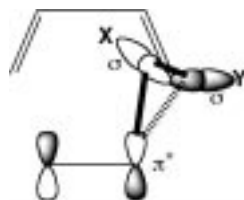


Figure 3. Cyclic orbital interaction and orbital phase properties in the geminal bond participation.

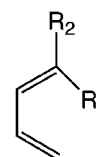
-0.7238 , $IBP = 0.1007$) most stabilize the transition state, as was expected from the frontier molecular orbital theory. The stabilizing interaction is greater than the intramolecular delocalization between the π bonds in the diene ($IBE = -0.6787$, $IBP = 0.0998$). The stabilization due to the reverse delocalization of π electrons from the dienophile to the diene is relatively low ($IBE = -0.3861$, $IBP = 0.0545$), in accordance with the usual observations that the diene is an electron donor in the Diels–Alder reactions.

A surprising difference was found in the σ electron delocalization from the C–H bonds geminal to the reacting π bonds in the diene to the π bond in the dienophile. The signs of the IBE and IBP values show that the delocalization from the σ_{C-HZ} orbital inside the six-membered ring of the transition structure to the π^* orbital of the dienophile is bonding (-0.0537 , 0.0075) as usual while that from the outside σ_{C-HE} orbital is antibonding (0.0227 , -0.0034). The absolute IBE and IBP values show that the bonding $\sigma_{C-HZ} - \pi^*$ interaction is greater than the antibonding $\sigma_{C-HE} - \pi^*$ interaction. The reverse delocalizations from the π bond of dienophile to the σ_{C-HZ} and σ_{C-HE} bonds of the diene occur to a less extent ($IBE = -0.0125$, -0.0015). The difference is less appreciable.

The antibonding delocalization is abnormal.^{3–5} The anomaly results from the orbital phase properties. The electron delocalizations from the σ bonds involve the interactions of the σ_{C-H} orbitals with the π^* orbital of dienophile. The σ bonds are geminal to each other and the interaction of the σ bonds is strong. The cyclic interaction occurs significantly among the two σ_{C-H} orbitals and the π^* orbital (Figure 3). Cyclic orbital interactions are controlled by the orbital phase continuity conditions:¹ (1) electron donating 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 promotes the electron delocalization. By applying the conditions to the cyclic interaction of the donating σ_{C-H} orbitals and the accepting π^* orbital, we found that the orbital phase is discontinuous. The delocalizations from the σ_{C-H} bonds to the π bond do not enhance each other. The interaction between the σ orbitals is intramolecular and strong as the Fock matrix element $|F_{ij}|$ ($=0.215$ au) showed. The σ_{C-HZ} orbital is spatially closer to the π^* orbital of dienophile than is the σ_{C-HE} orbital. The $\sigma_{C-HZ} - \pi^*$ overlap integral (0.102) is greater than the $\sigma_{C-HE} - \pi^*$ one (0.080). The $\sigma_{C-HZ} - \pi^*$ Fock matrix element (0.115 au) is greater than the $\sigma_{C-HE} - \pi^*$ one (0.098 au). Therefore the σ_{C-HZ} orbital prefers the in-phase combination with the π^* orbital or the bonding delocalization. This results in the antibonding $\sigma_{C-HE} \rightarrow \pi^*$ delocalization.

Reactivities of *Z*- vs *E*-1-Butadienes. The analysis of the electronic structure of the transition state in the

Chart 1



1E, $R_1=H$, $R_2=CH_3$	6E, $R_1=NH_2$, $R_2=F$	11E, $R_1=CH_3$, $R_2=SiH_3$
1Z, $R_1=CH_3$, $R_2=H$	6Z, $R_1=F$, $R_2=NH_2$	11Z, $R_1=SiH_3$, $R_2=CH_3$
2E, $R_1=H$, $R_2=NH_2$	7E, $R_1=OH$, $R_2=F$	12E, $R_1=NH_2$, $R_2=PH_2$
2Z, $R_1=NH_2$, $R_2=H$	7Z, $R_1=F$, $R_2=OH$	12Z, $R_1=PH_2$, $R_2=NH_2$
3E, $R_1=H$, $R_2=OH$	8E, $R_1=F$, $R_2=SiH_3$	13E, $R_1=OH$, $R_2=SH$
3Z, $R_1=OH$, $R_2=H$	8Z, $R_1=SiH_3$, $R_2=F$	13Z, $R_1=SH$, $R_2=OH$
4E, $R_1=H$, $R_2=F$	9E, $R_1=F$, $R_2=PH_2$	14E, $R_1=F$, $R_2=Cl$
4Z, $R_1=F$, $R_2=H$	9Z, $R_1=PH_2$, $R_2=F$	14Z, $R_1=Cl$, $R_2=F$
5E, $R_1=CH_3$, $R_2=F$	10E, $R_1=F$, $R_2=SH$	
5Z, $R_1=F$, $R_2=CH_3$	10Z, $R_1=SH$, $R_2=F$	

prototype of the Diels–Alder reactions revealed the interesting participation of the geminal σ_{C-H} bonds at the reacting centers in the diene. Electrons delocalize in a bonding manner as usual from the σ_{C-HZ} bonds to the π bond of dienophile while the delocalization from the σ_{C-HE} bonds is antibonding. This led to a prediction of the relative reactivities of *E*- vs *Z*-1-substituted dienes. Dienes with relatively electropositive atom or substituent at the *Z*-position are more reactive than those at the *E*-position. The high energy of the σ orbital facilitates the interaction with the π^* orbital of the dienophile. Furthermore, the σ orbital is polarized toward the carbon atom to enhance the interaction with the π^* orbital due to the increase in the orbital overlap.

The hydrogen atom is more electropositive than methyl carbon, amino nitrogen, hydroxy oxygen, and fluorine atoms. The *E*-isomers of the dienes **1–4** (see Chart 1) substituted by these groups at the 1-position have an electropositive C–H bond at the *Z*-position and then were predicted to be more reactive than the *Z*-isomers. This was in agreement with the calculated activation energies of the reactions with ethylene as a dienophile (Table 2).⁹ In fact, *E*-1-methyl- (Scheme 1) and methoxybutadiene were observed to be more reactive than the *Z*-isomers.¹³ However, the relative reactivities can be accounted for simply by the steric congestion at the transition state of the reactions of the *Z*-isomers.

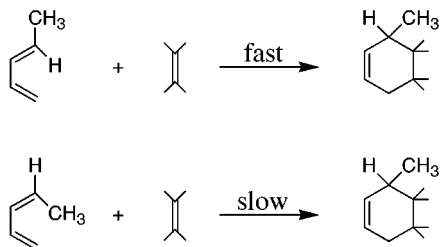
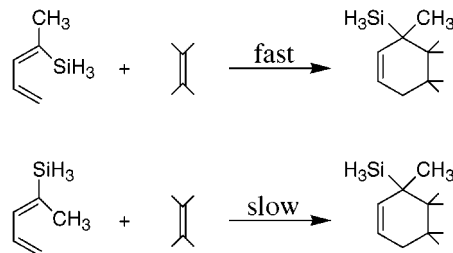
The dienes **1–4** have small electropositive hydrogens and large electronegative atom substituents. The geminal bond participation and the steric congestion lead to the same prediction of the relative reactivities of the *E*- vs *Z*-dienes. A small electronegative atom or substituent and large electropositive atom or substituent are required to demonstrate the significance of the geminal bond participation relative to the steric congestion. The fluorine atom is the most electronegative atom and sterically smaller than the relatively electropositive methyl, the amino, and the hydroxy groups. If the geminal bond participation is predominant, the *E*-isomer with the large groups at the *Z*-positions should be more reactive. We calculated the relative reactivities of the fluoro dienes **5–7** substituted by the methyl, amino, and hydroxy groups. The *E*-isomer of 1-amino-1-fluorobutadiene (**6**) was calculated to be more reactive than *Z*-isomer. This supported the predominance of the geminal

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Table 2. Activation Energies of the Diels–Alder Reactions of E- and Z-1-Substituted Butadienes with Ethylene

dienes	$\Delta E_E^{\ddagger a,b}$	$\Delta E_Z^{\ddagger a,b}$	$\delta\Delta E^{\ddagger b,c}$	dienes	$\Delta E_E^{\ddagger a,b}$	$\Delta E_Z^{\ddagger a,b}$	$\delta\Delta E^{\ddagger b,c}$
1	46.3 (23.7)	52.5 (29.2)	6.2 (5.5)	8	50.5 (26.9)	48.7 (25.4)	-1.8 (-1.5)
2	46.0 (23.7)	52.1 (30.0)	6.1 (6.3)	9	50.1 (26.6)	48.8 (25.7)	-1.3 (-0.9)
3	45.8 (23.5)	50.2 (27.6)	4.4 (4.1)	10	48.9 (26.0)	49.4 (26.4)	0.5 (0.4)
4	44.0 (21.8)	48.0 (24.8)	4.0 (3.0)	11	54.9 (31.3)	51.4 (28.5)	-3.5 (-2.8)
5	51.0 (27.6)	50.1 (26.8)	-0.9 (-0.8)	12	53.6 (31.0)	50.9 (27.8)	-2.7 (-3.2)
6	48.1 (25.6)	50.3 (27.6)	2.2 (2.0)	13	50.9 (27.4)	50.7 (27.1)	-0.2 (-0.3)
7	48.3 (24.6)	48.1 (24.8)	-0.2 (0.2)	14	47.2 (24.2)	49.6 (26.3)	2.4 (2.1)

^a Activation energies (kcal/mol) based on the *s-trans* dienes of the most stable rotamer. ^b RHF/6-31G* calculations with B3LYP/6-31G* calculations in parentheses. ^c $\delta\Delta E^{\ddagger} = \Delta E_Z^{\ddagger} - \Delta E_E^{\ddagger}$.

Scheme 1**Scheme 2**

bond participation over the steric congestion. However, the calculated relative reactivities of 4-fluoro-1,3-pentadiene (**5**) and 1-fluoro-1-hydroxybutadiene (**7**) are not in agreement with the predominance of the geminal bond participation. These results suggested that the methyl group in **5** should be still too bulky and that the electron-donating capability of the C–OH bond in **7** should be too low.

To demonstrate unequivocal evidence for the significance of the geminal bond participation, we designed the dienes **8–10** substituted at the 1-position by more electropositive groups, i.e., SiH₃, PH₂, and SH in place of CH₃, NH₂, and OH. The fluorine atom is similarly the counterpart. The calculated activation energies of the reactions of 1-fluoro-1-silylbutadiene (**8**) and 1-fluoro-1-phosphinobutadiene (**9**) showed that the *Z*-isomers, which react via the sterically congested transition states, are more reactive than the *E*-isomers. These results supported the predominance of the geminal bond participation. The opposite should have resulted from the steric hindrance. The *Z*-isomer of 1-fluoro-1-mercaptobutadiene (**10**) was calculated to be less reactive than the *E*-isomer. The disagreement with the geminal bond participation can be interpreted in terms of the low electron-donating capability of the σ_{C-S} bond.

For further examination of the geminal bond participation we compared the relative reactivities of the *E*- vs *Z*-isomers **11–14** with the substituent atoms in the same group of the periodic table. The second-row element substituents at the *Z*-position were predicted from the geminal bond participation to enhance the reactivity. The calculated reactivities of the *E*- vs *Z*-isomers of 2-silyl-2,4-pentadiene (**11**), 1-amino-1-phosphinobutadiene (**12**), and 1-hydroxy-1-mercaptobutadiene (**13**) confirmed the prediction. However, this is not the case with 1-chloro-1-fluorobutadiene (**14**), due to the small difference between F and Cl in the electronegativity. One of the most promising reactions to be examined in order to provide unambiguous experimental evidence for the geminal bond participation is illustrated in Scheme 2.

It is preferable to take the effects of electron correlation. We calculated the activation energies at the

Table 3. HOMO Energies (au)^a of *s-cis*-1-Substituted Butadienes

dienes	<i>E</i> -isomers	<i>Z</i> -isomers	dienes	<i>E</i> -isomers	<i>Z</i> -isomers
1	-0.3195	-0.3247	8	-0.3257	-0.3436
2	-0.2898	-0.2913	9	-0.3291	-0.3437
3	-0.3127	-0.2970	10	-0.3223	-0.3275
4	-0.3376	-0.3238	11	-0.3309	-0.3329
5	-0.3300	-0.3128	12	-0.3025	-0.2957
6	-0.3014	-0.2901	13	-0.3088	-0.3781
7	-0.3040	-0.3059	14	-0.3318	-0.3416

^a RHF/6-31G* calculations.

B3LYP/6-31G* level,⁹ which were reported¹⁴ to give the values matching the experimental results closely. The calculated reactivities of the *E*- vs *Z*-substituted butadienes were in good agreement with the RHF ones while the sole disagreement about **7** is not appreciable.

In their pioneering work, Sauer, Sustmann, and their colleagues¹³ proposed that the relative reactivities of the *E*- vs *Z*-1-substituted butadienes should be controlled by the HOMO energies of the *s-cis*-1-substituted butadienes. The HOMO energies (Table 3) account for the relative reactivities of the dienes **1**, **2**, **5**, **10**, **12**, and **14**. The relative reactivities of most of the dienes examined here cannot be explained by the HOMO energies.

Conclusion

We proposed a bond model for the transition states of organic reactions¹⁵ to investigate the bond interactions at the transition states and applied it to the prototype of the Diels–Alder reaction between butadiene and ethylene. The analysis of the electronic structures of the transition state disclosed the significant participation of the geminal σ bonds at the reacting centers in the diene. The electron delocalization to the π bond in the dienophile

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(15) Rastelli and co-workers proposed a method for analyzing the interactions of molecular subsystems (e.g. σ -bonds, π -systems, lone pairs, molecular fragments) at the transition states: (a) Rastelli, A.; Bagatti, M.; Ori, A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 29. (b) Rastelli, A.; Bagatti, M. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3913. (c) Rastelli, A.; Bagatti, M.; Gandolfi, R.; Burdisso, M. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1077. (d) Rastelli, A.; Bagatti, M.; Gandolfi, R. *J. Am. Chem. Soc.* **1995**, *117*, 4965.

from the geminal σ bonds at the *Z*-positions in the diene (at the pseudoaxial position of the six-membered ring of the transition structure) is bonding while that from the geminal bond at the *E*-positions or from the pseudoequatorial σ bonds is antibonding. The result led to the prediction that 1-substituted butadienes with a relatively electropositive atom or substituent at the *Z*-position are more reactive than those at the *E*-position. The effect of the geminal bond participation was confirmed by the calculated activation energies of the Diels–Alder reactions. The bond model for the transition state is useful.

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Supporting Information Available: Tables of data for the optimized transition structures and total energies (28 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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