Asymmetry in Symmetric Cycloadditions

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The Woodward−Hoffmann (W−H) rule and the Fukui's frontier-orbital theory (FMO) were assessed for the title reactions. Diels−Alder reactions of the normal electron demand were investigated with density functional theory calculations. The C_s symmetry is usually conserved in [4 + 2] reactions between 1,3-dienes and olefins of symmetric geometries. However, those between very nucleophilic dienes and olefins substituted by four electron-withdrawing groups take C_1-symmetry paths. This result is in contrast to the postulate of the W−H rule that the C_s symmetry should be conserved in "symmetry-allowed" paths. A [6 + 4] cycloaddition between tropone and cyclopentadiene was found not to take the C_s-symmetry path despite the symmetry-allowed reaction. Configuration analysis was carried out and gave the magnitude of various orbital interactions. The three-body orbital mixing leads to the symmetry lowering of reaction paths. FMO explains reasonably the anomaly of the cycloadditions of non-W−H rule in strong donor and acceptor reactants and in reactants with nearly degenerate frontier orbitals.

I. Introduction

Pericyclic reactions are composed of cycloadditions, cheletropic additions and eliminations, sigmatropic rearrangements, and electrocyclizations.[1] Reactivities of those reactions have been reasonably explained by the Woodward−Hoffmann (W−H) rule[2] and the Fukui's frontier-orbital theory (FMO).[3] The W−H rule is a symmetry conservation rule. A symmetry should be retained throughout reaction paths for "symmetry-allowed" reactions. The rule is in line with the general idea that needless geometric distortions in the course of reactions should be avoided as much as possible to take the minimum-energy trajectories. Reactions between conjugated systems with totally $4n$ π electrons belong to "symmetry-forbidden" paths and those with $(4n + 2)$ π electrons to "symmetry-allowed" paths. FMO is based on a perturbative treatment of two reactants and is under kinetic control.

Both the W−H rule and FMO explain that Diels−Alder reactions proceed readily as shown in Scheme 1. In Scheme 1a, electron configurations of reactants (ethylene and butadiene), S2 S2 A2, are the same as those of the product, cyclohexene. S2 means that a symmetric (S) orbital is occupied by two electrons. The occupied orbitals are correctly correlated, and accordingly, the C_s-symmetry conserved cycloaddition path is symmetry allowed. In Scheme 1b, both homo → LUMO and HOMO → lumo charge-transfer (CT) interactions are "in-phase" and take place effectively. The C_s-symmetry conserved path should be taken to maximize those interactions.

A reaction between tropone and cyclopentadiene has been extensively studied.[4] The [6 + 4] π electron reacting system is symmetry-allowed and should take the C_s-symmetry path. Both the W−H rule and FMO explain the path in Scheme 2. In Scheme 2a, electron configurations of reactants (tropone and cyclopentadiene), S2 S2 A2 S2 S2 A2, are the same as those of the cycloadduct (symmetry-allowed). In Scheme 2b, HOMO → lumo and homo → LUMO CT interactions are in-phase and take place effectively. The C_s-symmetry conserved path is favorable.

Despite success of the W−H rule and FMO, there are unclear points in them. The W−H rule describes regions of both kinetic and thermodynamic controls. The region cross description is questionable. FMO describes the perturbative region, and the description is not necessarily extended to transition states (TSs). To remove the uncertainty, Fukui proposed a theory of intrinsic reaction coordinate (IRC)[5] and attempted to connect analytically the perturbative region with TS. Recent progress of IRC calculations[6] makes it possible to trace the symmetry-allowed paths in realistic reacting systems.

In this work, paths of various Diels−Alder reactions and the tropone−cyclopentadiene reaction were investigated. It was found that the symmetry conservation rule is violated in some reactions. The one-center interaction is dominated over the in-phase CT and back CT interactions. The orbital mixing causes the violation.

II. Method of Calculations

Transition-state (TS) structures of Diels−Alder reactions and the tropone−cyclopentadiene reaction were determined with the B3LYP/6-31G* method.[7] The self-consistent reaction field (SCRF) = dipole solvent effect[8] was taken into account with the standard solvent, methylene chloride CH_2Cl_2 (dielectric constant = 9.08). After TS geometries were optimized, vibrational analyses were carried out to check whether they are correctly at saddle points. IRC calculations[6] were also performed

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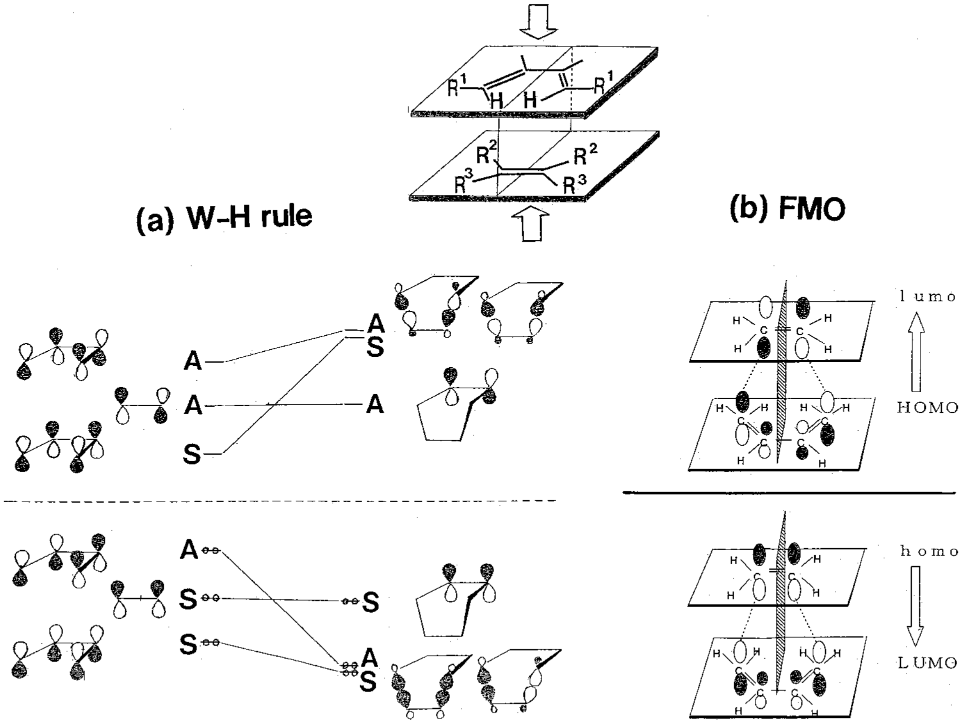
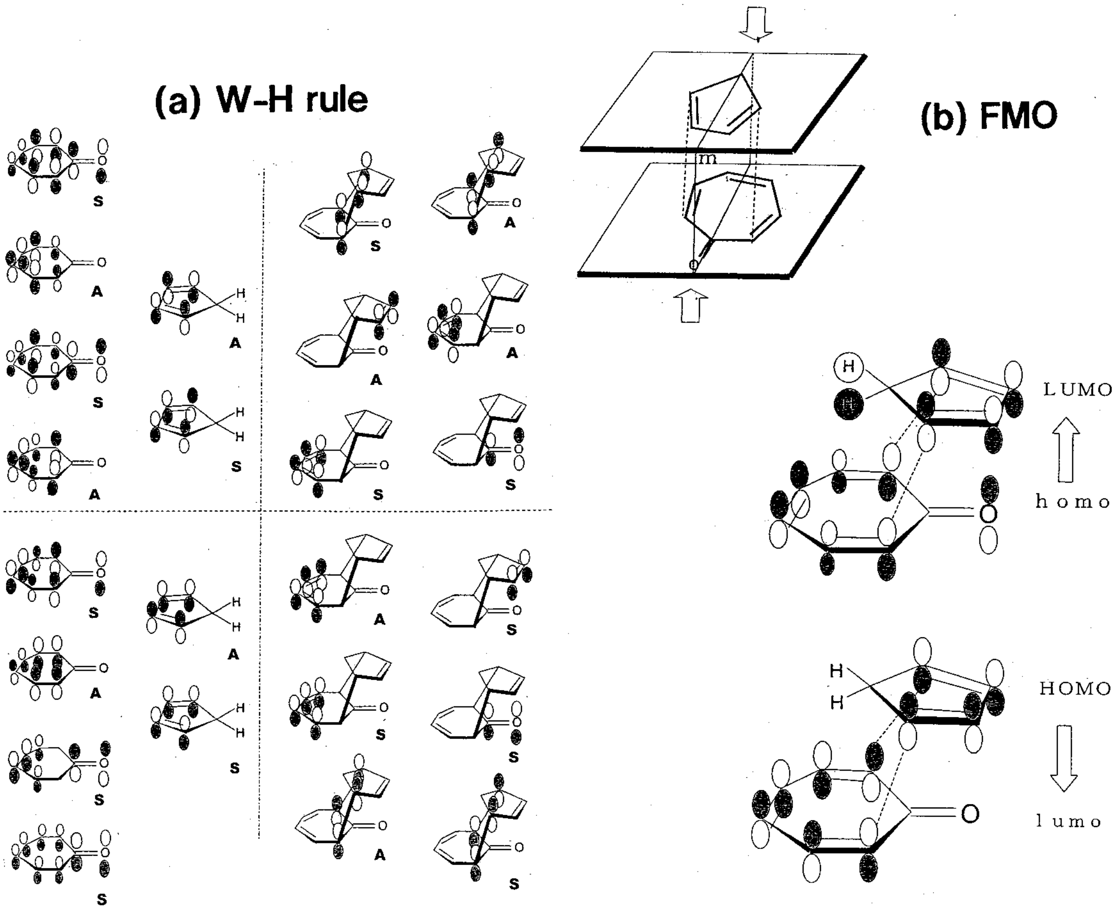
SCHEME 1: Two Ways of Explaining Ready Occurrence of Diels−Alder Reactions[a]



[a] S and A denote symmetric and antisymmetric orbitals with respect to the mirror plane.

SCHEME 2: Two Ways of Explaining Ready Occurrence of the Tropone−Cyclopentadiene Cycloaddition.



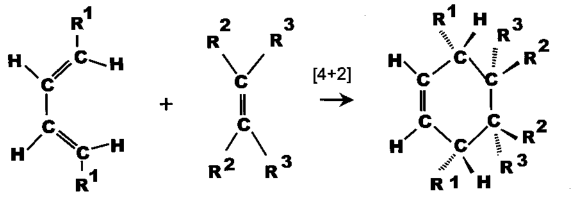
to examine the change of geometries along the reaction path. Those calculations were made using the Gaussian 98 program package.[9]

To investigate the extent of CT and polarization interactions, configuration analysis[10] was carried out for TS geometries. All of the calculations were made on the Compaq ES40 computer

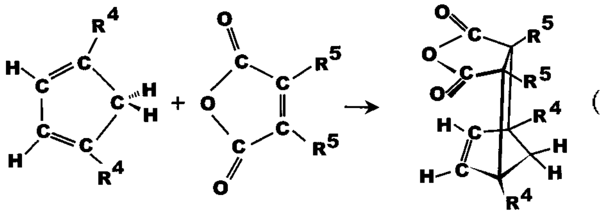
at Information Processing Centers (Nara University of Education and Nara University).

III. Results of TS and IRC Calculations

Diels−Alder reactions are enhanced by the combination of nucleophilic dienes and electrophilic olefins. According to the normal electron demand,[11] TS structures of those reactions were examined in eqs 1 and 2.



(1)



(2)

The substituent R1 in eq 1 or R4 in eq 2 is a methoxy group, −OMe. R2, R3, or R5 is a cyano group. Equation 1 shows a reaction between a linear diene and a linear olefin. Equation 2 shows that between cyclic reactants, substituted cyclopentadiene and maleic anhydride.

Figure 1 exhibits the reactions in eq 1. In accordance with the symmetry-allowed condition, TS geometries of parts A, B, and C have C_s symmetry (with respective sole imaginary frequencies, $\upsilon^{\ddagger}$). But, that of part D was found to be asymmetric! In part D, one bond-forming C···C distance is 1.926 Å and the other is 2.564 Å. The C_s-symmetry-constrained TS geometry was also calculated but has two imaginary frequencies, $\upsilon^{\ddagger} = 377.62$ and $\upsilon^{\ddagger} = 81.13$ icm^{-1} (not a real TS). The combination between a highly nucleophilic diene, 1,4-dimethoxy butadiene, and a highly electrophilic olefin, TCNE, has broken the W−H rule. Instead of TCNE, tetrafluoroethene (R2 = R3 = F) was employed as a tetra-substituted olefin, which reacts with 1,4-dimethoxy butadiene (R1= OCH$_3$). The B3LYP/6-31G* TS structure was calculated to have C_s-symmetry with two C···C distances, 2.259 Å, and a sole imaginary $\upsilon^{\ddagger} = 611.89$ icm^{-1}. Thus, the tetra substitution to olefin does not necessarily lead to a symmetry lowering of [4 + 2] cycloaddition paths.

Figure 2 shows endo-oriented reactions in eq 2. TS geometries of parts A and B have normal C_s symmetries (with respective sole imaginary frequencies). However, that of part C is asymmetric. As in Figure 1, the reaction between a highly nucleophilic diene and a highly electrophilic olefin has given the path of non-W−H rule. Scheme 1 must be reconsidered in view of the substituent effect in Figures 1 and 2. To this consideration, geometric changes along IRC paths would be contributive. Figure 3 shows them for the reaction in Figure 2C. Noteworthy is the almost symmetric geometry at the initial stage of the reaction, which is in contrast to the asymmetric one at the TS.

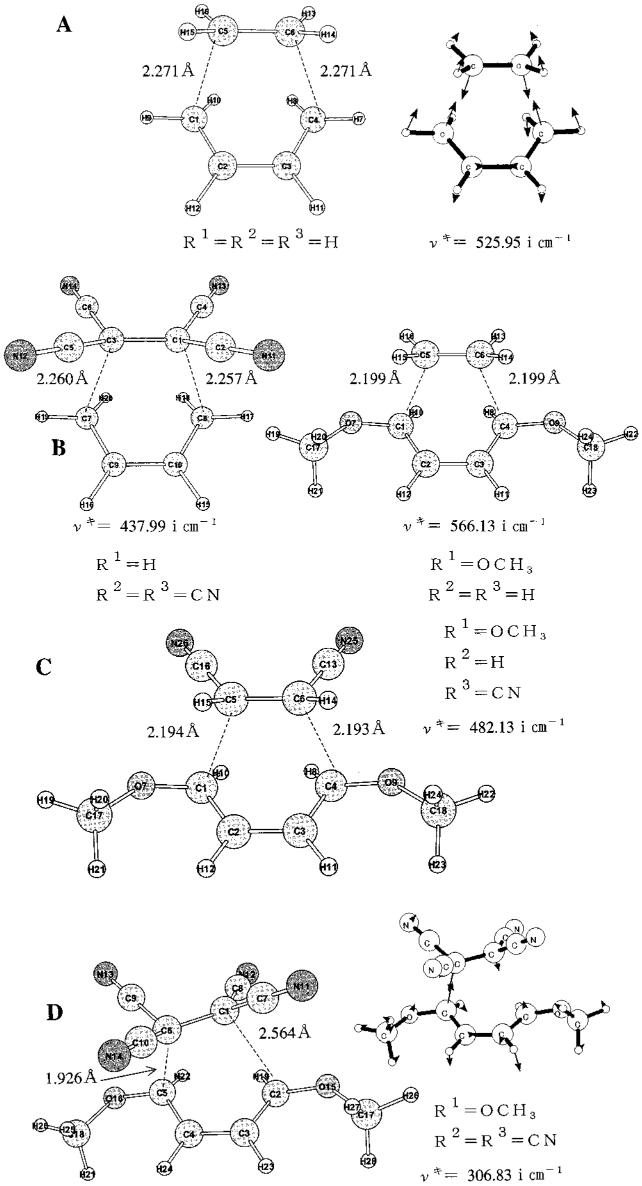
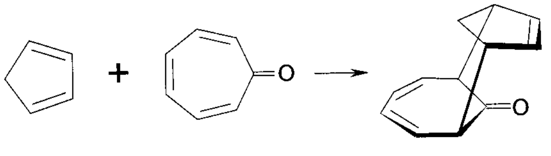


Figure 1. Transition-state (TS) structures of Diels−Alder reactions between linear dienes and olefins in eq 1. Their sole imaginary frequencies are shown, and for structures in parts A and D, the corresponding reaction-coordinate vectors are sketched. Geometries of structures in parts A, B, and C were found to have C_s symmetry.

The tropone−cyclopentadiene [6 + 4] cycloaddition (eq 3) is examined.



(3)

Figure 4 shows results of IRC calculations. Despite the prediction in Scheme 2a, the cycloaddition proceeds along symmetric ($S = -7.65$ bohr amu$^{1/2}$) → asymmetric (TS) → symmetric ($S = +7.83$ bohr amu$^{1/2}$) geometric changes. It is surprising that the famous reaction in eq 3 is not a combination of strong donor and acceptor and does not follow the W−H rule.

Asymmetric cycloaddition paths might compete with one-center addition paths. While the latter paths leading to singlet biradical intermediates were studied,[12] those to zwitterionic ones

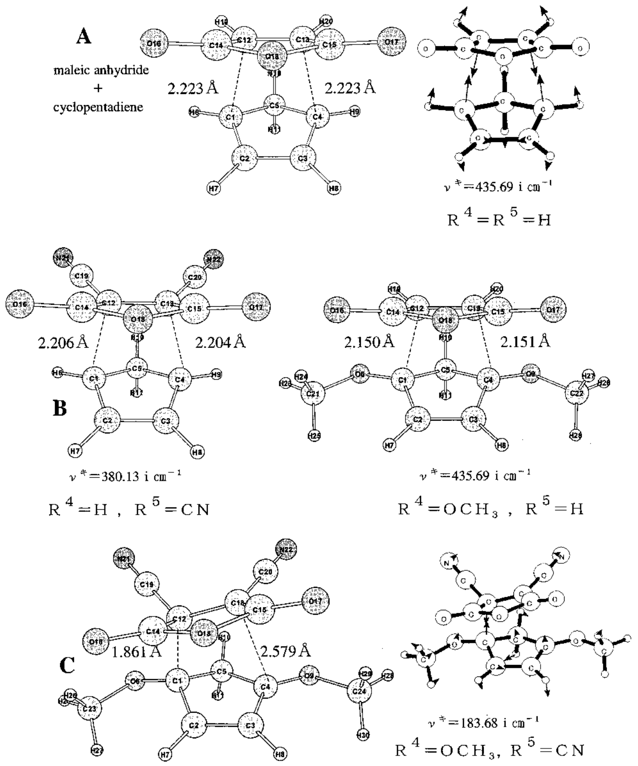
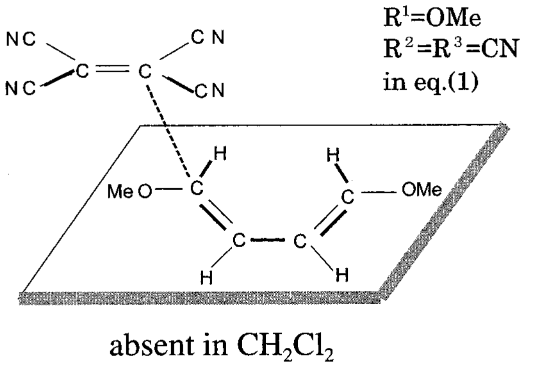


Figure 2. Endo-oriented TS structures of Diels−Alder reactions between cyclic dienes and cyclic olefins in eq 2. The parent system (R4 = R5 = H) is composed of cyclopentadiene and maleic anhydride. Geometries of structures in parts A and B were found to have C_s symmetry, while that of the structure in part C was found to have C_1 symmetry.

are rather few.[13] The combination of a strong donor diene and a strong acceptor olefin is expected to make the one-center addition more favorable. For the reactants with R1 = OMe and R2 = R3 = CN in eq 1, the one-center path has been examined, which is comparable to the TS in Figure 1D.



However, a zwitterionic intermediate cannot be obtained under the condition, solvent = CH_2Cl_2. A more nucleophilic diene, 1,4-diamino-butadiene (R1 = NH_2 in eq 1), is employed, and its reaction with TCNE was investigated. Figure 5 exhibits cycloaddition and one-center addition paths. Noteworthy is the result that the one-center addition path is more favorable than the asymmetric [4 + 2] cycloaddition path. A zwitterionic intermediate is formed. This species may quench a third polar reactant or solvent (e.g., methanol). Otherwise, its intervention leads to stereochemical scrambling of the cyclohexene products.[14] Thus, the asymmetry in [4 + 2] cycloaddition paths may give the product distribution; formation of the stereospecific cyclohexene is not exclusive.

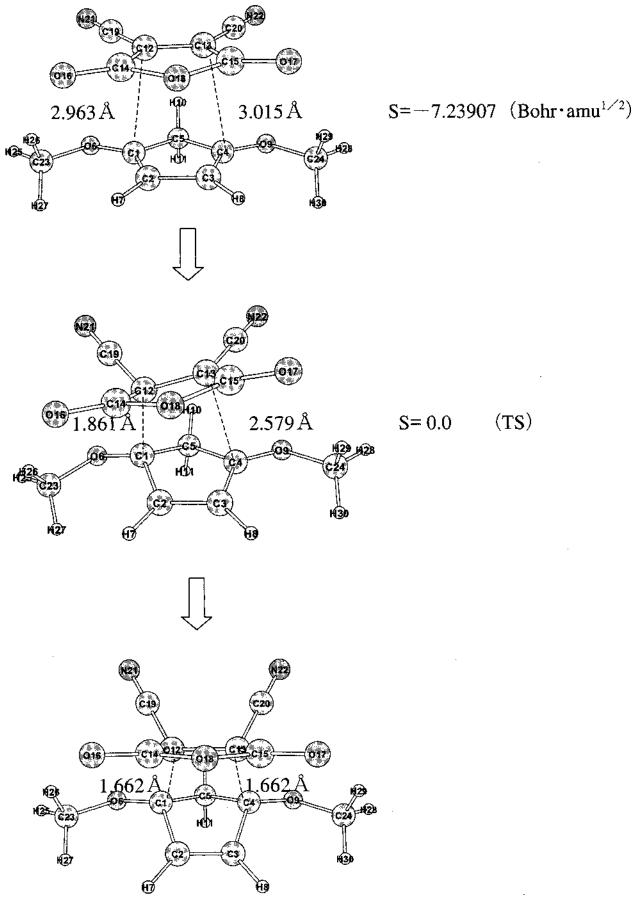


Figure 3. Geometric changes along the IRC of the reaction between 1,4-dimethoxy-1,3-cyclopentadiene and dicyano-maleic anhydride. The TS structure is the same as that in Figure 2C. At the later stage (after the TS), IRC calculations were diverged. By the use of the final point of the diverged IRC, the geometry optimization was performed. Its geometry (approximate IRC near the cycloadduct) is shown.

IV. Results of Configuration Analysis and Discussions of Orbital Interactions.

In eqs 1 and 2, combinations of the strong donor dienes and the strong acceptor olefins have given [4 + 2] cycloaddition paths that do not obey the W−H rule. In eq 3, even substituent-free reactants have given the [6 + 4] path with the C_s symmetry not conserved.

Figure 6 shows the energies of frontier and frontier-candidate orbitals. In Figure 6a, the MeO substitution to dienes raises naturally HOMO levels (by about 0.05 au). In Figure 6b, the cyano substitution to ethylene lowers lumo levels substantially, 0.320 au of ethylene → 0.162 au of dicyanoethylene → 0.064 au of TCNE. Noteworthy is the much smaller change of homo levels, −0.326 → −0.351 → −0.372 au. The same trend is shown in changes of lumo and homo levels of maleic anhydride and its dicyano substitute. The trend means that the HOMO−LUMO energy gap becomes very small by NC− substitution. That is, the cyano group enhances the homo → lumo excitation. The importance of the excitation in the interaction between a strong donor and a strong acceptor was already suggested.[15] The pseudoexcitation theory [15a] predicted generally that HOMO → LUMO and homo → lumo excitations contribute to the progress of reactions. In view of orbital energies in Figure 6, the homo → lumo excitation is more important than the HOMO → LUMO one for the system of 1,4-dimethoxy-butadiene and TCNE. Thus, the cooperation of the HOMO → lumo CT and

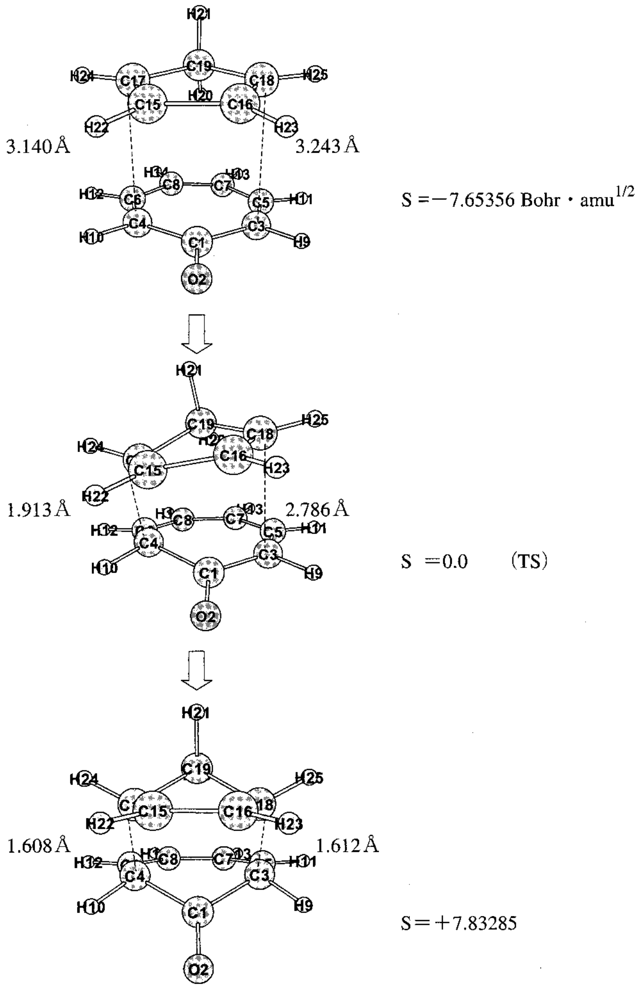
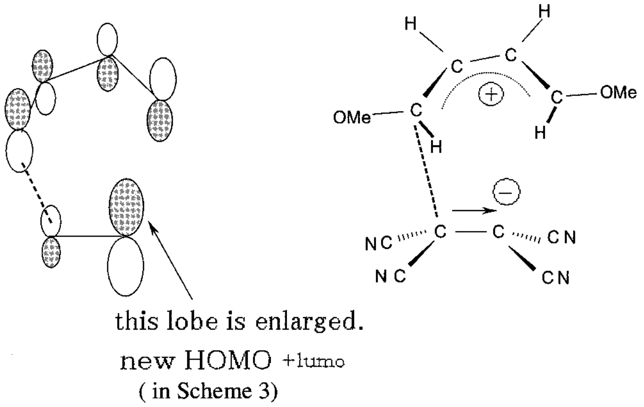


Figure 4. Geometric changes along the IRC of the reaction between tropone and cyclopentadiene in eq 3.

the homo → lumo excitation has given rise to the (HOMO − homo + lumo) three-body mixing.

To check weights of CT and excitation interactions, configuration analysis has been carried out. In Table 1, results for three reactions are displayed. For R1 = OMe and R2 = R3 = CN, those of C_s-constrained (not real TS) and real TSs are shown. In the parent (R1 = R2 = R3 = H) system, coefficients of HOMO → lumo and homo → LUMO are similar (0.278 14 and −0.271 73), which means that the system is neutral (not polarized) throughout the reaction course. As the substituents (MeO− and NC−) are introduced, HOMO → lumo interactions dominate over homo → LUMO ones according to the normal electron demand. The coefficients of the C_s TS and the real TS in the R1 = OCH3 and R2 = R3 = CN system are compared. The largest difference is that of homo → lumo.[16] The (C_s → C_1) symmetry lowering has made it possible to make the homo → lumo mixing [17] through diene orbitals, particularily, HOMO.

In Scheme 3, the mixing pattern of HOMO, homo, and lumo is shown. As shown in Figure 6, the homo level of TCNE is not as lowered. Through the (C_s → C_1) lowering, homo mixes well with HOMO. The level of "new HOMO" is raised relative to that of HOMO and is closer to that of lumo. The (new HOMO + lumo) interaction is larger than the (HOMO + lumo) one, which gives a very stabilized orbital, (new HOMO + lumo). In addition, this orbital may give the charge polarization along the olefin bond. Likewise, the (HOMO → LUMO) excitation enhances the polarization in the diene moiety.



The zwitterionic-like electronic distributions are subject to the solvation stabilization. Thus, the (C_s → C_1) symmetry

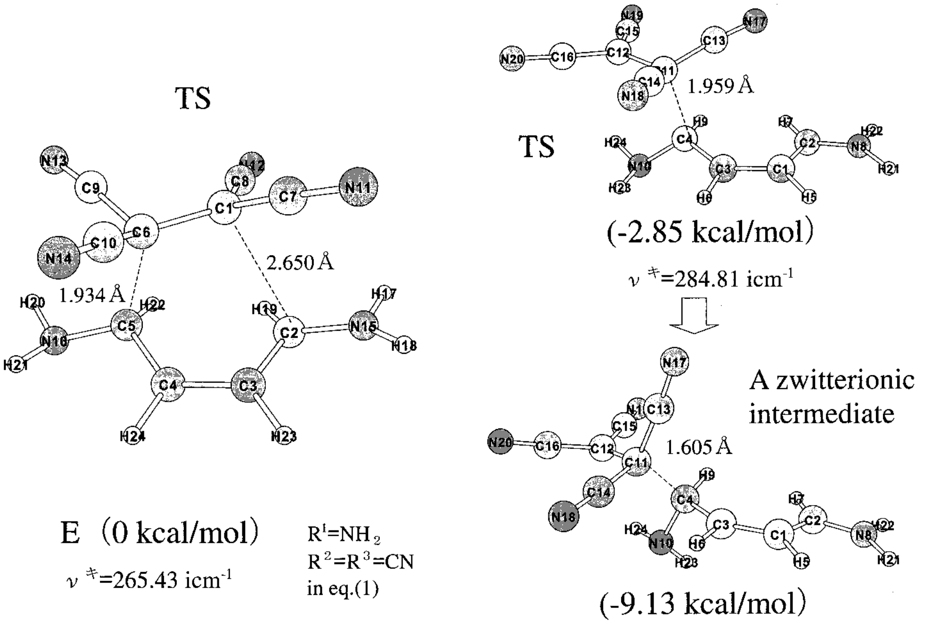


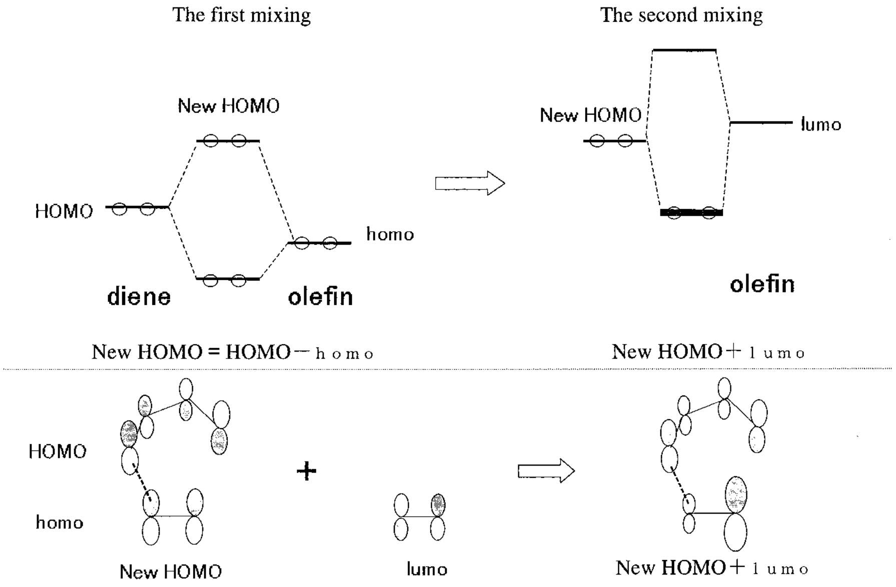
Figure 5. A reaction between TCNE (tetracyanoethylene) and 1,4-diamino-butadiene ($H_2N{-}CH{=}CH{-}CH{=}CH{-}NH_2$). In the left side, an asymmetric [4 + 2] cycloaddition TS is shown. In the right side, a one-center addition path leading to a zwitterionic intermediate is shown. Energies in parentheses are relative ones, and negative values stand for more stable systems. The solvent for SCRF calculations is dichloromethane (CH_2Cl_2).

TABLE 1: Coefficients of Configuration Analysis[a]

	reactants in eq 1[b]			
	butadiene + ethylene ($R^1 = R^2 = R^3 = H$)	butadiene + TCNE ($R^1 = H$ $R^2 = R^3 = CN$)	1,4-dimethoxybutadiene + TCNE (C_s TS) ($R^1 = OCH_3$, $R^2 = R^3 = CN$)	1,4-dimethoxybutadiene + TCNE (real TS) ($R^1 = OCH_3$, $R^2 = R^3 = CN$)
C_0	0.747 35	0.606 77	0.391 54	0.404 06
HOMO → lumo	0.278 14	−0.422 29	−0.409 72	−0.416 97
HOMO →→ lumo	0.050 77	0.144 59	0.210 84	0.211 87
homo → LUMO	−0.271 73	−0.185 08	−0.175 57	−0.155 90
homo → lumo	0	0	0	−0.072 07
HOMO → LUMO	0	0	0	0.058 92
HOMO − 1 → LUMO	−0.085 24	−0.079 17	−0.070 22	−0.060 75
HOMO → LUMO + 1	−0.057 37	−0.079 10	−0.089 68	0.073 63

[a] C_0 denotes adiabatic electron-configuration interaction. Capital-letter orbitals such as HOMO and LUMO belong to the diene and lowercase ones to the olefin. HOMO →→ LUMO means a doubly electron-transferred configuration. For electron-transferred configurations, the coefficients of more than 0.1 are displayed. For electron excitation configurations, those of more than 0.05 are shown. [b] Substituents are shown in parentheses.

SCHEME 3 The Double Mixing of Frontier Orbitals[a]



[a] The first mixing gives a destablized "new HOMO". New HOMO interacts more strongly than HOMO with lumo, which overcomes the first destabilization.

lowering converts the (HOMO + lumo) mixing to the (HOMO − homo + lumo) one. To ensure the three-body mixing, the lumo and HOMO levels should be low and high, respectively. Otherwise, the second mixing in Scheme 3 does not have merit to stabilize the system. The strong acceptor olefins and donor dienes are required to cause the symmetry-lowered addition path. At the initial stage of IRC, orbital interactions are weak, and the polarization ones (of the higher-order intermolecular overlaps[16]) are small. Only, the HOMO → lumo CT interaction controls the reaction path, which leads to the C_s symmetry.

The three-body mixing is in accord with the (homo → lumo) excitation in the "pseudoexcitation" theory.[15a] In the theory, the excitation is composed of two steps. The first is HOMO → lumo CT, and the second is the subsequent homo → HOMO back CT. Because the present three-body mixing describes the homo → lumo excitation via HOMO, the role of HOMO is common in the mixing and the pseudoexcitation.

In Figure 6, the cyclopentadiene HOMO (−0.260 au, antisymmetric "A") has an energy level similar to that of the tropone homo (−0.246 au, S). A three-body mixing (HOMO − homo + lumo), depicted in Scheme 4, may be brought about by the ($C_s \rightarrow C_1$) lowering.

In Table 2, coefficients of configuration analysis of C_s-constrained (not real) and real TSs are shown. Only the homo → lumo coefficient (0.050 98) of the real TS (at the middle of Figure 4) increases relative to that of the C_s-symmetry TS. The former contributes to the (HOMO − homo + lumo) three-body mixing. The other three-body mixing, HOMO + lumo + (lumo + 1), also works to stabilize the real TS. This mixing arises from CT, HOMO → lumo + 1 (0.02786) in Table 2, and has the same orbital reorganization at the reaction center as HOMO − homo + lumo. The role of HOMO + lumo + (lumo + 1) is understandable in the similar energy levels of tropone lumo (0.194 au) and lumo + 1 (0.220 au) in Figure 6b.

In a cheletropic addition reaction between butadiene and SO_2, the C_s symmtry was retained. On the other hand, a Lewis acid, BH_3, coordinated to SO_2 made a C_1-symmerty addition TS.[18] This anomaly was not analyzed and can be explained by the (HOMO + lumo + (lumo + 1)) three-body mixing. A S−O antibonding orbital (lumo + 1) is stabilized by the BH_3 coordination. BH_3 is coordinated in-plane to O=SO, and accordingly, lumo with the out-of-plane spatial extension is not as stabilized (the energy level not as lowered). On the other hand, lumo + 1 with the in-plane extension is stabilized by the coordination. Thus, the (HOMO + lumo + (lumo + 1)) three-body mixing is effective for the stabilization. The large-size lobe on the sulfur atom in lumo + 1 can overlap effectively with HOMO in the C_1-symmetry addition path. Because of the

SCHEME 4 In the Tropone−Cyclopentadiene Reaction, (HOMO + lumo) Single Mixing in the C_s Symmetry or (HOMO − homo + lumo) Double Mixing in the C_1 Symmetry Takes Place.

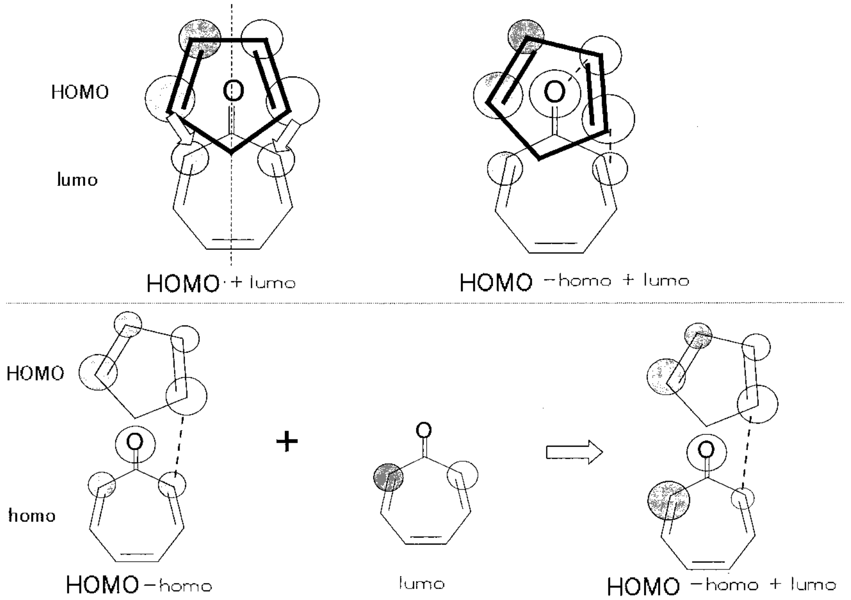
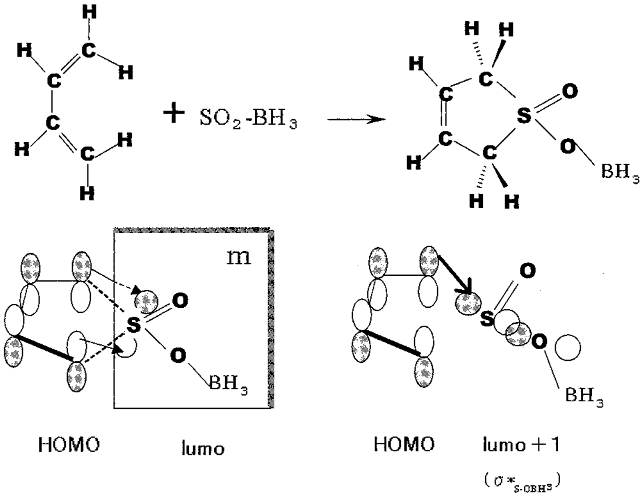


TABLE 2: Coefficients of Configuration Analysis[a]

	reactants in eq 3	
	cyclopentadiene + tropone (C_s TS)	cyclopentadiene + tropone (real TS)
C_0	0.498 64	0.523 89
HOMO → lumo	0.353 19	0.346 97
HOMO →→ lumo	0.125 08	0.114 30
homo → LUMO	0.277 88	0.252 40
HOMO → lumo + 1	0	(0.027 86)
HOMO − 1 → LUMO	0.058 53	(0.036 38)
HOMO → LUMO + 1	0.061 53	(0.045 72)
homo → lumo	0	0.050 98
homo − 2 → lumo	0.131 58	0.114 74
homo → lumo + 1	0.080 49	0.067 98

[a] Capital-letter orbitals belong to cyclopentadiene and lowercase-letter ones to tropone. Values in parentheses mean smaller ones than the criteria (more than 0.1 for electron-transferred configurations and more than 0.05 for excited ones).

effective overlap, the C_s symmetry is broken even at the initial stage of IRC according to the present calculation.



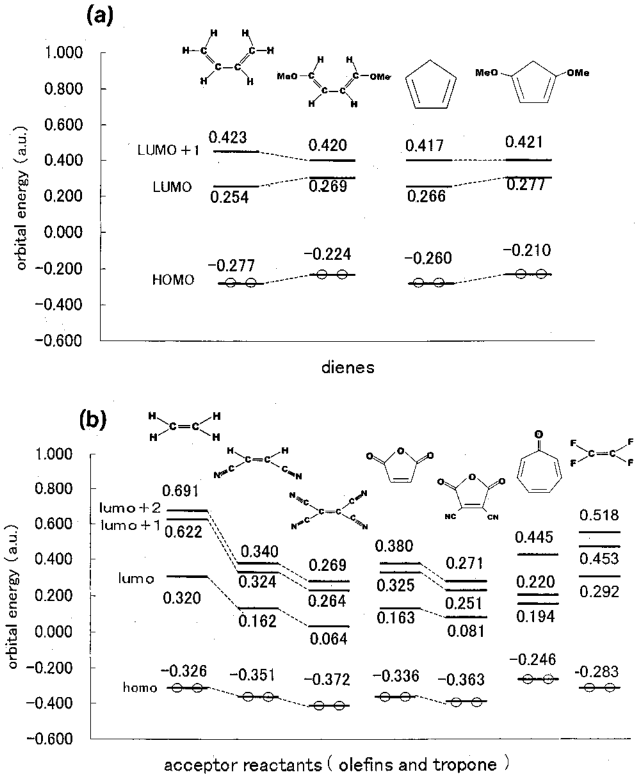


Figure 6. Energies of frontier orbitals of reactants used in the present cycloaddtions: (a) dienes; (b) olefins and tropone. Energy units are 1 au = 627.51 kcal/mol.

A Diels−Alder reaction between 1,4-dimethoxy-butadiene and tetrafluoro-ethene has been found to have C_s symmetry. At the right edge of Figure 6b, orbital energies of the olefin are shown. The lumo is high-lying (0.292 au), even higher than that (0.277 au) of a strong donor diene 1,4-dimethoxy-cyclopentadiene (at the right edge of Figure 6a). The three-body mixing is unlikely, and the C_s symmetry is retained at the TS.

V. Concluding Remarks

In this work, paths of Diels−Alder reactions of dienes and olefins with symmetric geometries were determined. They belong to the normal electron demand. While many reactions take the C_s-symmetry paths obeying the W−H rule, those of strong nucleophilic dienes and electrophilic olefins do not follow the symmetry-conservation rule. The breakdown is also observed in a typical [6 + 4] cycloaddition between tropone and cyclopentadiene. FMO theory explains reasonably geometric changes in terms of mixing of three frontier obitals, HOMO − homo + lumo or HOMO + lumo + (lumo + 1). The strong orbital mixing has given a Jahn−Teller[19] distortion of reaction paths against the W−H rule.

References and Notes

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