# Frontier Orbitals along Intrinsic Reaction Coordinates of Sulfur-Containing [4 + 2] and [8 + 2] Cycloadditions[1]

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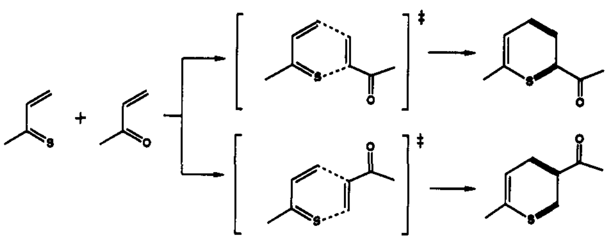
**Molecular orbital (MO) calculations of two cycloadditions, ethylene to 1-thiabutadiene and to tropothione, are made so as to compare the reactivities of [4 + 2] and [8 + 2] additions. Transition-state (TS) geometries are examined with various computational methods, followed by a search for intrinsic reaction coordinates (IRCs). Two concerted paths are almost synchronous. On account of the large lobe of frontier MOs (FMOs) on the sulfur atom, the small activation energies of the [4 + 2] and [8 + 2] additions are obtained. Even if the orbital phase in the free reactant does not give the favorable FMO interaction, it may be converted to the proper phase on the IRC route.**

## I. Introduction

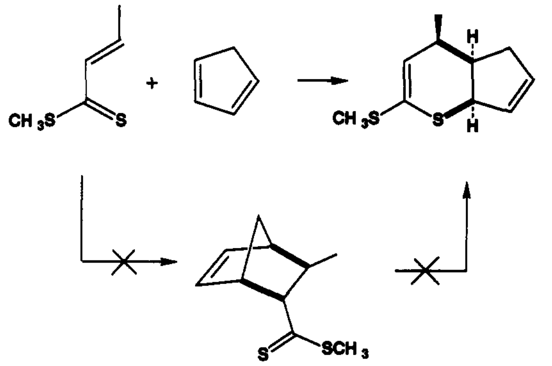
Cycloaddition is an effective method for synthesizing carbon cycles. These are typically symmetrically-allowed [4 + 2], [6 + 4], and [8 + 2] additions.[3] Among them, the Diels–Alder reaction giving rise to the cyclohexene derivative has been extensively studied with theoretical methods.[4] Also, some nitrogen- and oxygen-containing Diels–Alder reactions have been examined with semiempirical[5] and ab initio methods.[6] In contrast, thio-Diels–Alder reactions have not been investigated theoretically. They are known to be standard tools in the total synthesis of natural products.[7] For instance, 1-thia-1,3-butadienes react efficiently with olefins in eqs 1,[8] 2,[9] and 3[10] to prepare thiopyranyl compounds.

As an example of [8 + 2] hetero-cycloadditions, we have communicated a reaction between tropothione and cyclopentadiene to form an endo adduct in eq 4.[11]



(1)

Thio-Diels–Alder Reaction to form thiacyclohexene rings



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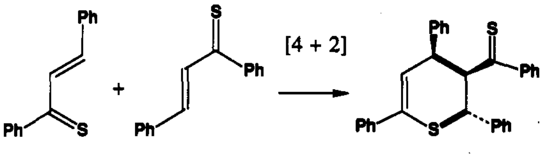
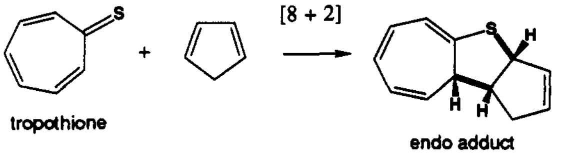
Thio-Diels–Alder Reaction between a thiabutadiene and cyclopentadiene



(3)

Dimerization of thiabutadiene derivative to form thiacyclohexene



(4)

| | Solvent | |
|---|---|---|
| | CHCl$_3$ | benzene |
| $\Delta H^{\ddagger}$ (kcal/mol) | 11.1 | 11.0 |
| $\Delta S^{\ddagger}$ (e.u.) | −37.8 | −39.6 |

In order to elucidate the reaction mechanism of these reactions, we study here the two model reactions eqs 5 and 6.

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[1] Abbreviations used: MO, molecular orbital; FMO, frontier MO; TS, transition state; RHF, restricted Hartree–Fock; STO, Slater-type orbital; MP2, second-order Møller–Plesset perturbation; IRC, intrinsic reaction coordinate.

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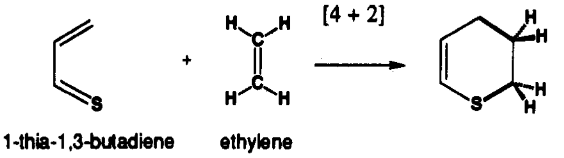
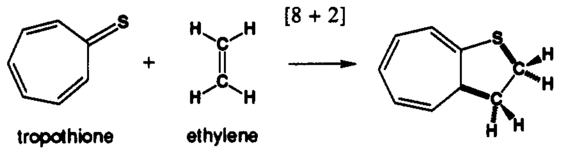


(5)



(6)

There are various questions to address for eqs 5 and 6. (a) Are really concerted paths likely with low activation energies? (b) Which is more efficient, the normal Diels–Alder or the sulfur Diels–Alder reactions? (c) Dependence of transition-state (TS) structures, activation enthalpies ($\Delta H^{\ddagger}$s), and entropies ($\Delta S^{\ddagger}$s) on computational methods. (d) Synchronousity of the C–C and C–S bond formation along the intrinsic reaction coordinate (IRC).[12] (e) How is the shape of FMOs of reactants distorted at the early stage of IRC? Since the FMO is based on the perturbation formula, this distortion should be in line with the progress of the reaction.

TS geometries and IRC of eqs 5 and 6 are examined in detail.

## II. Method of Calculations

Ab initio TS optimizations and vibrational analyses, RHF/STO-3G, RHF/3-21G*, RHF/6-31G$^{(*)}$, and MP2/6-31G$^{(*)}$, are carried out with GAUSSIAN 90.[13] The nonstandard 6-31G$^{(*)}$ basis set includes the 6d polarization function only on the sulfur atom. Single-point calculations, MP2/6-31+G*//MP2/6-31G$^{(*)}$, are also made to refine the obtained activation energies. Mass-weighted IRCs of eqs 5 and 6 are searched for using the method of Gonzalez and Schlegel,[14] with RHF/3-21G* and (60 + 60) points for forward and reverse directions. *Z* matrices used for TS and IRC searches are given in the supplementary material. All the ab inito calculations are performed on the CONVEX C-220 computer at the Information Processing Center of Nara University of Education.

## III. Results of Calculations

Figure 1 shows geometries of reactants and cycloadducts in eqs 5 and 6. Three reactants are computed to be planar, and tropothione is of $C_{2v}$ symmetry. Two cycloadducts are nonplanar, and in the seven-membered ring of the [8 + 2] adduct the hexatriene moiety is somewhat of the ring strain.

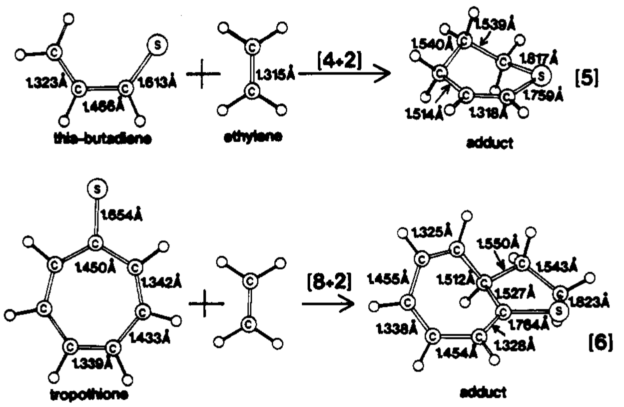


**Figure 1.** 3-21G* geometries of reactants and adducts. These data are also shown in Tables I and II. The observed C=S length of tropothione is 1.676 Å.[18] Empty circles stand for hydrogen atoms.

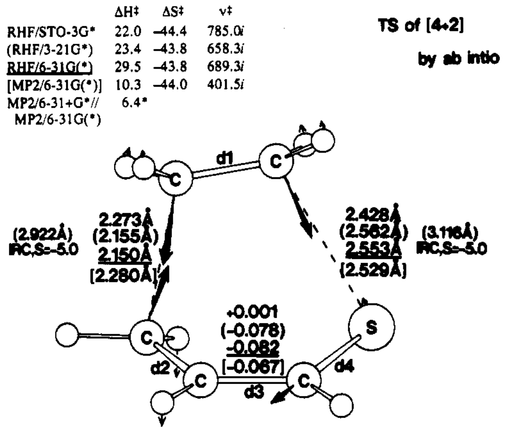


**Figure 2.** Calculated TS geometries of the [4 + 2] cycloaddition of ethylene to thiabutadiene in eq 5. $\Delta H^{\ddagger}$ is in kcal/mol, $\Delta S^{\ddagger}$ is in cal/(mol·K), and $\nu^{\ddagger}$ is the sole imaginary frequency in cm$^{-1}$. Convalent bond lengths d1, d2, d3, and d4 are displayed in Table I. Reaction-coordinate vectors corresponding to the sole imaginary frequency $\nu^{\ddagger}$ are also sketched. Negative numbers (–0.078), <u>–0.082</u>, and [–0.067] are net charges transferred from ethylene to diene calculated by (RHF/3-21G*), <u>RHF/6-31G$^{(*)}$</u>, and [MP2/6-31G$^{(*)}$] methods, respectively, which shows that the diene works as an electron acceptor at TS. $\Delta H^{\ddagger}$ of MP2/6-31+G*//MP2/6-31G$^{(*)}$ denoted by an asterisk is the difference of electronic energies. For the 3-21G* basis set, early-stage C···C distances at $S$ = –5.0 Bohr·amu$^{1/2}$ of IRC are also shown.

Figure 2 exhibits the TS geometry of eq 5. The intermolecular bond distances along two broken lines depend only slightly on computational methods. The C···C length is smaller than the C···S one. Vibrational analyses give only one imaginary frequency ($\nu^{\ddagger}$) by four methods, which indicates that the [4 + 2] addition is concerted. $\Delta H^{\ddagger}$ depends on the methods and is smaller by about 33 kcal/mol than the gas-phase Diels–Alder reaction between butadiene and ethylene.[15] $\Delta S^{\ddagger}$ is roughly –44 eu and is about twice the –20 eu of the Diels–Alder reaction,[4h] which demonstrates that the present TS structure is very compact. The net charge in the thiabutadiene moiety is negative except for that by RHF/STO-3G*, indicating that the diene works as an electron acceptor and that the reaction is of the reverse electron demand.[3] At an early stage of the addition, $S$ = –5.0 Bohr·amu$^{1/2}$ on IRC, the C···C distance of 2.922 Å is nearly the same as the C···S of 3.116 Å. The C···C and C···S bonds are made almost synchronously. Distances d1, d2, d3, and d4 are given in Table I and indicate that TS is situated at an early stage of eq 5.

Figure 3 exhibits TS geometries of eq 6. The change of activation enthalpy $\Delta H^{\ddagger}$ calculated by five methods is

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**Table I. Comparison of Covalent Bond Lengths between Reactants (Ethylene and Thiabutadiene) and [4 + 2] TS in Å by Four ab Initio Methods**[a]

| | | RHF | | | MP2 |
|---|---|---|---|---|---|
| | bond | STO-3G* | 3-21G* | 6-31G(*) | 6-31G(*) |
| | ethylene | 1.306 | 1.315 | 1.322 | 1.335 |
| d1 | IRC (−5.0) | | 1.316 | | |
| | TS | 1.352 | 1.371 | 1.380 | 1.395 |
| | adduct | | 1.539 | | |
| | C=C | 1.315 | 1.323 | 1.330 | 1.359 |
| d2 | IRC (−5.0) | | 1.325 | | |
| | TS | 1.356 | 1.379 | 1.388 | 1.394 |
| | adduct | | 1.514 | | |
| | C—C | 1.503 | 1.466 | 1.463 | 1.480 |
| d3 | IRC (−5.0) | | 1.457 | | |
| | TS | 1.425 | 1.386 | 1.386 | 1.425 |
| | adduct | | 1.318 | | |
| | C=S | 1.558 | 1.613 | 1.622 | 1.645 |
| d4 | IRC (−5.0) | | 1.614 | | |
| | TS | 1.622 | 1.658 | 1.670 | 1.679 |
| | adduct | | 1.760 | | |

[a] Bond Parameters d1, d2, d3, and d4 are defined in Figure 2. For 3-21G*, lengths at an early stage ($S = -5.0$ Bohr·amu$^{1/2}$) of the reaction and [4 + 2] cycloadduct are also shown. For instance, the distance d1 changes from 1.315 Å (ethylene) to 1.316 Å ($S = -5.0$) to 1.371 Å (TS) to 1.539 Å (adduct).

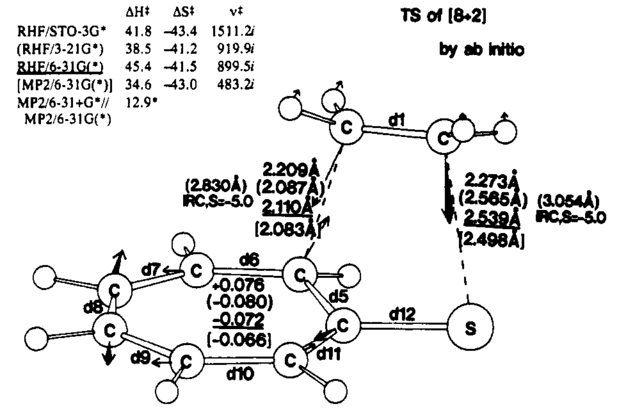

**Figure 3.** Calculated TS geometries of the [8 + 2] cycloaddition of ethylene to tropothione in eq 6. Bond parameters d1, d5, ..., d12 are shown in Table II. Same notations as in Figure 2 are used.

larger than that of the [4 + 2] TS in Figure 2. $\Delta S^{\ddagger}$ values of this [8 + 2] are similar to those of [4 + 2]. Thus, the present results predict that the [4 + 2] addition occurs much more readily than the [8 + 2] one. Only one imaginary frequency $\nu^{\ddagger}$ is obtained in each method and indicates that the present [8 + 2] proceeds concertedly. The reaction–coordinate vector corresponding to $\nu^{\ddagger}$ demonstrates that the new bond formation and the bond interchange take place simultaneously. Net charges in the tropothione side are negative except for that by RHF/STO-3G*, showing that the thione is an electron acceptor. Bond distances d1, d5, d6, ..., d12 are given in Table II. For the ethylenic C–C distance d1, that of the [8 + 2] TS is elongated more than that of the [4 + 2] TS in Table I. That is, the [4 + 2] TS is *earlier* than the [8 + 2] TS. The reliability of ab initio methods is examined. For TS structures, the MP/6-31G$^{(*)}$ is best in view of C–C distances (from d6 to d11, ca. 1.4 Å) inside the seven-membered ring. RHF/double-ζ level calculations are also acceptable qualitatively. However, for activation energies, single-point calculations (e.g., MP2/6-31+G*) are necessary. The measured activation energy of the [8 + 2] cycloaddition in eq 4 was 11 kcal/mol,[11] which is similar to the value of 12.9 kcal/mol of MP2/6-31+G*//MP2/6-31G$^{(*)}$ in Figure 3.

**Table II. Comparison of Covalent Bond Lengths between Reactants (Ethylene and Tropothione) and [8 + 2] TS in Å by Four ab Initio Methods**[a]

| | | RHF | | | MP2 |
|---|---|---|---|---|---|
| | bond | STO-3G* | 3-21G* | 6-31G(*) | 6-31G(*) |
| | ethylene | 1.306 | 1.315 | 1.322 | 1.335 |
| d1 | IRC (−5.0) | | 1.315 | | |
| | TS | 1.374 | 1.381 | 1.390 | 1.411 |
| | adduct | | 1.543 | | |
| | C—C | 1.499 | 1.450 | 1.450 | 1.467 |
| d5 | IRC (−5.0) | | 1.450 | | |
| | TS | 1.506 | 1.464 | 1.464 | 1.493 |
| | adduct | | 1.527 | | |
| | C=C | 1.328 | 1.342 | 1.351 | 1.385 |
| d6 | IRC (−5.0) | | 1.344 | | |
| | TS | 1.376 | 1.415 | 1.424 | 1.432 |
| | adduct | | 1.512 | | |
| | C—C | 1.471 | 1.433 | 1.433 | 1.444 |
| d7 | IRC (−5.0) | | 1.429 | | |
| | TS | 1.415 | 1.360 | 1.363 | 1.405 |
| | adduct | | 1.326 | | |
| | C=C | 1.327 | 1.339 | 1.347 | 1.383 |
| d8 | IRC (−5.0) | | 1.340 | | |
| | TS | 1.364 | 1.402 | 1.410 | 1.415 |
| | adduct | | 1.455 | | |
| | C—C | | = d7 | | |
| d9 | IRC (−5.0) | | 1.429 | | |
| | TS | 1.418 | 1.363 | 1.366 | 1.410 |
| | adduct | | 1.338 | | |
| | C=C | | = d6 | | |
| d10 | IRC (−5.0) | | 1.343 | | |
| | TS | 1.366 | 1.403 | 1.411 | 1.413 |
| | adduct | | 1.454 | | |
| | C—C | | = d5 | | |
| d11 | IRC (−5.0) | | 1.445 | | |
| | TS | 1.430 | 1.372 | 1.375 | 1.420 |
| | adduct | | 1.328 | | |
| | C=S | 1.576 | 1.654 | 1.666 | 1.680 |
| d12 | IRC (−5.0) | | 1.653 | | |
| | TS | 1.609 | 1.703 | 1.715 | 1.698 |
| | adduct | | 1.767 | | |

[a] Bond parameters d1, d5, d6, ..., d12 are defined in Figure 3. For 3-21G*, lengths at an early stage ($S = -5.0$ Bohr·amu$^{1/2}$) of the reaction and [8 + 2] cycloadduct are also shown. For instance, the distance d1 changes from 1.315 Å (ethylene) to 1.315 Å (S = −5.0) to 1.381 Å (TS) to 1.543 Å (adduct).

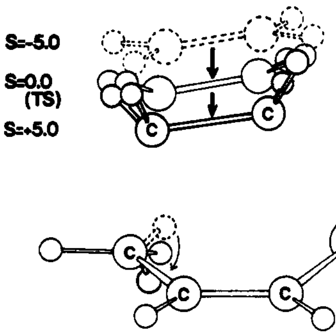

**Figure 4.** Snapshot of the [4 + 2] addition along IRC.

Figure 4 presents a geometric change along the [4 + 2] IRC. It is confirmed that C···C and C···S bonds are formed almost simultaneously.

In Figure 5, a geometric change along the [8 + 2] IRC is given. At the early stage $S = -5.0$, four reaction-center atoms provide almost the isosceles trapezoid form. This form indicates that the C···S bond formation is almost synchronous with the C···C formation initially in a way similar to the snapshot of Figure 4.

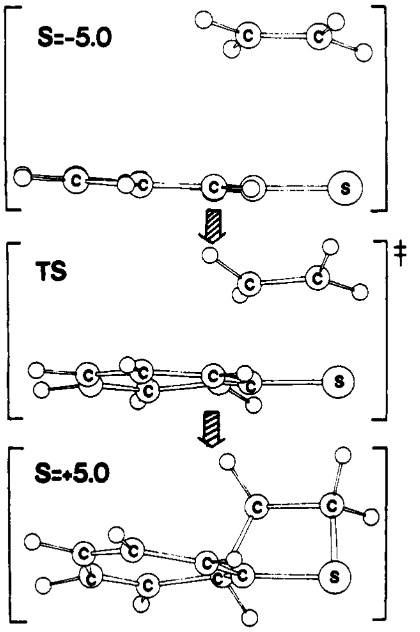

Figure 5. Snapshot of the [8 + 2] addition along IRC.

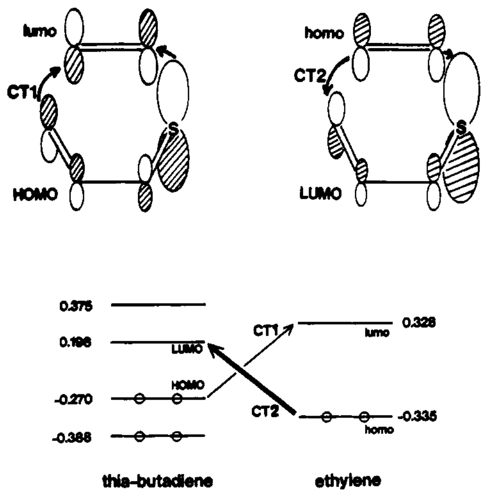

**Figure 6.** Two FMO interactions, CT1 and CT2, between thiabutadiene and ethylene. Since the (homo–LUMO) energy gap is smaller than the (HOMO–lumo) one, the reverse-electron-demand-type reaction is verified. Orbital energies are calculated with RHF/STO-3G* and are in a.u.

## IV. FMO Analysis of [4 + 2] and [8 + 2] Cycloaddition

In the previous section, reaction routes and energies of eqs 5 and 6 have been discussed. Here, it is examined how the frontier-orbital interaction controls them in the course of reaction coordinates. Figure 6 shows the [4 + 2] FMO scheme. The large lobe on the sulfur atom may work effectively to form the initial C⋯S bond. The reverse electron demand, i.e., CT2 > CT1, is derived from comparison between (homo–LUMO) and (HOMO–lumo) energy gaps. Thus, for [4 + 2], inclusion of the sulfur atom is found to enhance the reactivity relative to the normal Diels–Alder reaction. This enhancement has been reflected in the small activation energy 6.4 kcal/mol of MP2/6-31+G*//MP2/6-31G(*) in Figure 2.

Figure 7 shows the [8 + 2] FMO scheme. CT3 is of the anti-symmetric MO overlap and corresponds beautifully to the concerted process of the new bond formation and the bond interchange in the seven-membered ring. That is, loss of the HOMO density leads to the elongation of three double bonds and the shortening of three single bonds in the ring. However, the charge donation from ethylene to tropothione is not in line with the concertedness. That is, LUMO or (LU+1)MO cannot be the frontier orbital alone, and CT4 and CT5 must occur simultaneously. The problem of the concertedness vs CT4 and CT5 is considered next. In Figure 8, a typical [8 + 2] FMO scheme is described. While the (HOMO → lumo) CT corresponds correctly to CT3 in Figure 7, the (homo → LUMO) CT appears to be different from CT4 and CT5. So far, FMOs of isolated reactants have been examined.

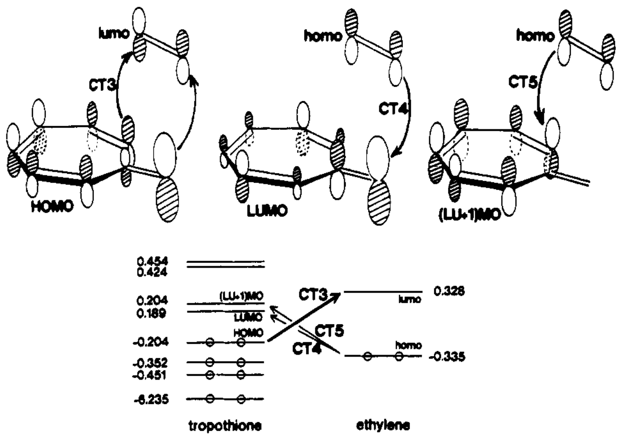

**Figure 7.** Three FMO interactions, CT3, CT4, and CT5. (LU+1)MO of tropothione is equivalent with LUMO of hexatriene. While CT3 is of the antisymmetric overlap and perfectly in-phase, CT4 and CT5 are imperfect for the concerted C–C and C–S bond formation.

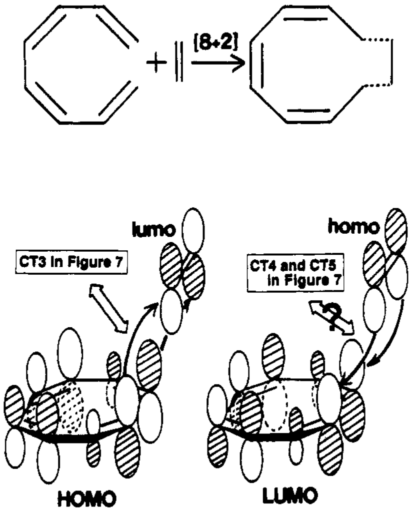

**Figure 8.** Typical [8 + 2] FMO interaction between octatetraene (HOMO and LUMO) and ethylene (homo and lumo) leading to cyclodecatriene.

Since the FMO scheme is based on the perturbation, the change of the shape of FMOs along IRC is scrutinized. Figure 9 displays the change. Even if the reaction proceeds to some extent, shapes of HOMO and lumo in CT3 are not changed so much. This result demonstrates that the good orbital phase is hardly affected by the geometric distortion along IRC. In contrast, the feature of CT4 and CT5 changes drastically along IRC. CT4 becomes a perfect FMO interaction (*in phase*! in Figure 9), and CT5 is not a FMO one (*symmetry forbidden*!) any more at $S = -1.0$ Bohr·amu$^{1/2}$. CT4 at $S = -1.0$ is now concerned with the concertedness and is similar to the typical (homo →

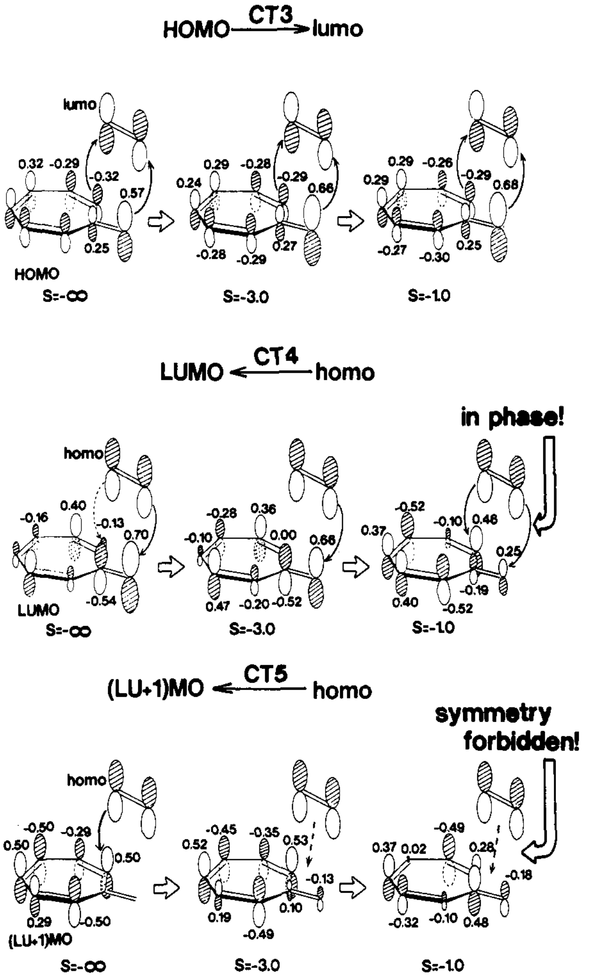

**Figure 9.** Changes of RHF/STO-3G* FMO shapes of tropothione and ethylene along IRC. The in-phase nature of CT3 is maintained even in distorted geometries of reactants. On the other hand, CT4 becomes beautifully in-phase of the symmetric FMO overlap, and CT5 becomes symmetry forbidden.

LUMO) CT in Figure 8. This change of CT4 is favorable for the progress of the [8 + 2] reaction. Thus, even if the phase relation is not suitable to the concertedness in reactants ($S = -\infty$), the IRC geometric change is found to improve the phase relation. The idea of collaboration of the phase refinement and the geometric change has been first suggested by Fukui and Fujimoto.[16]

In the free tropothione, it is not clear whether almost degenerate LUMO and (LU+1)MO are frontier orbitals or not in Figure 7. However, as the reaction proceeds, an appropriate frontier vacant orbital has appeared. Next interest lies in the way of MO mixing for the orbital. In Figure 10, the mixing process of two vacant MO's is shown. Through the geometric distortion of tropothione, almost degenerate two MO's are thought to be reorganized into *plus* and *minus* products. Indeed, these expected shapes of LUMO + (LU+1)MO and (LU+1)MO − LUMO have been obtained already in *in phase*! and *symmetry forbidden*! of Figure 9. Now, LUMO + (LU+1)MO is the frontier orbital on IRC.

The role of FMOs should become important more and more as the reaction proceeds for the larger extent of charge transfer. In fact, orbital-energy levels of HOMO and (new) LUMO of tropothione come closer along IRC, which contributes really to this acceleration.

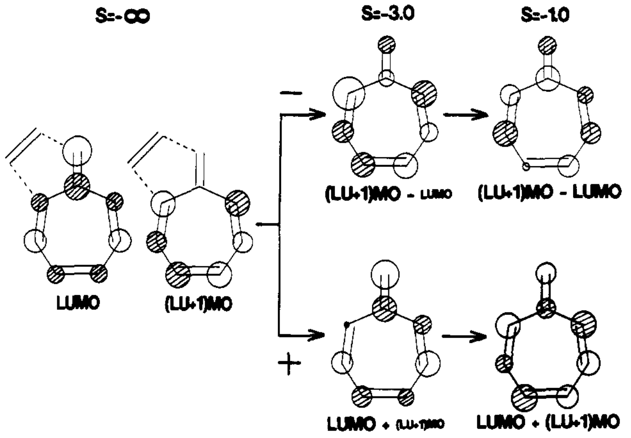

**Figure 10.** Combination scheme for explaining the change of shapes of LUMO and (LU+1)MO along IRC. The plus combination gives rise to the in phase! in Figure 9. The minus one does symmetry forbidden!.

## V. Concluding Remarks

In this work, two sulfur-containing cycloaddition reactions of eqs 5 and 6 have been investigated theoretically.

(1) Four ab initio methods give similar TS geometries. The activation entropy hardly depends on the computational method and is ca. −42 eu in both [4 + 2] and [8 + 2] reactions. This value is in good agreement with observed data[11] in eq 4. On the other hand, extended basis sets and inclusion of the electron correlation are needed to provide reasonable activation energies.

(2) Both [4 + 2] in eq 5 and [8 + 2] in eq 6 are found to take place concertedly with small activation energies. This high reactivity is ascribed to the large lobe of the sulfur atom. The C···C and C···S bond formation is almost synchronous.

(3) The sulfur-containing [4 + 2] addition is of the reverse electron demand and is much more efficient than the normal Diels–Alder reaction.

(4) The reactivity of [8 + 2] addition is smaller than that of [4 + 2] addition, probably owing to the delocalization of HOMO and LUMO inside the seven-membered ring of tropothione.

(5) Even if the orbital shape does not give the favorable FMO interaction in the reactant geometry, the shape is readjusted suitably on IRC. Thus, it is demonstrated for the first time that the FMO interaction becomes more and more important as the reaction proceeds.

The present study has dealt with [4 + 2] and [8 + 2] reactions by RHF and MP2 wave functions and accordingly with only concerted paths. FMO analyses in Figures 6–10 are also limited to concerted mechanisms. Biradical mechanisms might be involved as other reaction routes. These must be traced by MC-SCF wavefunctions, which is almost technically infeasible for the [8 + 2] reacting system. However, experimental values of eq 4 and computed ones in Figure 3 of the activation entropy ca. −40 eu are in close agreement with those of typical concerted cycloadditions[17] and strongly suggest that the

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[8 + 2] reaction takes place concertedly. Thus, although biradical paths are not treated, the present results are thought to be meaningful.

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**Supplementary Material Available:** *Z*-matrices of TS geometries optimized with four methods and shown in Figures 2 and 3 (3 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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