Triplet–Singlet Intersystem Crossing as the Second Step of the Cycloaddition of Triplet Penta-1,4-diene. An *ab initio* MO Study

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The mechanism of the second step in the photosensitized cycloaddition reaction of penta-1,4-diene has been investigated. This step, which starts from an aliphatic cyclic intermediate on the first excited triplet (T_1) surface, consists of an intersystem crossing from the T_1 state to the ground singlet state (S_0) and ring closure on the S_0 surface. For two possible reaction paths, cross addition and parallel closure, we have calculated by an *ab initio* MO method, the lowest point on the crossing seam between the S_0 and T_1 states, which can be regarded as the transition state for this second step. The triplet cyclic intermediate for cross addition, **2**, requires only *ca.* 1 kcal mol^{-1}† to reach the lowest crossing point accompanied by 90° internal rotation of the terminal methylene group with relatively small changes in the skeletal structure. On the other hand, the triplet cyclic intermediate for parallel closure, **4**, requires *ca.* 5 kcal mol^{-1}, accompanied by a drastic change in the skeletal molecular structure. The calculation confirms that this second step is not the rate-determining step of the entire cycloaddition reaction.

It is well known in the field of photochemistry that a series of non-conjugated acyclic dienes can be converted into bicyclic aliphatics through a triplet excited state upon sensitization by the mercury ($^3P_1$) atom.[1–3]

In our previous papers,[4,5] we have shown that: (*a*) the energy difference between the *cis–trans*‡ **1** and the envelope **3** forms of the reactant, penta-1,4-diene, in the first excited triplet (T_1) state is very small, and both forms are probably produced in nearly equal quantities in the initial stage of the reaction; (*b*) the transition state TS2 for the parallel closure on the T_1 surface is substantially lower in energy than that, TS1, for the cross closure, supporting the experimental dominance of the parallel closure;[2] (*c*) the energy difference between the two transition states, TS1 and TS2, is closely related to the strain energies of the aliphatic cyclic intermediates, **2** and **4**, which were formed after the initial closure. The potential energy profiles calculated for this first step from **1** and **3** to **2** and **4**, respectively, are shown in Fig. 1.

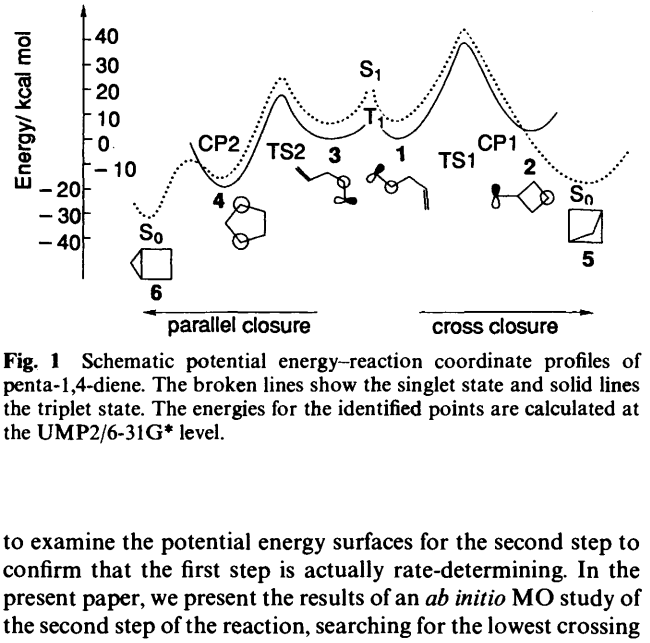

Fig. 1 Schematic potential energy–reaction coordinate profiles of penta-1,4-diene. The broken lines show the singlet state and solid lines the triplet state. The energies for the identified points are calculated at the UMP2/6-31G* level.

Thus, for both parallel and cross closure reactions, we have followed the first step from triplet pentadienes over barriers to the triplet diradical intermediates. In order to complete the reaction, one has to go through the second step from the triplet intermediates to the closed shell bicyclic products, as shown schematically in Fig. 1. Since the singlet diradicals are expected to be connected adiabatically to the closed shell bicyclic products, with or without a small barrier, there should be $(n - 1)$-dimensional seams of crossing between the n-dimensional singlet and the triplet surfaces, which are located between the intermediates and the products but not far from the intermediates. In this situation, the lowest points on the seams of crossing between the two states can be considered as the surface hopping transition states for this second step of the closure reactions.[6]

Though our previous study has shown that the experimental selectivity of parallel *vs.* cross closure can be explained by comparison of the barrier heights in the first step, we would like to examine the potential energy surfaces for the second step to confirm that the first step is actually rate-determining. In the present paper, we present the results of an *ab initio* MO study of the second step of the reaction, searching for the lowest crossing point between the first triplet and the singlet state.

Computational Method

In this section, first we discuss the method for determining the lowest crossing point between a singlet and a triplet state. At first we expand the singlet UHF and the triplet UHF wave functions in terms of spin eigenfunctions [eqn. (1)]. The

$$\begin{aligned}\Phi(^1\mathrm{UHF}) &= c_1\Psi_1 + c_3\Psi_3 + c_5\Psi_5 + \cdots \\ \Phi(^3\mathrm{UHF}) &= \qquad\quad a_3\Psi_3' + a_5\Psi_5' + \cdots \end{aligned} \tag{1}$$

corresponding energies are given by eqn. (2). We will seek the

$$\begin{aligned}E(^1\mathrm{UHF}) &= c_1^2\varepsilon_1 + c_3^2\varepsilon_3 + c_5^2\varepsilon_5 + \cdots \\ E(^3\mathrm{UHF}) &= \qquad\quad a_3^2\varepsilon_3' + a_5^2\varepsilon_5' + \cdots \end{aligned} \tag{2}$$

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† 1 cal = 4.184 J.

‡ *cis–trans* refers to the conformation around the C(2)–C(3) and C(3)–C(4) axes as s-*cis* and s-*trans*, or otherwise.

seam of crossing between the two UHF states, which satisfies eqn. (3). In our previous paper[5] we have found that the

$$E(^1\mathrm{UHF}) - E(^3\mathrm{UHF}) = 0 \quad (3)$$

contribution of the quintet and higher multiplets to the UHF triplet wave function of the present system is rather small. The same is expected for the UHF singlet wave function. In fact, at the lowest crossing points the calculated $\langle S^2 \rangle$ values of 2.03 and 1.01–1.03 for the triplet and singlet states, respectively, support this argument; the former is close to the value of 2.0 for the pure triplet wave function and the latter to the value of 1.0 for the 1:1 mixture of the singlet and the triplet biradical with little contaminations from the higher multiplicities. Therefore we can practically assume in eqn. (2) that the energy contribution of the quintet and higher multiplets cancel between the two states and that $c_1^2 + c_3^2 = a_3^2$ and $\varepsilon_3 = \varepsilon'_3$. The latter assumption was used in the approximate projected UHF and UMP method by Yamaguchi and his co-workers, who obtained satisfactory results.[7] Then eqn. (3) leads to eqn. (4). That is to

$$\varepsilon_1 = \varepsilon_3 \quad (4)$$

say that the seam of crossing found with the unprojected UHF energies, eqn. (3), is approximately equal to the seam obtained with the more reliable projected UHF energies, eqn. (4). We use the method developed by two of the authors[8,9] to find the lowest energy point on the $(n - 1)$-dimensional seam of crossing between two n-dimensional surfaces by searching for the minimum of the expression $\{E(^1\mathrm{UHF}) + E(^3\mathrm{UHF})\}/2$ under the conditions of eqn. (3).

All of the MO calculations were performed by using the GAUSSIAN 82 program packages,[10] and the geometry was fully optimized without any symmetry restriction. The structures thus determined for **4** and for the lowest point on the seam of crossing starting from **2**, have C_2 and C_s symmetry, respectively, whereas the structures of **2** and the lowest point on the seam of crossing from **4** have no symmetry.† The basis sets used were the 3-21G[11] and 6-31G*.[12] The UHF/6-31G* calculations were performed at the 3-21G UHF optimized geometries. Electron correlation was taken into account using the second order Møller–Plessett (MP2) perturbation procedure with the 6-31G* basis set.[13] Though at the lowest points on the crossings of seam they must be the same, the triplet and singlet energies in the UHF/6-31G* and UMP2/6-31G* calculations for the UHF/3-21G optimized structures could be different. Therefore, we calculated both singlet and triplet energies at the UHF/6-31G* and UMP2/6-31G* level.

Results

Transition State Geometries.—The optimized geometries of the transition states, *i.e.*, the lowest points of the triplet–singlet crossing for cross and parallel closure are shown in Fig. 2 as CP1 and CP2, respectively, and are compared to those of triplet intermediates, **2** and **4**, the starting points of this second step of the reaction. It has been shown[6] that at the minimum of the seam of crossing between the two surfaces, the direction of gradient on one surface is parallel to that on the other surface [eqn. (5) where $\mathbf{g}_\mathrm{T}$ and $\mathbf{g}_\mathrm{S}$ are gradient vectors for the triplet

$$\mathbf{g}_\mathrm{T} = k\mathbf{g}_\mathrm{S} \quad (5)$$

and the singlet potential energy surface at the lowest crossing point]. If k in eqn. (5) is positive, their directions are exactly equal, and if k is negative, they are exactly opposite. This is one of the reasons why the direction of gradient with proper mass factor, *i.e.*, the direction of the steepest descent, can be considered as the direction of the reaction coordinate at the surface hopping transiton state.[6]

Though the geometry of CP1 has been determined without symmetry constraint, one can say that it has converged to a C_s structure. The most important geometrical difference between CP1 and the intermediate **2** is that the terminal methylene group has rotated *ca.* 90°, putting its half-occupied orbital and the C(4) half-occupied orbital in the same plane. This is the angle where the singlet state would have the lowest and the triplet would have the highest energy and the singlet–triplet separation would be the smallest. Other differences are seen in the four-membered ring itself. The nearly coplanar ring skeleton in **2** becomes substantially puckered and the C(2)–C(4)–H angle is reduced by 29° to 148° in CP1. We note here that the changes in bond lengths are at most 0.01 Å.

At CP1, k in eqn. (5) is calculated to be 0.82, indicating that the reaction coordinate vectors on both states have the same direction and that the energy gradient vector on the singlet surface is larger than that on the triplet surface. The reaction coordinate vector starting from CP1 shown in Fig. 2 indicates that the C(1)–C(2) bond becomes shorter and that the C(2)–C(3)–C(4)–C(5) skeleton becomes more planar, if the reaction coordinate is followed. This actually means that the reaction coordinate on the triplet surface is a path connecting CP1 to **2**. Since the reaction coordinates on both states have the same direction, the reaction coordinate from CP1 on the singlet surface would pass through the structure similar to **2** and eventually lead to the product **5**. Based on these results, we depicted the overall potential energy profiles for the cross closure as shown in Fig. 1.

The geometrical changes going from the intermediate **4** to CP2 are quite different in nature from those for **2** $\longrightarrow$ CP1. While the changes in bond lengths are small, as in CP1, there are substantial changes in the skeletal angles. The five-carbon skeleton in **4** becomes folded by 29° along the symmetry axis through the C(3) atom and the midpoint of the C(1)–C(5) bond. The C(2)–C(3)–C(4) angle narrows by 4°. Furthermore, the H(3)–C(2)–C(3)–C(4) and H(4)–C(4)–C(3)–C(2) dihedral angles change by 66° and 39°, respectively.

At CP2 k in eqn. (5) is calculated to be 1.85, indicating that the reaction coordinates on both states have the same direction, and that the energy gradient vector on the triplet surface is larger than that on the singlet surface. In addition, geometry optimization starting from CP2 on the singlet surface gave a structure similar to **4**, consistent with the reaction coordinate vector starting from CP2 shown in Fig. 2. These results suggest that the potential energy profiles for parallel closure are as shown in Fig. 1. Therefore, though the structure changes indicate clearly that bond formation in the singlet between the two radical centres, C(2) and C(4), has already begun at CP2, Fig. 1 suggests that there is a small barrier on S_0 to be overcome after passing through CP2. The UHF expectation values of $\langle S^2 \rangle$ at CP2 and **4** are close to unity, indicating that the singlet state around these structures is singlet diradical and thus the singlet UHF wavefunction is nearly a 1:1 linear combination of pure singlet and triplet eigenfunctions. Therefore, the singlet UHF potential energy surface reflects features in the triplet UHF potential energy surface. The minimum on the singlet surface, similar to **4**, and thus the barrier, may be an artifact of the triplet contamination. Therefore, the reaction from CP2 to **6** would be an easy process, and one can regard CP2 as the

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† Though in our previous paper[5] we have determined the structures of **2** under the C_s symmetry constraint and of **4** under the C_{2v} symmetry constraint, they were found not to be true equilibrium structures because of the eclipsing CH bonds. However, these more highly symmetric structures are less stable than the true equilibrium structures reported here only by 0.002 and 0.3 kcal mol^{-1} for **2** and **4**, respectively. Therefore, the conclusions in our previous paper are unchanged.

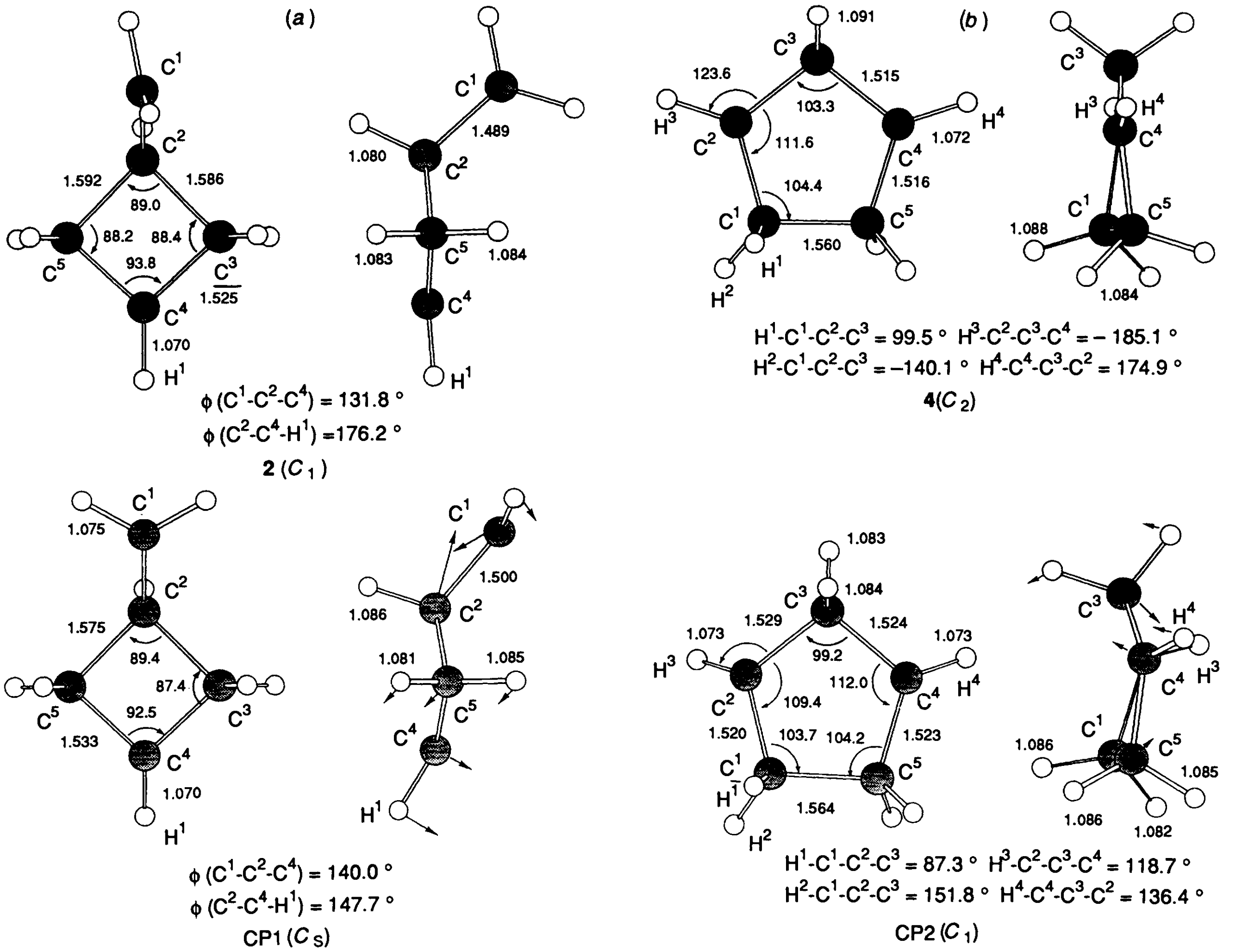

Fig. 2 Optimized geometries (in Å and deg) of the T_1 state and of the energy minimum crossing points between the triplet and the singlet state of penta-1,4-diene at the UHF/3-21G level. Arrows are the reaction coordinate vectors at the crossing points.

transition state between **4** and **6**. Note that, as discussed in the Computational Method section, triplet contamination does not affect the location of CP2.

Relative Energies.—The energies of the transition states CP1 and CP2, *i.e.*, the lowest points on the seam of crossing between the triplet and singlet states, relative to the corresponding intermediates, **2** and **4**, respectively, as well as the total energies of the triplet intermediates, **2** and **4**, calculated at various levels of calculations at the UHF/3-21G optimized geometries are shown in Table 1. The potential energy profiles for the second step from **2** to CP1 to **5** and from **4** to CP2 to **6** are shown in Fig. 1 together with those for the first step obtained in our previous paper.[5] The energy difference between the intermediate **2** and the transition state CP1 is found to be very small (*ca.* 1 kcal mol^{-1} at our highest calculation level of UMP2/6-31G*). This is not surprising because the geometry of CP1 is very similar to that of **2**, *i.e.*, the transition state is located very close to the intermediate, except for the CH_2 rotation. On the other hand, the difference between **4** and CP2 is *ca.* 5 kcal mol^{-1} at the highest level of calculation. As was shown in the preceding section, there is a substantial change in geometrical parameters between the intermediate **4** and the transition state CP2 for this path. A drastic skeletal reorganization has to take place to reach CP2, which requires a large energy.

Table 1 Total energies (in hartree) of the triplet intermediates, **2** and **4**, and energies (in kcal mol^{-1}) of the corresponding lowest triplet–singlet crossing points CP1 and CP2, respectively, relative to the intermediates, at different levels of calculation at the UHF/3-21G optimized geometries

	UHF/3-21G	UHF/6-31G*	UMP2/6-31G*
2	−192.793 35	−193.871 16	−194.467 56
CP1	1.8	0.8,[a] 1.0[b]	0.8,[a] 1.1[b]
4	−192.837 51	−193.913 01	−194.508 20
CP2	5.1	5.8,[a] 5.1[b]	5.6,[a] 4.4[b]

[a] Triplet energies. [b] Singlet energies.

Discussion

A computational method has been successfully applied to find the energy minimum crossing point between the first excited triplet T_1 and the singlet state S_0, which can be regarded as the transition state for intersystem crossing, during the second step of the cycloaddition reaction of penta-1,4-diene. For the cross closure, the energy difference between the triplet intermediate **2** and the transition state (CP1) is very small, 1 kcal mol^{-1} at the best calculation level. This energy comes from the methylene internal rotation about the single bond. The geometry difference between the triplet state **4** and the transition state (CP2) is fairly large, involving a skeletal geometry change of the pentacycle from a planar to a folded form. Thus the energy required to reach CP2 from **4** is larger, *ca.* 5 kcal mol^{-1} at the best calculation level.

We have shown previously that the dominance of the parallel closure process over the cross closure process can be reasonably explained in terms of the barrier heights of the first cyclization step on the triplet state.[5] What we have shown in the present paper is that once intermediates are formed in the triplet state, as the second step they can easily make intersystem crossing to the singlet state and reach the final doubly cyclized products. The present calculation thus confirms that this second step is not rate-determining for the entire reaction. The first step is in fact the rate-determining step, as we proposed in our previous paper.[5] One may note that in the second step the cross closure is easier than the parallel closure, whereas in the first, rate-determining step the opposite is true.

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