

Revisiting the S_1/S_0 Degeneracy Space along the Exocyclic Methylene Twist Motion of Fulvene through a Two-Step Procedure

Masato Sumita and Kazuya Saito*

Department of Chemistry, Graduate School of Pure and Applied Sciences,
University of Tsukuba, Tsukuba 305-8571, Japan

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Abstract: We have characterized the degeneracy space (DS) between the ground (S_0) state and the first excited (S_1) state along the exocyclic methylene twist motion of fulvene, using our calculation strategy, i.e., a two-step procedure with CASSCF. The origin of the “cancellation error” on locating degeneracy points under geometrical constraints is analyzed, leading to a method to assess adequacy of the strategy. According to our estimation, these S_1/S_0 DPs are optimized for energy within $2.0 \times 10^{-3} E_h \text{ \AA}^{-1}$ (the value of root-mean-square). From the obtained S_1/S_0 DS, we provide some information about the exocyclic methylene rotation by 180° .

1. Introduction

Recent theoretical calculations elucidated the importance of the conical intersections which are the real state crossing between the same spin multiplicity states.^{1,2} A degeneracy point (DP), which is an apex of a conical intersection, is not an isolated point but consecutive space (see the next section about the details). The method to locate stationary DP (e.g., the lowest energy degeneracy point: LEDP) has been already established.^{3,4} However, some theoretical calculations indicated the importance of exploring the degeneracy space (DS).^{5–7} Hence, the method to explore the DS as a function of an arbitrary internal coordinate of the molecule is desired. Some methods characterizing the DS along an arbitrary internal coordinate of molecules have been reported. In the method based on Lagrange multipliers for optimization in the DS,³ the determination of the section of the DS along a variable is possible.⁸ In the projected gradient method,⁴ when one uses the method with a geometric constrain beyond symmetry, the point at which energies are not degenerated is located. This undesirable result is called a “cancellation error” which has been discussed, and some methods to circumvent the problem have been proposed.^{7,9–12} According to these discussions, the origin of cancellation error is due to the loss of the orthogonality between a degeneracy lifting space and its complement space. We will however show that it is not the case.

We have circumvented the cancellation error by a two-step procedure.^{9,10,13} We however did not assess how well energy was minimized with the two-step procedure. The goal of this paper is to clarify how well energy is minimized using the procedure and what condition is required for the procedure. To this end, we selected fulvene as a calculation target.

Fulvene is known as one of the isomers of benzene and a product of its photoisomerization.^{14–17} The radiationless decay from the first excited (S_1) state in fulvene is observed.^{18–21} Theoretically, this radiationless decay can be explained by the existence of some DPs.^{12,22–24} These theoretical results suggested the possibility of the exocyclic methylene rotation by 180° . On the other hand, cis–trans photoisomerization is experimentally observed in the fulvene derivative. The photoisomerization of *E*–*Z*-2-*tert*-butyl-9-(2,2,2-triphenylthylidene)fluorene is recently observed experimentally.²⁵ This means that fulvene is useful as photo-switches if suitable substitutions are selected. To select the suitable substitutions, it is necessary to know the condition that makes it possible for the exocyclic methylene to rotate by 180° . Bearpark et al. suggested that the 0–0 excitation to S_1 is needed for the rotation.²² In this paper, considering the existence of the S_1/S_0 DPs, we additionally discuss the condition of the exocyclic methylene rotation by 180° . Bearpark et al.¹² have already revealed that three S_1/S_0 DPs (DP_{planar}: C_{2v} planar structure, DP₆₃: exocyclic methylene is rotated by about 63° with C_2 , and DP_{perp}: exocyclic

* Corresponding author e-mail: kazuya@chem.tsukuba.ac.jp.

methylene is perpendicular to a five-membered ring with C_{2v}) exist in the same S₁/S₀ DS which is predicted to be chemically relevant to cis–trans photoisomerization in contradiction to the suggestion by Deeb et al.²⁶ However, we have some questions about the previous mapping S₁/S₀ DS.¹² Here we will give more reliable results in the geometry with better energy degeneracy.

In section 2, we analyze the origin of the “cancellation error” and suggest the method to assess the validity upon using our computational strategy.^{9,10,13} In section 4, picking up the exocyclic methylene rotation of fulvene, we will show the valid condition in applying the two-step procedure based on section 2. Utilizing the procedure, the possibility of the methylene rotation in a fulvene molecule by 180° is discussed.

2. Theoretical Discussion

To describe the conical intersection, an apex of which is a DP, two coordinates are needed.^{1,27} One is a gradient difference vector (GD)

$$\mathbf{g} = \nabla(E_1 - E_0) \quad (1)$$

and the other is a derivative coupling vector (DC)

$$\mathbf{h} = \langle \Psi_1 | \nabla \Psi_0 \rangle \quad (2)$$

In eqs 1 and 2, the gradient ∇ is a vector operator in nuclear coordinates. Ψ_1 and Ψ_0 are wave functions of the upper and lower states, respectively. Their energies are denoted as E_1 and E_0 . The pair (\mathbf{g}, \mathbf{h}) is usually called a branching plane or a g-h plane.^{1,27} In the complement orthogonal space to the branching plane, the degeneracy is preserved. In this paper, we refer to this complement space as a degeneracy space (DS) which is sometimes called a conical intersection hyperline or seam.^{1,27} The DS is $(n - 2)$ -dimensional space for two states, where n is the number of molecular internal degrees of freedom. We denote unit vectors, \mathbf{x}_1 and \mathbf{x}_2

$$\mathbf{x}_1 = \frac{\mathbf{g}}{|\mathbf{g}|}, \quad \mathbf{x}_2 = \frac{\mathbf{h}}{|\mathbf{h}|} \quad (3)$$

on the branching plane and $(n - 2)$ -dimension internal coordinates orthogonal to the branching plane as $\mathbf{x}_3, \mathbf{x}_4, \dots, \mathbf{x}_n$. \mathbf{x}_i ($i = 3, 4, \dots, n$) is referred to as intersection adapted coordinates.²⁷ Intersection adapted coordinates are different from nonredundant internal coordinates because each of the \mathbf{x}_i ($i = 1, 2, \dots, n$) is represented as a linear combination of some variables like bond lengths, bond angles, and/or dihedral angles. To locate the lowest energy degeneracy point (LEDP) in DS, some optimization methods have been developed.^{3,4,28} The projected gradient method⁴ is extensively used. If this method is used together with a geometric constraint beyond molecular symmetry, however, a point at which the energy of two states are not degenerated is finally reached. We have pointed out that this error is due to constraining the variables that have components in the branching plane.⁹ In the following discussion, we show that the error is due to constraining the variables that have components in both the branching plane and the intersection adapted coordinates.

In the projected gradient method, the following gradient is used

$$\mathbf{g}^{\text{CIO}} = P \nabla E_1 + 2(E_1 - E_0) \nabla(E_1 - E_0) \quad (4)$$

where P is the projection operator onto the $(n - 2)$ -dimensional intersection adapted coordinates. That is to say, P deducts DC and GD from ∇E_1 . Here, we write the GD in a non-normalized form for simplicity although the GD in eq 4 is practically coded in a normalized form, \mathbf{x}_1 .

Hereafter, we regard E_1 as a function of internal molecular coordinates, v_i ($i = 1, 2, \dots, n$), and define \mathbf{e}_i as a unit vector in the direction of the displacement of v_i . \mathbf{e}_i must be orthogonal to each other. For instance, \mathbf{e}_i can be obtained by orthogonalizing the unit vector of a physically significant set like bond lengths, bond angles, and dihedral angles.²⁹ Then, ∇E_1 can be represented by derivatives with respect to v_i ($i = 1, 2, \dots, n$).

$$\nabla E_1 = \frac{\partial E_1}{\partial v_1} \mathbf{e}_1 + \frac{\partial E_1}{\partial v_2} \mathbf{e}_2 + \dots + \frac{\partial E_n}{\partial v_n} \mathbf{e}_n \quad (5)$$

For convenience, we classify the components of ∇E_1 into four groups.

$$\begin{aligned} \nabla E_1 &= \frac{\partial E_1}{\partial v_L} \mathbf{e}_L^T + \frac{\partial E_1}{\partial v_M} \mathbf{e}_M^T + \frac{\partial E_1}{\partial v_S} \mathbf{e}_S^T + \frac{\partial E_1}{\partial v_P} \mathbf{e}_P^T \\ &= \sum_h \frac{\partial E_1}{\partial v_{L,h}} \mathbf{e}_{L,h} + \sum_i \frac{\partial E_1}{\partial v_{M,i}} \mathbf{e}_{M,i} + \sum_j \frac{\partial E_1}{\partial v_{S,j}} \mathbf{e}_{S,j} + \sum_k \frac{\partial E_1}{\partial v_{P,k}} \mathbf{e}_{P,k} \quad (6) \end{aligned}$$

where v_L is the group of the components which has no overlap with the branching plane. Both v_M and v_S are the groups of the components having overlap with the branching plane, but v_S is the variable that is constrained. On the other hand, v_P is the group of the components that lie within the branching plane. Corresponding unit vectors are denoted by $\mathbf{e}_L, \mathbf{e}_M, \mathbf{e}_S$, and \mathbf{e}_P and distinguished by an additional subscript. After applying P , eq 6 becomes

$$\begin{aligned} P \nabla E_1 &= \sum_h \frac{\partial E_1}{\partial v_{L,h}} \mathbf{e}_{L,h} + \sum_i c_{M,i} \frac{\partial E_1}{\partial v_{M,i}} \mathbf{e}_{M,i} + \sum_j c_{S,j} \frac{\partial E_1}{\partial v_{S,j}} \mathbf{e}_{S,j} \quad (7) \end{aligned}$$

where coefficients, $c_{M,i}$ and $c_{S,j}$, satisfy

$$\begin{aligned} c_{M,i} &= 1 - \mathbf{x}_1 \cdot \mathbf{e}_{M,i} - 1 - \mathbf{x}_2 \cdot \mathbf{e}_{M,i} \\ &= 1 - c'_{M,i} \quad (8a) \end{aligned}$$

$$\begin{aligned} c_{S,j} &= 1 - \mathbf{x}_1 \cdot \mathbf{e}_{S,j} - 1 - \mathbf{x}_2 \cdot \mathbf{e}_{S,j} \\ &= 1 - c'_{S,j} \quad (8b) \end{aligned}$$

The branching plane component should be represented by the deducted component. Then we write the component of the second term in eq 4 as

$$\nabla(E_1 - E_0) = \sum_i c'_{M,i} \frac{\partial E_1}{\partial v_{M,i}} \mathbf{e}_{M,i} + \sum_j c'_{S,j} \frac{\partial E_1}{\partial v_{S,j}} \mathbf{e}_{S,j} + \sum_k \frac{\partial E_1}{\partial v_{P,k}} \mathbf{e}_{P,k} \quad (9)$$

Equation 4 then becomes

$$\mathbf{g}^{\text{CIO}} = \sum_h \left(\frac{\partial E_1}{\partial v_{L,h}} \right) \mathbf{e}_{L,h} + \sum_i \left(c_{M,i} \left(\frac{\partial E_1}{\partial v_{M,i}} \right) + 2(E_1 - E_0) c'_{M,i} \left(\frac{\partial E_1}{\partial v_{M,i}} \right) \right) \mathbf{e}_{M,i} + \sum_j \left(c_{S,j} \left(\frac{\partial E_1}{\partial v_{S,j}} \right) + 2(E_1 - E_0) c'_{S,j} \left(\frac{\partial E_1}{\partial v_{S,j}} \right) \right) \mathbf{e}_{S,j} + \sum_k 2(E_1 - E_0) \left(\frac{\partial E_1}{\partial v_{P,k}} \right) \mathbf{e}_{P,k} \quad (10)$$

Although the third summation term is eliminated for geometric constraint, we keep this term for clear discussion. The following condition is also implicitly imposed because of the orthogonality between the intersection adapted coordinates and branching plane:

$$P \nabla E_1 \cdot \nabla(E_1 - E_0) = \sum_i c_{M,i} c'_{M,i} \left(\frac{\partial E_1}{\partial v_{M,i}} \right)^2 + \sum_j c_{S,j} c'_{S,j} \left(\frac{\partial E_1}{\partial v_{S,j}} \right)^2 = 0 \quad (11)$$

According to eq 10, the convergence condition then reads

$$\frac{\partial E_1}{\partial v_{L,h}} = 0 \quad (12a)$$

$$c_{M,i} \frac{\partial E_1}{\partial v_{M,i}} + 2(E_1 - E_0) c'_{M,i} \frac{\partial E_1}{\partial v_{M,i}} = 0 \quad (12b)$$

$$c_{S,j} \frac{\partial E_1}{\partial v_{S,j}} + 2(E_1 - E_0) c'_{S,j} \frac{\partial E_1}{\partial v_{S,j}} = C_{S,j} \quad (12c)$$

$$2(E_1 - E_0) \frac{\partial E_1}{\partial v_{P,k}} = 0 \quad (12d)$$

Here, $C_{S,j}$ is finite. Equation 12(a) shows that optimization will be successful if the variables that have no overlap with the branching plane are employed. As for eq 12(d), two situations are possible. One is $E_1 - E_0 = 0$ and the other is $\partial E_1 / \partial v_{P,k} = 0$. The former condition is, however, ruled out by the following reason: Multiplying eq 12(b) by $c_{M,i} (\partial E_1 / \partial v_{M,i})$ and using eq 11

$$\sum_j c_{S,j} c'_{S,j} \left(\frac{\partial E_1}{\partial v_{S,j}} \right)^2 = 2(E_1 - E_0) \sum_i c'_{M,i} \left(\frac{\partial E_1}{\partial v_{M,i}} \right)^2 \quad (13)$$

is obtained. Apart from special cases (e.g., the value of $v_{S,j}$ corresponds to that of a LEDP), $c_{S,j} c'_{S,j} (\partial E_1 / \partial v_{S,j})^2$ is not zero from eq 12c. The right-hand side of eq 13 is not zero, accordingly. Namely, the optimization converges to the point where two states do not degenerate (i.e., $E_1 \neq E_0$). This is really a “cancellation error”. If either $c_{S,j}$ or $c'_{S,j}$ is zero, then

Table 1. Values of the Difference ($E_1 - E_0$) (in E_h) and the Gradient, Eq 4 to θ , and $0.5\sqrt{2(E_1 - E_0)|C_{S,\theta}|}$ (in $E_h \text{ \AA}^{-1}$) along θ in the First Step^a

θ (deg)	$(E_1 - E_0)$	$C_{S,\theta}$	$0.5\sqrt{2(E_1 - E_0) C_{S,\theta} }$	RMS
0	0.00000	0.00000	0.00000	0.00000
5	0.00002	-0.01530	0.00005	0.00030
10	0.00008	-0.00890	0.00005	0.00058
15	0.00016	-0.01294	0.00012	0.00085
20	0.00028	-0.01647	0.00019	0.00108
25	0.00041	-0.01928	0.00028	0.00127
30	0.00053	-0.02115	0.00035	0.00140
35	0.00064	-0.02185	0.00039	0.00145
40	0.00070	-0.02119	0.00040	0.00141
45	0.00070	-0.01902	0.00036	0.00127
50	0.00061	-0.01530	0.00027	0.00102
55	0.00042	-0.01018	0.00015	0.00068
60	0.00017	-0.00405	0.00004	0.00027
63.1	0.00000	0.00000	0.00000	0.00000
65	0.00010	0.00235	0.00002	0.00016
70	0.00031	0.00791	0.00010	0.00053
75	0.00038	0.01125	0.00016	0.00074
80	0.00028	0.01103	0.00013	0.00072
85	0.00009	0.00686	0.00005	0.00044
90	0.00000	0.00000	0.00000	0.00000

^a The RMS values of the projected gradient which is obtained after the second step is also listed.

the cancellation error does not occur because there are no dependences between $\partial E_1 / \partial v_{M,i}$ and $\partial E_1 / \partial v_{S,j}$ by eq 11. If both $c_{S,j}$ and $c'_{S,j}$ are not zero, then the cancellation error occurs. Therefore, in contradiction to the previous suggestion (the orthogonality between the first and second term in eq 4 is lost due to the constraint), to keep the orthogonal condition [eq 11], the first term offsets the second term in eq 4.

Recently, this cancellation error has been circumvented by several methods.^{7,9–12} Migani et al.⁷ circumvented it by scaling the second term in eq 4 with a factor of 100. Yamazaki et al.¹¹ circumvented it by orthogonalizing the internal coordinates of molecules. With the gradient of which the constraint is applied before the projection of ∇E_1 onto the intersection adapted coordinates, Bearpark et al.¹² have succeeded to map the S_1/S_0 DS along the exocyclic methylene rotation of fulvene with a maximum energy gap of 0.4 kcal mol⁻¹. It is, however, noteworthy that the points at which a maximum energy gap is approximately 0.4 kcal mol⁻¹ (see Table 1) can be located by using the default gradient (our first step). That is, there is no difference in effect between the default gradient⁴ and the modified gradient.¹²

On the other hand, in our easy computational strategy, after optimization using eq 4 (i.e., converging to the geometry satisfying eq 12), we carried out the geometry optimization using only the second term in eq 4.^{9,10,13} We have used this computational strategy without estimating how well energy is minimized within the intersection adapted coordinates. Here we try to assess the validity of the strategy. Multiplying eq 12b by $c_{M,j} (\partial E_1 / \partial v_{M,i})$ and using eq 11, we obtain

$$\sum_i c_{M,i}^2 \left(\frac{\partial E_1}{\partial v_{M,i}} \right)^2 = 2(E_1 - E_0) \sum_j c_{S,j} c'_{S,j} \left(\frac{\partial E_1}{\partial v_{S,j}} \right)^2 \quad (14)$$

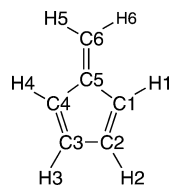


Figure 1. Atom numbering using throughout this paper.

This equation indicates the variables which have overlap with both the branching plane and the intersection adapted coordinates cannot work as an independent variable for optimization due to geometric constraint. In turn, the second step optimization is successfully limited in effect within the intersection adapted coordinates if eq 14 is small enough. The two-step procedure is, in this sense, not for improving the energy degeneracy but for the better geometry in the DS. Validity (or limitation) of the strategy can be assessed by using eq 14 as will be shown later.

3. Computational Details

All calculations in this paper were carried out using the CASSCF method implemented in GAUSSIAN 98³⁰ with the correlation-consistent polarized valence double-zeta (cc-pVDZ) basis set. An active space of six electrons in six orbitals was used, corresponding to π orbitals. CASSCF were carried out using the S₁/S₀ state-averaged orbital, with the two states weighted equally.

To characterize S₁/S₀ DS, we carried out two-step optimizations described in the previous section. In the first step, we used eq 4 as gradient until the square root of eq 14 becomes sufficiently small as will be shown in the next section. In the second step, we used only the second term in eq 4.

Starting from C_{2v} planar structures, the S₁/S₀ DS was scanned in C₂ symmetry along the exocyclic methylene twist motion with a step size of 5° up to C_{2v} twisted structures.

Our calculation is not definitive because the CASSCF does not take into account effects of dynamical electronic correlation. However, the behavior we have predicted in this paper would not be affected qualitatively by it.

4. Results and Discussion

The atomic numbering is shown in Figure 1. Hereafter, θ denotes the twist angle of the exocyclic methylene. In Figure 2, we show the example of the two-step procedure locating DP at $\theta = 45^\circ$.

In eq 14, we have shown that the variables, v_M , that have overlap with both the intersection adapted coordinates and the branching plane are dependent on the constrained variables that also have overlap with these two spaces. From eq 14, the square root of the gradient for v_M in the intersection adapted coordinates is given by

$$\sqrt{\sum_i c_{M,i}^2 \left(\frac{\partial E_1}{\partial v_{M,i}} \right)^2} = \sqrt{2(E_1 - E_0) \sum_j c_{S,j} c'_{S,j} \left(\frac{\partial E_1}{\partial v_{S,j}} \right)^2} \quad (15)$$

According to eq 15, how geometries are well optimized in intersection adopted coordinates depends on the magnitude of $E_1 - E_0$ and the gradient with respect to constrained

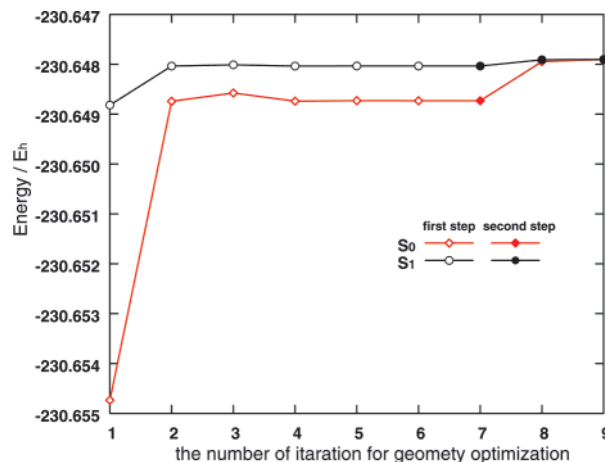


Figure 2. The example of the two-step procedure in locating DP at $\theta = 45^\circ$. The starting structure was produced by replacing the value of θ of the DP at $\theta = 40^\circ$ by 45° . Open symbols (diamond and circle) indicate the first step iteration. Filled symbols (diamond and circle) indicate the second step iteration. At iteration number 6, the first step (using the default gradient \mathbf{g}^{CIO} (eq 4)) was completed, whereas the second step (using the second term of \mathbf{g}^{CIO} (eq 4)) started from iteration number 7.

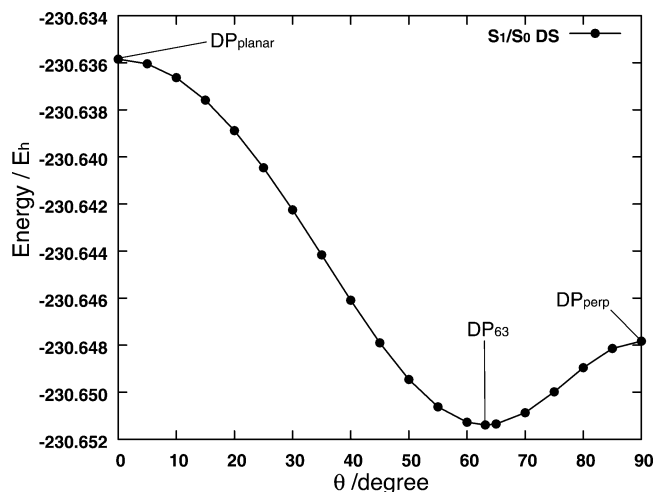


Figure 3. The result of the S₁/S₀ DS along θ .

variables ($\partial E_1 / \partial v_S$) in the first step [using the default gradient, eq 4]. The value of ($\partial E_1 / \partial v_{S,j}$) can roughly be estimated by $C_{S,j}$ in eq 12c. As $C_{S,j}$ includes the normalization factor of the GD, the values of $C_{S,j}$ are larger than ($\partial E_1 / \partial v_{S,j}$). In the system we targeted, only one variable, θ , is constrained. It is known that mutual transformation between forces represented by Cartesian coordinates and by nonredundant internal coordinates is possible.³¹ Furthermore, the physically significant set can be written by the linear combination of \mathbf{e}_i . Therefore, the right-hand side of eq 15 can be written by using θ .

$$\sqrt{\sum_i c_{M,i}^2 \left(\frac{\partial E_1}{\partial v_{M,i}} \right)^2} = \sqrt{2(E_1 - E_0) c_{S,\theta} c'_{S,\theta} \left(\frac{\partial E_1}{\partial v_{S,\theta}} \right)^2} \leq \sqrt{2(E_1 - E_0) c_{S,\theta} c'_{S,\theta} C_{S,\theta}} \quad (16)$$

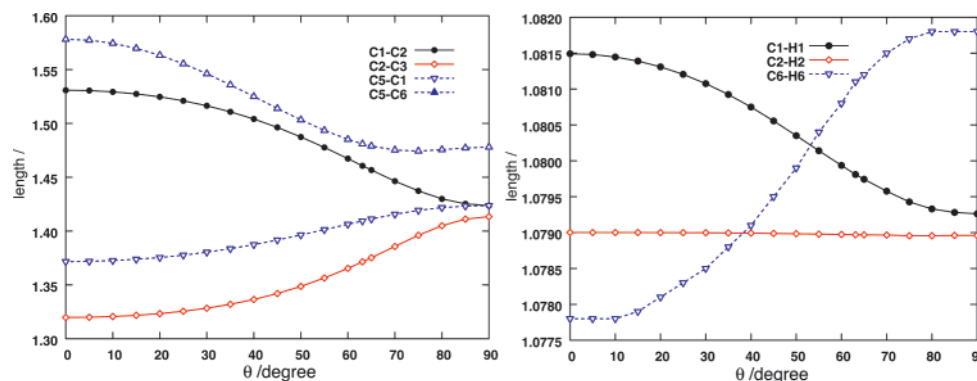


Figure 4. Geometric change along S_1/S_0 DS. (a) carbon-carbon bond lengths and (b) carbon-hydrogen bond lengths.

The values of the $\sqrt{(E_1 - E_0)}$, which is the square root of the difference between energies of the S_1 and S_0 and $C_{S,\theta}$ that is the value of eq 4 as the gradient along θ , are given in Table 1. Furthermore, the upper bound of $\sqrt{c_{S,\theta}c'_{S,\theta}}$ can also be estimated by the inequality between arithmetic and geometric means, i.e., $\sqrt{c_{S,\theta}c'_{S,\theta}} \leq 0.5$. The degree of optimization in the variables which overlap with both intersection adapted coordinates and the branching plane can therefore be estimated as $0.5\sqrt{2(E_1 - E_0)}C_{S,\theta}$ approximately. From Table 1, the gradient of E_1 with respect to the variables which correspond to ν_M is approximately 0.0004 (in $E_h \text{ \AA}^{-1}$). From our experience, this magnitude is small enough to reoptimize from each point obtained in the first step to locate the S_1/S_0 DP using the second term of eq 4. We show the root-mean-square (RMS in Cartesian coordinate) of projected gradient on E_1 [the first term in eq 4] whose component of exocyclic methylene rotation is given in Table 1. According to the values of RMS of Table 1, the geometry of the finally obtained DP is optimized within $1.5 \times 10^{-3} E_h \text{ \AA}^{-1}$ at worst. These RMS values are comparable to those of the residual gradient optimized “loosely” by GAUSSIAN 98. There is one more important condition for validity of the two-step procedure. The tendency of change of the value of the RMS indicates a similar change of the value of (16) along θ . This means the final geometry may be in the same intersection adapted coordinates of the geometry which is obtained in the first step. From our experiences, if the tendency of the change of the final RMS is different from that of eq 16, resultant DS would not be meaningful. In Figure 2, we show the example of the two-step procedure locating DP at $\theta = 45^\circ$.

Now, it is in order to see some details of the characterized DS. The S_1/S_0 DS characterized S_1/S_0 using the above strategy is shown in Figure 3. A recent second-order derivative calculation in the S_1/S_0 DS²⁴ has revealed that DP_{planar} and DP_{perp} are second- and first-order saddle points, and DP_{63} is almost the global minimum on the S_1 excited state and S_1/S_0 DS though its energy is slightly lowered by pyramidalization.³² Our result is favorably compared with the second derivative calculation. The energies of the two states agreed within $10^{-5} E_h$ for all the DPs located. Starting from DP_{planar} , we have characterized the S_1/S_0 DS along θ up to DP_{perp} . This result also tells us that θ is the variable which has overlap with

both the intersection adapted coordinates and the branching plane. Unless so, the first step optimization should converge to DP.

The origin of degeneracy of DP_{planar} and DP_{perp} is different. In DP_{planar} , the degeneracy occurs by elongating the exocyclic double bond and enhanced allylic character. On the other hand, in DP_{perp} ,²² the degeneracy stems from the D_1/D_0 symmetry required conical intersection of the cyclopentadienyl radical.^{33,34} The bonds that compose the five-membered ring become more similar to each other. Indeed, the bond lengths of C1-C2, C5-C1, and C2-C3 become about 1.4 Å equally. In spite of the different origin of the DP, Figure 4 shows that the electronic structure is continuously changed from DP_{planar} to DP_{perp} . This demonstrates that DP_{planar} and DP_{perp} are in the same DS.

The behavior of the exocyclic double bond C5-C6 is very interesting. We expected that the tendency of the geometric change of C5-C6 is changed in the vicinity of DP_{63} corresponding to the global minimum on the S_1 state. However, around DP_{63} (i.e., around $\theta = 60^\circ$), there are no particular changes. This implies that the electronic structure is not changed around DP_{63} . Instead, the tendency of the geometric change of C5-C6 is changed around DP_{75} . Hence, we can imagine that the DPs between $\theta = 0^\circ$ and $\theta = 75^\circ$ will be photochemically discriminated from the DPs between $\theta = 80^\circ$ and $\theta = 90^\circ$. To clarify the final product via the S_1 state, we have performed S_0 geometry optimizations using a state-averaged orbital from structures near DP_{63} , DP_{75} , and DP_{80} . Starting structures were generated by distorting the DP geometries in the direction of GD. These results indicate that the product whose exocyclic methylene is rotated by 180° is available from DP_{80} but not from DP_{63} and DP_{75} . Therefore, if the S_1 excited fulvene can reach the DPs between $\theta = 80^\circ$ and $\theta = 90^\circ$, then the exocyclic methylene rotation by 180° is possible. If DPs in this area are stabilized by the proper substitution so that the S_1 excited fulvene can reach this area, then cis-trans photoisomerization will become possible. In the dibenzofulvene system whose $E-Z$ photoisomerization is observed recently,²⁵ adding the benzene to fulvene may give rise to the stabilization of the DPs between $\theta = 80^\circ$ and $\theta = 90^\circ$.

5. Conclusion

We have shown that the cancellation error is due to the constraint of the variables that have components in both the branching plane and the intersection adapted coordinates. Accordingly, the valid condition for the two-step procedure is limited. Taking into account the limitation, we have characterized the S₁/S₀ DS along the exocyclic methylene rotation coordinate of fulvene within $1.5 \times 10^{-3} E_h \text{ \AA}^{-1}$ in energy at worst.

Our calculation, which we have shown in this paper, is limited to C₂ symmetry. Though systems which have no symmetry like ref 25 should be explored, the following conclusion would be worthy to be noted. The photophysical/photochemical behavior changes in the continuous DS. The DPs where the photochemical property changes are not the saddle point on the S₁/S₀ DS within C₂ symmetry. That is, the product obtained via S₁/S₀ DPs in the vicinity of DP₆₃ does not change. It is difficult for the exocyclic methylene to rotate by 180°, when the S₁ excited fulvene transits to S₀ via DPs between DP_{planar} and DP₇₅. However, in DPs between DP₈₀ and DP_{perp}, the exocyclic methylene rotation is expected. Therefore, photochemically, DP_{80-perp} may be discriminated from DP_{planar-75}.

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Supporting Information Available: Cartesian coordinates of DPs geometries discussed in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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