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The Role of the Intersection Space in the Photochemistry of Tricyclo[3.3.0.0^{2,6}]octa-3,7-diene

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CASSCF and CASPT2 methods were used to study the photochemistry of tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (TOD). The analysis of different S_{1} reaction paths as well as the topology of the S_{1}/S_{0} intersection space allows us to establish two novel properties associated with the photochemical behavior of this compound: (i) simple low-lying intersection space domains can mediate different photoproducts, and (ii) TOD photochemistry is probably mediated by two disconnected intersection space domains, related to the formation of cyclooctatetraene and semibulvalene in different time-scales. It is shown that these domains are chemically distinct since the first, leading to COT, mediates barrierless pericyclic reactions while the second, leading to SBV, is accessed through the formation of an excited-state biradical intermediate. To the best of our knowledge, in the domain of single molecule photochemistry, TOD represents the first example where a different chemical role of distinct low-lying intersection spaces has been computationally documented. The observed photoproducts can be rationalized in terms of branching space diagrams, constructed by determining the branching space (derivative coupling and gradient difference vectors) for each conical intersection involved in the photochemical process.

Conical Intersections (CI) are fundamental mechanistic keys to understanding photochemical processes.1 Usually, only one CI structure is considered when dealing with the mechanism of a photochemical reaction. Nevertheless, conical intersection points are elements of the intersection space: an N-2-dimensional subspace of conical intersections (where N corresponds to the vibrational degrees of freedom of the reacting system),2 and consequently, full segments of this subspace can be involved in the decay process.3 The segment of the intersection space accessible by the system are likely to be “chemically homogeneous” (i.e., photoproducts originating from all the points of the segment are the same), nevertheless, in principle, it may be possible that a finite intersection space segment provides different reaction channels leading to different photoproducts.1(b),3

In this work we present an investigation of the photochemistry of tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (TOD, see Scheme 1) and provide evidence in favor of the existence of two chemically distinct intersection spaces S_{1}/S_{0} involved in the decay process. Furthermore, we show that the distinct accessibility of these intersection spaces leads to complex photochemical behavior, where the different photoproducts (semibulvallene, SBV and 1,3,5,7-cyclooctatetraene, COT) are formed on different time-scales because of the different paths followed (i.e., activationless for COT and through an intermediate for SBV) in the relaxation process on the excited state (S_{1}).

SCHEME 1: TOD Ground State Equilibrium Structure (Numbering Used in the Text) and the Experimentally Observed Photoproducts: 1,3,5,7-Cyclooctatetraene (COT) and Semibulvalene (SBV) in Approximate Proportion of 2:1

Experimental results indicate that irradiation of TOD at ~60 °C leads to the concomitant formation of SBV and COT in an approximate ratio of 2:1 (See Scheme 1).4 The low-temperature ensures that the isomerization of TOD to SBV is negligible in the time-scale of the complete photochemical reaction (i.e., ~1 h). Different mechanisms have been proposed for the photochemical rearrangement of TOD to yield COT and SBV, involving a [2+2] retro-cycloaddition for COT and a concerted suprafacial[1,3]-sigmatropic shift for SBV, or the formation of COT and SBV via a highly vibrationally excited biradical intermediate.5 Nevertheless, none of the mechanisms have been validated by experimental or theoretical studies.

Our theoretical investigation gives, for the first time, an insight into the mechanism of the photoreaction. It is shown that COT is formed mainly via an efficient ultrafast internal conversion process (that may occur in the femtosecond time-scale) where decay to the ground state occurs through an intersection space domain comprising two qualitatively different mechanisms of reaction: a [2+2] cycloaddition for a D_{2} symmetry CI, and a photocyclization where a single σ transannular bond is formed/broken for a C_{2} symmetry CI. On the
The role of the interconversion space in TOD


The Role of the Intersection Space in TOD

Results and Discussion

1. Photochemical Reaction Paths. The singlet absorption spectrum of TOD, a nonconjugated diene hydrocarbon, shows specific behavior since it cannot be considered as the sum of the two isolated double bond spectra. As shown earlier, hyperconjugation through the highly strained cyclobutane central ring, couples the double bonds, giving an S1 excitation energy (≈300 nm) lower than the corresponding S1 band of two non-interacting double bonds (≈250 nm). This fact indicates that the molecular orbitals of the central cyclobutane ring must be enclosed in the active space of the multiconfigurational calculations (see also Computational Details) because of the role in the hyperconjugation. This is consistent with the computed CASPT2 S0 → S1 excitation energy (≈272 nm, see Table 1).

Zero-point vibrational energy correction leads to a more stabilized S1 state (by ~9 kcal/mol), giving a S0 → S1 absorption wavelength (≈298 nm) that is in very good agreement with the experiment. At the FC point, the S1 potential energy curve (second derivatives) presents five negative values, corresponding to vectors of D2, C2, C1 (two fold degenerate) and D2 symmetry, which are orthogonal to the energy gradient vector.7

These five negative eigenvalues of the Hessian also reveal that the initial relaxation directions from the FC point on S1 can occur as a combination of five directions (apart of the energy gradient vector). Accordingly, the possible initial relaxation directions from the FC point were searched by performing minimum energy path (MEP) computations starting from structures with a small initial distortion (0.03 au/Å) along the modes associated with the five negative curvatures. The results demonstrate that, initially, the computed MEPs are almost co-incident and lead to a common transient tetraradicaloid structure corresponding to a bifurcation point, BP1, where the two double bonds (C1≡C4 and C7≡C8) are almost broken reaching a value for the CC distance of ~1.5 Å, which corresponds to a single bond (see Figure 1). The bifurcation points are characterized by a zero eigenvalue of the diagonal projected Hessian (see computational details). The formation of this unstable structure is also characterized by expansion of the CC bond of the central strained cyclobutane ring, which provides a stabilization of the system by allowing a through bond coupling of the radical centers.5

Two of the three MEPs (of symmetry D2 and C2) finish in a Conical Intersection (CI1 and 2 respectively), while the C2 MEP finishes in a biradical species (BR). The three MEPs diverge due to the presence of two bifurcation points (BP1 and BP2 points) on S1 (marked with blue circles).

Contrary, SBV is mainly formed via an S1 intermediate biradical species, which can evolve rapidly (with low energy of activation) to reach a second intersection space domain, which provides an efficient funnel for radiationless decay to the ground state and SBV formation.

### Table 1: CASSCF and CASPT2(6-31G(d)) Energies for the Significant Points of the PES

<table>
<thead>
<tr>
<th>Structure</th>
<th>CASSCF(8, 8)-31G(d)</th>
<th>CASPT2(8, 8)-31G(d)</th>
<th>Relative energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>S1</td>
<td>S0</td>
<td>S1</td>
</tr>
<tr>
<td>TOD (D2h)</td>
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<td>TOD (D2h)</td>
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<td>-307.46165</td>
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</tr>
<tr>
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<td>-308.41001</td>
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<tr>
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</table>

* Absolute energies in a.u. * CASPT2 eigenvalues were examined in order to eliminate contributions from intruder states (weight of the reference function > 0.74 in all cases). " Relative to TOD (S0 equilibrium geometry) CASSCF energies in kcal/mol. The relative CASPT2 energies are given in parenthesis. 5 Oscillator strength for the S0 → S1 FC transition in TOD equal to 0.0851. Electronic energies with zero point energy (ZPE) corrections obtained by CASSCF(8,8)-31G* analytical frequencies. In this case relative energies are taken from the ZPE corrected energy on the Absolute minimal energy conical intersection of the subspace. Data taken from ref 17b.

Figure 1. Plot of the three qualitatively different MEPS related to the relaxation processes after the S0 → S1 FC transition for TOD. The MEPS are displayed as a function of a and z coordinates. Two of the three MEPs (those of symmetry D2 and C2) finish in a Conical Intersection (CI1 and 2 respectively), while the C2 MEP finishes in a biradical species (BR). The three MEPS diverge due to the presence of two bifurcation points (BP1 and BP2 points) on S1 (marked with blue circles).

Contrary, SBV is mainly formed via an S1 intermediate biradical species, which can evolve rapidly (with low energy of activation) to reach a second intersection space domain, which provides an efficient funnel for radiationless decay to the ground state and SBV formation.
space, that is, the linear two-dimensional subspace of coordinates where the energy degeneracy is lifted, to characterize these conical intersections, i.e., to predict and rationalize the possible relaxation paths on \( S_0 \) and consequently the possible formed photoproducts. The branching space diagrams for CI\(_1\) and CI\(_2\) are given in Figure 2.

These diagrams suggest that CI\(_1\) may mediate an intramolecular cycloreversion while CI\(_2\) may mediate a radical photocyclization. In order to confirm this prediction, we computed equally spaced MEPs in the branching space according to the prescriptions defined in ref 10. Different minima on \( S_0 \), associated with different photoproducts, were reached. Accordingly, from the CI\(_1\) (\( D_2 \) symmetry), reversion to the reactant (TOD) as well as the formation of cyclooctatetraene (COT) was confirmed. On the other hand, from CI\(_2\) (\( C_2 \) symmetry) the computed MEPs were consistent with the formation of COT as well as trans,cis,trans,cis-COT (t,t-COT)\(^{11}\) (notice that the large value of the \( C_1-C_2 \) distance (2.39 Å) in CI\(_2\) is likely to be responsible for the lack of a photocyclization product from this funnel; only when such a distortion is reduced (for example 2.11 Å in CI\(_3\), see below) the photocyclization may occur). Since no barriers were detected along either the \( S_1 \) or \( S_0 \) MEPs, the described photochemical pathways which involve decay at CI\(_1\) and CI\(_2\) must be related to ultrafast dynamics (i.e., no intermediate is populated in the excited-state and the decay to the ground state occurs via a CI) (see Figure 3).

CI\(_1\) and CI\(_2\) are qualitatively different in both the geometrical structure of the conical intersections and the structure of the branching space. These changes are obviously enough to prompt the formation of different photoproducts. As seen above, already the analysis of the derivative coupling (DC) and gradient difference (GD) vectors (Figure 2) revealed the possibility of a \([2+2]\) photocycloreversion process (involving the central moiety of TOD) for CI\(_1\) and a radical photocyclization for CI\(_2\), where the two interacting central carbon atoms are closer than the other.

Figure 2. Branching space diagrams for CI\(_1\) of \( D_2 \) symmetry (a) and CI\(_2\) of \( C_2 \) symmetry (b) are shown. GD and DC vectors expands the two-dimensional branching space that lifts out the energy degeneracy. CI\(_1\) corresponds with a \([2+2]\) cycloaddition (given by the GD vector), while CI\(_2\) is related with a radical photocyclization (GD vector). The DC vector stands by the \( \pi \)-charge coupling in both cases.
two central atoms (see branching space diagrams in Figure 2; anyway, note that photocyclization from CI2 is aborted, as seen above).

The second type of TOD photochemical reaction pathway revealed by our MEP computations involves population of a biradical intermediate on S1 (BR12) (see Figure 1). In fact, the MEP associated with a distortion along the normal mode of symmetry C_s with imaginary frequency (see above), reaches an energy minimum (BR) with a biradical character on S1. From BR, the system can reach, trough three different transition states (TS CI3, TS CI4 and TS CI5) three new CIs (CI3, CI4 and CI5 of C1, Cs, and Cs symmetry respectively).

TS CI3 is located ~15.5 kcal/mol above BR at the CASSCF level of theory. Nevertheless, single-point CASPT2 correction to the energy along the computed IRC linking BR with CI3, leads to a flat transition state region, with only a ~4 kcal/mol activation energy (see Table 1 and Figure 4). To better characterize BR and check if this is a real minimum or a non-stationary point, we have re-optimized this point using a CASPT2 numerical gradient with a CASSCF(6,6)/6-31G(d) zeroth-order wave function, including in the active space only the π-type molecular orbitals. A rapid convergence to a stationary point suggests that BR is a S1 minimum also at the CASPT2 level. On performing single-point correction at the improved CASPT2/CASSCF(8,8)/6-31G(d) level the energy of activation is corrected to an improved value of ~6 kcal/mol (see Table 1).

Similar to CI3, also CI4 and CI5 are accessed from BR by overcoming a transition state on S1 (TS CI4 and TS CI5, respectively). The energy profile along the MEP computed at the CASSCF level predicts 5.8 and 6.5 kcal/mol energy of activation for the TS CI4 and TS CI5, respectively. In order to obtain at least a qualitative value for the activation energy at the CASPT2 level of theory, we have performed a linear scan (in internals coordinates) from BR to CI4 and CI5. The results (see supporting material) predict a unique maximum along the path, with activation energies of 8.69 and 5.57 kcal/mol, respectively. Obviously, these values of energy of activation represent upper

Figure 3. Energy (in au) profile of the complete relaxation process for the ultrafast photochemical reaction of TOD after the FC transition to S1 as a function of internal coordinates. Relaxation on S1 (red arrows) allows the system to reach two different CIs (CI1 and CI2) of symmetry D2 (left) and C2 (right). The ultrafast decay to the ground state (blue arrows) via the conical intersections yield the formation of several photoproducts (TOD, COT, and t,t-COT).

Figure 4. CASSCF IRC for TS CI3 and single-point CASPT2 correction to the energy. Filled symbols correspond to CASPT2 computations, while open symbols to CASSCF. Circles correspond to S1 state and squares to S0. Relative energy in kcal/mol is referred to the S0 BR energy.
limits. Therefore, CASPT2 energies of activation are estimated by single-point corrections on the CASSCF transition state geometries with upper limits given by CASPT2 maxima along the scans. Consequently, the CASPT2 activation energies should be around 3.9 kcal/mol with an upper limit of 8.7 kcal/mol for TS C134, and around 0.2 kcal/mol with an upper limit of 5.6 kcal/mol for TS C15. In view of the small activation energies, we predict a short lifetime for BR, which will evolve along the three different pathways leading to CI3, CI4, and CI5. The accessibility of each pathway must be related to the corresponding activation energy; therefore, the efficiency should follow the order: TS C15 > TS C14 > TS C13. The MEP computed on S0 from the CIs10 forms different photoproducts. Thus, for CI3 the ~50% of the computed MEPs is related to the formation of COT, while ~40% is related to the formation of SBV and only ~10% is related to the formation of the t-COT isomer. Therefore, this CI3 seems to be an efficient channel to the formation of COT as well as SBV photoproducts, which are, as it has been noted before, the main photoproducts of the photochemical reaction. CI4 and CI5 are responsible for the formation of BRs, through the formation of a biradical structure on S0 with symmetry C2v, which corresponds to the transition state connecting two equivalent SBV in a Cope rearrangement process (Figure 5).13 There is also the possibility of forming other biradical species (BR C134 and BR C15, see Figure 5) in the nonradiative decay through CI4 and CI5, due to σ bond formation. However, these channels for relaxation in the ground state are less favored compared with the formation of SBV because the accessibility of the valleys on the PES aids the formation of SBV, i.e., the beginning of the valley in the ground state PES associated with the formation of the biradical species, BR C14 and BR C15, is more far from the cusp of the CI than that corresponding to the formation of the SBV. Thus, the valley for the formation of the biradical species BR C14 is located at 0.2 amu1/2 bohr,14 while that corresponding to the formation of SBV is located at 0.02 amu1/2 bohr from CI4. For CI5 the situation is analogous, the formation of the SBV being related to a path starting in the neighborhood of the CI (0.02 amu1/2 bohr), while the path for the formation of the σ bond and the corresponding biradical species is located at 0.28 amu1/2 bohr far away. Therefore, both CI4 and CI5 should be efficient funnels principally for the formation of SBV (and other biradical species to a minor extent).

The computed MEPs are in agreement with the main predictions that can be made from the analysis of the branching space for both CI4 and CI5 (see Figure 5). While this analysis provides a rationale for photoproducts formation,
only MEP computations tell us which photoproduct can be really formed.

Finally, it should also be possible for BR to decay radiatively to the ground state by forming the corresponding biradical structure on S0. This biradical is close to the transition state structure for the Cope rearrangement interconverting two equivalent SBVs. Therefore, the formation of SBV is predicted by radiative decay to S0 through the BR intermediate on S1. Moreover, this process is predicted to be a minor event due to the short lifetime expected for BR, as the small barrier to CI5 reveals.

In summary, for the second type of reaction pathway, a biradical species (BR) is populated in the S1 state. In both radiative and nonradiative decay processes to the ground state, the main photoproduct formed is the SBV, while COT can also be formed as a minor product in conjunction with t-COT and some biradical species.

2. Intersection Space Analysis. Using the conical intersection optimization method, we have been able to demonstrate the CI1, CI2, and CI3 converge to the same optimized conical intersection CIM (i.e., a stationary conical intersection point, featuring a vanishing gradient in the intersection space). Therefore, the two immediately accessible CIs must belong to the same intersection space. In fact, during optimization the energy degeneracy is maintained, with the S0=S1 energy gap always \( < \approx 2.5 \text{ kcal/mol} \) and the step-size always low enough (maximum 0.1 bohrs or radians) to avoid discontinuity in the paths. This indicates that there is a continuous line of conical intersections connecting CI1, CI2, CI3, and CIM that, therefore, must belong to the same domain of a stationary CI. Furthermore, we have been able to demonstrate that CIM pertains to the intersection space in which a lower energy conical intersection (CIA) is contained. We have performed single-coordinate and double-coordinate relaxed scans in the S1/S0 intersection space to prove that CIM and CIA are linked by a continuous space of intersection points (See Computational Details and Figure 7). The results indicate that CIM is a transition state in the intersection space and that a MEP on this space leads to the minimum CIA (See Figure 7). According to our previous works, CIA (a conical intersection of symmetry \( C_{2v} \)) is involved in the nonradiative decay process of excited COT. Indeed, CIA controls the photoinduced ring inversion and bond shifting of COT as well as the formation of two equivalent semibullvalene (SBV) photoproducts through a transition state for the Cope rearrangement.

Therefore, here we present an example in which different regions of the same continuous intersection space (i.e., the regions related with the stationary conical intersections CIA and CIM) provide diverse photochemical pathways for different valence isomers of the same compound (COT and TOD, respectively).

In common with CI1, CI2, CI3, CIM, and CIA, we have provided evidence that CI4 and CI5 belong to the same intersection space by locating a transition-state structure in the intersection space connecting both structures (see Supporting Information).

The analysis of the branching spaces associated with the two crossing seams suggests that these are not connected: in order to connect by a continuous hyperline the stationary conical intersections CIM with CI4 or CI5 it is necessary to form the central \( \sigma \) bond. The branching space for the CIM is qualitatively equal to that of the CI2 (see Figure 2), therefore any distortion...
Figure 7. Relaxed double-coordinate scan (energies in a.u.) on the region of the intersection space linking the CIA and CIM conical intersections (see Computational Details). The surface was obtained by fitting a total of 1369 optimized points in the S1/S0 intersection space to a polynomial function on “X” and “Y” with 55 parameters. The “X” and “Y” coordinates are given by the “1−2−3−4” dihedral angle and its C2 symmetry equivalent (where C2 symmetry is maintained for X=Y).

used to form this central bond makes the molecule to leave the intersection space. Thus, it is very much unlikely that a continuous crossing seam exists connecting these two families of CIs, at least in the low-energy region of the intersection space.

**Computational Details**

Most of the gradient computations (optimizations and minimum energy paths) were performed at the CASSCF(8e,8MO) level with a 6-31G(d) basis set. Analytical frequencies were performed at the same level of theory using the Gaussian98 suite of programs.18 Single-point energy corrections at the CASPT2 level of theory and CASPT2 optimization of the BR structure using numerical gradients, were performed using the MOLCAS 6.0 suite of programs.19 (Table 1)

The active space for the CAS calculation was chosen to include the hyperconjugation effect between the two double bonds through the cyclobutane central ring, by including σ orbitals of the central ring in the active space. The four σ-type orbitals (2 occupied and the lowest 2 unoccupied), as well as four σ-type orbitals pertaining to the central cyclobutane ring were included in the active space. The σ-type orbitals are the lowest unoccupied and higher occupied and takes into account equal contribution of the four C atoms of the ring. Further single-point computations which include up to 12 electrons and 12 MO were performed to test the influence of the inclusion of all σ electrons for the central ring. No significant contributions of the new configurations respect to using the 8MO,8e scheme were found, which validates the selection of the 8MO,8e active space.

All the computed relaxation pathways (MEPs and initial relaxation directions) were performed at the CASSCF level of theory. In the S1 relaxation process the eigenvectors of the diagonalized Hessian matrix and the gradient vectors were taken as initial relaxation directions for computing the MEP. For the study of the relaxation process on S0 after passing through the funnel provided by the different conical intersections, twenty initial relaxation directions equally spaced in the branching space10 were taken as initial relaxation directions. In addition, initial relaxation computations were performed to determine the beginning of the valley corresponding to the formation of the photoproducts from the CI4 and CI5 conical intersections.14

Stationary points were fully optimized and characterized using analytical frequency calculations at the CASSCF level. The bifurcation points were located by diagonalizing the projected Hessian matrix20 for every point along the MEP on S1; thus, the points of the MEP with closer to zero eigenvalues of the projected Hessian have been identified as bifurcation points. In the case of conical intersections, those involved in ultrafast processes (CI1 and CI2) were determined by computing the state-averaged MEP on S1, where the conical intersections are the final points of the corresponding MEP. The same situation is valid for CI3, CI4, and CI5, but here the MEP involves the associated transition state. The structures of CI4 and CI5 found with this procedure are virtually the same as those obtained from full optimizations in the intersection space by using standard methods of conical intersection optimizations as implemented in Gaussian98.18 Finally, the relaxed scans involving CIM and CIA on the intersection space were performed at the CASSCF(8e,8MO)/6-31G(d) level of theory for the single-coordinate, and due to the large number of optimizations (a total of 1369) the double-coordinate relaxed scan was performed at the CASSCF(8e,8MO)/STO-3G level using constrained optimizations in the intersection space.

**Conclusions**

By constructing the branching space diagrams for the most representative conical intersections involved in the photochemistry of TOD (CI1, CI2, CI4, and CI5), we could account for the experimentally observed photoproducts (COT and SBV). These diagrams seem to be very useful in predicting the photochemical behavior of a chemical system, even for molecules showing complex photochemical behavior, as for TOD. Nevertheless, only by the analysis of the computed MEPs and relaxation processes both on the excited and the ground state, qualitative information on the efficiency and time scale for the process can be obtained. By performing different MEPs on S1, we have found two bifurcation points. In particular, three main different minimum energy paths exist on S1, which are related
to different photochemical processes. By following these MEPs, different conical intersection domains can be reached, which are related to different photochemical reactions and trigger the formation of the two main photoproducts: TOD and SBV. Because of the variety of the conical intersections involved in the decay to \( S_0 \), a deeper analysis of the intersection space was necessary to better understand the photoproduct formation. Thus, by carrying out the study of the topology of the intersection space as well as the related relaxation paths on \( S_0 \), we have found that the simple low lying intersection space domain including CI1, CI2, and CI3 (as well as CI4, which is related to COT photochemistry) is responsible for COT formation. Since this segment of intersection space is directly accessible via barrierless routes on \( S_1 \), we expect COT formation to be efficient and ultrafast, as well as the main photoproduct afforded by the photochemical reaction, in agreement with the experiments. Similarly, a second intersection space domain has been located (including CI4 and CI5) which is unconnected to the first and mediates SBV photoproduction formation through barrier (although small) controlled paths (i.e., longer time-scales), thus affording the secondary photoproduction. Therefore, the two intersection space domains which are “chemically” distinct, are related to the formation of the two main photoproducts in a different time-scale: COT (involving an ultrafast barrierless process) and SBV (involving an excited-state biradical intermediate and a barrier activated process). Together with the formation of COT, the first intersection space domain is responsible for the back formation of TOD and t-t-COT to a minor extent, which at room temperature should isomerize to yield the most stable conformation: COT. Moreover, there are qualitative differences between the conical intersections belonging to this intersection space, since CI1 corresponds with a \([2+2]\) cycloaddition while CI2 formally corresponds with a photocyclization process (although this is aborted).

In contrast, the second type of photochemical behavior implies the population of a relatively unstable biradical intermediate on \( S_1 \) (BR). From this intermediate, it is possible to reach two different CIs belonging to the same segment of the intersection space. These CIs (CI4 and CI5), in addition to providing a route for radiationless decay and SBV formation, may also be responsible to the formation (to a minor degree) of other biradicals.

In conclusion, the experimentally detected photochemical products SBV and COT are correctly predicted to be formed in a different amount and in different time-scales (ultrafast for the primary COT product, and via a slower biradical-mediated process for the secondary SBV product) and involve different conical intersections which belong to different intersection space domains.

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**Supporting Information Available:** Cartesian coordinates, transition state structure, and scans from BR to CI4 and CI5.

This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**


5. A total of 8e, 8MO has been chosen for the active space, corresponding to 4e, 4MO for the two double bonds (\( \pi \) orbitals) and 4e, 4MO (two first HOMOs and two first LUMOs) for the central cyclobutane ring (\( \pi \) orbitals).

6. The negative eigenvalues of the Hessian matrix determined for the FC geometry on \( S_1 \) are \(-844, -761, -593 (x^2) \) and \(-322 \text{ cm}^{-1}\) with symmetries \( D_2, C_3, C_2 \) (2-fold), and \( D_3 \) respectively. The corresponding eigenvectors, which were all orthogonal to the gradient, give the direction of energy decrease within a second order approximation for the PES around the FC geometry on \( S_1 \).

7. These five directions provide a five-dimensional subspace of energy decreases in a second order approximation, while the orthogonal force (i.e., minus energy gradient) vector provides a first-order decrease in the energy. Therefore, any linear combination of these six vectors gives a six-order dimensional subspace of potential energy decrease within first- and second-order expansion of the PES.

8. The \( \sigma \) coordinate corresponds with the average value of the length for the two opposite \( \sigma \) CC bonds of the central cyclobutane ring which are broken in the relaxation process on \( S_1 \) (e.g., \( C_1=C_2 \) and \( C_3=C_4 \)). The \( \pi \) coordinate stands for the average value of the length for the CC double bonds (i.e., \( C_1=C_4 \) and \( C_2=C_3 \)).

9. 20 MEPs in \( S_0 \) were computed for every CI, taking as initial direction to follow the corresponding 20 equally spaced vectors (0.1\( \text{\AA} \) radians) belonging to the plane defined by the gradient difference (GD) and derivative coupling (DC) vectors of each CI.

10. Unless the experimentally observed photoproducts (SBV and COT in an approximate ratio of 1:2) are involved, the formation of structural isomers of COT which rapidly isomerize to COT is not excluded, even at temperatures as low as \(-60 \text{ °C}\). See ref 4.

11. The BR intermediate on \( S_1 \) has biradical character, but with a contribution from a tetra-radical form.


13. Due to the relatively large distance between C atoms for the formation of the C–C bond in CI4 and CI5 to yield BR\( \text{C}_4 \) and BR\( \text{C}_5 \), we have located the distance (from the tip of the CI) of the beginning of the corresponding valley on the ground state for each photoproduct (i.e., BR\( \text{C}_4 \) and BR\( \text{C}_5 \) and SBV). This is an index of the relative accessibility of each relaxation process. In practice, this distance has been computed by incrementing the initial relaxation direction displacement for MEPs computation by steps of 0.02 \text{amu}^{1/2} \text{bohr units from both CI4 and CI5}.

14. By performing MEP computations in the intersection subspace (with a standard conical intersection optimization algorithm as implemented in the Gaussian suite of programs. See ref 18), CI1 has been located from CI1 and CI2.

15. By a domain of a stationary CI (i.e., vanishing gradient in the intersection space) we mean a continuous subspace of CIs in which the stationary CI is included. This implies that, for every CI point of this subspace, a MEP exists in the intersection space that connects that point to the stationary CI.

