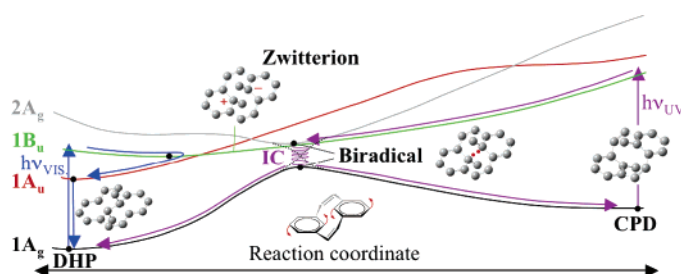# Toward a Mechanistic Understanding of the Photochromism of Dimethyldihydropyrenes

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A mechanism accounting for the photochromic properties of dimethyldihydropyrene (DHP)/metacyclophanediene (CPD) is proposed based on high-level CASSCF/CASPT2 ab initio calculations. The very low ring-opening quantum yield observed upon irradiation of DHP is explained by the quenching of the photoisomerization channel by internal conversion of the initially excited zwitterionic state to the lowest excited state minimum, where the system can fluoresce or decay back to the ground state via another internal conversion. On the other hand, irradiation of CPD leads to the formation of a biradical excited state minimum along the ring-closure reaction path. Internal conversion back to the ground state can then occur at a well-characterized conical intersection, leading to the DHP photoproduct. Thus, our results point unambiguously toward a stepwise mechanism involving the formation of a biradical intermediate on a singlet excited state. The fact that this intermediate does not correspond to the lowest excited state minimum is mainly responsible for the inefficiency of this system.

Introduction

Dimethyldihydropyrenes (DHPs) are part of a family of photochromic compounds, which can be converted between two isomers.[1] They belong to the diarylethene class of photochromes. The closed-ring isomer (DHP), in which the transannular bond is formed, is the thermally stable isomer. It absorbs strongly in the visible region and can be converted to its open-ring form, the cyclophanediene (CPD), by irradiation with visible light. The CPD isomer, which absorbs strongly in the ultraviolet (UV) region, can be switched back to the DHP isomer either by irradiation with UV light or thermally (see Scheme 1). Such systems, like many other photochromic compounds, have a large number of applications in the fields of nonlinear optics and optical switches.[2-4]

SCHEME 1
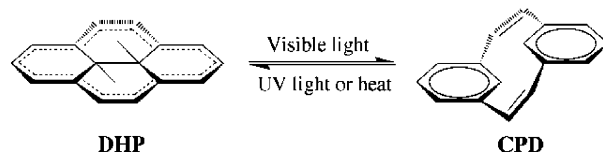
A great deal of interest and research has gone into DHP and its derivatives. The vast majority of the work has focused on improving their synthesis[5,6] and designing sophisticated systems by using DHP-based architectures.[6-8] Only fairly recently did the group of Mitchell and Bohne focus their attention onto the

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mechanism of the (photo-)isomerization.[9–11] They used absorption and fluorescence spectra combined with laser flash photolysis studies to determine the quantum yields of the different photophysical and photochemical processes involved. These processes include fluorescence, isomerization, internal conversion to the ground state, and intersystem crossing to the triplet excited state. Their main experimental observations can be summarized as follows. For DHP, the fluorescence, isomerization, and intersystem crossing quantum yields are very low, leaving the internal conversion to ground state DHP as the main decay pathway. For CPD, the isomerization quantum yield increases substantially but is significantly lower than unity. Moreover, unlike DHP, no emission at all was detected for CPD.

The low isomerization quantum yield and rate constant observed for irradiated DHP combined with the long lifetimes associated with the weakly emitting DHP indicate that the transannular bond cleavage is intrinsically a low-efficiency process[10] (although the efficiency can be modulated to some extent with the use of suitable substituents).[11] Two hypotheses have been suggested to explain this inefficiency. First, the isomerization could involve a concerted mechanism with a low reaction probability (activated process). Second, the photocleavage of the transannular bond could involve the intermediate formation of a biradical from the singlet excited state. Unfortunately, the current state of the experiments does not permit one to differentiate between these two possible mechanisms.[10]

The main goal of this study is to use high-level quantum chemical calculations to find which of these two mechanisms is responsible for the low efficiency of the DHP photochromism. Our results point toward a mechanistic picture, which is summarized in Figure 1.

The reaction coordinate, from DHP to CPD (structures **I** and **II**, respectively), can be described as a synchronous flapping motion of the benzene rings. This is accompanied by the transannular bond breaking and a change of conjugation of the π system, as the planar character imposed by the transannular bond in DHP is lost upon forming CPD (compare structures **I** and **II**). Along this reaction coordinate, a large potential energy barrier on the ground state (GS) potential energy surface connects the thermodynamically stable DHP to the less stable CPD. Unlike other photochromic systems that we have recently studied,[12–14] the excited state dynamics is intrinsically very complex in nature, involving more than one excited state. At least three electronic singlet excited states (LE, Z, and B in Figure 1) need to be considered since they participate directly in the photophysical or photochemical processes investigated. The first excited state, denoted LE for "locally excited", corresponds to a covalent resonant structure with a different π delocalization from GS and yielding uniformly expanded longer bonds (similar to the anti-Kékule state of benzene). The second excited state is the zwitterionic (Z) HOMO $\rightarrow$ LUMO state, and the third state, denoted B for biradicaloid, corresponds to
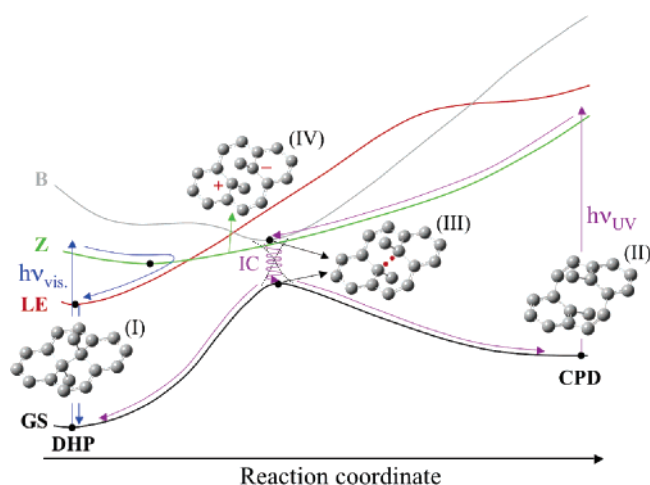

FIGURE 1. Outline of the proposed mechanism for dimethyldihydropyrene (DHP)/cyclophanediene (CPD) photochromism. The blue arrows indicate the most likely reaction pathway after irradiation of DHP (structure I). The purple arrows indicate the most probable reaction pathways after irradiation of CPD (structure II). The central mechanistic point is a GS/B conical intersection in the region of a biradicaloid minimum (structure III) leading to ultrafast internal conversion (IC) back to the ground state. Hydrogen atoms are hidden from the structures for clarity. GS, LE, Z and B denote ground state, locally excited, zwitterionic, and biradicaloid states, respectively.

a covalent state whose minimum has a biradicaloid structure (**III**). The only possible decay channel from excited state to ground state that can explain the reversible photoisomerization was identified as an interstate crossing (conical intersection) between B and GS. Provided the biradicaloid minimum (**III**, Figure 1) can be populated (as shown in detail later in the Results section), this conical intersection can be accessible, leading to an extremely efficient internal conversion. However, this is not the lowest excited state minimum that we have located on the potential energy surfaces, which is one of the main reasons for the inefficiency of this system.

Upon excitation of DHP to the "bright" Z state, we believe that the system will decay by internal conversion to the lowest LE excited state (Figure 1). However, we were unable to find a pathway that leads to the biradical structure on the B state. Population of the lowest LE DHP minimum accounts for the observed fluorescence (Kasha's rule)[15] with the absence of Stokes shift.

On the other hand, upon excitation of CPD to the same zwitterionic state, a spontaneous barrierless ring-closure reaction takes place. The system is driven toward the region of the biradical structure, where population of the biradicaloid minimum is now possible via internal conversion. The system can then decay to the ground state by internal conversion at the well-characterized B/GS conical intersection (see Results section), following a similar mechanism encountered in photochromic diarylethenes.[13] The fairly small ring-closure quantum yield could be attributed to return to the initial CPD (see Figure 1) and other decay channels following initial excitation and leading to population of other excited states. Moreover, the absence of CPD emission[10] can be explained by the lack of excited state minimum on the CPD region of the potential energy surface.

The qualitative description of the results presented above will be substantiated in the Results section by a more thorough

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analysis based on quantitative information obtained from our ab initio study. After a brief description of the different theoretical methods used to perform these ab initio computations, we present the results obtained along with a detailed description of the topological features of the potential energy profiles, and the electronic states and molecular structures involved. In particular, structures of conical intersections playing a major role in the photophysical and photochemical processes will be characterized.

Methods

Photoinduced isomerization reactions of large hydrocarbons can be very challenging for theoretical studies. Because of the large reorganization of the electronic system occurring along the reaction path, a multiconfigurational wave function method is required to account for the electronic motion. The most appropriate approach in this context is to calculate the wave function by using the complete active space self-consistent field (CASSCF) theory.[16] However, this method suffers from a lack of electronic correlation, and it is often necessary to include the dynamical electron correlation at a higher level treatment to correct this deficiency. The complete active space second-order perturbation theory (CASPT2) is one of the most efficient methods in this regard.[16]

The ground electronic state and the first four singlet excited electronic states of DHP/CPD have been computed with CASSCF by distributing 16 π electrons in 16 π orbitals (16e,16o), generating around 8.7×10^6 electron configurations in C_{2h} symmetry. The triplet state was not studied in detail, as it is not involved in the photoswitching process. In particular, it was shown experimentally that, although the triplet state is formed, it does not influence the isomerization quantum yields.[10,11] The basis set used was Dunning's cc-pVDZ,[17] which efficiently describes correlation effects. Geometry optimizations (energy minimizations only) were performed with C_{2h} symmetry constraints, the symmetry of the DHP and CPD ground state structures.[18] The C_{2h} symmetry had to be imposed at this level of calculation as reducing the symmetry would lead to an unworkable number of electron configurations. Thus, only configurations belonging to a specific irreducible representation of the C_{2h} point group are generated for each electronic state. Calculations with lower symmetry had to be performed by using a reduced (12e,12o) active space. This was used in particular to optimize conical intersections. Transition moments were also computed at this level. Energy single-point calculations were performed at linearly interpolated structures between the different stationary points on each potential energy surface to approximate the different excited state reaction paths.

As geometry optimization at the CASPT2 level is not feasible at present for such a large system (no analytical gradients available), CASPT2 calculations were performed at the CASSCF optimized structures and linearly interpolated structures by using CASSCF-(12,12) reference wave functions. The reason behind the use of the reduced (12e,12o) active space in the CASSCF reference wave functions is to avoid the problem with the bottleneck of the CASPT2 method due to the large number of active orbitals.[19] The quality of the CASPT2(12,12) results was ensured by benchmark calculations using a multireference second-order perturbation theory (MRPT2) approach using the full (16e,16o) active space as reference. To avoid intruder state problems in the excited state calculations, a level shift as proposed by Roos and Andersson[20] was used and taken to be

0.4 hartree in all calculations. Basis set effects were assessed by using larger basis sets (aug-cc-pVDZ[21] and cc-pVTZ[17]) and shown to be small. Note, however, that even with perturbation theory, there is no guarantee that different states encountered along the same reaction pathway will be described equally well. Thus, even at this high level of calculation, the results are expected to be only semiquantitative. All calculations were performed with the quantum chemistry packages MOLPRO[22] and Gaussian.[23]

An attempt to use the molecular mechanics−valence bond (MMVB) method[24] showed that the current version of MMVB is not able to treat the DHP/CPD systems because it cannot describe all the electronic states involved. This is probably due to a poor parametrization of MMVB for such states at present. However, we hope that future developments of this method will allow one to describe the complex potential energy surfaces and dynamics of these systems.

Results and Discussion

Molecular Structures and Potential Energy Profiles. CASSCF(16,16)/cc-pVDZ calculations were used to compute the potential energy profile of the DHP/CPD isomerization. CASPT2 was then used at the CASSCF geometries to take into account the dynamic correlation effects. The results are displayed in Figure 2. The reaction coordinate is represented by a dihedral angle ϕ between four adjacent carbon atoms as shown in Figure 3. This angle gives a measure of the degree of planarity of the system, and therefore reflects the increasing lack of planarity of the peripheric ring in going from the essentially planar DHP to the highly stepped CPD (see discussion below).

The most noticeable feature of the potential energy profiles in Figure 2 is their apparent complexity. The four computed excited states are all intertwined, with numerous surface crossings occurring along the reaction coordinate. Moreover, all these states seem well separated energetically from the ground state (GS) surface. Let us describe succinctly the main features of each of these potential energy curves.

Two minima were found on the GS potential energy surface. These two structures, denoted DHP-GS and CPD-GS, are displayed in Figure 3, and correspond to the DHP and CPD isomers, respectively. In the DHP minimum, the transannular bond is fully formed and the remaining 14 π electrons are delocalized along an almost planar ($\phi = 177°$) [14]annulene outer ring at the periphery of the system, in agreement with X-ray data.[25] This aromatic character of DHP is also expected from Hückel's rule. On the other hand, in the CPD minimum, there are 16 π electrons and the ring is highly nonplanar ($\phi = 120°$). Thus, Hückel's rule does not apply and the delocalization or aromatic character comes only from the benzene rings, which are linked by two localized ethylenic bridges. This change of structural feature from DHP to CPD was also well described by density functional theory (DFT) calculations.[18,26]

The DHP minimum lies 11.4 and 30.2 kcal/mol below the CPD minimum at CASSCF and CASPT2 levels, respectively.

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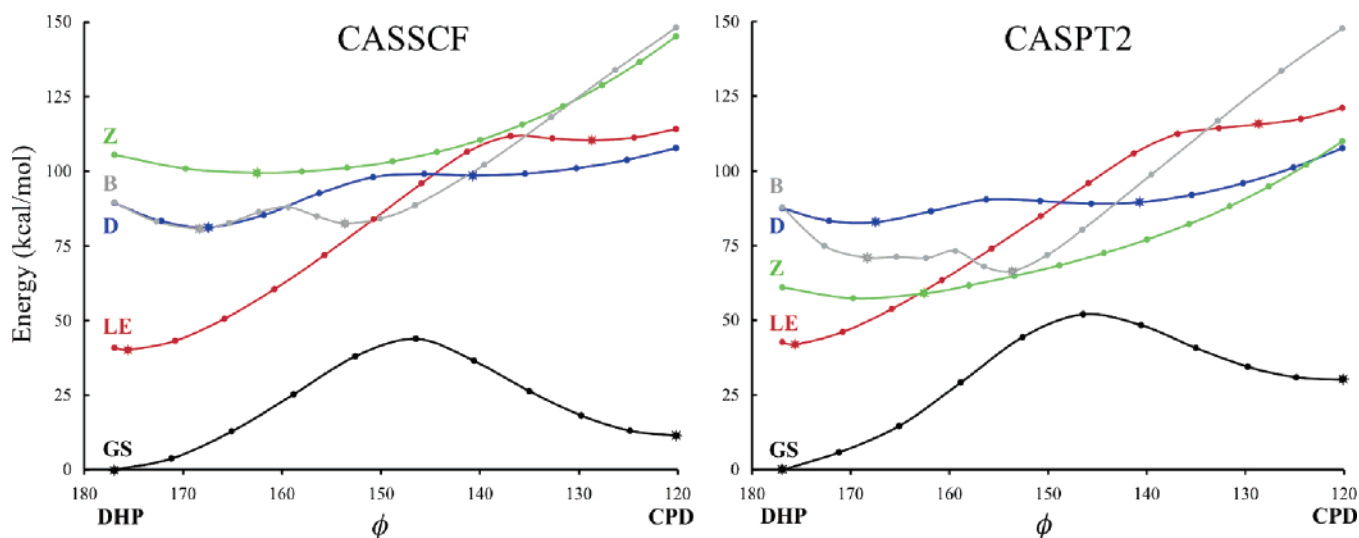(26) Clark, A. E. *J. Phys. Chem. A* **2006**, *110*, 3790−3796.

FIGURE 2. CASSCF(16,16)/cc-pVDZ and CASPT2(12,12)/cc-pVDZ potential energy profiles for DHP/CPD isomerization. The dihedral angle ϕ, shown in Figure 3, is used to describe the reaction coordinate along the C_{2h}-preserving symmetry. The star points correspond to energy minimized structures at CASSCF level (see Figure 3).
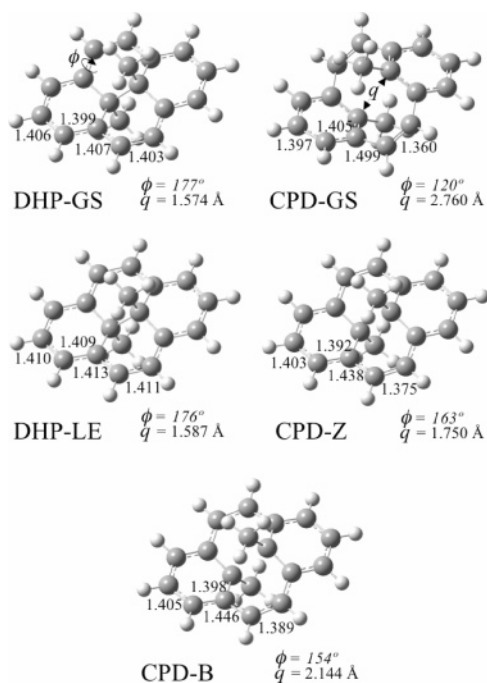

FIGURE 3. CASSCF(16,16)/cc-pVDZ optimized structures in C_{2h} symmetry. ϕ is a dihedral angle measuring the planarity of the system. q is the transannular distance.

These values surround the ΔH values of 23.2[18] and 20.6[26] kcal/mol computed with DFT. DHP is connected to CPD by a large potential energy barrier of 44 and 52 kcal/mol at CASSCF and CASPT2 levels, respectively. Although these values of the GS barrier are very approximate since no transition state was optimized, they are in good agreement with the activation enthalpy of 43.5 kcal/mol obtained with DFT.[18] Note that the ring-closure potential energy barrier is reduced from 32.5 kcal/mol with CASSCF to 21.9 kcal/mol with CASPT2. The latter value is in much better agreement with the DFT value of 20.3 kcal/mol,[18] and the experimental one of 22.4 kcal/mol.[27]

This relatively small potential energy barrier, compared to the ring-opening barrier, accounts for the possible thermal ring-closure reaction, although forbidden by the Woodward−Hoffmann rule[28] (see Figure S1 in the Supporting Information for the symmetry of the HOMO).

The lowest excited state at the DHP Franck−Condon (FC) geometry is the LE state. The vertical excitation energy is 42.7 (40.9) kcal/mol at the CASPT2 (CASSCF) level. Remarkably, there is a closed-ring minimum very close to the FC geometry. This structure, noted DHP-LE in Figure 3, differs from DHP-GS only in the slightly more pronounced delocalization character of the outer ring. As a consequence, the vertical emission energy from DHP-LE is very close to the absorption energy (41.6 and 39.6 kcal/mol at the CASPT2 and CASSCF levels, respectively). A shallow minimum was found on the CPD side of the potential energy surface (CPD-LE, Figure S2 in the Supporting Information). This minimum lies 70 kcal/mol above DHP-LE, and the ring-closure barrier is only 1.4 kcal/mol at the CASSCF level. Note, however, that this minimum and the ring-closure barrier vanish with use of CASPT2 theory.

The second excited state is the zwitterionic Z state. Its electronic wave function is described mainly by a HOMO → LUMO excitation. The vertical excitation is 61.1 kcal/mol at the DHP FC geometry. Only one minimum (CPD-Z) was located on this potential energy surface. Its structure is displayed in Figure 3 and has a zwitterionic structure as shown in Figure 1. On this potential energy surface, it is clear that the ring-closure reaction is barrierless (as predicted by the Woodward−Hoffmann rule, see Figure S1 in the Supporting Information) at both CASSCF and CASPT2 levels. Note, however, that CASSCF, although correct qualitatively, describes the energies of this state very poorly on a quantitative level. Indeed, the Z state appears as the highest excited state among the four computed with CASSCF. This is due to the fact that dynamic correlation is very important in such a state due to the important ionic configurations. This correlation energy is only properly taken into account at the CASPT2 level.

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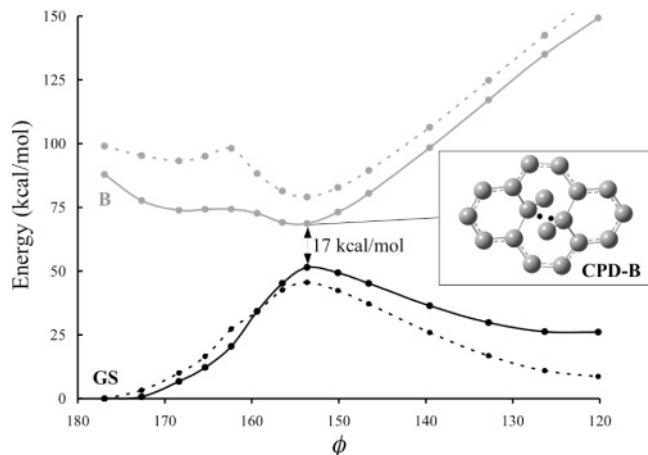
FIGURE 4. CASSCF(12,12)/cc-pVDZ reference energies (dashed lines) and CASPT2/cc-pVDZ energies (full lines) along the B state reaction path. State-averaged orbitals were used. The dihedral angle ϕ, shown in Figure 3, is used to describe the reaction coordinate.

The next excited state is a doubly excited state, denoted D, at the DHP FC geometry. The vertical excitation energy is 87.5 (89.4) kcal/mol at the CASPT2 (CASSCF) level. This state presents two minima within the C_{2h} point group, one closed-ring (DHP-D) and one open-ring minima (CPD-D) (see Figure S2 in the Supporting Information). As for the LE state, the open-ring isomer is higher in energy than the closed-ring isomer and separated by a small ring-closure potential energy barrier (ca. 1 kcal/mol). Note that this state is not represented in Figure 1, as it does not play a direct role in the photoisomerization (see the discussion of the mechanism below).

Finally, the fourth excited state at the DHP FC geometry is the biradicaloid state noted B. At this geometry, it is nearly degenerate with the D state. Its vertical excitation energy is 87.9 (89.5) kcal/mol at the CASPT2 (CASSCF) level. It also has two minima within the C_{2h} point group. The closed-ring minimum (DHP-B, Figure 3) is slightly higher in energy (5 kcal/mol) than the open-ring minimum (CPD-B, Figure 3) at the CASPT2 level and the ring-closure barrier is around 6 kcal/mol. The most interesting feature of this potential energy surface is the nature of the CPD-B minimum. This minimum corresponds to a biradical structure, similar to the ground transition state encountered during the homolytic transannular bond breaking. The transannular distance q is 2.14 Å (see Figure 3), with each atom carrying a single electron (see the inset in Figure 4). The GS and B states actually belong to the same electronic symmetry and can thus interact via strong electronic coupling. This electronic coupling results in an avoided crossing between the GS and B states in the region of the GS transition state, giving rise to the CPD-B biradical minimum. To highlight this, the GS state was recomputed along the approximate reaction path ϕ on the B state. The result is shown in Figure 4, and illustrates the resulting avoided crossing. The energy gap between the two states at the CPD-B biradical minimum is 17 kcal/mol. This value is too large for efficient radiationless decay to the ground state. Therefore, this biradical minimum cannot directly serve as a "funnel" for this decay.

In Search of the Photochemical Funnel. It is now widely recognized that ultrafast radiationless decay occurs in critical regions called conical intersections.[29] From the early 1990s, numerous such photochemical funnels have been identified in basic organic chromophores.[29b−d] The results of these investiga-
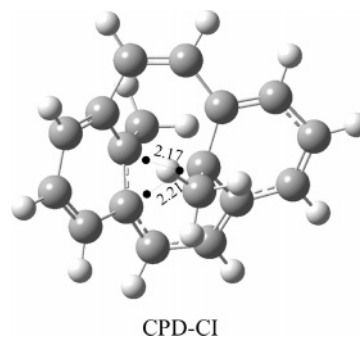

FIGURE 5. Central GS/B conical intersection involved in the photoisomerization of DHP/CPD. The three weakly coupled π-electrons forming a nearly isosceles triangle are represented. Distances are in Å.

tions have shown that, in all of these cases, it is possible to locate a low-lying conical intersection with a structure related to the observed photoproducts. More recently, the authors have investigated a number of photochromic systems and they showed that conical intersections also played a central role in the mechanism of such molecular switches.[12−14]

The conical intersection responsible for the nonradiative decay back to the ground state occurring along the DHP/CPD isomerization reaction has been identified. Its structure is denoted CPD-CI and it is shown in Figure 5. It belongs to a well-known class of conical intersections involving three weakly coupled π-electrons. This type of conical intersection is well documented[30−32] and, in particular, it has been encountered in the study of the photochromic diarylethenes.[13] The three weakly coupled π-electrons form a nearly isosceles triangle, and the structure presents an alternation of single and double bonds, whereas the π-system is delocalized in CPD-B. CPD-CI lies 12.4 kcal/mol above CPD-B at the CASSCF(12,12)/cc-pVDZ level. As explained in ref 13, the accessibility to this surface crossing can occur via vibrational motion in the appropriate modes, which leads to the crossing seam. This can occur once the system is vibrating in the CPD-B potential energy well. Moreover, this conical intersection is the photoisomerization (or photochemical) funnel in the sense that, upon decay at this crossing, the system can evolve to both photoproducts, DHP-GS and CPD-GS.

Another conical intersection providing a nonradiative decay channel to the ground state was found. Its structure is shown in Figure 6. It is noted DHP-CI because the transannular bond is formed and therefore this structure is located on the DHP side of the potential energy surfaces. As in CPD-CI, three weakly

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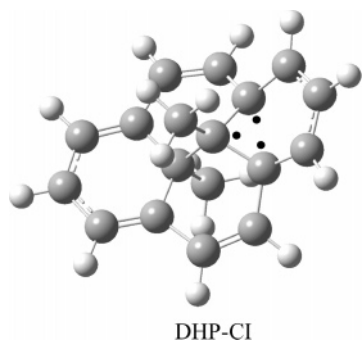
FIGURE 6. GS/LE conical intersection involved in the photostabilization of DHP. The three weakly coupled π-electrons forming a "kink" in the benzene ring are shown.

coupled π-electrons are involved and lead to a triangular arrangement forming a "kink" in one of the benzene rings. The DHP-CI results from a crossing between the states GS and LE and, in contrast with CPD-CI, offers a photostability (or photophysical) funnel for DHP. Indeed, decay at this surface crossing can only lead back to DHP-GS. This kind of photostability funnel was also found in diarylethenes.[13] Although DHP-CI lies around 50 kcal/mol above DHP-LE at the CASSCF(12,12)/cc-pVDZ level, CASPT2 calculations at this geometry show that this energy may not be accurate as the states split by 7 kcal/mol at this level. This is due to important dynamic correlation effects taking place at very distorted structures like DHP-CI. A theoretical study of hexatriene showed that a similar type of conical intersection might lie at a much lower energy when dynamic correlation is included.[33]

Interpreting the Experimental Results: Our Proposed Mechanism. Following irradiation, excited DHP can decay by fluorescence, isomerization to CPD, intersystem crossing to the triplet state, or internal conversion back to the ground state. The group of Mitchell and Bohne observed that upon excitation of DHP in the visible region at 380 nm, the sum of the quantum yields for the first three processes is 0.013 suggesting that most of the singlet excited state (98.7%) decays back to the ground state of DHP by internal conversion.[10] The lowest energy absorption band of DHP was observed at 641 nm (44.6 kcal/mol), which is in good agreement with the vertical excitation energy to the LE state (42.7 kcal/mol) calculated with CASPT2. We found the Z state to lie 61.1 kcal/mol above the ground state at the FC geometry. This is also in good agreement with the second absorption maximum observed at 470 nm (60.8 kcal/mol). This state has a larger molar absorptivity in agreement with the larger transition dipole moment calculated for the Z state (1.8 D) relative to the LE state (0.1 D). Two intense absorption maxima at higher energy were observed experimentally.[10] These peaks correspond to higher excited states, which were not computed in this study as the D and B states are symmetry-forbidden. The excitation wavelength used in the experimental setup and the results of the absorption spectrum described above suggest that the initially excited state of DHP is the Z state. Relaxation on the corresponding potential energy surface toward the CPD-Z minimum leads the system in the region of a crossing with the LE state (see Figure 1). The system then decays to the lowest LE excited state, and further relaxation leads to population of the DHP-LE structure. At this minimum,

decay can occur by fluorescence in agreement with Kasha's rule.[15] The calculated vertical emission energy to the ground state is 41.6 kcal/mol, only 1.1 kcal/mol less than the vertical absorption energy. This is due to the very similar geometrical structures of DHP-GS and DHP-LE. Consequently, there is no Stokes shift noticeable, in agreement with the experimental observation.[10] However, the fluorescence quantum yield is only 0.0006, and the main decay channel is assumed to be internal conversion back to DHP-GS. As shown in the previous section, we found a conical intersection, DHP-CI, which could provide a funnel for such decay. Unfortunately, the position of this funnel is computed to be too high in energy to explain such a high internal conversion quantum yield. Nevertheless, as explained earlier, it could be due to the inaccuracy of the energies for such a structure due to the lack of dynamic correlation at the CASSCF level. In addition, the low DHP → CPD isomerization quantum yield (0.006) can be explained by the fact that population of the intermediate biradical CPD-B required to access the isomerization funnel (CPD-CI) is quenched by the internal conversion to the lowest LE state. Also, population of the CPD-B intermediate is an activated process as it lies 7.5 kcal/mol above the CPD-Z minimum. This is in agreement with an experimental study[27] showing that for a DHP derivative (1,3,6,8-hexamethyl-DHP), the ring-opening quantum yield decreased as the temperature was decreased.

Irradiation of CPD in the UV region results in CPD → DHP isomerization with a quantum yield ranging from 0.1 to 0.4 depending on substituents.[10] The vertical excitation energy to the Z state is 79.8 kcal/mol at the CASPT2 level. It is probably the initially excited state considering its larger transition dipole moment (1.3 D) than that of the higher LE state (0.4 D), which lies 90.9 kcal/mol above CPD-GS at the FC geometry. However, direct population of the LE state is also possible. Relaxation on the Z state leads a barrierless ring-closure of CPD due to the attractive Coulombic interaction between the partial charges (see Figure 1). As the system relaxes toward CPD-Z, the only minimum located on this potential energy surface, the system reaches a region of near degeneracy with the B state at the biradicaloid minimum, CPD-B. At this geometry, the Z state is in fact 3.7 kcal/mol above CPD-B at the CASPT2 level, showing that a surface crossing (which cannot be optimized at present, as it requires post-CASSCF treatment) occurs between the Z and B states in the vicinity of this biradical minimum. Thus, efficient radiationless decay can take place to the B state leading to the population of the biradical CPD-B. Note that a similar outcome is expected following photoexcitation to the LE state. This state also leads to a barrierless ring-closure of CPD but crosses the B state at a higher energy (see Figure 1), before relaxation on the B state leads to formation of CPD-B. Moreover, another possible channel to CPD-B is by two successive internal conversions. First, the initial Z state can decay in the FC region of CPD to the dark D state, before another decay to the B state takes place (see the CASPT2 energy profile in Figure 2). All these hypotheses strongly suggest the population of a biradical intermediate, in agreement with one of the suggestions put forward by the group of Mitchell and Bohne.[10] Once this intermediate is formed, the system can decay to the ground state at a nearby conical intersection, CPD-CI, leading either back to CPD-GS or to the DHP-GS photoproduct. The low ring-closure quantum yield can be attributed to radiationless decay channels in addition to the ones leading to the formation of the biradical intermediate CPD-B and to the

(33) Celani, P.; Ottani, S.; Olivucci, M.; Bernardi, F.; Robb, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 10141−10151.

fact that decay at the photoisomerization funnel CPD-CI can also lead the system to return to the reactant. In addition, the absence of CPD fluorescence can easily be explained by the fact that there is no low-lying excited state minimum on the potential energy surfaces in the CPD region.

Note also that the singlet biradical CPD-B will not intersystem cross to the triplet biradical, because the radical centers are held in close proximity by the molecular framework, leading to a large singlet−triplet energy splitting. At the CASSCF level, the triplet lies 30 kcal/mol below the singlet biradical CPD-B. Thus, the triplet state is not expected to play an important role in the photoswitching mechanism, in agreement with experimental observations.[10,11]

Conclusions

High-level ab initio calculations of the ground and first singlet excited states of dimethyldihydropyrene (DHP)/metacyclophanediene (CPD) were performed to rationalize the mechanism behind the photochromic properties of this system. The topology of the potential energy profiles obtained from these calculations points unambiguously toward a stepwise mechanism involving the formation of a biradical intermediate on a singlet excited state (B state). Efficient internal conversion to the ground state is then possible by accessing a nearby conical intersection (CPD-CI), leading to the formation of the photoproducts. The low quantum yield for the ring-opening reaction of irradiated DHP is mainly due to the quenching of the biradical formation by internal conversion to a lower singlet excited state (LE state), also responsible for the observed fluorescence with no Stokes shift. The low fluorescence quantum yield may be explained by the presence of another conical intersection (DHP-CI) acting effectively as a photophysical funnel, although more accurate energetics would be required to assert this point. On the other hand, irradiation of CPD can lead to a spontaneous formation of the biradical intermediate via several routes, explaining the larger ring-closure quantum yield observed experimentally. The absence of CPD emission can be explained by the fact that there is no low-lying intermediate on the potential energy surfaces in the CPD region. Although there is a high level of confidence in the proposed mechanism, the authors wish to highlight that describing all the excited state reaction pathways is beyond current computational resources, hence the title.

Finally, the group of Mitchell and Bohne[11] found that [*e*]-annelated dimethyldihydropyrenes have much larger photochemical ring-opening quantum yields than the parent DHP shown in Scheme 1, making them potentially more useful as building blocks for photoswitchable materials. Although the theoretical study of these much larger systems is not feasible at present with the high level of calculation used in this work, we can predict, based on our proposed mechanism, that the biradical intermediate has to be more accessible energetically. Therefore, we expect that the biradicaloid minimum (CPD-B) would be further stabilized in these systems relative to the DHP-LE and CPD-Z minima.

Supporting Information Available: Table of Cartesian coordinates of optimized CASSCF structures shown in Figures 3, 5 and 6; Figure S1 for the frontier orbitals, HOMO and LUMO, of CPD; Figure S2 for CPD-LE, DHP-D, and CPD-D optimized structures; Tables S1 and S2 for CASSCF and CASPT2 energies, respectively; and complete refs 22 and 23. This material is available free of charge via the Internet at http://pubs.acs.org.

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