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Beyond the van der Lugt/Oosterhoff Model: When the Conical Intersection Seam and the S_1 Minimum Energy Path Do Not Cross

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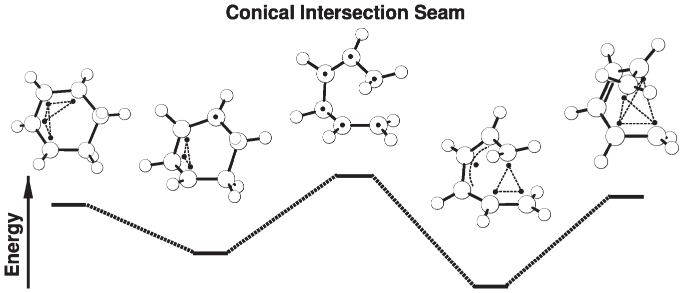

The photoinduced ring-opening reaction of cyclohexadiene (CHD) is a textbook example for electrocyclic reactions. In this paper we report the complete “minimum energy path” of the low-lying region of the conical intersection space reaching from the closed to the open ring side. The general role of conical intersections (CoIns) is to provide the locus for ultrafast transfer between electronic states, in the present case, to the closed or open form in the ground state after photoexcitation. The seam was calculated with use of an analytic approach in which the intersection space in the vicinity of a CoIn is described to second order. The topography of the seam was investigated, revealing minimum energy and transition state structures. In addition the energy profile of the seam was rationalized with valence bond (VB) theory. The geometrical changes along the seam have been related to the motions along the excited state minimum energy path (S_1-IRC-MEP) in a conceptual model highlighting the quasiparallel orientation of seam and IRC-MEP. Our model shows that even though the van der Lugt and Oosterhoff concept predicts the formation of an avoided crossing along the S_1-IRC-MEP, it provides an incomplete description of the decay process to the ground state. The latter requires, in addition, vibrational motions orthogonal to the MEP, directed toward the CoIn seam.

Introduction

The photoinduced isomerization of 1,3-cyclohexadiene (CHD) to cZc-hexatriene (HT) is experimentally, as well as theoretically, a prototypical photochemical reaction involving an extended seam of conical intersections (CoIns). Indeed, the CHD to HT reaction was one of the first systems used to elucidate the fundamental role of CoIns in ultrafast photochemical processes.[1-6] The mechanistic importance of an extended CoIn seam on quantum dynamics was shown for this system.[7-9] Furthermore, it was one of the first examples

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to illustrate the possibility of following a minimum energy path (MEP) in the intersection space.[2] The aim of this paper is to demonstrate the existence and mechanistic importance of an extended CoIn seam, which lies almost parallel to the excited state MEP, stretching from reactants to products.

The traditional view of the nonadiabatic decay during photochemical reactions as devised by van der Lugt and Oosterhoff[10,11] rests upon the concept of an avoided crossing arising from the correlation of the potentials of the reactant ground state and a two-electron excited state of the product along a common reaction coordinate. In conjugated polyenes this implies certain symmetry constraints, e.g., the conservation of C_2-symmetry in CHD. However, detailed theoretical treatments,[2,12,13] as well as experimental observations,[3] predict strong acceleration in symmetry breaking directions, thus indicating that excited state motions must deviate from the ground state reaction path. Fuss et al. incorporated these findings in a symmetry breaking ballistic motion model of the wavepacket on the excited state in order to explain the short reaction time of ~140 fs (Figure 1).[3] A complementary study by Olivucci et al.[2] documented the role of a CoIn seam extending to molecular structures close to C_2-symmetric geometries. Subsequent quantum dynamics calculations highlighted the C_2-conserving CoIn as dominant for the relaxation pathway.[9] In this paper, we provide further arguments for the existence of an extended seam lying approximately parallel to the excited state MEP (S_1-IRC-MEP) and controlling the ultrafast decay to the ground state. We shall demonstrate the existence of a complete minimum energy S_0/S_1-CoIn seam (seam-MEP) for the conrotatory ring-opening reaction of CHD, covering the region from the closed (CHD) to the open-ring structure (HT), providing an outlet toward S_0 from a large part of the conrotatory S_1 MEP.

In summary, unlike other prototypical ultrafast reactions such as the cis–trans photoisomerization of *s-cis*-butadiene[14] and protonated Schiff bases[15,16] or the internal conversion in DNA bases[17] where the S_1 relaxation is strongly directed toward the minimum of the crossing seam (“sand-in-the-funnel“ picture), for the CHD-HT isomerization, the S_1-IRC-MEP and the seam-MEP do not intersect. Rather, the seam-MEP is nearly parallel to the S_1-IRC-MEP in the $3N - 6$ space despite exhibiting different curvature (minima and transition states) in certain localized regions. Vibrational energy in the orthogonal degeneracy creating/lifting modes of the branching space perpendicular to the initial reaction coordinate drives the system to the seam. On the basis of these findings a qualitative 3D representation is used to elucidate the idea of parallel MEPs.

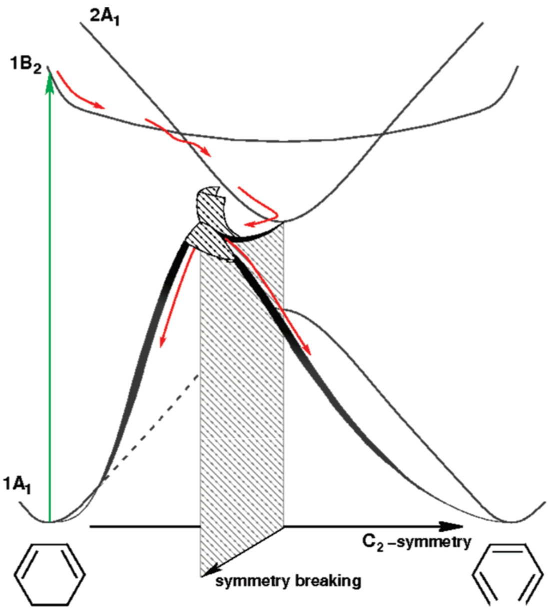

FIGURE 1. Qualitative potential curves for the CHD ring-opening with assignment of the directions of motion. The excited state symmetry preserving path reflecting the ground state isomerization (as in the van der Lugt/Oosterhoff picture) leads to an avoided crossing with a large gap due to the electron correlation of both A_1 states. The S_1 minimum, as well as the CoIn, lie out of the drawing plane and are reached by symmetry breaking deformations, i.e., motions independent of the ones on the S_0 state. Acceleration in symmetry breaking direction is observed already at the $1B_2/2A_1$-CoIn.

Conceptual Discussion

Seam-MEP. An analytic approach, accurate to second order,[18] was used to calculate the seam-MEP connecting the seam critical points such as transition states and minimum energy structures. The underlying theoretical concepts are briefly summarized in the following section. The reader is referred to the references provided therein for a more precise mathematical derivation.

Current practical applications for the optimization of stationary CoIn points rely on a first order approximation,[19−22] i.e., are based on gradients only. At a CoIn point this approximation allows the definition of a $3N - 8$ dimensional subspace, the so-called intersection space (IS),[23] which conserves the degeneracy of the crossing states for infinitesimal displacements along any IS coordinate. A continuous hyperline of minimum energy in this subspace, accessible during a particular photochemical process, is called a conical intersection seam. Two degeneracy lifting vectors can be constructed orthogonal to the IS that span a plane around a CoIn point, referred to as the branching space (BS).[23] Displacement in the BS yields the well-known double cone structure.[24] These

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vectors are labeled gradient difference (GD) and derivative coupling (DC).[25] Due to the first order approximation used, the local BS and IS vectors, derived at a certain CoIn, are only tangential to the generally curved global BS and IS and they are only valid in close vicinity of a CoIn. As a result a motion in the locally defined IS lifts the degeneracy as well as a motion in the BS and the first order BS and IS need to be redefined at every point along the seam. Their local character forbids any statement about the curvature of the global IS around a stationary CoIn.

Recent implementation of an analytic approach, based on a truncated second order Taylor expansion around a CoIn, allows one to derive generalized curvilinear coordinates, for which the degeneracy is retained correctly to second order.[26,27] Along these coordinates the region around a CoIn can be explored yielding additional information about the seam. Furthermore the seam-MEP can now be computed[18] via a modified version to the intrinsic reaction path following the scheme proposed by Gonzalez and Schlegel.[28]

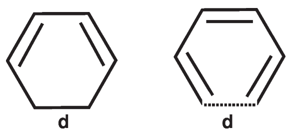
Computational Details

All calculations were done withng the CASSCF method and a standard Pople basis set 6-31G*.[29] The active space consisted of the 6 orbitals and 6 electrons in the π-space of HT and of the 4 π-orbitals and 4 π-electrons plus 2 σ-orbitals and 2 σ-electrons of CHD, respectively. With the basis set and the CASSCF active space used the $1B_2$ (Figure 1) is higher in energy than the $2A_1$ (Figure 1) in the FC region. A basis set including Rydberg functions together with dynamic correlation corrections obtained with CASPT2 is needed[7] to obtain the correct order of states. Away from the FC region the $2A_1$ becomes the first excited state (S_1) and the energetic order is described correctly by CASSCF. When S_1 and S_0 states approach each other they are described equally well. Therefore a correlation correction is not performed as our aim is to outline the role of the seam-MEP versus the S_1-IRC-MEP in the context of the electrocyclic reaction and not to provide accurate absolute values. The $1A_1$- and $2A_1$-IRC-MEPs were obtained with MO-coefficients optimized only for the state of interest, i.e., without state averaging (SA). SA-CASSCF with equal weights for both states was applied in the optimization of the seam-MEP, whereas the coupled perturbed MCSCF equations were explicitly solved. All stationary points as well as the seam-MEP were calculated with a development version of the quantum chemistry package Gaussian.[30] Analytical frequency calculations in the IS for obtaining the saddle point character of all stationary points along the seam-MEP were performed with use of the algorithm described in ref 27.

Results and Discussion

The van der Lugt reformulation of the Woodward–Hoffmann rules[31] has proven over the years to be a good first approximation for many "slow" photochemical processes. For a number of ultrafast reactions the energy gap between both correlated states remains so large along the theoretically calculated adiabatic symmetry-conserving path that an effective and fast non-adiabatic transition is impossible, in contradiction to what is observed experimentally. In this case, the role of real crossings displaced from the symmetry-conserving path is indispensable mechanistically (Figure 1) and the weakly avoided crossings of the van der Lugt picture become real crossings along a displacement orthogonal to the reaction path.

SCHEME 1



For molecules with more than two atoms the noncrossing rule derived by von Neuman and Wigner[32] does not provide any restrictions as to whether two states of the same symmetry can cross or not. Furthermore, there exist $3N - 8$ reactive coordinates (with N being the number of atoms) along which the degeneracy is preserved. So by stating that a conical intersection mediates a nonradiative decay to a lower state one has to bear in mind that this feature is not restricted to a single point on the PES but rather expands over a hyperspace of points of degeneracy. In the following the major structures in the IS for the photochemical isomerization of CHD to cZc-HT are studied and their relevance is discussed.

Comparison of the S_1-IRC-MEP and the Seam-MEP. The Cartesian coordinates of selected points from the S_1-IRC-MEP and the seam-MEP are included in the Supporting Information. The reaction coordinate is dominated by the internuclear distance d between the two terminal carbon atoms (Scheme 1). The C–C distance and the relative energies of all stationary structures are summarized in Table 1. The values are in a good agreement with earlier[1] and more recent[33] reports. The "mapping" of a seam segment between CoIn_{min} and CoIn_{C2} has been previously reported by Garavelli et al.[2] Since no structural data were given no comparison with the obtained seam-MEP could be performed. The energetic profiles of the S_1-IRC-MEP and the seam-MEP plotted along d are given in Figure 2.

On the basis of the quantitative results of Figure 2 and the geometries obtained along both MEPs a qualitative 3D representation of the ground and first excited states for the CHD/cZc-HT isomerization is presented in Figure 3. The black dashed lines follow the IRC-MEPs on both S_0 and S_1 with A_1 electronic character, describing the conrotatory CHD-HT interconversion along the C_2-conserving coordinate (RC). An effective BS coordinate lying orthogonal to the RC can be defined at every point along the MEP as a linear combination of the local BS vectors: $\alpha\text{DC} + \beta\text{GD}$. Displacement along the BS coordinate connects points of the S_1-IRC-MEP to the corresponding structures along the seam. We want to point out that S_1-IRC-MEP and seam-MEP are not strictly parallel in the $3N - 6$ dimensional IS. In general they can be curved with respect to each other

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TABLE 1. Energy Gap, Relative Energies, and Internuclear Distance between Both Terminal Carbon Atoms for All Points of Relevance Discussed in This Paper

	CHD	CHD*	Min_{S1}	TS_{S0}	HT	$CoIn_{TS2}$	$CoIn_{bu}$	$CoIn_{TS1}$	$CoIn_{min}$	$CoIn_{C2}$
ΔE_{S0-S1} (kcal/mol)	152.80	70.77	35.82	45.21	140.94	0.00	0.00	0.00	0.00	0.00
ΔE_{S0} (kcal/mol)[a]	0.00	44.76	66.00	61.44	18.37	123.93	114.80	130.92	107.50	125.64
ΔE_{S1} (kcal/mol)[b]	0.00	−37.28	−50.98	−46.15	6.51	−28.87	−38.01	−21.89	−45.30	−27.17

[a] Ground state minimum of CHD chosen as reference point for estimating the relative energy on S_0. [b] Franck−Condon point of CHD chosen as reference for estimating the relative energy on S_1.

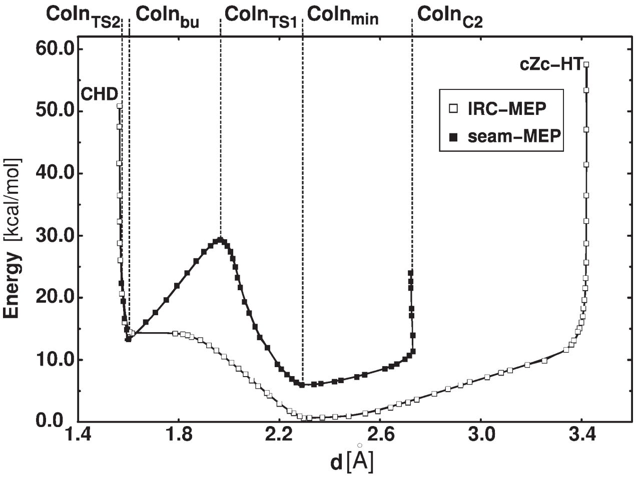

FIGURE 2. Plot of the IRC-MEP on the $2A_1$ surface and seam-MEP energy along the internuclear distance *d* between both terminal carbon atoms.

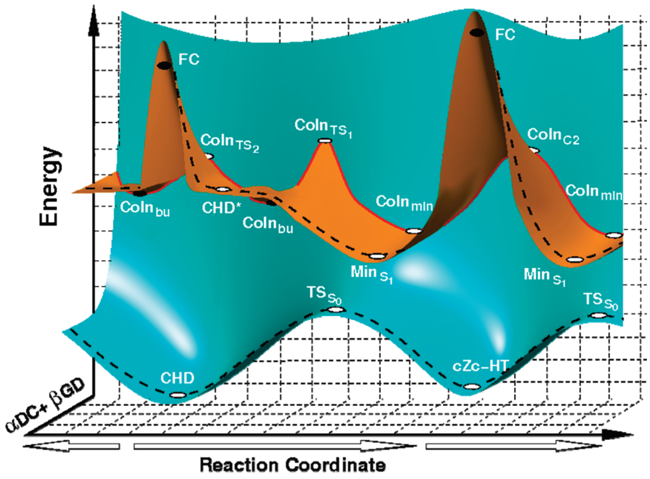

FIGURE 3. Schematic representation of the S_0 and S_1 potential energy surfaces with A_1 electronic character (see the Computational Details) for the ring-opening/ring-closure reaction in the CHD/cZc-HT system including the CoIn seam (seam-MEP, solid red line). The reaction coordinate (RC) describes the conrotatory CHD-HT conversion along the minimum energy reaction path (IRC-MEPs, dashed lines). The orthogonal BS vector is defined at every point along the seam-MEP as a linear combination of the local BS vectors (αDC + βGD). Critical points along the MEPs are denoted. The C_2-symmetry of the initial structures is used to construct the equivalent landscape at both sides of the FC points.

(i.e., partially differing motions invoked in the IS). Still as long as both MEPs do not intersect (i.e., the BS remains orthogonal to the S_1-IRC-MEP) the quasiparallel model is valid. A more rigorous proof is provided in the Supporting Information.

The C_2-symmetry of the initial structures was used to construct the landscape around the equilibrium structures on S_0 and at both sides of the FC points. Thus two equivalent thermal pathways arise from each of the ground state minima as denoted by the white arrows on the X-axis. Furthermore, both FC points on the $2A_1$ surface exhibit a saddle point character along the S_1-IRC-MEP. The C_2-symmetry is also found on the seam for $CoIn_{C2}$ and $CoIn_{TS2}$. The higher symmetry determines their stationary point character and allows for an optimization using standard gradient driven algorithms. The classic van der Lugt avoided crossing can be seen in the vicinity of TS_{S0} and Min_{S1} while the minimum of the seam-MEP lies at $CoIn_{min}$, which is displaced along αDC + βGD.

IRC-MEPs. We now give some more detailed discussion of the IRC-MEP characteristics. On the S_0 surface two minima, corresponding to the open- and closed-ring isomers, respectively, and a TS_{S0} were located. The ground state reaction coordinate involves simultaneous σ-bond breaking/forming and reorganization of the π-electronic system under conservation of the symmetry.

On the S_1 excited state a shallow closed ring minimum (denoted as CHD* in Figure 3) of nearly C_2-symmetry was located, induced by C=C stretch and C_2-symmetric wagging deformations (i.e., conrotatory C=C torsion) in the butadiene moiety. The σ-bond is thereby only slightly stretched. Both the geometrical and electronic structures of the butadiene fragment at that geometry are basically the same as those of the C_2-minimum found on the $2A_1$ excited state surface of *s-cis*-butadiene[34] itself, which demonstrates that at the FC point the initial relaxation involves the 4 π-electronic system. The interactions of the π-electrons with the σ-bond initiating the electrocyclic pathway are turned on only later, when the molecule is distorted strongly enough, as pointed out by Fuss.[3] On displacement from the CHD* region, the direction of motion changes and the σ-bond starts to stretch. Mutual asymmetric distortions of the terminal atoms lead to the global pericyclic minimum on S_1 (denoted as Min_{S1} in Figure 3) with C_1-symmetry and a geometry slightly differing from the transition state on S_0. Interestingly, the $2A_1$ minimum and the $1A_1$ maximum arising from the same avoided crossing do not fully coincide geometrically. This can be attributed to the different electronic nature of both states at the avoided crossing (see ref 13 for a more detailed discussion). Two transition states connecting CHD* to Min_{S1} and $CoIn_{bu}$, respectively, were found (not shown in Figure 3; geometries and normal modes included in the Supporting Information) that lie less than 0.1 kcal/mol above CHD*. Early CASSCF studies with 4-31G and DZ+d[1] show a basis set dependency of the height of these

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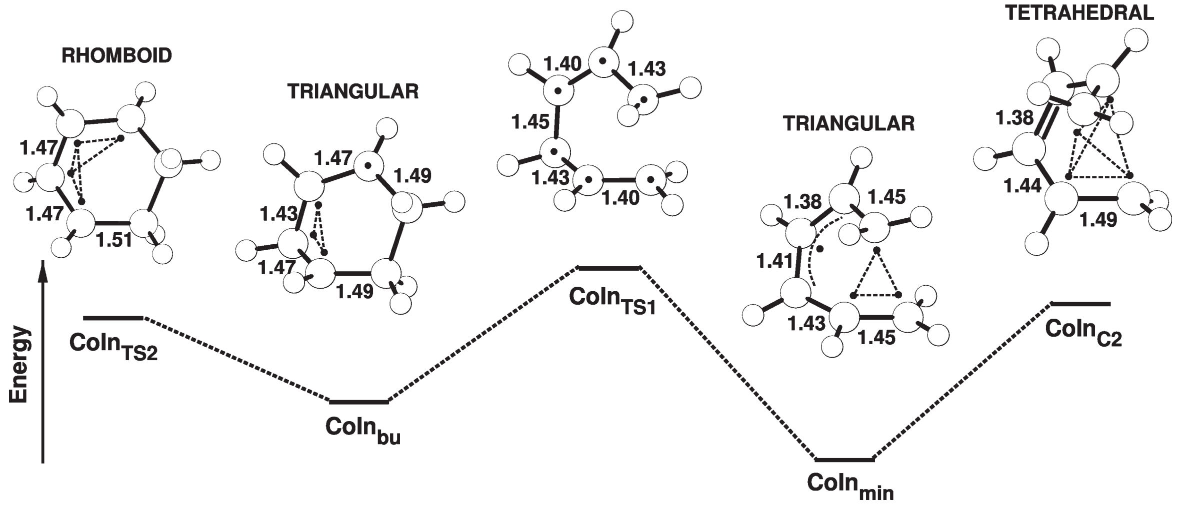

FIGURE 4. Optimized geometries and valence bond treatment of the electronic structure for the stationary points along the seam-MEP. Dashed lines indicate weakly interacting electrons in varying geometrical arrangements which are loosely coupled to isolated radical centers. C−C bond lengths are given in support of the geometrical models. The energetic stability depends on the electronic correlation.

barriers, which almost vanish for larger basis sets. In fact, recent calculations of Tamura et al. using a 6-31G(d,p) basis set as well as accounting for dynamic correlation effects[33] do not report any intermediate structures on the excited PES. However, resonance Raman[35,36] and transient-ionization[3] spectroscopy do show that the ring-opening reaction is initiated by distortions in the butadiene moiety as described above, indicating that either $1B_2$-$2A_1$ character exchange on S_1 occurs already before reaching CHD* or that the deformations on the $1B_2$- and $2A_1$-state are similar.

Seam-MEP. The S_1-IRC-MEP gives only insights into the behavior of vibrationally cold molecules. Motion from the S_1-IRC-MEP toward the conical seam is a central mechanistic feature for the photoreaction. Thus we now turn to the description of the structures along the seam-MEP. Previous CASSCF studies on the S_0/S_1 CoIn seam located two different geometries that are stationary points on the seam: CoIn_{C2}[2] and CoIn_{min}[1] (structures shown in Figure 4). Recently the structure of CoIn_{bu}, an intersection for which the σ-bond is still intact (1.59 Å), was also reported[13] (Figure 4). However, decay through this CoIn was proposed to be a minor route, using the argument that it possesses higher energy compared to CoIn_{min}. Our calculations demonstrate that CoIn_{bu} lies on the same extended seam containing CoIn_{C2} and CoIn_{min} and predict a lower energy (~6 kcal/mol below the previously reported energy) as well as an almost barrier-free transition from CHD*. This suggests bifurcation of the reaction pathway on S_1 into two channels, a σ-bond conserving (photophysical) one via CoIn_{bu} and the surrounding area as well as a σ-bond breaking one (photochemical) via the CoIn segment between CoIn_{min} and CoIn_{C2}. Photophysical deactivation through an intersection similar to CoIn_{bu} has been discussed by Boggio-Pasqua et al. for a group of aromatic derivatives of cyclohexadiene, diarylethenes.[37]

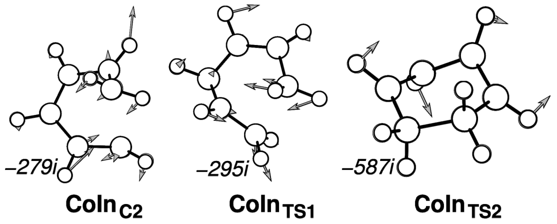

FIGURE 5. Normal modes corresponding to the imaginary frequencies of the transition state structures along the seam-MEP.

Two additional new CoIn geometries lying on the same seam, CoIn_{TS1} and CoIn_{TS2}, are documented (Figure 4). These critical points together with the original MEP provide a complete seam-MEP between CHD* and cZc-HT*. Seam frequency analysis (Figure 5) reveals that CoIn_{C2}, CoIn_{TS1}, and CoIn_{TS2} are all first-order saddle points in the intersection space (normal modes to the imaginary frequencies are included in the Supporting Information). CoIn_{C2} and CoIn_{TS2} exhibit C_2-symmetry and each of them connects two equivalent asymmetric minima, CoIn_{min} and CoIn_{bu}, respectively (Figure 3). CoIn_{TS1} has a C_1-symmetry and represents the lowest lying saddle point in the IS between CoIn_{bu} and CoIn_{min}. It has an interesting chemical relevance since it resembles a bond-breaking/making TS along the seam. At this point relaxation to the open-side isomer competing with the photodeactivation is facilitated. CoIn_{bu}, CoIn_{TS1}, and CoIn_{TS2} are located on the closed-ring isomer side ($d < 2.0$ Å, see Figure 2), whereas CoIn_{C2} lies in the open-ring region ($d \approx 2.7$ Å). CoIn_{min} appears in an intermediate geometry region ($d \approx 2.3$ Å).

In summary, the extended CoIn seam runs quasiparallel to the S_1-IRC-MEP preserving the degeneracy of S_0 and S_1. However, we observe helical twisting deformations along the CoIn_{C2}-CoIn_{min}-branch that are essentially different from the motions along the S_1-IRC-MEP even though the distance d between the terminal carbon atoms is growing. This implies that the seam-MEP is actually curved with respect to the S_1-IRC-MEP. Tamura et al.[13] have recently reported an asymmetric twisted open-ring CoIn ($d \approx 2.9$) exhibiting the

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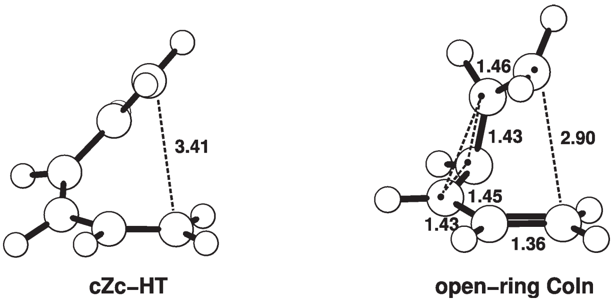

FIGURE 6. Comparison of the structures of cZc-HT and the open-ring CoIn first introduced by Tamura et al.;[13] Valence bond treatment of the open-ring CoIn demonstrates its relation to $CoIn_{bu}$. Dashed lines indicate weakly interacting electrons in a triangular arrangement, which are loosely coupled to an isolated radical center. C−C bond lengths are given in support of the geometrical model.

same $-(CH)_3-$ kink pattern as $CoIn_{bu}$ (see Figure 6). The structural similarity to HT lets us speculate that this CoIn belongs to an extension of the seam-MEP toward the open-ring geometry that resembles the motions along the S_1-IRC-MEP. Nevertheless, the instability of the open-ring CoIn (~15 kcal/mol above $CoIn_{min}$) should make this part of the seam hardly accessible.

VB Rationalization of the Extended Seam. For symmetric nonpolar conjugated polyenes like CHD and HT the valence bond (VB) theory provides a useful tool to rationalize the structure and energy profile of the seam by using simple bonding arguments.[38] Figure 4 presents an analysis of the low-energy covalent VB configurations, which arise due to different interaction patterns of the four π- and two σ-electrons of CHD along the seam-MEP. In $CoIn_{TS2}$ and $CoIn_{bu}$ the σ-bond between the terminal C-atoms is not broken yet. The remaining four π-electrons are unpaired and interact according to a rhomboidal ($CoIn_{TS2}$) or a triangular ($CoIn_{bu}$) pattern. It can be shown that exactly these three- and four-center patterns are responsible for the emergence of CoIns.[39] The triangular alignment is a prominent feature of nonpolar polyenes and is referred to as a $(CH)_3$-kink.[38,40,41] We attribute the destabilization of $CoIn_{TS2}$ to the symmetry constraint rather to a less favorable electronic configuration. After the σ-bond breaking is initiated a new more stable configuration, $CoIn_{min}$, arises involving one allyl radical and only three unpaired electrons in an isosceles triangular alignment. Since the unpaired electrons in $CoIn_{bu}$ and $CoIn_{min}$ are located on different centers a complete decoupling of all six electrons is necessary in order to connect both minima in the intersection space. We attribute the high energy of $CoIn_{TS1}$ to the absent electron coupling. $CoIn_{C2}$ arises through the tetrahedral arrangement of four unpaired electrons. The remaining two electrons form a π-bond. The introduction of a symmetry in the system and the decomposition of the allyl fragment are the reasons for the significant energetic destabilization as compared to $CoIn_{min}$.

Implications for the Mechanism of the Photoreaction. Direct photoexcitation of CHD promotes the system to the optically allowed S_1-state of B_2-symmetry. Within a few femtoseconds the B_2-state decays to the spectroscopically dark $2A_1$-state.[3,5,6] The σ-bond destabilization motions, needed for the photoreaction to proceed, are, however, not yet activated. As long as both σ-electrons are paired twisting motions in the butadiene fragment can drive the system to $CoIn_{bu}$, thus promoting internal conversion back to CHD. Using the CHD ground state equilibrium structure as reference $CoIn_{bu}$ lies higher (by ~10 kcal/mol) than the experimental FC point ($1A_1 \rightarrow 1B_1$ absorption maximum at ~270 nm[3,6]). However, the dynamic correlation correction is expected to lower its energetic position by more than 20 kcal/mol.[42] Thus we suggest that $CoIn_{bu}$ is reachable from a static point of view but only a minor part of the system proceeds through this loss channel due to the weak energetic stabilization. The higher energy of $CoIn_{bu}$ compared to $CoIn_{min}$ together with observed experimental yield of about 40%[43] for the ring-opening reaction indicates that only a minor part of the system proceeds through the photostable channel. The electrocyclic reversion triggered by the weakening of the terminal σ-bond results in the formation of a global minimum on the excited state with avoided-crossing nature, rationalized by the van der Lugt/Oosterhoff model as already discussed. Distortions of the carbon frame, orthogonal to the S_1-IRC-MEP, lead to the seam and allow for an ultrafast decay. The higher lying $CoIn_{C2}$ can also be reached, when momentum and energy conservation of a wavepacket prepared by fs-light pulse is taken into account. In principle relaxation to the ground state can occur anywhere on the seam between $CoIn_{min}$ and $CoIn_{C2}$. Quantum dynamical calculations suggest that $CoIn_{C2}$ plays an even more important role for the internal conversion from the S_1 to the S_0 state than $CoIn_{min}$.[7,9]

Conclusion

In the Woodward−Hoffmann treatment of photochemistry as reformulated by van der Lugt and Oosteroff the excited state and ground state reaction paths were assumed to be similar with the "photochemical funnel" occurring at an avoided crossing. In this classic example, we have demonstrated that the ground state and excited state reaction paths are indeed very similar and one can indeed visualize the avoided crossing photochemical funnel in two dimensions (Figure 3, TS_{S0} and Min_{S1}). However, the CoIn seam allowing fast and direct relaxation is displaced from the excited state/ground state MEP along skeletal deformations (αDC + βGD in Figure 3.), i.e., the branching space of the CoIn is orthogonal to the MEP. This is one of the first examples where the complete MEP in IS space between reactants and products has been mapped out and characterized with respect to a prototypical photoreaction. Studies on CHD derivatives like diarylethenes[37] and fulgides[44] report of CoIn values similar to the ones described in this paper and suggest that the introduced quasiparallel alignment of IRC- and

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seam-MEP constitutes a common feature for a variety of excited state reactions.

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Supporting Information Available: Conceptual discussion on the quasiparallelism of IRC-MEP and seam-MEP supported by a graphical representation, table of Cartesian coordinates of optimized CASSCF structures along the seam-MEP and the S_1-IRC-MEP, Cartesian coordinates of optimized CASSCF structures for both TS connecting CHD* to Min_{S1} and CoIn_{bu}, respectively, and of the normal modes corresponding to the imaginary frequency, Cartesian coordinates of the normal modes corresponding to the imaginary frequencies for CoIn_{TS2}, CoIn_{TS1}, and CoIn_{C2}, and complete ref 30. This material is available free of charge via the Internet at http://pubs.acs.org.