

Relationship between Photoisomerization Path and Intersection Space in a Retinal Chromophore Model

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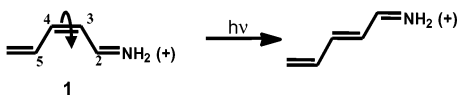
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Abstract: A low-lying segment of the intersection space (IS) between the excited-state and the ground-state energy surfaces of a retinal chromophore model has been mapped using ab initio CASSCF computations. Analysis of the structural relationship between the computed IS cross-section and the excited state $Z \rightarrow E$ isomerization path shows that these are remarkably close both in energy and in structure. Indeed, the IS segment and the $Z \rightarrow E$ path remain roughly parallel and merge only when the double bond reaches a 70° twisting. This finding supports the idea that, in certain chromophores, a more extended segment of IS, and not a single conical intersection, contributes to the decay to the ground state.

1. Introduction

The computational investigation of a photochemical reaction requires the characterization of the associated photochemical funnel.¹ This is defined as the point of the excited-state reaction path (ESRP) where the reactant decays to the ground state and prompts photoproduct formation. In many singlet reactions the funnel corresponds to a conical intersection between the excited (S_1)- and ground (S_0)-state energy surfaces.¹ Conical intersections are not isolated points of the n -dimensional potential energy surface (n is the number of vibrational degrees of freedom) but belong to a maximally $(n - 2)$ -dimensional set of intersection points called intersection space (IS).² In the past methods have been developed to compute conical intersection structures using an energy criteria.^{3,4} Indeed, the lowest-energy point of IS has been often taken as a model of the photochemical funnel.



Computationally ESRPs are defined as minimum-energy paths (MEP) in mass-weighted coordinates.³ When the reaction is barrierless, these correspond to single steepest-descent paths starting at the Franck–Condon (FC) point.^{5,6} Recently, the

mapping of different ESRPs has shown that, in several cases, such paths do not end up at the lowest-energy point of IS but at a structurally and energetically different conical intersection point.^{7,8} To this category belong molecules that undergo photoinduced ring-openings^{9,10} and Z/E isomerizations.¹¹ The minimal model of the retinal chromophore of rhodopsin (the human visual pigment), the Z -penta-3,5-dieniminium cation **1**, is one of these compounds.¹¹

As shown in Figure 1a, the S_1 $Z \rightarrow E$ photoisomerization path of **1** terminates at a 70° twisted conical intersection structure (CI_{70°) rather than at the lowest-energy conical intersection (CI_{92°). Since the degree of twisting and general structure of the photochemical funnel are basic factors controlling the reaction-time scale and quantum yield, the investigation of the relationship between ESRP and IS appears to be of great interest. Below we use CASSCF computations¹² to demonstrate that the ESRP coordinate of **1** not only enters IS at

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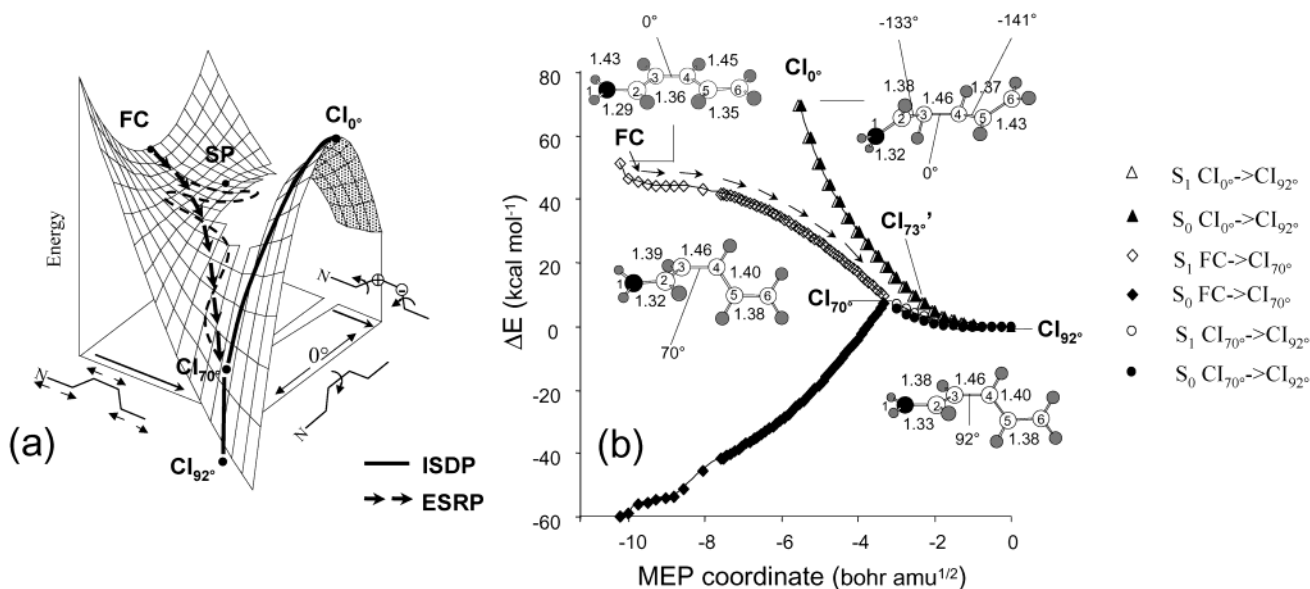


Figure 1. (a) Structure of the S₁ energy surface of **1**. The surface fault marks the structural difference between ESRP and ISDP (see text). SP is a planar transition structure. The ISDP line corresponds to the seam of intersection of the S₁ and S₀ potential energy surfaces. However, for simplicity, the intersecting S₀ surface is not shown. (b) Energy profiles along the computed ESRP (FC → CI₇₀[°]) and IS cross-section (CI₀[°] → CI₉₂[°]) for the S₁ Z → E isomerization of **1**. The structure parameters are in Å and degrees.

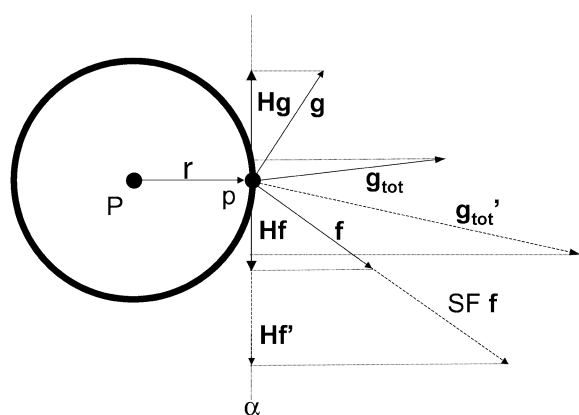


Figure 2. Projection of the vectors **g** and **f** on the plane tangent to the hypersphere at **p** (see Appendix in ref 9 for the formulation of the original procedure). **P** and **r** indicate the center and the radius of the hypersphere, respectively. Notice that **Hg** and **Hf** have opposite directions and cancel each other.

CI₇₀[°] but then remains substantially coincident with it up to CI₉₂[°] (CI₇₀[°] → CI₉₂[°]). Furthermore, we show that the same IS segment extends backward toward the FC point of the system (CI₀[°] → CI₇₀[°]). Thus, in this region, it is roughly parallel to the ESRP.

2. Computational Methods

The CASSCF S₁ and S₀ energies and gradients have been computed at the two-root state-average (0.5 weights) level with a 6-electron-6- π -orbital-active space and the 6-31G* basis set. The ESRPs are unambiguously determined by using a methodology that we have described elsewhere.³ To compute¹² the one-dimensional CI₀[°] → CI₉₂[°] cross-section of IS we use a new strategy to locate *steepest-descent paths within the IS* (ISDP).⁹ This strategy¹³ can be described as a combination of the intrinsic relaxation direction (IRD) method for finding local steepest-descent directions from a nonstationary point¹⁴ and of the conical intersection optimization (CIO) method for locating conical intersections as stationary points within the intersection space.¹⁵ Such a strategy has been recently described and applied to the mapping

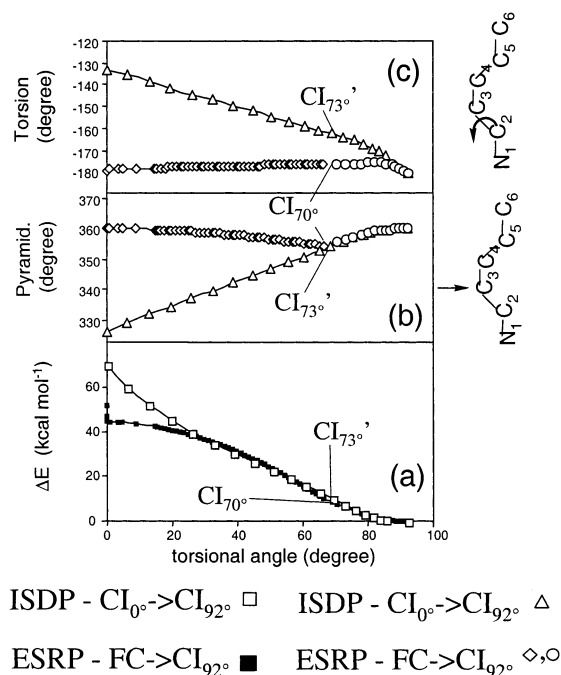


Figure 3. Change in (a) S₁ energy, (b) pyramidalization at C₃ (given as the sum of the three bending angles centered on C₃) and (c) C₁–C₂–C₃–C₄ torsion as a function of the isomerization angle (i.e., the C₂–C₃–C₄–C₅ torsion).

of the IS of cyclohexa-1,3-diene.⁹ Briefly, an IRD is usually calculated by locating the energy minimum on a hyperspherical cross-section of the *n*-dimensional potential energy surface centered on an initial point,

- Although developed independently—as it was originally designed with the target of avoiding the use of Lagrangian multipliers—the methodology may be related to the previously reported Lagrangian multiplier methods for locating conical intersection such as the one developed by us (Ragazos, I. N.; Robb, M. A.; Bernardi, F.; Olivucci, M. *Chem. Phys. Lett.* **1992**, *197*, 217–223) and by Yarkoni (see ref 4).
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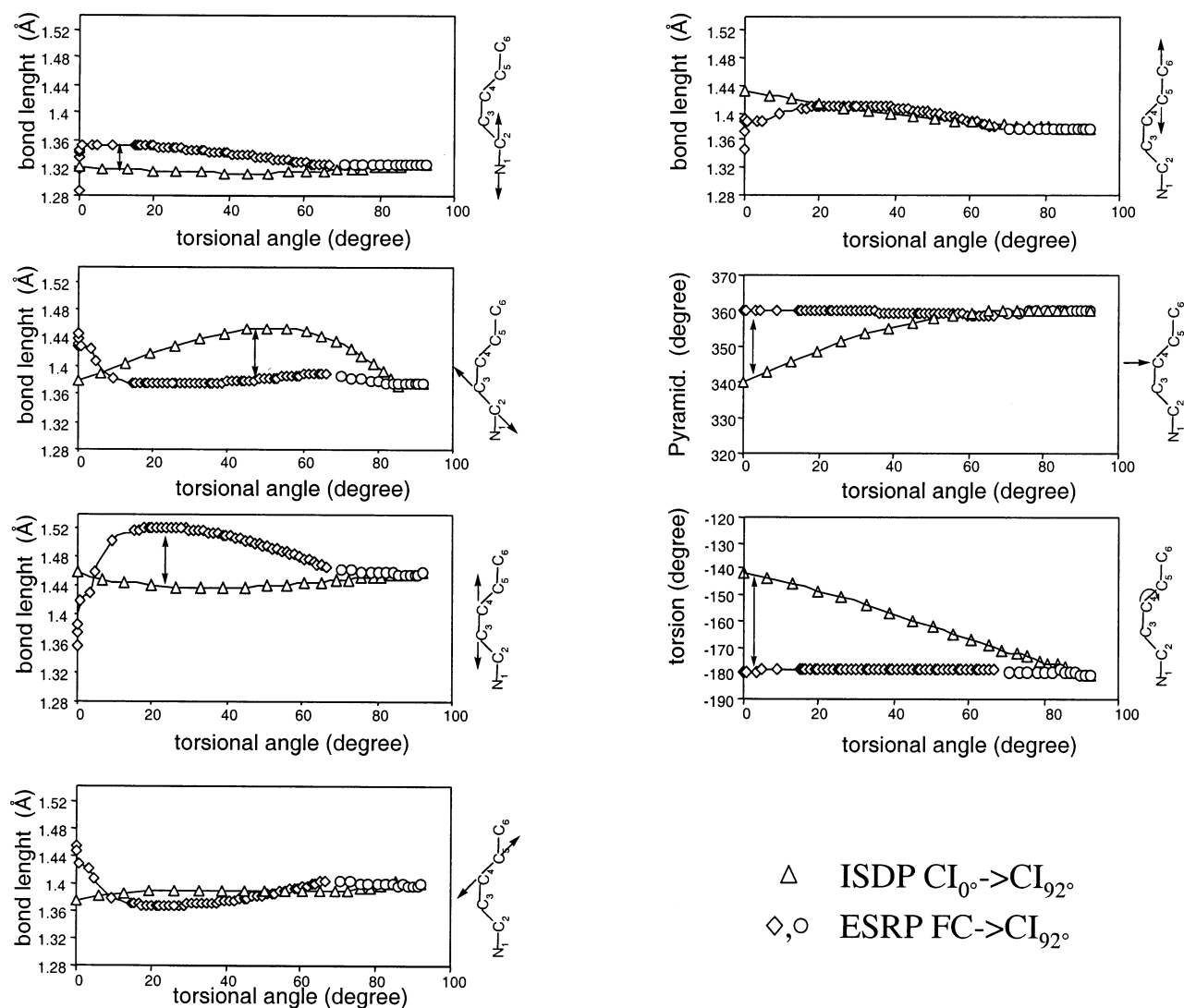


Figure 4. Change in (a) N_1-C_2 , (b) C_2-C_3 , (c) C_3-C_4 , (d) C_4-C_5 , (e) C_5-C_6 bond lengths, (f) C_4 pyramidalization (given as the sum of the three bending angles centered on C_4), and (g) C_4-C_5 torsion as a function of the isomerization angle (i.e., the $C_2-C_3-C_4-C_5$ torsion). The vertical arrows indicate the geometric parameters responsible for the separation between the $FC \rightarrow CI_{70^\circ}$ ESRP and the high-energy part of the $CI_{0^\circ} \rightarrow CI_{92^\circ}$ IS cross-section.

P. The vector connecting P to the minimum corresponds to the steepest-descent direction at P. The basic idea behind the strategy used to compute an ISDP is to require that both P and the optimized energy minimum are conical intersections. Thus, in this work we take a conical intersection point P as the starting point for the IRD search. Then we locate an energy minimum on a hypersphere imposing the condition $\mathbf{H}\mathbf{g}_{\text{tot}} = \mathbf{H}\mathbf{g} + \mathbf{H}\mathbf{f} = 0$ where $\mathbf{H}\mathbf{g}$ and $\mathbf{H}\mathbf{f}$ correspond to the projections of the vectors \mathbf{g} and \mathbf{f} (\mathbf{g} is the projection of the excited-state gradient on IS, and \mathbf{f} is the S_1-S_0 gradient difference^{3,15}) onto a plane tangent to the hyperspherical cross-section of radius r centered on P. The vector connecting P to the located energy minimum P' defines the local steepest-descent direction *within* the IS. A complete steepest-descent path can then be generated moving the center of the hypersphere on P' and repeating the procedure.

The $CI_{0^\circ} \rightarrow CI_{92^\circ}$ cross-section is defined by two branches. The first branch ($CI_{70^\circ} \rightarrow CI_{92^\circ}$) corresponds to the ISDP starting from CI_{70° (i.e., the last ESRP point) and is determined with the procedure described above. The second $CI_{0^\circ} \rightarrow CI_{70^\circ}$ branch has been determined with the following procedure. First, as detailed in section 2.1, we compute a suitable starting point CI_{0° by locating the lowest-energy conical intersection (with the CIO method) under a planarity constraint for the C_3-C_4 double bond (i.e., fixing 0° twisting). Then, we compute the ISDP starting at CI_{0° and obtain the full $CI_{0^\circ} \rightarrow CI_{92^\circ}$ path.

2.1. Computation of CI_{0° . To locate the CI_{0° conical intersection point that corresponds to the lowest-lying point with a 0° $C_2-C_3-C_4-C_5$ torsion, we have used a bottom-to-top strategy. The use of this strategy was necessary because the direct search for a conical intersection (i.e., employing the CIO method) with a 0° constrained $C_2-C_3-C_4-C_5$ torsion and starting at FC (or at a relaxed excited state planar structure) led to convergence failure. Thus, we performed a series of conical intersection optimizations (again with a constrained $C_2-C_3-C_4-C_5$ angle) starting at the optimized lowest-energy conical intersection point CI_{92° and minimizing the S_1-S_0 gradient difference \mathbf{f} . In each step we take as the guess geometry, the structure optimized in the previous step with the constrained torsional angle further reduced by $5^\circ-15^\circ$. While this procedure yields a low-lying CI_{0° (ca. 18 kcal mol^{-1} above the FC point), the strategy does not fully guarantee that the located structure corresponds to the lowest-energy conical intersection with a 0° $C_2-C_3-C_4-C_5$ torsion. The consequence of this is that we cannot exclude that our computed CI_{0° is a few kcal mol^{-1} higher in energy than the actual minimum.

2.2. Computation of the Steepest-Descent Path within IS. To solve an optimization problem occurring during the calculation of the $CI_{0^\circ} \rightarrow CI_{92^\circ}$ IS cross section, it was necessary to modify the methodology⁹ briefly described above. In fact, while in the reported procedure one minimizes the projection ($\mathbf{H}\mathbf{g}_{\text{tot}}$) of the gradient $\mathbf{g}_{\text{tot}} = \mathbf{g} + \mathbf{f}$ on the

Table 1. CASSCF 6-31G* Absolute (E) and Relative (ΔE)^a Energies for the Z-Penta-3,5-dieniminium Cation

structure	state	E (a.u.)	ΔE (kcal mol ⁻¹)
FC ^b	S ₀	(-248.26236) ^c	—
	S ₁	(-248.07879) ^c	—
	S ₀	-248.24918 ^d	-59.43
LP ₆₆ ^c	S ₁	-248.07206 ^d	51.72
	S ₀	-248.1422 ^d	7.70
CI ₇₀ ^c	S ₀	-248.13875 ^d	9.87
	S ₁	-248.1456 ^d	5.56
CI ₉₂ ^c	S ₀	-248.14278 ^d	7.34
	S ₁	-248.15455 ^d	-0.05
CI ₀ ^c	S ₀	-248.15447 ^d	0.00
	S ₁	-248.04326 ^d	69.79
CI ₇₃ ^c	S ₀	-248.04302 ^d	69.94
	S ₁	-248.14250 ^d	7.56
SP	S ₀	-248.14247 ^d	7.53
	S ₁	(-248.08904) ^c	—

^a Energies relative to the lowest-energy conical intersection point, CI₉₂^c.

^b The energies of the first five points along the photoisomerization minimum-energy path have been scaled, by means of state-average single-point energy calculations, to match the energies of all remaining points in Figure 1b computed at the state-average CASSCF level. ^c Single-state energies (in parentheses). ^d State-average energies.

hypersphere of search radius r , in the new procedure one minimizes the projection of the gradient $\mathbf{g}_{\text{tot}}' = \mathbf{g} + (\text{SF})\mathbf{f}$ where SF is a scaling factor.

The change is required because, in the specific case of the system under investigation, a cancellation effect manifests itself making $\mathbf{H}\mathbf{g}_{\text{tot}} = \mathbf{H}\mathbf{g} + \mathbf{H}\mathbf{f}$ small even if the components $\mathbf{H}\mathbf{f}$ (the projection of \mathbf{f} on the hypersphere surface) and $\mathbf{H}\mathbf{g}$ (the projection of \mathbf{g} on the hypersphere surface) are large. This accidental cancellation drives the search toward points where $E_2 \neq E_1$ (E_2 and E_1 are the energies of the S₁ and S₀ states). Choosing SF = 100 leads to convergence recovery ($E_2 - E_1 < 0.001$ au and $\mathbf{H}\mathbf{g} < 0.02$ au at the optimized point). The origin of the cancellation effect is schematically illustrated in Figure 2 and is due to the fact that, in our system, the $\mathbf{H}\mathbf{g}$ and $\mathbf{H}\mathbf{f}$ vectors happen to have opposite directions when the C₂-C₃-C₄-C₅ torsion is close to planarity. This effect is also the source of the small energy gap reported for certain optimized CI structures (e.g., CI₇₀^c in Table 1).

3. Results and Discussion

Below we shall discuss the nature of the relationship between the ESRP and the IS of **1**. The energies of the critical points discussed in the text are collected in Table 1. In Figure 1b we show that the minimum-energy intersection CI₉₂^c is located 52 kcal mol⁻¹ below the FC point. The CI₀^c point is 18 kcal mol⁻¹ above FC, whereas CI₇₀^c is 7 kcal mol⁻¹ above CI₉₂^c. Reaction coordinate analysis demonstrates that, topographically, ESRP extends along the CI₇₀^c → CI₉₂^c segment of IS.

The ESRP is sequentially dominated by two modes (see Figure 1a). These are an in-plane stretching mode and the isomerization mode.¹¹ The coordinate describing the CI₀^c → CI₉₂^c segment of IS is more complex. In fact, this can be seen as a combination of the same isomerization mode with a C₂-C₃/C₄-C₅ conrotatory torsion and C₃ and C₄ pyramidalization.¹⁶ The “distance” between the ESRP and ISDP coordinates decreases monotonically up to the CI₇₀^c region where the paths merge (see Figure 1a). This region must constitute the major decay channel, and mechanistically, the excited-state branch of the reaction coordinate ends at this point. The degree of merging at CI₇₀^c is documented in Figure 3.

(16) The pyramidalization is reminiscent of the conical intersection structure found in ethylene. Ben-Num, M.; Martinez, T. J. **2000**, 259, 237–248.

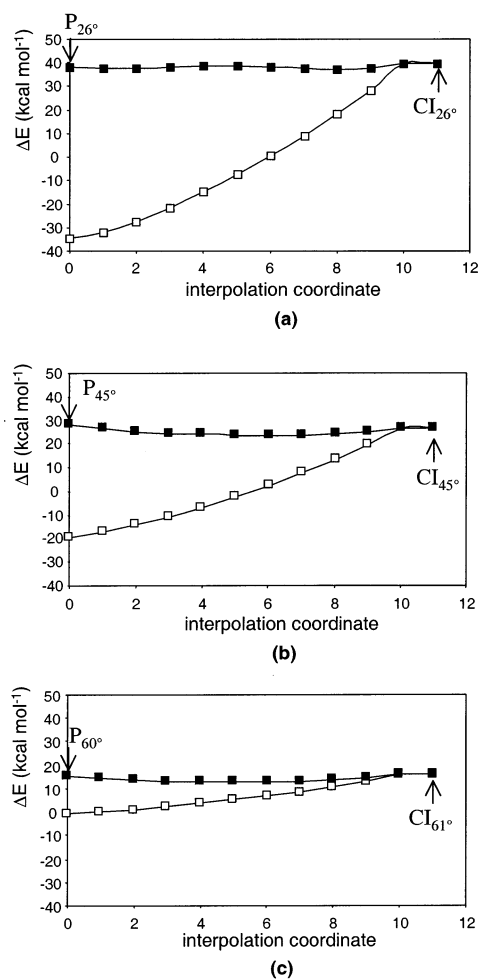


Figure 5. Energy profiles along the interpolated coordinates connecting pairs of structures located along the FC → CI₇₀^c ESRP and CI₀^c → CI₉₂^c IS, respectively. P and CI indicate points of the FC → CI₇₀^c and CI₀^c → CI₉₂^c coordinates, respectively. Each pair is characterized by the same value of the C₂-C₃-C₄-C₅ torsional parameter that corresponds to (a) 26°, (b) 45°, and (c) 61°. The energy values are relative to CI₉₂^c. Notice that the three profiles show no barrier separating the ESRP and the IS cross-section. (■) and (□) indicate the S₁ and S₀ energies, respectively.

Comparison of CI₇₀^c with the CI₇₃^c point shows that the energy (Figure 3a) and most geometrical parameters (for instance see Figure 3b) have the same values. However, the two structures are not fully equivalent mainly due to a 10° and 0.05 Å difference in the C₂-C₃ stretching and torsion, respectively (Figure 3c). Below we consider these paths equivalent (i.e., CI₇₃^c ≈ CI₇₀^c). The geometric changes along the ESRP and ISDP of the residual structural parameters that complement the analysis of the reaction coordinate as a function of the isomerization angle are shown in Figure 4.

Due to the two-mode nature of the ESRP ca. 10 kcal mol⁻¹ excess energy will initially populate vibrational modes orthogonal to the isomerization coordinate (see Figure 1).¹¹ Thus, the existence of a low-lying IS segment in the vicinity of ESRP may have an impact on the S₁ dynamics. In Figure 3a we show that from 0° to 25° twisting ISDP is higher in energy than the ESRP. However, these paths become substantially degenerate in the 25°–90° region. The energy profiles illustrated in Figure 5 show that there is no energy barrier preventing the access to IS from the ESRP in the 25°–90° region.

This implies that a limited amount of vibrational energy can effectively displace an ESRP structure toward IS. Two limiting situations are possible: (i) the vibrational excess energy populates modes that displace the S_1 structure toward IS, and (ii) it populates modes parallel to IS. In the first case one should have an early $S_1 \rightarrow S_0$ decay with a decrease in lifetime and quantum yield. (The decrease in quantum yield is related to the lower degree of torsional deformation of the reactant at decay. A second factor that may affect the quantum yield is the shape of the S_0 and S_1 surfaces at decay.¹⁷) In the second case the population is “protected” against early decay. This second case applies to **1** where only totally symmetric stretching modes are initially excited (see the schematic trajectory in Figure 1a). This mode cannot displace the molecular structure toward any point of the highly twisted and pyramidalized IS coordinate. This conclusion is supported by semiclassical trajectory computations that show that **1** performs a couple of stretching oscillations before accelerating along the orthogonal isomerization coordinate.¹⁸

4. Conclusions

In conclusion we have documented the relationship between ESRP and a low-lying segment of IS in a biologically related chromophore. The result suggests that the investigation of extended segments of IS may be required to fully characterize a photochemical mechanism. Dynamics computations will be presented in future work which complement this picture.

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Supporting Information Available: Cartesian coordinates of the structures discussed in the text (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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