

Conical Intersection Mechanism for Photochemical Ring Opening in Benzospiropyran Compounds

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Received May 27, 1997[⊗]

Abstract: The photoinduced ring-opening process in spiropyran compounds has been modeled through CASSCF calculations on the lowest excited state (S_1) of benzopyran. The documented S_1 reaction coordinate is characterized by a ring-opening transition state connecting a cyclic intermediate to a much more stable acyclic structure. Remarkably this structure does not correspond to a real S_1 intermediate but to a crossing point (i.e., a conical intersection) between the excited- and ground-state energy surfaces. At this crossing the excited-state system can undergo fully efficient decay to S_0 . Using the parent pyran molecule as a model, we have characterized two ground-state valleys which develop from the crossing point. The first valley leads to reactant (pyran) regeneration. The second valley leads to *cZc*-penta-2,4-dienal indicating that the primary ring-opened photoproduct is formed in an unstable conformation. The benzopyran/pyran reaction coordinates suggest that the first step in the benzospiropyran photochromic reaction must correspond to the excited-state ring opening of the benzopyran moiety. It is shown that while this process can be controlled by a small energy barrier, it ultimately leads to ultrafast radiationless decay at a structure where the C–O bond distance is ca. 2.3 Å. Upon ground-state relaxation this structure can generate either a *cZc* precursor of merocyanine (via full ring opening) or the starting benzospiropyran (via ring closure). This mechanistic picture seems to be consistent with the present experimental knowledge.

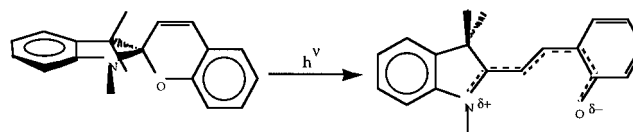
Introduction

Spiropyrans^{1,2} constitute an intensively studied class of photochromic materials. Spiroprans consist of a pyran fragment (usually part of a larger aromatic system) and another moiety containing conjugated rings that are held orthogonal by a common "spiro" carbon atom. Scheme 1 shows the structure of colorless indolinobenzospiropyran where the pyran ring is embedded in a benzopyran moiety.

Upon UV irradiation, the C–O bond breaks allowing the molecule to unfold. The "isolated" π systems, which are orthogonal and noninteracting in the spiro form, become extensively conjugated in the opened form, and a strong absorption is seen in regions of the visible spectrum where the unfolded system does not absorb (the open form belongs to the general family of merocyanine dyes). The C–O cleavage is thermally and/or photochemically reversible. Following irradiation in the visible region,³ merocyanine compounds revert back to the more stable spiro form, and the intense color fades on a time scale of seconds to minutes at room temperature.

Recently, the results of time-resolved spectroscopic studies^{4,5} have provided information on the dynamics of the initial step

Scheme 1



of the photochromic process in benzospiropyran compounds. It has been shown that⁴ (i) an excited-state (A^*) or vibrationally hot ground-state (X) "metastable" species is produced within 100 fs, (ii) this metastable species seems to decay within 200 fs leading to reactant back-formation and/or vibrational relaxation which is completed in a few picoseconds to form a transient acyclic merocyanine precursor, and (iii) the merocyanine product is formed from the vibrationally relaxed precursor with a time constant of 100 ps. While the exact nature of the metastable species (A^* or X) remains to be determined, the observed subpicosecond time scale is indicative of nonadiabatic motion along a coordinate leading from excited-state benzospiropyran to vibrationally hot ground-state species within a single vibrational oscillation. Such motion can only occur if the ring-opening coordinate in the excited state *continues directly* onto the ground-state potential energy surface thus avoiding excited-state equilibration. In other words, the coordinate describing the evolution of the molecular structure during the initial reactive motion must have an excited state and one or more ground-state branches. In this paper we focus on the investigation of such a reaction coordinate.

In spite of the technological importance of spiropyrans,² very little information about the structure of the potential energy surfaces that control the ring-opening reaction is available from theoretical studies. This may be due to the large size of the system that makes the use of suitable quantum chemical methodologies impossible. Nevertheless it has been recognized that the absorption spectrum of the spiro compound is, in first approximation, the sum of the spectra of the individual

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[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1997.

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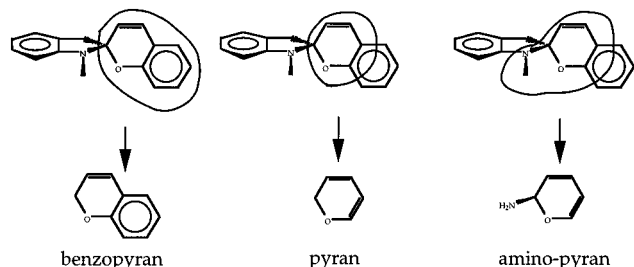
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Scheme 2



moieties.^{6ab} This is due to the orthogonality of the π systems which does not allow interaction between the rings. Thus, the ring opening-reaction is initiated with absorption of light at 290–308 nm where spiropyran has a strong absorption maximum^{4,5} which can be attributed to the benzopyran moiety^{6a} (Scheme 2). Furthermore, studies by Becker and co-workers on β -naphthospiropyran proved that only the chromene (β -naphthopyran) moiety exhibits photochromism.^{6c,d}

The results discussed above support the idea that the benzopyran could be taken as a model compound to study the benzospiropyran photochromic ring-opening reaction and the subsequent evolution toward a stable merocyanine.

While some theoretical work has been recently carried out at the *ab initio* level on the ground state of pyran⁷ (see Scheme 2), the excited states of benzopyran have been studied using only semiempirical methods coupled with single-excitation configuration interaction at equilibrium geometries^{8a} or along reaction coordinates obtained through constrained optimizations^{8b} (see also ref 7c for a discussion about reaction coordinates used in ref 8b).

In this paper, the nonadiabatic reaction coordinate of benzospiropyran compounds has been modeled through CASSCF calculations on the excited state of benzopyran. The S_1 branch of the coordinate is characterized by a ring-opening transition state (with a barrier of a few kcal mol⁻¹) connecting a cyclic intermediate to a much more stable, almost acyclic, S_1 structure. Remarkably this structure does not correspond to a real S_1 intermediate but to a crossing point (i.e., a conical intersection) between the excited- and ground-state energy surfaces. At this crossing, the excited-state system can undergo fully efficient decay to S_0 . The subsequent relaxation processes leading to production of merocyanine or benzospiropyran back-formation have been modeled using the “minimal” pyran and 2-aminopyran (see Scheme 2) models.

Computational Methods

The strategy for carrying out excited-state mechanistic studies has recently been reviewed,⁹ so we mention only the essential details here. The MC-SCF energy and gradient computations have been carried out using a complete active space (CAS) with basis sets available in Gaussian 94.¹⁰ In all our calculations, only singlet states have been considered. (Triplet states are only involved in nitrospiropyran photochemistry.^{1a,4,11}) The photoproduct formation and reactant back-formation paths are computed by using a new methodology^{12a} to locate

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the initial direction of relaxation (IRD) vectors from the conical intersection point. The intersection point is essentially a singularity on the ground-state potential energy surface similar to the tip of a cone. From such a point, different relaxation paths may develop leading to different ground-state intermediates or products. The IRD vectors are computed by locating *all* “constrained” energy minima existing on a hyperspherical cross section on S_0 and centered on the crossing point. Each structure located in this way defines the terminus of a different IRD vector. Once the IRDs have been determined, the associated relaxation path or valley can be characterized by plotting the gradient (i.e., the direction of the steepest descent) and by computing the *steepest descent line in mass-weighted Cartesians* using the IRD vector to define the initial direction to follow.^{12b}

To investigate the benzopyran ring-opening reaction coordinate, we have used an active space comprising the six “benzenoid” orbitals, the π/π^* orbitals of the C–C double bond, the σ/σ^* orbitals of the C–O single bond, and the n orbital centered on the oxygen atom which is conjugated with the aromatic ring to give 12 active electrons in 11 orbitals.^{10b} To model S_0 relaxation coordinates the much smaller pyran model system can be used. In this case, the active space involves eight electrons in seven orbitals and includes the 4π orbitals of the “butadiene-like” subspecies, the σ/σ^* orbitals of the single bond C–O, and the n orbital on the oxygen. We shall demonstrate that the conical intersections optimized in benzopyran and pyran are remarkably similar at the electronic level and have very similar geometries. Thus the choice of pyran to model the relaxation pathways on S_0 can be justified.

Both the benzopyran and pyran models presented do not contain nitrogen. However, it could be argued that conjugation between the N atom and the breaking C–O bond might alter the electronic nature of the CI involved in decay by allowing a zwitterionic state to be stabilized. To check this, the CI has also been optimized for aminopyran adding the nitrogen lone pair to the pyran active space. Again the CI optimized in this “augmented” model was very close to that in pyran justifying the exclusion of nitrogen.

All the critical points for benzopyran have been initially optimized with the 6-31G basis set, and single-point calculations have been performed at 6-31G* to improve energetics. *We stress that the accurate evaluation of the reaction energetics (i.e., the accurate computations of energy barriers, excitation energies, etc.) is not within the scope of this work which mainly concentrates on the energy surface topology and reaction coordinate structures.* Selected geometries (namely, the CI, the S_1 minimum, and the S_1 transition state toward ring opening) have been reoptimized at 6-31G* level due to the sensitivity of these structures to inclusion of polarization functions. Conical intersection geometry in pyran has been optimized at both 6-31G and 6-31G* levels. Similarly, the relaxation pathways have been calculated at 6-31G* level. For the aminopyran CI optimization, the 6-31G* basis was augmented with a shell of diffuse SP functions on C, N, and O.

Due to the size of the active space, it was impossible to calculate analytical frequencies at the critical points reported in the paper, and numerical frequencies would have been exceedingly expensive. Accordingly, the nature of the critical points presented in this paper has been determined only from the inspection of the final updated Hessian calculated.

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(12) (a) Celani, P.; Robb, M. A.; Garavelli, M.; Bernardi, F.; Olivucci, M. *Chem. Phys. Lett.* **1995**, *243*, 1–8. (b) At an optimized point on the hypersphere, the gradient is zero in the subspace on the $n - 1$ variables excluding the constraint corresponding to the radius of the hypersphere. The gradient in the full n -dimensional space (the “residual forces”) points in the direction of the steepest descent path in mass-weighted coordinates and corresponds to the initial relaxation direction.

Scheme 3

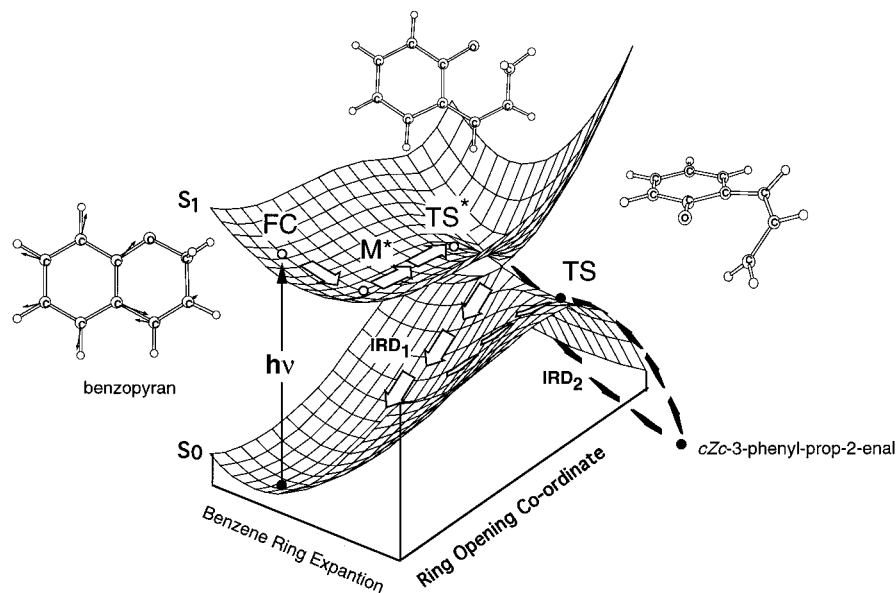


Table 1. Single-Point Calculations^a CASSCF(12,11)/6-31G* at CASSCF(12,11)/6-31G-Optimized Geometries

	S ₀	S ₁	ΔE(S ₁ –S ₀)	ΔE(S ₁)
minimum S ₀	–420.43778	–420.26674	107.3	5.0
minimum S ₁	–420.42279 ^b	–420.27478	92.9	0.0
	–420.42484 ^{b,d}	–420.27639 ^d		0.0
TS S ₁	–420.40118 ^b	–420.26624	84.7	5.4
	–420.39775 ^{b,d}	–420.26780 ^d		5.4
CI S ₁ /S ₀ ^{c,d}	–420.34028	–420.34019	0.1	–41.0

^a Absolute energies in Hartrees. ΔE in kcal mol^{–1}. ^b CI approximation to the energy of S₀ calculated with orbitals optimized for S₁. ^c State average energy. ^d 6-31G* basis set used for optimization.

Results and Discussion

A schematic overview of the benzopyran ring-opening path obtained from our computations is presented in Scheme 3. From the Franck–Condon region (FC), the reaction path proceeds via a transition state (TS*) to a conical intersection (CI), where fully efficient decay to S₀ is possible. Using the smaller pyran, we found only two relaxation pathways from the conical intersection: the first path (IRD₁) goes toward spiropyran, and the second (IRD₂) produces a ring-opened merocyanine conformer. The region of the thermal transition state (TS) has been investigated by other workers^{7c} and will not be discussed further. The energetics are summarized in Table 1, while the geometries are collected in Figures 1–7.

Reaction Path from the Franck–Condon Region via the Transition State to the Conical Intersection. Our computations are limited to the study of the S₁ surface of benzopyran. We have made the assumption that this state is reached either following decay from a higher excited state or possibly by direct absorption. The S₁ state at the FC geometry closely resembles the ¹B_{2u} anti-Kekulé state in benzene (i.e., the minus combination of the two VB Kekulé functions). The lack of symmetry lifts the degeneracy of the benzene-like molecular orbitals, and the transition is no longer symmetry forbidden. The Franck–Condon excitation energy from the optimized S₀ geometry of benzopyran is about 107 kcal mol^{–1} at CASSCF(12,11)/6-31G* level. Dynamic correlation energy would be expected to decrease the gap just slightly because S₁ is essentially covalent as in benzene. The S₁ state is essentially a combination of two single excitations involving HOMO–1 → LUMO and HOMO → LUMO+1 which are predominantly localized in the benzenoid ring. Thus one may estimate oscillator strength with a

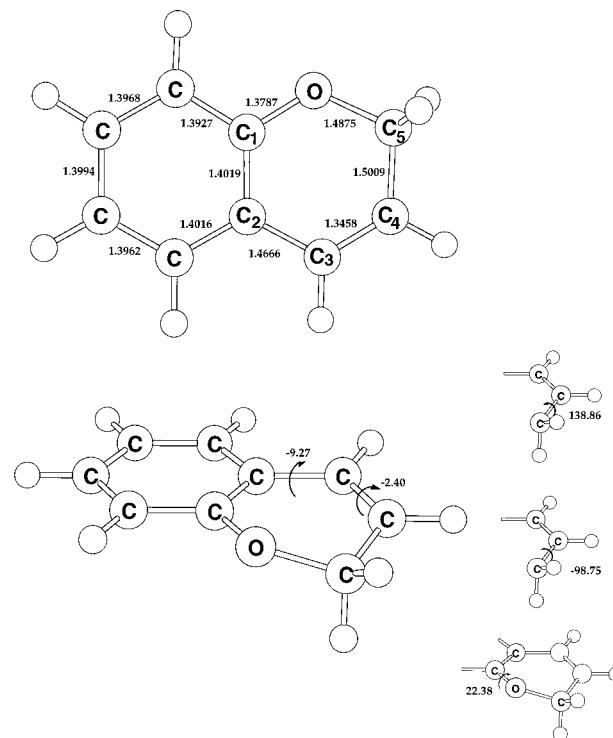


Figure 1. Equilibrium geometry (angstroms and degrees) for benzopyran in the ground state. Structure optimized at CASSCF, 12 electrons/11 orbitals, level and 6-31G basis set.

simple CI restricted to single excitations (CIS) but using the more correct CASSCF energy gap. This estimation gives a value of 0.0145 for the oscillator strength corresponding to a weak transition.

Figure 1 shows the ground-state equilibrium geometry (FC) of benzopyran, and Figure 2 shows the pattern of excited-state forces at this geometry. The benzene-like anti-Kekulé nature of the state is immediately evident in the forces corresponding to the “symmetric” expansion of the benzenoid ring. Indeed relaxation from the FC geometry does not break the C–O bond; rather, the system relaxes to the excited-state intermediate M* shown in Figure 3 (only 5 kcal mol^{–1} below the FC energy). The M* region is very shallow. By stretching the C–O bond, the excited benzopyran reaches the TS* (Figure 4) on the path

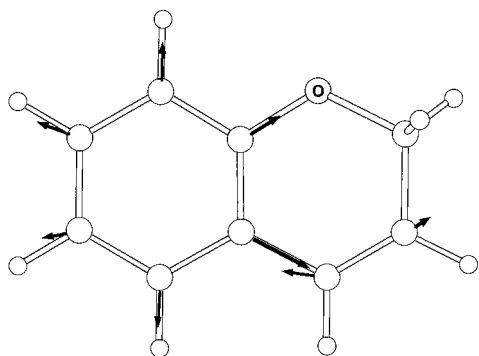


Figure 2. Forces (CASSCF(12,11) level and 6-31G basis set) at FC geometry (ground-state equilibrium geometry in Figure 1) on S_1 .

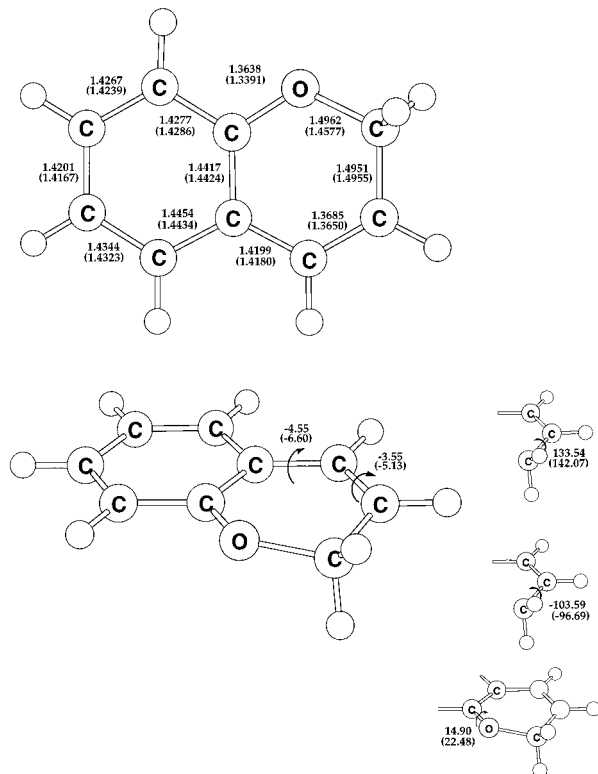


Figure 3. Equilibrium geometry (angstroms and degrees) for benzopyran on S_1 optimized at CASSCF(12,11) level and 6-31G basis set (6-31G* in parentheses).

toward the ring-opened region of the potential surface. The ring-opening reaction coordinate involves elongation of the C–O bond coupled with a very large rotation of the methylene group which becomes almost coplanar with the rest of the side chain. The barrier required for ring opening is about 5 kcal mol⁻¹.

At M^* and TS^* , the gap between S_1 and S_0 is more than 60 kcal mol⁻¹. However, as the C–O bond breaks, the surfaces come progressively closer together and ultimately (C–O distance 2.35 Å in benzopyran) reach the conical intersection (geometry shown in Figure 5) where S_1 and S_0 are completely degenerate. Very remarkably, such a conical intersection belongs to a class of conical intersections which has already been documented in the past. In particular both the geometrical and electronic structures show that the intersection arises because of the degeneracy of the S_0 and $n - \pi^*$ S_1 states of this system (where “ n ” is the oxygen lone pair). This same situation has been documented in *s-cis*-acrolein¹³ and the ethyleneformaldehyde dimer¹⁴ and provides a mechanistic rationalization for photochemical formation of oxetene and oxetane, respectively.

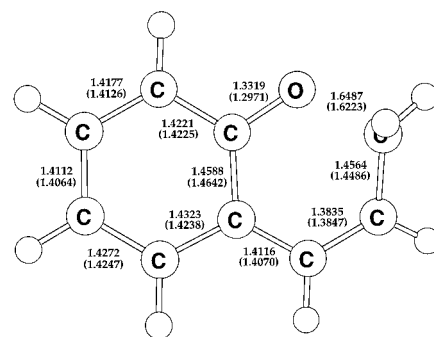


Figure 4. Transition state optimized at CASSCF(12,11) level with 6-31G basis set (6-31G* in parentheses) for ring opening on S_1 (angstroms and degrees).

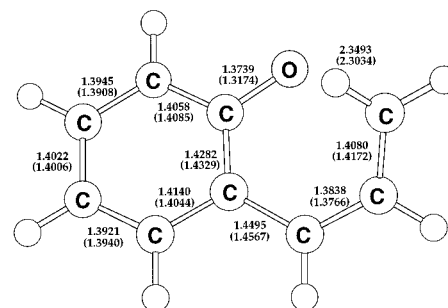


Figure 5. CASSCF(12,11) geometry of the conical intersection between S_1 and S_0 in benzopyran optimized with 6-31G (6-31G* in parentheses) basis set.

The different electronic structure of the S_1 state (essentially a benzene-like anti-Kekulé structure) intermediate M^* and of the S_1 state (essentially an $n - \pi^*$ structure) at the conical intersection suggests that the TS^* corresponds to an avoided

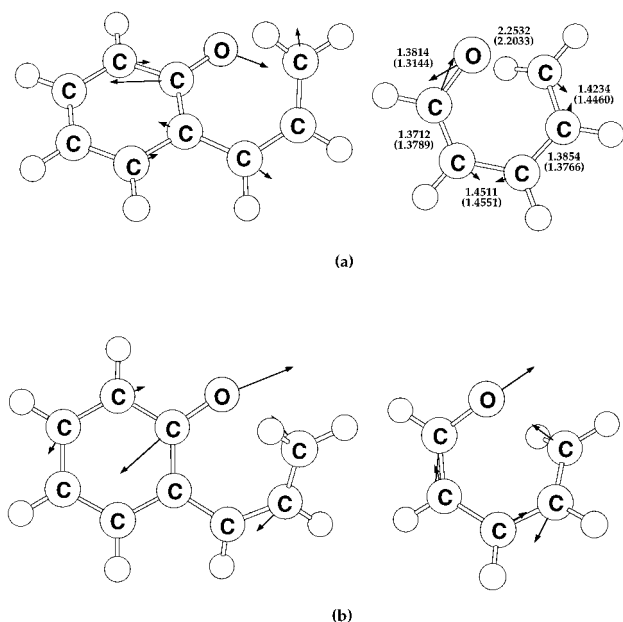


Figure 6. Derivative coupling vector (a) and gradient difference vector (b) in benzopyran (left-hand side) and pyran (right-hand side). The CASSCF(8,7) geometry of the conical intersection between S_1 and S_0 in pyran optimized using 6-31G (6-31G* in parentheses) basis set is shown in the right of panel a.

crossing between two excited-state energy surfaces. Thus, at TS^* the electronic configuration of the excited-state system changes from anti-Kekulé to $n - \pi^*$ and this change is driven by the C–O bond fission. This interpretation of TS^* leads to the conclusion that the benzene ring in the benzopyran molecule acts as an “antenna” capable of harvesting a photon of the right wavelength. The photon energy is then transferred to the incipient carbonyl bond by ring opening. The same mechanism must operate in more complex molecules like chromene (the chromophore of β -naphthospiropyrans) where the absorption maximum is red-shifted due to the naphthalene “antenna”.

Two Relaxation Pathways from the Conical Intersection: Toward Spiropyran and toward Ring-Opened Merocyanine. While pyran itself could never be a reasonable model for investigating the S_1 reaction coordinate in benzopyran and its derivatives (including benzospiropyrans), we believe that this simple system can be used to investigate the $S_1 \rightarrow S_0$ decay and ground-state relaxation processes. From Figures 5 and 6 it is clear that the essential features of the conical intersection structure are the same for benzopyran, pyran, and aminopyran (Scheme 2). Figure 6 reports the optimized geometries at 6-31G and 6-31G* levels for the pyran conical intersection. The geometry is remarkably similar to benzopyran CI (apart from the obvious case of the bond in common with the benzene ring). Figure 6 also shows the nonadiabatic derivative coupling and the gradient difference vectors which define the branching plane for the benzopyran and pyran conical intersections. Clearly they span the same plane in each case. To test for importance of N conjugation at the CI, we repeated the optimization for aminopyran adding a set of diffuse SP functions and the n orbital centered on the nitrogen to the active space. Figure 7 reports the geometry of the conical intersection found in aminopyran (optimized using the 6-31+G* basis set). The similarity with the conical intersection in pyran confirms that N conjugation is not crucial.

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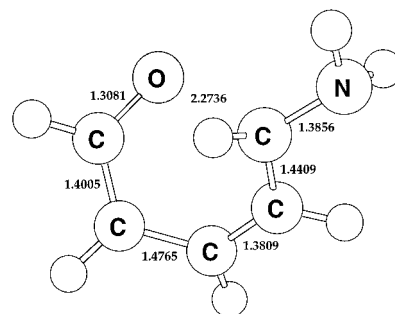


Figure 7. CASSCF(10,8) geometry of the conical intersection between S_1 and S_0 in aminopyran optimized with 6-31G* basis set.

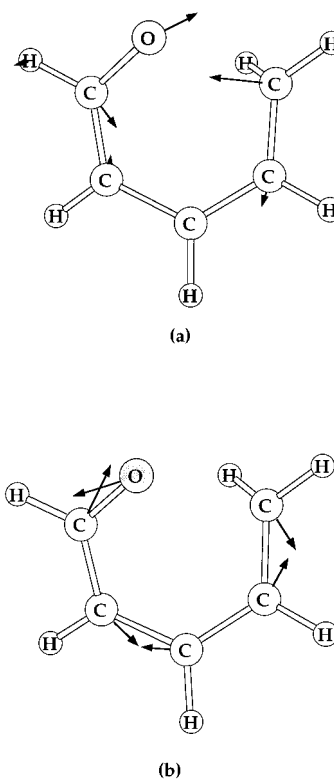


Figure 8. Residual forces^{12b} at the beginning of the relaxation channels on S_0 . The geometries differ only by a very small amount from the conical intersection itself and are not shown: (a) channel toward pyran and (b) channel toward 2,4-pentadienal.

Calculation of the relaxation pathways on S_0 suggests which photoproducts may be generated by decay at the conical intersection. Since pyran is a good model for benzopyran (near the conical intersection region), it has been used to locate the possible S_0 relaxation valley accessible from the optimized intersection point. The intersection point is a singularity (i.e., a “spike” on the ground-state potential energy surface) very similar to the tip of a cone. From such a point different potential energy valleys may develop leading to different ground-state intermediates or product. As mentioned above, these valleys are located using a novel methodology¹² which involves the search for steepest descent directions from a singularity (IRDs). Two different IRDs (IRD₁ beginning at the geometry shown Figure 8a and IRD₂ beginning at the geometry shown Figure 8b) have been located. The final product generated by relaxation along the corresponding valley can be identified by looking at the direction of the residual forces^{12b} at the optimized points (Figure 8) or by computing the steepest descent line using, for instance, the IRC method^{10a} starting from the optimized points using the residual forces as initial search direction. In our case,

the final products can be easily recognized as *cZc*-penta-2,4-dienal (from IRD₂) and pyran (from IRD₁).

It is important to point out that knowledge of the relaxation valleys provides information on the shape of the ground-state energy sheet which will surely control the relaxation process occurring after S₁ → S₀ decay. (The actual dynamics of this relaxation, the extent of the branching between different valleys, and the final quantum yields require dynamic studies that are not yet feasible on systems of this size.) However, the valleys do indicate that the ring-opened primary photoproduct (IRD₂, Figure 8b) will have a curly *cZc* (i.e., *cis-cis-cis* conformation following the notation in ref 5) conformation. Thus the production of the more stable *cZt* (i.e., *cis-cis-trans*) conformers must occur from the initial conformer (it has been recognized that only merocyanine compounds with a central *trans* configuration are stable¹⁵). This is corroborated by CASSCF studies on *o*-quinodimethane¹⁶ where the *s-cis* conformer (analogous electronically to the *s-cis*-benzopyran) is in the center of a flat region with no barrier to isomerization to *s-trans* and an energy stabilization of about 5 kcal mol⁻¹.

The IRD₁ valley (defined in Figure 8a) leads to pyran. A similar valley in the full system must account for benzopyran regeneration, via ring closure. It may be argued that since the IRD₂ valley (to *cZc*-penta-2,4-dienal) appears to represent the "natural" continuation of the M* → TS* → CI S₁ path described above, for inertial reasons one expects a higher yield of ring-opened product with respect to reactant regeneration.

Conclusion

The ring-opening reaction coordinate in benzopyran has been determined through CASSCF calculations on the S₁ excited state. The ground-state coordinates which describe the relaxation processes occurring after decay to S₀ have been investigated on the smallest model pyran system. The important points of the proposed mechanism are as follows (see Scheme 3).

(1) A ring-opening transition state (TS*) connecting a cyclic intermediate (M*) to a much more stable (>40 kcal mol⁻¹ below M*) acyclic structure has been located on the S₁ state.

(2) The S₁ acyclic species corresponds to a conical intersection (CI). The presence of such a low-lying intersection renders the lifetime of any S₁ ring-opened structure negligible (in the sense that after TS* the system will decay immediately to the ground state). *Thus the magnitude of the benzopyran S₁ lifetime must depend on the S₁ barrier height.* A previous study^{8b} did not find the degenerate region of the conical intersection when the C–O bond is almost completely broken due to the poor level of theory.

(3) Two relaxation coordinates from CI have been documented. These demonstrate that decay from CI can produce open *cZc*-3-phenylprop-2-enal or revert to pyran, with the first decay process probably more efficient for inertial reasons.

Our computations can be used to interpret the results of recent ultrafast studies on indolinbenzospiropyrans.^{4,5} As mentioned

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before the size of the benzopyran system does not allow for an accurate evaluation of the energetics along the S₁ pathway. Therefore the computed 5 kcal mol⁻¹ barrier for TS* might change after inclusion of correlation energy. (However, the barrier will not be large!) Let us now assume that this barrier is negligible and that the S₁ surface is initially very flat. (A large *initial* energy slope along the ring-opening coordinate seems unlikely due to the required change in the excited-state electronic structure—from benzene anti-Kekule to *n* – π*—described above.) Under these conditions, the computed reaction coordinate suggests that, after photoexcitation to the FC geometry, the system will relax to M* along an *unreactive coordinate* (see arrows in Figure 2 and Scheme 3). In order to achieve ring opening, part of the kinetic energy will have to be redistributed among other molecular vibrational modes, especially the C–O bond stretch. Such a process will take a few hundred femtoseconds.¹⁷ After even partial energy redistribution, the system will start to decay through the CI channel generating a change in the transient spectra. This view seems consistent with the 100 and 200 fs processes observed in indolinbenzospiropyran transient absorption spectra. The observed, almost instantaneous rise in absorption (<100 fs) may be attributed to formation of the transient excited-state species A*. The following 200 fs absorption change may then be assigned to decay of A* with formation of vibrationally hot merocyanine which then undergoes cooling in picoseconds to form the primary photoproduct.

The above view is, of course, tentative. The obvious requirement is that vibrational energy redistribution (IVR) in excited-state benzospiropyrans occurs in ca. 200 fs on a substantially barrierless (but initially flat) potential energy surface. Recent studies on short polyenes (*all-trans*-hexatriene)¹⁷ have demonstrated that in *all-trans*-hexatriene the time scale for IVR on S₁ is 250–500 fs. The mechanism proposed in ref 4 is different from the one proposed above since these authors suggest direct production of a metastable vibrationally hot merocyanine (X) in <100 fs which partially regenerates the reactant via ring closure on a 200 fs time scale. While we cannot at the moment provide unambiguous evidence in support of this view (which would require accurate quantum chemical computations on their experimental system), our reaction coordinate suggests that product back-formation on a short time scale is also possible by decay at the same conical intersection with relaxation along the IRD₁ path.

Acknowledgment. This research was supported in part by the EPSRC (U.K.) under Grant GR/K04811 and by an EU TMR network grant (ERB 4061 PL95 1290, Quantum Chemistry for the Excited State). All computations were carried out in an IBM-SP2 funded jointly by IBM-UK and HEFCE (U.K.). We are also grateful to NATO for a travel grant (CRG 950748).

JA9717323

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