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Accidental degeneracy in the spiropyran radical cation: charge transfer between two orthogonal rings inducing ultra-efficient reactivity†

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Photochromism of the spiropyran radical cation to the corresponding merocyanine form is investigated by a combination of electrochemical oxidation, UV/vis absorption spectroscopy, spectroelectrochemistry and first-principles calculations (TD-DFT, CAS-SCF and CAS-PT2). First, we demonstrate that the ring-opening of mono-spiropyran occurs upon one-electron oxidation and that it can be driven photochemically as well as thermally, with trapping of the merocyanine by protonation. Second, in order to explain this experimentally observed spectroelectrochemical behaviour we suggest a theoretical mechanism based on the reactivity of the two lowest electronic excited-states, which promotes effective electron transfer from the indoline (nitrogen-ring) to the pyran (oxygen-ring) moieties (and *vice versa*) through a conical intersection seam of degeneracy. Characterisation of the minimum energy conical intersection on this crossing revealed that it presents a rare diabatic trapping topology. The excited state molecule cannot escape from crossing the intersection seam due to the presence of only one degeneracy-lifting coordinate that efficiently channels into the formation of the merocyanine photoproduct, so giving rise to a "kitchen sink" funnel-like effect. Therefore, assuming rapid relaxation after vertical excitation to a higher electronic state, photoconversion cannot be avoided in the D_1 electronic state, which rationalises the remarkably efficient visible light driven excited-state reactivity observed experimentally.

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1 Introduction

Since their discovery by Fischer and Hirshberg in 1952,¹ the members of the spiropyran photochrome family have received much attention due to their numerous industrial applications (e.g., ophthalmic glasses, optical switches, optical memory and

non-linear optical devices).^{2–5} This versatile class encompasses organic photoswitches consisting of two planar heterocycles, one with a nitrogen atom (indoline) and another with an oxygen atom (pyran), connected through a common tetrahedral carbon atom (C_{spiro}) that both enforces the orthogonality between the two rings and prevents the mutual conjugation of their respective π -electron systems.

Neutral spiro-type compounds have been studied extensively, both theoretically and experimentally, especially for their photochemically and thermally driven switching processes.^{2–5} Irradiation of spiropyran with UV light results in the opening of the spiro moiety of the neutral, non-planar spiropyran structure (SP) leading to a thermally unstable zwitterionic planar merocyanine

Scheme 1 Photochromism between the ring-closed spiropyran (SP) and the ring-open merocyanine (MC) forms in spiropyran-type compounds. The (T)rans-(T)rans-(C)isomer of the MC form is displayed.

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† Electronic supplementary information (ESI) available: Plots of the molecular orbitals included in the active spaces employed; Cartesian coordinates and energies of all optimised geometries; CAS-PT2 absolute energies; Mulliken populations of the spin density partitioned onto atomic sites. See DOI: 10.1039/c6cp06907j

form (MC) (Scheme 1). Subsequent irradiation with visible light results in an increase in the rate of the otherwise thermal recovery of the SP form.

Likewise, their respective singlet cationic counterparts have been shown to display photochromism in both solution^{6,7} and crystalline state.^{8,9} These have been employed in a variety of applications. For example, salts of spiropyrans have been used for the development of hybrid multi-functional materials, in which the spiropyran acts as a photochemical molecular switch perturbing the magnetic properties of the crystal lattice.¹⁰ Other uses are related to biological applications, where a water-soluble photochrome is needed.^{11–13} Although the thermal reversibility of this transformation has been exploited extensively in applications, thermally stable MC isomers have been attained in solution, as shown by Minkin and coworkers⁷ through the addition of cationic substituents, by Kortekaas *et al.* through protonation of the pyran oxygen atoms of bis-spiropyrans,¹⁴ and in the solid state when embedded in a silica gel.⁹

Although the photochromism of spiropyrans has been known for over half a century, their electrochromism has received detailed attention only recently. Ivashenko *et al.*¹⁵ demonstrated that oxidatively driven ring-opening of the nitro-spiropyran compound **1** shown in Scheme 2(a) does not occur, but instead the indole moiety undergoes rapid aryl–aryl dimerisation upon oxidation by a mechanism analogous to the dimerisation of *N,N*-dimethylaniline (DMA) to *N,N,N,N*-tetramethylbenzidine (TMB).^{16–18} Introduction of a methyl group at the *para*-position of the indoline unit blocks this coupling reaction resulting in reversible redox behaviour [compound **2** in Scheme 2(b)]. Remarkably, the reversibility of the cyclic voltammogram of this latter compound indicates that rapid oxidatively driven ring-opening does not occur with respect to the time scale of cyclic voltammetry.¹⁵ More recently, Kortekaas *et al.*¹⁴ reported the redox chemistry of a spiropyran dimer. In this system oxidation did not result in ring opening either, yet upon irradiation with visible light the dicationic form underwent conversion to the

doubly oxidised MC form, with the latter species trapped by protonation.

Although unexpected, the production of a stable radical cationic species, the spiro moiety remaining intact, and its parallel photochromic behaviour comparable to neutral spiropyrans opens up a wealth of possibilities in regard to multi-state, multi-addressable switching systems (*i.e.*, simultaneous pH, light, redox and thermal control).¹⁹ For example, a combination of acid- and photo-responsiveness in neutral spiropyrans has been shown to afford a bi-responsive system as a Self-Assembled Monolayer (SAM) functionalised electrode.²⁰ Irradiation with UV light generates the MC form, which can be switched between the protonated and zwitterionic forms by controlling the pH of the solution, which provides an electrode in which conductivity is controllable both photochemically and by changing the acidity. This also raises the question as to whether or not the photo-switching observed in the oxidised state is particular to the aforementioned systems, or is a general phenomenon occurring in the more readily accessible spiropyran monomers. Therefore, we performed the first joint theoretical–experimental investigation of the photochromic properties of the mono-spiropyran radical cation.

From the experimental side, we demonstrate that ring-opening of the mono-spiropyran compound **2** from the SP to the corresponding MC form occurs upon one-electron oxidation and that it can be driven photochemically as well as thermally, with trapping of the MC by protonation. Following this, we gain additional insights into the underlying molecular mechanisms thanks to first-principles calculations performed at different levels of theory (TD-DFT, CAS-SCF, and CAS-PT2) and relying on several chemical model systems. The fundamental origin of the light driven opening observed in spiropyran radical monomers is rationalised using a reaction mechanism in which the shape of the Potential Energy Surface (PES) of the two first electronic states and the topology of the Conical Intersection (CI) seam suggests a highly efficient photochromic conversion. These studies highlight the remarkable untapped potential for redox gated photochemical bidirectional switching with visible light.

The proposed theoretical mechanism for the SP radical cation photoconversion cannot be fully explained without using theoretical concepts that can be relatively unfamiliar to the non-specialised reader and hence these are briefly summarised in the following. In the theoretical study of the relaxation of an electronically excited molecule, a vital initial step is the understanding of the shapes of the PESs involved and their respective conical intersection crossing seams. The first determines the nuclear deformations after vertical excitation at the Franck–Condon (FC) region, while the second channels the radiationless decay towards lower electronic states.^{21,22} A conical intersection seam is a region on the molecular PES where two or more electronic states have the same energy which provides the funnel for population transference between these electronic states. CIs are defined by two coordinates, the so-called Derivative Coupling Vector (DCV) and Gradient Difference Vector (GDV), *i.e.*, branching space, which correspond to two directions in the space of molecular geometrical deformations that linearly lift the degeneracy.^{23,24}

Scheme 2 The oxidative electrochemistry of the spiropyran form is characterised by a chemically irreversible oxidation at ca. 1.1 V vs. SCE. Compound **1** undergoes rapid aryl–aryl dimerisation upon oxidation, while compound **2** maintains the SP structure.

In general these two coordinates, which are precisely defined quantities that can be computed explicitly, are combinations of changes in the bond lengths and bond angles of the molecular species under investigation. The representation of the electronic energy, *e.g.*, the PES, as a function of the branching space coordinates for a given CI geometry takes the form of a double cone in the region of the degeneracy. Two aspects should be underlined: (i) the apex of the cone corresponds in general to an optimised molecular geometry where the DCV and GDV quantities are evaluated. These vectors provide a description of the acting forces during the radiationless decay and the directions in which any photoproducts might be generated after decay; (ii) the remaining $3N - 8$ nuclear degrees of freedom (where N is the number of atoms) define the so-called intersection space, in which the degeneracy of the electronic states is preserved. Complementarily to the DCV and GDV, characterisation of this space^{25–28} (see ref. 27 and 28 for a complete description) provides information about the directions in the “surroundings” of the conical intersection geometry in which the degeneracy is preserved and thus alternative regions (higher or lower in energy) where radiationless decay might occur.^{29–32}

In the case of neutral spiropyrans, the accepted excited state decay mechanism involves a series of low-lying S_1/S_0 CIs that are accessible after vertical excitation to S_1 and can develop into either the SP or the MC form.^{33–36} We emphasize that recent static^{37,38} and dynamic³⁹ studies suggest that only one of these CIs has chemical significance (hydrogen-out-of-plane valley), as the others become avoided crossings when both static and dynamic electron correlation effects are simultaneously taken into account. Regardless of which region of the conical intersection seam is responsible for the photoisomerisation, the $C_{\text{spiro}}\text{--O}$ bond dissociation is generally accepted as the initial reaction step, which eventually develops into the formation of the planar MC form.

2 Methods

2.1 Experiment

Unless stated otherwise all reagents were obtained from commercial sources and used as received without further purification. Methyl-nitro-spiropyran, *i.e.*, 2-(3',3',6'-trimethyl-6-nitrospiro[chromene-2,2'-indol]-1'-yl)ethyl octanoate, was available from earlier studies.¹⁵ Solvents were spectrophotometric grade (UVASOL Merck). Electrochemical studies were performed using either a CH Instruments 760B or 1200B potentiostat. For cyclic voltammetry a three-electrode arrangement with a reference electrode (Ag/AgCl), Pt wire auxiliary electrode and glassy carbon working electrode were used. Voltammetry and spectroelectrochemistry were carried out in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile. UV/vis absorption spectra were acquired on an Analytik Jena Specord S600 diode array spectrophotometer. Spectroelectrochemistry was carried out using an OTTL cell⁴⁰ (a liquid IR cell modified with Infrasil or quartz windows, a platinum mesh working and counter electrode and an Ag/AgCl wire reference electrode).

2.2 Theory

In order to describe the experimental target system, 2^+ in Scheme 2(b), at the Complete Active Space Self-Consistent Field (CAS-SCF) level, the natural choice would be a CAS(21,20) description. In other words, the use of an active space consisting of 21 electrons in 20 Molecular Orbitals (MOs) including all π MOs, the to-be-broken $\sigma\text{--}\sigma^*$ MOs describing the $C_{\text{spiro}}\text{--O}$ bond, as well as the two lone pairs of the oxygen atom. Computations with such an extended active space are not feasible, hence we turned to three smaller but closely related model systems of increasing complexity (see Scheme 3). Our strategy is therefore to use a combination of hierarchical model systems and levels of theory (TD-DFT, CAS-SCF, and CAS-PT2) in order to reach a general picture for the photoconversion from SP to MC in monospiropyran radical cation compounds.

Model I is the simplest model, the effects of the heteroatoms are omitted since it contains carbon and hydrogen atoms only. This gives a simplified picture for the electron transfer between two symmetric orthogonal rings. Model II adds into the description the effects of both the oxygen and nitrogen atoms. As we will show below, photoinduced electron transfer from the indoline to the pyran rings along the $C_{\text{spiro}}\text{--O}$ cleavage coordinate induces the opening of the later ring and thus photochromism. Finally, model III is the closest to the experimental compound, and hence the most realistic.

Stationary points were optimised at the CAS-SCF level without imposing any symmetry constraint and numerical frequency calculations were systematically used in all of our computations to ascertain the nature of the stationary points. The Hartree–Fock method was used for model I. For models II and III a CAS(11,10) active space consisting of eight π, π^* MOs plus the two σ, σ^* MOs corresponding to the $C_{\text{spiro}}\text{--O}$ bond was employed. In the first case, this corresponds to the full π active space, while for the second, to a truncated active space comparable to the one employed in ref. 38. In order to check the reliability of the truncated active space for model II, two more π and π^* MOs were added, *i.e.*, CAS(15,14). The respective MOs are given in the ESI.†

All CAS-SCF calculations were performed using the standard 6-31G(d) atomic basis set and the Gaussian 09 package.⁴¹ Conical intersections were optimised using the standard algorithm in Gaussian 09.⁴² When state-averaged orbitals were used the orbital rotation derivative contribution from the CP-MCSCF

Scheme 3 Model systems for spiropyran radical cations. These model systems are very simplified, but they allow us to obtain useful insights by looking at the differences among them. In the first, one can evaluate electron transfer between two symmetrical π -rings, while in the second the effect of the heteroatoms is added. Finally, model system III is the closest to the experimental target system 2^+ as it includes the previously neglected ring conjugation.

equations to the gradient (which is usually a small correction and zero at an intersection seam geometry) was neglected.

To account for dynamic electron correlation, CAS-PT2 calculations were carried out by using the MOLCAS 7.8 software.⁴³ For each optimised geometry, two-root state-averaged calculations with equal weight were performed at the CAS-SCF/6-31G(d) level of theory and were followed by single root CAS-PT2/6-31G(d) calculations relying on the SA-CAS-SCF wavefunctions. An imaginary shift of 0.1 a.u. was applied to avoid the effects of intruder states while losing only a minimal amount of dynamic correlation energy.

3 Results and discussion

3.1 Experimental results

3.1.1 Photochemical switching of 2. The photochemical switching of the SP form of compound **2** to its MC form under UV irradiation ($\lambda_{\text{exc}} = 365$ nm) is manifested in the appearance of a visible absorption band at 587 nm [(i) black to red in Fig. 1]. However, this MC form starts to revert thermally to the SP within a few seconds of cessation of irradiation. Addition of acid to the MC form, however, results in a blueshift to 446 nm [(ii) red to blue in Fig. 1] and substantially retards the thermal reversion to the SP form [(iii) blue to green in Fig. 1]. Photochemical switching is still possible in the presence of acid since UV irradiation at 365 nm directly results in the appearance of the absorption band at 446 nm.

The effect of protonation is to lower the energy of the MC form by stabilisation of the phenolate anion. However even with excess of acid, reversion to the SP form occurs spontaneously. Hence rather than turning on and off of the thermal pathway, pH can be used to readily tune the response (recovery) rate of the neutral spiropyran.

3.1.2 Cyclic voltammetry. The cyclic voltammetry of compound **2**, in dichloromethane, was reported earlier by Ivashenko *et al.*;¹⁵ a single reversible oxidation wave was observed at *ca.* 1.0 V vs. SCE, indicating that the mono-cation 2^+ was chemically stable on the electrochemical timescale (*i.e.*, seconds). In the present study, its voltammetry was studied in acetonitrile and ethanol (*i.e.*, more polar solvents), in which it

Fig. 1 UV/vis absorption spectrum of compound **2** in acetonitrile (i) upon UV irradiation at 365 nm, (ii) immediately after addition of $\text{CF}_3\text{SO}_3\text{H}$ and (iii) thermal recovery 5 min after addition of $\text{CF}_3\text{SO}_3\text{H}$.

Fig. 2 Cyclic voltammetry of compound **2** in acetonitrile (0.1 M TBAPF₆), normalised to the square root of the scan rate (black – 0.01 V s⁻¹, blue – 0.05 V s⁻¹, and red – 0.5 V s⁻¹).

would be expected that the mono-cation would be destabilised and thus ring-opening observed.

In acetonitrile, dichloromethane and ethanol, with $\text{TBASO}_3\text{CF}_3$ as well as with TBAPF_6 , a reversible one-electron redox couple is observed at *ca.* 1.0 V. The scan rate dependence of the cyclic voltammetry of **2** in acetonitrile (Fig. 2) shows that the redox couple is electrochemically reversible ($E_{\text{p,a}} - E_{\text{p,c}}$ is *ca.* 60 mV). However, at lower scan rates the difference in $I_{\text{p,a}}$ and $I_{\text{p,c}}$ confirms that it is not chemically reversible; *i.e.*, the chemical follow-up reaction is slower than the timescale of the voltammetry. Notably, however, additional redox waves at less positive potentials are not observed, indicating that the product is either redox inert or has a more positive redox potential than the one of the SP form.

Therefore as previously reported,¹⁵ the spiropyran compound **2** undergoes reversible one-electron redox chemistry with formation of the mono-cation 2^+ in the SP form. In other words, there is no ring-opening or change in structure on the electrochemical timescale. However, once oxidised to its monocationic state, 2^+ undergoes thermal ring opening (and protonation) to the corresponding merocyanine form. The ring opening is accelerated by irradiation also as observed for the related double spiropyrans discussed above.¹⁴ Oxidation effectively reverses the direction of photochemical and thermal ring-opening and cyclisation and protonation serves to stabilise the merocyanine forms in both oxidation states.

3.1.3 UV/vis absorption spectroelectrochemistry. *In situ* UV/vis absorption spectroelectrochemistry was carried out on compound **2** to explore its chemical stability upon oxidation. At moderate scan rates (*e.g.*, 0.1 V s⁻¹), an increase in absorbance at 300 nm and the appearance of an absorption band at *ca.* 470 nm (blue in Fig. 3) occurs upon oxidation, with a near complete recovery of the original spectrum (black in Fig. 3) upon reduction at *ca.* 0.8 V (red in Fig. 3). The reversibility of the changes in the absorption spectrum, although not complete, indicate that the absorption band can be assigned to the radical monocation 2^+ in the SP form.

When the potential is held at 1.3 V, the absorption band at *ca.* 470 nm undergoes a blueshift over 60 s, yet, little change in the absorbance below 350 nm is observed. Upon cycling to lower potentials, the spectrum does not change further until a

Fig. 3 Top: UV/vis absorption spectra of compound **2** (black) and its oxidised form **2⁺** obtained initially upon oxidation at 1.3 V vs. SCE (blue) and after reduction at 0.8 V vs. SCE (red). Bottom: Cyclic voltammetry in acetonitrile (0.1 M TBAFPP₆) recorded at 0.1 V s⁻¹.

potential of <0.4 V is reached. At <0.4 V a slow decrease in the absorbance at *ca.* 420 nm is observed but again the absorption spectrum at <350 nm does not change significantly. Reoxidation at 1.3 V leads to a regeneration of **2⁺** to a small extent but primarily the oxidised species that absorbs at 430 nm recovers. The thermal conversion of the **2⁺** from SP to MC is accelerated by irradiation with visible light (*i.e.*, either by recording spectra

Fig. 4 UV/vis absorption spectra of compound **2** (black) and its oxidised form **2⁺** (blue) obtained initially upon oxidation at 1.3 V vs. SCE and after holding the potential at 1.3 V for 1 min (red) in acetonitrile (0.1 M TBAFPP₆). The inset shows the changes that occur over the intervening 60 s.

more frequently or by irradiation with a LED at 470 nm). The shift is similar to that observed earlier for a double-spiropyran system.¹⁴ It should be noted that the pH of the solution decreases when the potential is held at 1.3 V due to oxidation of adventitious water present and increases when the potential is held at below 0.3 V due to proton reduction at the platinum electrode.

The time-dependent changes observed can be understood by considering that there are two distinct processes. First, oxidation of the spiropyran is followed by a spontaneous ring-opening through a thermally activated process, which is accelerated by visible irradiation. Second, the production of protons at the platinum electrode results in the protonation of the MC form. The latter process can be reversed by an increase of the pH upon electrolysis at low potentials.

3.2 Theoretical analysis

3.2.1 Photoinduced ring-opening for the radical cations.

First, let us discuss the structures and the reaction pathways on the D₀ and D₁ PESs that are relevant for the photoconversion mechanism of model **II** (see Scheme 3) at the CAS-SCF level. The ground-state minima corresponding to the spiropyran (SP), open (OP) and merocyanine (MC) isomers were located together with a CI between the SP and OP forms. In these structures the C_{spiro}–O bond progressively dissociates along the reaction coordinate described by these geometries, with the C_{spiro}–O bond distance varying from 1.42 Å in the SP minimum, 1.60 Å in the CI and finally 2.66 Å in the OP minimum (see Fig. 5).

We focus our discussion around the sketch shown in Fig. 6, which illustrates the photochemical mechanism of spiropyran radical cations according to the selected computational model. Fig. 6 provides the potential energies for the D₀ (green, bottom) and D₁ (orange, top) electronic states at the SP geometry represented in the space of two independent nuclear coordinates.

Fig. 5 Optimised structures of model **II** at the CAS(11,10)/6-31G(d) level. C_{spiro}–O bond distances are in angstroms. The stationary points on the ground state (a, b and d) are radical cation minima as confirmed by numerical frequency calculations whereas c is the conical intersection between the closed and open forms. The (*T*)*trans*–(*T*)*trans*–(*C*)*is* isomer of MC is displayed.

Fig. 6 Sketch of the proposed mechanism for reactivity in spirocyan radical cations. The energies for the D_0 (green, bottom) and D_1 (orange, top) electronic states at the SP geometry are represented in the space of two nuclear coordinates: (i) the GDV computed at the CI (reaction coordinate) and (ii) out-of-plane distortion (intersection seam coordinate).

These correspond to: (i) the GDV computed at the CI, which mainly involves the shortening/elongation of the internuclear $C_{\text{spiro}}\text{--O}$ distance, that is, the reaction coordinate; and (ii) the out-of-plane distortion that leads to the open form once the $C_{\text{spiro}}\text{--O}$ bond has been broken. According to this sketch derived from the CAS-SCF computations, we expect that after vertical excitation from D_0 to D_1 of the SP form (or to a higher electronic state and subsequent relaxation down to D_1 , as we discuss below), the forces at the FC point will lead to the CI and induce the formation of the ground-state OP minimum. This reactivity, which is the central mechanistic feature for the proposed mechanism, is further supported by the topology around the CI optimised geometry described in the following.

The DCV and GDV computed at the CI geometry are highly collinear (see Fig. 7), which has dramatic consequences on the mechanistic picture (these two vectors lift the D_1/D_0 degeneracy of the seam). Due to this collinearity, the CI hyperline has a dimension of $(N - 1)$ instead of $(N - 2)$,⁴⁴ where N is the number of nuclear degrees of freedom. Therefore, the degeneracy preserving coordinate shown in Fig. 6 (out-of-plane distortion) is not unique: in fact, any nuclear coordinate orthogonal to the reaction

Fig. 7 The branching space at the D_1/D_0 CI in Fig. 5: Gradient Difference Vector (GDV, left) and Derivative Coupling Vector (DCV, right). The angle between DCV and DGV is 163.0 degrees.

coordinate preserves the degeneracy. This rare topology of the intersection seam means that it cannot be avoided thus creating a diabatic trapping⁴⁵ for both electronic states and hence an ultra-efficient photochromic reaction takes place. Due to the absence of other lifting-degeneracy coordinates besides the GDV, we can think of it as a ‘kitchen sink’ funnel-like effect in which the excited state molecule cannot escape from crossing the intersection seam in the same way as the liquid cannot escape from meeting the hole at the bottom of a sink.

Diabatic trapping can be expected in topologies where the vectors corresponding to the branching space are nearly collinear⁴⁴ or the DCV has a small length.⁴⁵ In fact, the derived landscape, plotted in Fig. 6, is similar to the one encountered for the photochemical dissociation of bromoacetyl and bromopropionyl chlorides,^{46–49} the electron transfer in the bis(methylene)adamantane (BMA) radical cation,⁴⁵ the photoinduced isomerization of the photoactive yellow protein chromophore^{50,51} and the nitro-nitrite isomerization in nitroamide and nitromethane hindering the reactivity.⁵² This non-adiabatic hindering is an atypical feature only found so far to slow down the chemical reaction of the desired product on the lower surface of the crossing seam in the aforementioned examples, hence the naming as a diabatic trap. However, interestingly in the present case the same diabatic trapping induces a very high reactivity after vertical excitation since we are interested in the upper surface product (orange surface in Fig. 6). This feature has not been found so far in the photochromic conversion of the neutral spirocyan, which explains the remarkably efficient visible light driven excited-state reactivity observed experimentally for the radical cation.

Finally, as model **II** can be viewed as too simplified and as CAS-SCF only accounts for static correlation, the effect of increasing the conjugation of the pyran and indoline rings as well as the impact of dynamic electron correlation were evaluated. In order to assess the first, geometry optimisations of the relevant structures were carried out for model **III** at the CAS-SCF level, while to evaluate the second, complete active space second-order perturbation theory (CAS-PT2) energy evaluations were performed for both the models **II** and **III**. These geometries and their respective energies are given in the ESI† and Table 1, respectively. As we can see these CAS-PT2//CAS-SCF results confirm the existence of the CI degeneracy for both models **II** and **III** when adding dynamic electron correlation (-2.87 and -0.23 kcal mol⁻¹ energy gap, respectively). Similarly, there are no significant differences in the SP core when comparing the respective geometries of the two models (see the ESI†). In terms of the collinearity of the CI both models **II** and **III** have a strong character, which is denoted by the angle between the DCV and GDV being 163.0 and 160.8 degrees respectively, using a CAS(11,10)/6-31G(d) description. This near collinearity was also confirmed (149.8 degrees) by an optimisation of the CI for model **III** employing a larger active space, *i.e.*, CAS(15,14)/6-31G(d). An angle of 90 degrees would correspond to the common case of an orthogonal branching space, while 180 degrees to a complete collinearity between the two vector components.

3.2.2 Electron transfer between two orthogonal rings. After describing the mechanism of the ring opening in the spirocyan

Table 1 CAS-SCF energies and CAS-PT2 energy gaps at the optimised geometries [CAS(11,10)/6-31G(d) level of description] for models **II** and **III**. Energies are in kcal mol^{−1} selecting the SP minimum as reference and using two-root state-averaged orbitals. For CAS-PT2, the energy differences between the D₁/D₀ electronic states are given in brackets

Geometry	Model II		Model III	
	<i>E</i> (D ₀)	<i>E</i> (D ₁)	<i>E</i> (D ₀)	<i>E</i> (D ₁)
SP	0.0	72.4	0.0	39.4
OP	−11.4	58.4	−3.2	56.4
CI	29.6	29.8 (−2.87)	19.1	23.6 (−0.23)
MC (TTC)	−16.6	37.3	—	—

radical cation, we now turn towards a comparison between models **I** (symmetric rings) and **II** (asymmetric rings). As model **I** belongs to the *C*₂ point group, a symmetry induced CI is responsible for the electron transfer between the two rings, which can be interpreted by simple symmetry arguments. At the HF/6-31G(d) level of theory, the Highest Occupied Molecular Orbital (HOMO) and HOMO−1 of the neutral form are degenerate and consist in the π -bonding orbitals localised on each of the CC double bonds (see Fig. 8), that do not interact together. As expected these correlate with the A and B irreducible representations, respectively.

The removal of one electron, either from the HOMO or HOMO−1 to generate the cationic species is subject to an asymmetric distortion. In other words, the unpaired electron is localised at either of the CC double bonds, the *C*₂ symmetry is lost and the degeneracy between the MOs is lifted. The asymmetric redistribution of the electronic charge can be quantified by computing the so-called spin density ($\rho_\alpha - \rho_\beta$). The UHF/6-31G(d) MOs and the corresponding spin density obtained for model **I** after symmetry breaking due to oxidation are shown in Fig. 8. As we can see the spin density plots correlate well with the unrestricted MOs for these asymmetric nuclear geometries and localise the electron/charge on either of the CC bonds, as expected.

Fig. 8 The symmetry-induced degeneracy for model **I** (*C*₂). The central part corresponds to the neutral system. The character of the electronic spin density of the radical cation form (left and right) can be correlated to the topology of the singly occupied molecular orbital (SOMO) orbital.

This simple analysis is more difficult for the spiropyran due, on the one hand, to the lack of *C*₂ symmetry, and, on the other to the larger number of relevant π MOs. Nevertheless, by examining the spin density population at each ring, we can trace this behaviour in a fashion that is independent of the symmetry group and number of MOs. Fig. 9 illustrates the D₀ and D₁ electronic energies of a linear extrapolation in model **II** along the GDV coordinate at the CI and gives the spin density for each electronic state at *x* = 0.4 and *x* = −0.4 in the horizontal axis. For simplicity, we compute the spin density and partition it onto the atomic sites *via* the standard Mulliken Population analysis (see the ESI†). The total sum of Mulliken population values for each ring and the C_{spiro} atom are displayed in Fig. 9.

Each electronic state has a distinctive chemical character, which is denoted by the spin density distribution. For instance, at the lowest energy closed geometry (negative side of the *x*-axis in Fig. 9) the unpaired spin is nearly evenly located between the pyran (O) and indoline (N) rings but with the majority of the distribution on the latter. Electronic vertical excitation from the blue into the orange curve induces a transfer of the spin density into the pyran ring. The opposite transfer from pyran to indoline can be seen by looking at the vertical excitation on the lowest energy open geometry (positive side of the *x*-axis), *i.e.*, moving vertically along this graph changes the electronic character. In contrast, the electronic energy value for each electronic state (blue and orange curves) depends dramatically on the GDV coordinate, which mainly consists in the C_{spiro}–O bond breaking. Therefore, moving horizontally along this graph – either to the right along the orange curve or to the left along the green curve – stabilises the associated spin density character and analogously to the crossing at *C*₂ nuclear geometries in model **I**, one finds an “accidental” nuclear geometry (the CI) in which the two electronic states are degenerate. As for the

Fig. 9 Extrapolation of the electronic energy in kcal mol^{−1} along the Gradient Difference Vector (GDV) computed at the lowest energy conical intersection for model **II**. Blue and orange curves correspond to the energies of the two possible electronic states. The numerical values of the spin density for each ring and C_{spiro}, extracted from the Mulliken population analysis, are displayed (see the ESI† for all values).

symmetric case in which the breaking of the symmetry removes any degeneracy by locating the charge on either ring, the dissociation of the $C_{\text{spiro}}\text{-O}$ bond in model **II** plays an equivalent role. Elongation/contraction of this distance controls the stabilisation of the charge either on the pyran or the indoline rings, while the orthogonality and rigidity between the two rings derived from the C_{spiro} atom imposes a “hidden” symmetry with analogous consequences to the effects derived from the C_2 point group in the most simplified model.

3.2.3 UV electronic spectra. Last, since the present theoretical modelling was restricted to the ground and first excited states, the theoretical UV/vis absorption spectra should be addressed. Thus the transition energies of the lowest excited electronic states were investigated using Time-Dependent Density Functional Theory (TD-DFT). This theoretical spectral analysis neglects vibrational and geometric reorganisational effects. Nevertheless despite these limitations, the use of vertical TD-DFT computations is in general a valuable first approximation.⁵³

The positions of the maxima together with the corresponding oscillator strengths for the experimental target 2^+ computed using the CAM-B3LYP exchange–correlation functional⁵⁴ indicate that the strongest absorptions (high oscillator strengths) correspond to excitations towards higher-lying excited states. Indeed, the vertical excitation to the first four excited states are associated with negligible oscillator strengths, while transitions to the fifth and sixth excited states should give rise to relatively weak absorption bands. These appear at 413 nm ($D_5 \leftarrow D_0$, $f = 0.16$) and 376 nm ($D_6 \leftarrow D_0$, $f = 0.04$). Therefore, as the most intense bands observed experimentally take place in the 400–500 and 300–350 nm domains (Fig. 4), irradiation of the spiropyran radical cation 2^+ in the UV should result in excitation into these higher excited states.

At this stage, we cannot rule out the presence of additional CIs with higher excited-states, so that the relevant photochemistry would occur at higher energy and not be affected by the lower-lying conical intersections found here. However, this would imply that the relaxation to the lowest excited-state would not be the favoured mechanism when excitation to high-energy states is performed. In addition, confirmation of the presence of high lying CIs would require the mapping of the PES of higher excited states, which goes beyond the scope of the present work. In consequence, assuming rapid internal conversion after vertical excitation into higher lying excited states, our analysis of the D_1 PES indicates that photoconversion cannot be avoided on this electronic state, rationalising the efficient conversion to the MC form observed experimentally.

4 Conclusions

The combined experimental/theoretical study of the visible light driven ring-opening of the spiropyran radical cation presented here highlights the remarkable untapped potential for redox gated photochemical bidirectional switching with visible light. First, the efficient photochemically induced conversion from the oxidised spiropyran to the merocyanine form, observed previously both in solution and in polymer films,

Fig. 10 Photochemical reaction pathways in the mechanism proposed for spiropyran radical cation photoconversion from SP to MC.

although unexpected, has been shown to be an intrinsic property of the one-electron oxidised spiropyran unit. Second, the computational analysis of the topology of both the ground and first excited electronic states of the spiropyran monocation has revealed that the observed photoreactivity could be explained by the shape of the conical intersection seam, thus providing a possible mechanistic explanation (summarised in Fig. 10).

Indeed, assuming rapid relaxation from higher excited electronic states, there is only one coordinate lifting the degeneracy in the D_1/D_0 intersection seam resulting in a radiationless decay that can occur anywhere along a wide range of nuclear geometries. The unusual topology of this region may play a decisive role for the photochemical reactivity in spiropyran radical cations since this funnel induces a diabatic trapping of the electronic states, which should efficiently channel conversion from SP to MC and *vice versa* in what we described as a “kitchen sink” effect on the upper surface in Fig. 6. To the best of our knowledge, this is one of the very first examples of such topology in a photochromic system.

From a theoretical point of view, we aimed here at justifying the experimental evidence by providing a microscopic explanation of the photoconversion process. However, an extra fundamental challenge for theoretical chemistry is the design of new photochromic compounds, which could be addressed by hindering/promoting the lower/upper surface reactivity through the appropriate substitutions and/or changes in oxidation state. Therefore, even though the present study presents only a partial static picture focussed on the topologies of the ground and first excited states, the outlined mechanism provides the necessary foundation for further computational works and raises the opportunities for exploration of spiropyran radical cations (as well as other molecules displaying this topology) as a new approach to photoswitching.

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