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Bipyridyl Derivatives as Photomemory Devices: A Comparative Electronic-Structure Study

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Abstract: The two isoelectronic bipyridyl derivatives [2,2′-bipyridyl]-3,3′-diamine ($BP(NH_2)_2$) and [2,2′-bipyridyl]-3,3′-diol ($BP(OH)_2$) are experimentally known to undergo very different excited-state double proton transfer processes that result in fluorescence quantum yields that differ by four orders of magnitude. Such differences have been theoretically explained in terms of topographical features in the potential energy surface and the likely presence of conical intersections. The hypothetical hybrid compound [2,2′-bipyridyl]-3-amin-3′-ol ($BP(OH)(NH_2)$) presents intermediate photochemical features of its "ancestors". In this report we analyze the photochemical properties of a whole family of "dark" (not fluorescent) states that can be accessed from each bipyridyl derivative upon irradiation of light of a given wavelength and their potential application as photomemory devices. In the light of our density functional theory (DFT), time-dependent DFT (TDDFT), and complete active space self-consistent field (CASSCF) calculations, $BP(NH_2)_2$ is the more likely candidate to become a photomemory device.

Keywords: bipyridyls · computer chemistry · conical intersections · photochemistry · proton transfer · reaction mechanisms

Introduction

Intramolecular proton (or hydrogen) transfer is a fundamental chemical reaction that plays a crucial role in a variety of fields that extend from biological processes to technological applications. Because of this, intramolecular proton transfer in the ground electronic state has attracted considerable attention from experimentalists, which has led to the development of powerful techniques to investigate the mechanism of these processes.[1] With this increase in knowledge these reactions were also investigated theoretically with the use of progressively more accurate methods.[2] Nowadays, we have a rather clear picture of the structure and dynamics of these processes in the ground electronic state.[3]

With the advent of progressively faster time-resolved techniques that have reached the femtosecond timescale,[4] it has been possible to see the evolution of a chemical process in real time. This technical evolution has led to a blossoming of knowledge about systems undergoing excited-state intramolecular proton transfer (ESIPT). The advent of femtochemistry has settled an old dispute about the timescale of ESIPTs, which are now known to be ultrafast processes lasting no more than a few hundreds of femtoseconds.[5–7]

Probably the most thoroughly studied molecules exhibiting ESIPT are several families of aromatic systems with intramolecular hydrogen bonds. The interest in these systems was, at first, mostly technologically driven because of their potential use as photostabilizers and sunscreens for the protection of organic polymers and biological tissues (including our own skin).[8,9] The generic mechanism of photostabilizers involves an ultrafast proton (or hydrogen) transfer in the excited state followed by fluorescent or radiationless decay of the excited phototautomer leading to a very unstable structure in the ground state that quickly reverts to the original species. Figure 1a schematically shows the process involved in the simplest mechanism: The molecule absorbs radiation at a short wavelength λ_1. Once in the singlet excited state (S_1) the ESIPT process takes place through a barrierless (or

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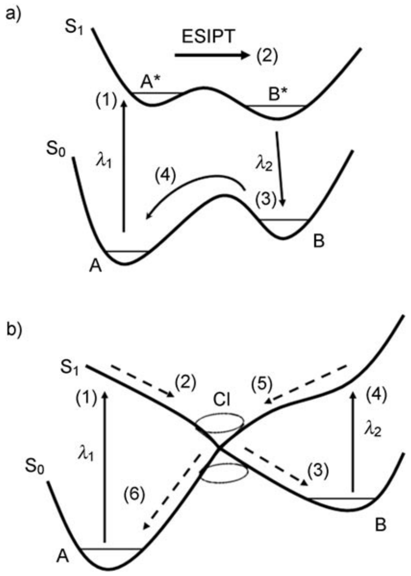


Figure 1. Schematic representation of the processes involved in the photocycle of a) a photostabilizer and b) an ideal optical photoswitch. ESIPT in (a) refers to the excited-state intramolecular proton-transfer process and the double cone in (b) refers to a conical intersection (CI) region of low energy. λ_1 is the wavelength that photoexcites A and λ_2 in (a) is the emission of B* and in (b) it indicates the wavelength that excites B. The numbering of events follows the sequence of the photocycle steps. Figure 1a is clearly related to that already used by us in ref. [36] whereas Figure 1b is based on Figure 1 in ref. [28].

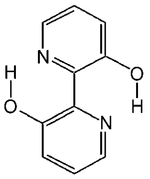
near barrierless) energy profile. The phototautomer, the more stable species in S_1, fluoresces, returning to the ground state S_0 by emitting a longer wavelength λ_2 so that by the end the system has absorbed high-energy (dangerous) radiation and emitted a far less energetic (harmless) one. As stated above, the tautomer obtained in S_0 is very unstable and quickly reverts to the initial species that is able to repeat the whole photocycle. This correlative sequence of processes is represented in Figure 1a by the numbers (1)–(4).

This simple and easy-to-understand picture is not, however, the usual case as most of the photostabilizers do not actually emit any radiation (that is, they do no fluoresce). In these cases the deactivation of the excited state has to take place through a radiationless path. A likely mechanism for the highly effective deactivation of fluorescent states[10] involves the curve-crossing of the initially accessed (bright) state with a nonfluorescent dark state that would be responsible for the deactivation process. This rather intriguing hypothesis was not proved until quite recently when increasing computational power allowed accurate electronic-structure calculations of excited electronic states. In our present-day picture of reactions in excited electronic states, such true crossings between different electronic states (conical intersections) are ubiquitous and essential to explain the photochemistry and photophysics of virtually any molecular system.[11] The presence of conical intersections in ESIPT processes (or more generally in hydrogen-bonded molecular complexes) was anticipated some years ago,[12,13] but it was not explicitly demonstrated until quite recently with the advent of powerful theoretical techniques able to unequivocally locate such a crossing between different electronic states.[14–19]

In its plainest form, the mechanism of a photostabilizer that fully quenches fluorescence is shown in Figure 1b: After photoexcitation in which light of λ_1 is absorbed, the ESIPT process leads to a tautomer that is not stable with respect to a deforming coordinate (usually torsion of the aromatic rings and/or pyramidalization of the proton acceptor group). By following this coordinate a conical intersection (CI) with the ground state is reached. At this geometry, an $S_1 \rightarrow S_0$ nonadiabatic transition occurs within a fraction of the time of a torsional process, that is, the transition is ultrafast.[20] Once the system is again in the ground state the most likely process involves the return to the (more stable) initial species in the ground state thus closing the photocycle in the usual manner. Alternatively the CI may also connect with a different tautomer in the ground state. If this isomeric species is stable enough, a so-called photochromic species is obtained as the final product of the photoexcitation.

A huge variety of organic (and inorganic) compounds exhibit photochromism although they are usually grouped within a few families of compounds.[21] The chemical reactions these compounds may undergo after photoexcitation is also very varied. Among them, the family of aromatic Schiff bases is to be highlighted because the photochromism in these compounds is produced through an ESIPT process.[22,23] Recently, interest in photochromic systems has suddenly increased because of the intriguing possibility of using them as molecular optical switches or photomemory devices. The use of organic molecules for the future realization of digital processors and storage media at the miniaturized level is at present a hot topic in applied science.[24–27] A molecule that exhibits the simple behavior shown in Figure 1b could be a good candidate for a molecular photomemory device if the photochromic species is stable enough. To accomplish this, additional stabilization of this isomer should be possible, for example, through the formation of a new hydrogen bond. In addition, the photochromic form should absorb at a very different wavelength in comparison with the original absorption (λ_2 in Figure 1b) and this excitation would have to revert the system to the original form also through an ultrafast process. The numbers (1)–(6) in Figure 1b reveal the whole sequence: 1) Photoexcitation of species A, 2) a barrierless photochromic process in S_1, 3) transition via a conical intersection to yield species B in S_0, 4) photoexcitation of species B, 5) reversal of the photochromic process, and 6) closing of the photocycle again via the conical intersection finally reverting to species A in S_0. Finally, to be able to "read" the memory, there should exist a physical property, easy to measure, that could be used to discriminate clearly between the two isomers. This idea has recently been proposed by Sobolewski who has theoretically designed a molecule that would fulfill all these conditions.[28]

In recent years we have studied a series of isoelectronic molecules with [2,2′-bipyridyl]-3,3′-diol (hereafter referred to as $BP(OH)_2$), one of the simplest molecules that is experimentally known to suffer a double proton transfer in the excited state.[29–33] In addition to studying the parent molecule,[34] we have also investigated the isoelectronic derivatives [2,2′-bipyridyl]-3,3′-diamine ($BP(NH_2)_2$)[35] and [2,2′-bipyridyl]-3-amin-3′ol ($BP(OH)(NH_2)$).[36] In spite of the similarities between the three molecular systems (the only change being the substitution of one or two hydroxy groups by amino ones), they show quite different photochemical behavior. One of the most striking differences arising from time-resolved femtochemistry experiments is the fluorescence quantum yield, which differs by more than four orders of magnitude between $BP(OH)_2$ and $BP(NH_2)_2$.[37] Our previous theoretical work, mainly devoted to a systematic analysis of the stationary points in both the ground (S_0) and first singlet-excited (S_1) electronic states, provided a good theoretical basis to explain the differences between both systems and the hybrid $BP(OH)(NH_2)$ for which no experimental data is yet available.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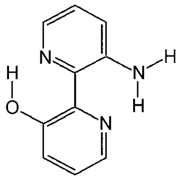
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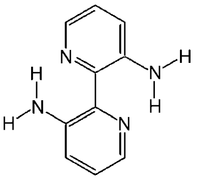
$BP(NH_2)_2$

One of the key features that differentiate the three systems so significantly is the likely presence of conical intersections (CIs) between S_1 and S_0. These CIs appear in regions of the potential energy surface that correspond to a single proton transfer upon rotation of the two pyridyl rings and it appears that they are energetically accessible from the Franck–Condon initial excitation area in all the systems considered. In our previous work,[34–36] the different photochemical behavior of the three systems was discussed in light of the different energies and geometries of the stationary points in S_0 and S_1 and the CIs. However, in these analyses the fate of the molecule beyond the CI was not considered. Up to this point, we could conclude that these systems have the corresponding potential profile to become good photostabilizers. In this paper we go a further step and look more carefully at the molecular motions that may occur in S_0 after passing the CI. In this way we disclose the presence of an, up to now, unknown set of photochromic structures that cannot be directly accessed by photoexcitation but which may eventually become the product of the complete photochemical process. If these "dark" molecular species happened to be the main product after passage through the CI, the bipyridyl systems studied here could be one of the smallest and simplest photostable molecular memories known so far. Our theoretical work may then open the door to exciting new possibilities in the design of sub-nanostructures as building blocks for the next generation of digital processors and storage devices.

Results and Discussion

As stated in the Introduction, we have previously performed several studies on three isoelectronic bipyridyl derivatives.[34–36] In this paper we reconsider these three systems. We shall begin the study with $BP(NH_2)_2$, the molecule with the lowest quantum fluorescence yield as this points to a more likely access of the conical intersection and, consequently, to the dark states. Later on we will consider the $BP(OH)_2$ molecule, the best-studied system from both experimental and theoretical points of view. Finally, we will analyze the hybrid $BP(OH)(NH_2)$, which has been synthesized but studied no further, but is very interesting in relation to our work here due to the asymmetry of the molecule that allows for a larger number of reaction paths. As there is no way of discussing our new results (the dark states) without also considering the "bright" states that were previously identified (using the same level of calculation) and analyzed by us,[34–36] Figures 2–9 show the structures in two different formats: bold letters, numbers, and characters refer to the dark states (new results) whereas normal letters, numbers, and characters represent the bright (previously obtained) states of the different studied systems.[38] This differentiation also allows for a clearer discussion.

$BP(NH_2)_2$: We theoretically analyzed $BP(NH_2)_2$ in a previous work.[35] In that work the stationary states of the ground (S_0) and first singlet-excited (S_1) electronic states, the latter resulting from an allowed $\pi \rightarrow \pi^*$ excitation, were carefully located. The results are summarized in Figures 2 and 3. Figure 2 shows the energies of the different stationary points (and the conical intersection structure) on both the S_0 and S_1 potential energy surfaces and the reaction paths (as discussed in the Computational Details section) that connect them. Figure 3 gives a schematic view of the most relevant structures found along the different photochemical paths as well as the atomic numbering used to refer to the atoms involved in a particular intramolecular motion. It is hard to follow Figure 2 without taking a look at Figure 3 and thus both figures will be analyzed together. Even though Figure 2 shows the structures along a unique direction, all the reaction paths are clearly multidimensional. Solid lines connecting any pair of stationary points (minima or transition states) indicate a single proton transfer. Arrows at the foot of the figure indicate the transferring atom. Dashed lines are used to indicate out-of-plane motions (mainly rotation around the C1−C2 bond).

On the bright side of the S_0 potential energy surface, $BP(NH_2)_2$ possesses only one minimum-energy structure. As in our previous work, we name it diamine (DA) to indicate the positions of the transferring hydrogen atoms. This is the only existing chemical species prior to any photochemical reaction. Note that the fully optimized minimum is not per-

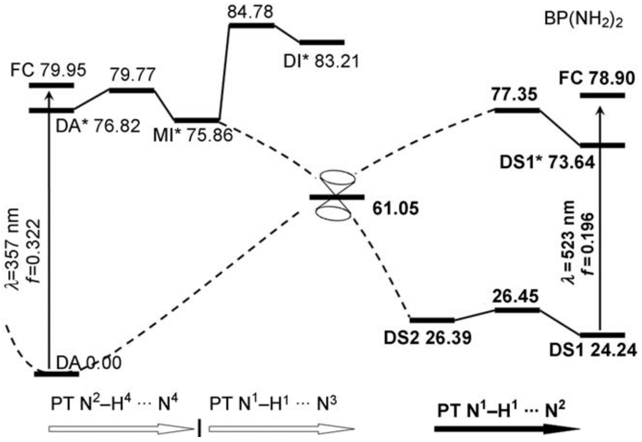

Figure 2. Relative energies (in kcal mol^{-1}) of the planar structures in S_0 (bottom) and S_1 (top) relevant to the double proton transfer and the rotation of the two pyridine rings in $BP(NH_2)_2$. Solid lines represent reaction paths that maintain the planar symmetry whereas out-of-plane reaction paths are indicated by dashed lines. A double-cone symbol is posted on the region of the conical intersection between S_0 and S_1. Arrows at the bottom indicate the proton that is transferred along any given path. The vertical arrows correspond to light absorptions relevant to the whole photochemical process (see text). Normal letters, numbers, and characters are used for processes in the bright zone that were studied in previous work,[35] whereas the dark region, discussed for the first time here, is indicated by bold letters, numbers, and characters.

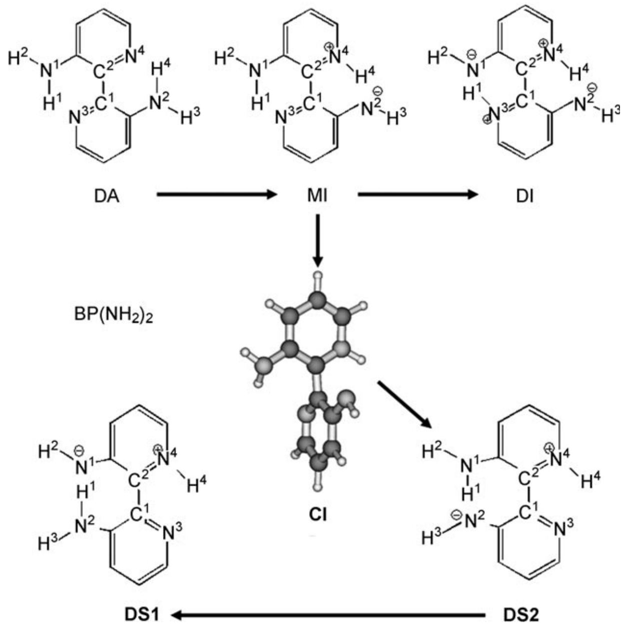

Figure 3. Schematic structures and atom-numbering of the geometries of the stationary points and the conical intersection region of $BP(NH_2)_2$ in S_0 and S_1. The meaning of the bold letters is as described in Figure 2.

fectly planar as a small amount of pyramidalization takes place in the amino groups and the two pyridyl rings are also slightly rotated. However, all the energies considered in Figure 2 refer to fully planar geometries (with the obvious exception of the conical intersection, as noted below). This does not produce large energy differences (for example, the difference in energy between the planar and optimized DA structures in S_0 is just 0.39 kcal mol^{-1}). Irradiation with light of 357 nm, similar to the maximum absorption experimentally measured at 370 nm,[37] puts the system in the excited S_1 state. This electronic transition is clearly allowed as it has an oscillator strength (*f*) of 0.322 (also indicated in Figure 2). Because of the Franck–Condon (FC) principle, the initial geometry accessed (leftmost FC in Figure 2) in S_1 is not the relaxed one corresponding to the DA* minimum, which lies 3.13 kcal mol^{-1} below the FC structure (note that, as is customary, we are using an asterisk to refer to excited-state structures). In fact, the energy of the FC structure allows the system to overcome the small energy barrier for the transfer of a proton thus enabling the so-called monoimine structure (MI*) to be accessed. Mulliken charge analysis of MI* shows a charge separation between the two aromatic rings of 0.467 a.u., consistent with the values found for typical zwitterionic species.[39] On the other hand, the second proton transfer, which would lead to the diimine (DI*), is not energetically accessible and so only a single proton transfer can take place in this system upon irradiation.

As in S_0 there is no minimum in the monoimine region, the overlap between the vibrational wavefunctions in S_0 and S_1 is quite weak. Consequently, fluorescence from MI* is not a favored process and competitive nonradiative processes may come into play. A possible channel of deactivation would be a back-proton transfer leading back to DA*, which is more able to fluoresce. However, as hinted at in our previous work, there is a lower-energy conical intersection (CI) region between the ground and first singlet-excited electronic states that can be accessed from the MI* structure upon rotation around the C1–C2 bond (that is, rotation of the two pyridyl rings). Given the multiconfigurational character of these regions, we have used, in a first step, the CASSCF approach to properly locate the conical intersection. In a second step, we have taken this geometry and employed the TDDFT method to find a minimum-energy structure in the CI region by optimization of the geometry structure corresponding to the excited-state (S_1) energy minimum, requiring that a degeneracy constraint with a lower potential energy surface (S_0) is satisfied at the end of the optimization (typically the degeneracy $S_0 \rightarrow S_1$ is less than 1.5 kcal mol^{-1}). The geometry thus obtained does not differ much from that obtained by the CASSCF approach. We are aware that the TDDFT method used in this paper is not suited to properly locating and characterizing conical intersections. However, it has been shown[40] that the approach may still provide a good approximation of the location of such structures and allow their energy to be determined provided that one is lucky or smart enough to know where the CI is to be found.

The most prominent geometrical parameter that defines the CI region is the rotation angle around the C1–C2 bond of around 90° such that the two pyridine rings are almost orthogonal in the CI. This structure is also characterized by the pyramidalization of the NH_2 group with a dihedral angle H2-N1-C-C2 of around 135°.

Even if the TDDFT energy of the CI is just qualitatively accurate, its value, well below the energies of all the other excited-state geometries, clearly points to a very easy internal conversion deactivation through this structure. In fact this is the most likely explanation of the very low fluorescence quantum yield (10^{-5}) measured for $BP(NH_2)_2$.[37] A question that has not yet been considered but is of crucial importance is: What is the fate awaiting the system beyond the CI? In our previous work it was implicitly assumed that the system, once again in the S_0 ground state, would revert to the original DA structure thus closing the photochemical cycle that would be ready to start again. In this sense $BP(NH_2)_2$ would be qualified as a good photostabilizer as it would absorb UV radiation without emitting dangerous radiation (in fact without emitting any radiation). To determine the fate of the process beyond the CI we followed the gradient difference vector direction, which is one of the two independent vectors of the branching space.[41] In the present case, this fate can be easily ascribed to the inter-ring C1−C2 rotational angle. The breaking of symmetry between S_0 and S_1 leads, on one side, to the initial DA structure and, on the other, to a rotated DA isomer. If this structure is stable (as we have found in our calculations), a photochromic product can be obtained. In Figures 2 and 3 we have labeled this new species as DS2.

As shown in Figure 3, the DS2 structure also has two intramolecular N−H···N bonds. The fully optimized DS2 geometry is also nonplanar, although, as stated above, the energies shown in Figure 2 correspond to planar geometries. Now the energy difference between the optimized (nonplanar) and planar geometries is a little larger (1.31 kcal mol^{-1}), probably because the new intramolecular hydrogen bond N2···H1 implies a more crowded cycle of seven atoms instead of the (more usual) six atoms involved in the DA structure. In any case, it did not come as a surprise to find that an intramolecular proton transfer may take place in DS2 to give the more stable DS1 tautomer. The barrier for the proton transfer between the two tautomers is almost nonexistent, 0.06 kcal mol^{-1} above DS2 and DS1 is 2.15 kcal mol^{-1} lower in energy than DS2. Given the excess energy that the system coming from S_1 is expected to possess, DS1 is the more likely final product, that is, the photochromic species, to result from the initial photoexcitation of DA. As can clearly be seen in Figure 3, DS1 is, in fact, a tautomer of the original DA structure as an equivalent DS1 form could be obtained by direct transfer of H2 between N1 and N4 (of course such a transfer cannot take place directly). DS1 has a high energy (24.24 kcal mol^{-1}) relative to the lowest DA minimum such that its presence would not be of relevance were it not for the likelihood of the photochemical route just discussed.

Now we can discuss the potential of $BP(NH_2)_2$ as a photomemory device. If the dark states are the main product after passage through the CI region (with our pure electronic calculations we have no possibility of further evaluating this point) then DS1 is expected to be a fairly stable species as the energy barrier for reverting to DA in the ground electronic state is quite large. The only possible way for DS1 to revert to DA would be a new irradiation, which we have calculated would require a wavelength of 523 nm. As is shown in Figure 2, the first allowed transition from DS1 has an oscillator strength of 0.196. The accessed excited state is the S_1 $\pi\pi^*$ excited state in which DS1* exists as a minimum-energy structure with the transition state for the back-proton transfer from N2 to N1 estimated to lie 3.71 kcal mol^{-1} above DS1*. However, as shown in Figure 2, the Franck–Condon vertical excitation (rightmost FC in Figure 2) puts the system higher in energy than that so that ESIPT is, again, energetically feasible. We have not been able to locate a minimum corresponding to the DS2* structure as the optimization provokes an internal rotation around the C1−C2 inter-ring bond leading again to the conical intersection region. Once there, the system will most likely proceed to DA. If this is so we will have a good molecular photomemory device. Thus, at first sight, the whole scheme shown in Figure 2 corresponds to a system that could be used as a molecular photomemory device. The whole scenario is somewhat more complicated than that previously schematized in Figure 1b, but it clearly fulfils all the expected conditions for a photomemory.

Thus, to summarize: 1) $BP(NH_2)_2$ is a bistable system, 2) the two stable structures in S_0 absorb (with high oscillator strength) at different wavelengths, 3) irradiation of one species mostly leads to the other species in an ultrafast process (there is no energy barrier to be surmounted in any direction), and 4) the two forms of $BP(NH_2)_2$ have to be differentiated by some physical property. Here an obvious choice is the permanent molecular dipole moment as the symmetric DA structure has a zero molecular dipole moment whereas DS1 is not at all symmetric and has quite a prominent molecular dipole moment of 1.826 D. If the calculations presented here are further confirmed, $BP(NH_2)_2$ may become one of the simplest isolated molecules known so far that is able to act as an efficient photomemory device.

Finally, it may be of interest to compare the intramolecular hydrogen bonds between the original DA structure and the most stable dark state DS1. Table 1 presents the geometrical data (distances) as well as the electronic characteristics analyzed by using Bader's atoms-in-molecules (AIM) formulation.[42] The electron density at the bond critical points is a measure of the strength of the bond. As usual, it can be di-

Table 1. Geometrical distances, electronic densities, and Laplacians at the bond critical points of the X−H···Y bonds of $BP(NH_2)_2$.[a]

Structure	Bond	r [Å]	ρ [e Å^{-3}]	$\nabla^2\rho$ [e Å^{-5}]
DA	N1−H1	1.017	0.332	−1.78
	H1···N3	1.868	0.0387	0.107
	N2−H4	1.017	0.332	−1.78
	H4···N4	1.868	0.0387	0.108
DS1	N2−H1	1.055	0.296	−1.51
	H1···N1	1.631	0.0640	0.127
	N4−H4	1.033	0.327	−1.77
	H4···N3	1.837	0.0424	0.121

[a] See Figure 3 for the atomic labeling.

rectly related to the corresponding bond distances. As for the Laplacian of the charge density, also shown in Table 1, negative values were obtained for all the X−H covalent bonds (charge is concentrated in this region), whereas positive values, which indicate charge depletion, are seen for the hydrogen bonds H···X. A comparison of the two hydrogen bonds present in the structures of DA and DS1 shows that the covalent X−H bonds are stronger in the case of DA, whereas the intramolecular H···X bonds are stronger in the case of DS1. In fact it is quite surprising to see how the N−H bond of the amino group increases on going from the DA to the DS1 structure (from 1.017 to 1.055 Å). As discussed above, this geometrical distortion is probably a consequence of the overcrowded seven-membered ring that is involved in the intramolecular hydrogen bond between H1 and N1 in DS1. The fact that the electronic densities at the bond critical points are not so different between the two cases sustains this hypothesis.

$BP(OH)_2$: This molecule is the most thoroughly studied of the three isoelectronic systems considered here and was also the subject of the first electronic calculations performed by us some time ago.[34,35] In the search for molecular photomemory devices it is not as interesting as $BP(NH_2)_2$ because of the relatively high fluorescence yield of 0.32, which, in principle, would hinder the presence of other photochemical paths such as the one eventually leading to dark states. However, we carried out a study on $BP(OH)_2$ identical to that performed on $BP(NH_2)_2$ and the results obtained are graphically displayed in Figures 4 and 5 (entirely equivalent to Figures 2 and 3 for $BP(NH_2)_2$). Overall, the whole scenario is not very different to that found for $BP(NH_2)_2$ although some subtle differences lead to quite a different photochemistry.

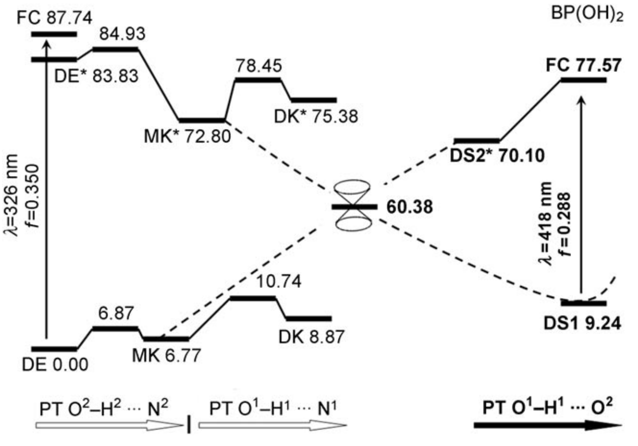

Figure 4. Relative energies (in kcal mol^{-1}) of the minimum-energy structures in S_0 (bottom) and S_1 (top) relevant to the double proton transfer and the rotation of the two pyridine rings in $BP(OH)_2$. Normal letters, numbers, and characters are used for processes in the bright zone that were studied in previous work,[34,35] whereas the dark region, discussed for the first time here, is indicated by bold letters, numbers, and characters. Other symbolization used in the figure are defined in Figure 2.

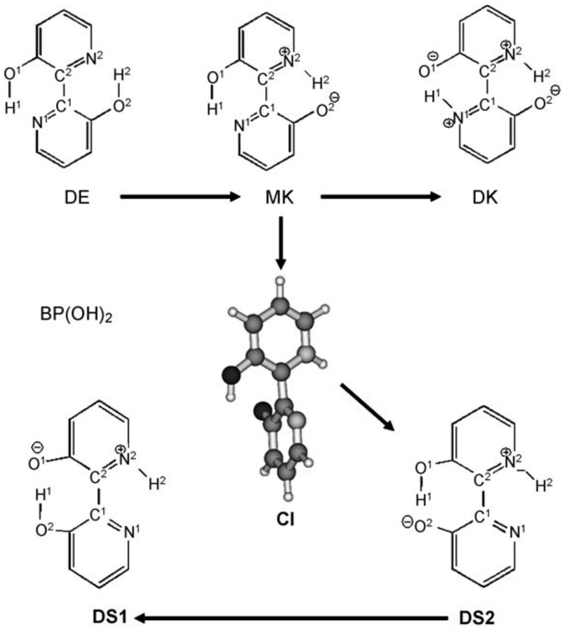

Figure 5. Schematic structures and atom-numbering of the geometries of the stationary points and the conical intersection region of $BP(OH)_2$ in S_0 and S_1. The meaning of the bold letters is as described in Figure 4.

The number of stationary points in the "bright" zone of Figure 4 is greater than observed for $BP(NH_2)_2$: The ground electronic state S_0 displays three minima corresponding to three possible protonation states. The most stable species is the dienol (DE) form. A single proton transfer leads to the monoketo (MK) intermediate and a further proton transfer to the (final) diketo (DK) tautomer. The transition states linking the different minima have also been located and are shown in Figure 4. All the directly located stationary states are fully planar. The first singlet-excited electronic state S_1 comes from a $\pi \rightarrow \pi^*$ excitation. The $S_0 \rightarrow S_1$ transition is allowed (oscillator strength = 0.350) and the excitation wavelength has a maximum absorption, Franck–Condon vertical transition, at 326 nm at our level of calculation (the experimental value is 340 nm). The relative stabilization of the tautomers dramatically changes in S_1 and the most stable one is the MK* structure, again a typical zwitterionic structure with a charge separation of 0.485 a.u. between the two rings. However, all the tautomeric forms are energetically available in S_1 as the FC structure is higher in energy than any of them and also higher than the estimated energies of the transition states, as seen in Figure 4.

A conical intersection has also been located for $BP(OH)_2$. The methodology used was the same as that outlined in the previous case and the characteristics of the CI structure located are also quite similar to those discussed for $BP(NH_2)_2$ with the two pyridine rings almost orthogonal to each other. The energy of this structure is also well below all the other ones in S_1 so that again the CI is energetically accessible from the S_1 potential energy surface. This again opens the door to the dark states, which can be obtained by relaxation of the CI to the ground state if the rotation between the two pyridyl rings does not bounce back (reverting to the original DE structure in S_0) but keeps going to yield a 180° rotated planar structure. In this case the direct product of the rotation, DS2 using the previous nomenclature, is not a stable structure as full optimization also leads to the spontaneous transfer of H1 from O1 to O2 such that relaxation of the conical intersection directly leads to the DS1 tautomer.

The DS1 isomeric form of $BP(OH)_2$ is a photochromic species. It is a very stable structure and will only revert to the initial DE structure upon irradiation of a given wavelength, 418 nm according to our calculations. With this wavelength the DS1 structure is excited to the S_1 $\pi\pi^*$ state with a high oscillator strength (0.288). In contrast to the situation in S_0, there is no minimum-energy structure DS1* in S_1 and the only located minimum corresponds to DS2*. This structure can be accessed directly from the Franck–Condon excitation and it has enough energy to lead to the CI region from which the system can evolve back to the bright states. Then the direct product of the full rotation is MK as it is a stable form of $BP(OH)_2$. However, MK will be reached with plenty of energy so that it will easily evolve to the more stable DE tautomer, thus closing the whole photochemical cycle.

Bader's AIM analysis of the DE and DS1 isomers of $BP(OH)_2$ is presented in Table 2. The results are quite similar to those previously discussed for $BP(NH_2)_2$. Note that here the N2–H2···N1 intramolecular hydrogen bond in DS1 is quite weak. This result could be anticipated as it forms through a five-membered cycle. This prevents an additional path connecting DS2 to a structure mirroring DS1 involving the intramolecular transfer of the H2 atom. Curiously enough, for $BP(NH_2)_2$ this intramolecular hydrogen bond was as strong as for the others. As in the previous case, the calculated dipolar moment of the DS1 photochromic species is large (5.890 D) and this physical property could be easily used to differentiate the DS1 state from the original DE symmetrical structure, which has a zero dipole moment. In the end, we have a very similar situation to the one discussed for $BP(NH_2)_2$ and, again, the conditions for a good photomemory device are fully accomplished. Without a molecular dynamics study of the competing processes considered here it is hard to tell whether the dark states will play an important role in the whole photochemistry of $BP(OH)_2$. As this (very complex) dynamics study is well beyond the scope of this paper we can only rely on the experimental data that indicate a high fluorescence yield so that passing through the CI is probably not the preferred deactivation path of the photoexcited species, although there may still be a non-negligible fraction of molecules following this path. Clearly additional studies (both experimental and theoretical) are necessary to acquire a better knowledge of the fascinating possibilities of this deceivingly simple molecular system.

Table 2. Geometrical distances, electronic densities, and Laplacians at the bond critical points of the X–H···Y bonds of $BP(OH)_2$.[a]

Structure	Bond	r [Å]	ρ [e Å^{-3}]	$\nabla^2\rho$ [e Å^{-5}]
DE	O1–H1	1.005	0.318	−1.75
	H1···N1	1.673	0.0581	0.123
	O2–H2	1.005	0.318	−1.75
	H2···N2	1.673	0.0581	0.123
DS1	O2–H1	1.052	0.271	−1.26
	H1···O1	1.410	0.0988	0.120
	N2–H2	1.029	0.330	−1.80
	H2···N1	1.941	0.0341	0.123

[a] See Figure 5 for the atomic labeling.

$BP(OH)(NH_2)$: For this asymmetric system there are two different paths for the intramolecular double proton transfer depending on whether the first transfer involves the amino group (N channel) or the hydroxy group (O channel). So as not to make the discussion too cumbersome, the two cases will be discussed together. Figures 6 and 7 show the results for the N channel and Figures 8 and 9 refer to the O channel. For the bright states we are using the same nomenclature as in our previous theoretical work:[36] The initial form is the enol amine (EA) and the product of the double proton transfer is the keto imine (KI) structure. A single hydrogen transfer leads from EA to the enol imine (EI) or the keto amine (KA) for the N and O channels, respectively. As in $BP(NH_2)_2$, the stationary points are usually slightly out-of-plane although in Figures 6–9 a planar geometry has been imposed with the obvious exception of the conical intersections in which the two pyridyl rings are twisted by almost 90° and have a significant degree of pyramidalization around the nitrogen atoms. In fact, the geometries obtained here are similar to those properly located at the CASSCF level presented in our previous study of this molecule.[36]

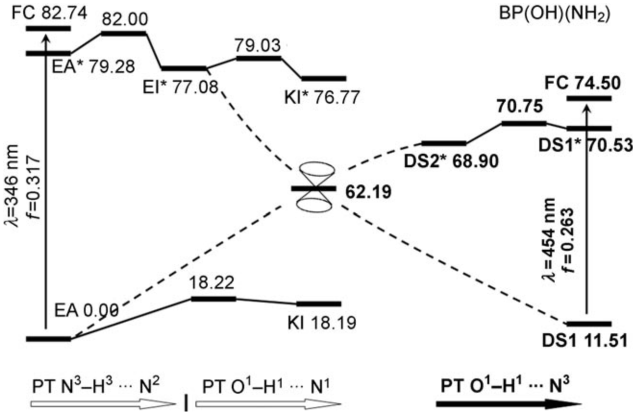

Figure 6. Relative energies (in kcal mol^{-1}) of the planar structures in S_0 (bottom) and S_1 (top) relevant to the double proton transfer and the rotation of the two pyridine rings in $BP(OH)(NH_2)$ along the N channel. Normal letters, numbers, and characters are used for processes in the bright zone that were studied in a previous work,[36] whereas the dark region, discussed for the first time here, is indicated by bold letters, numbers, and characters. Other symbolization used in the figure are defined in Figure 2.

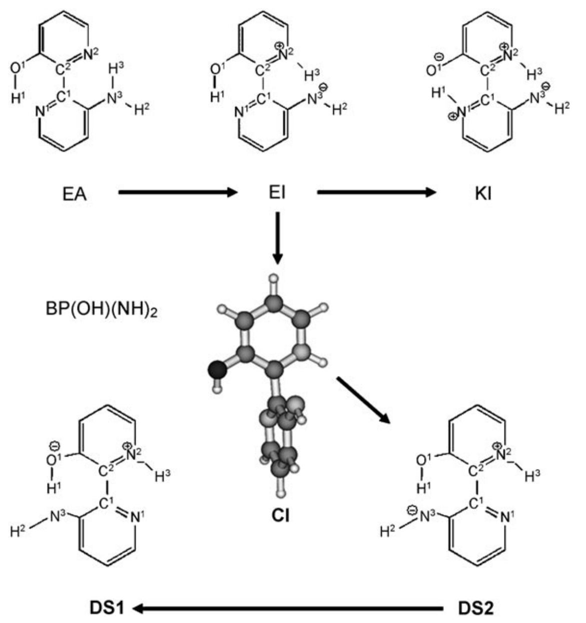

Figure 7. Schematic structures and atom-numbering of the geometries of the stationary points and the conical intersection region of BP(OH)-(NH_2) in S_0 and S_1 found along the N channel. The meaning of the bold letters is as described in Figure 6.

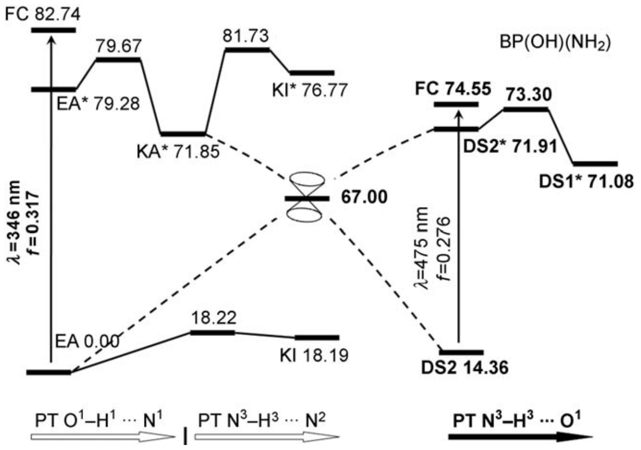

Figure 8. Relative energies (in kcal mol^{-1}) of the planar structures in S_0 (bottom) and S_1 (top) relevant to the double proton transfer and the rotation of the two pyridine rings in BP(OH)(NH_2) along the O channel. Normal letters, numbers, and characters are used for processes in the bright zone that were studied in a previous work,[36] whereas the dark region, discussed for the first time here, is indicated by bold letters, numbers, and characters. Other symbolization used in the figure are defined in Figure 2.

There are two minimum-energy structures in the "bright" region of S_0, although the KI tautomer is barely stable as it lies only 0.03 kcal mol^{-1} below the transition state linking it to the original, and more stable, EA tautomer. The transition to the S_1 state from EA is allowed (oscillator strength = 0.317) and, as usual, it corresponds to a $\pi \rightarrow \pi^*$ electronic excitation. From the vertical accessed state (FC structure in Figure 6 and Figure 8) several proton transfers are available.

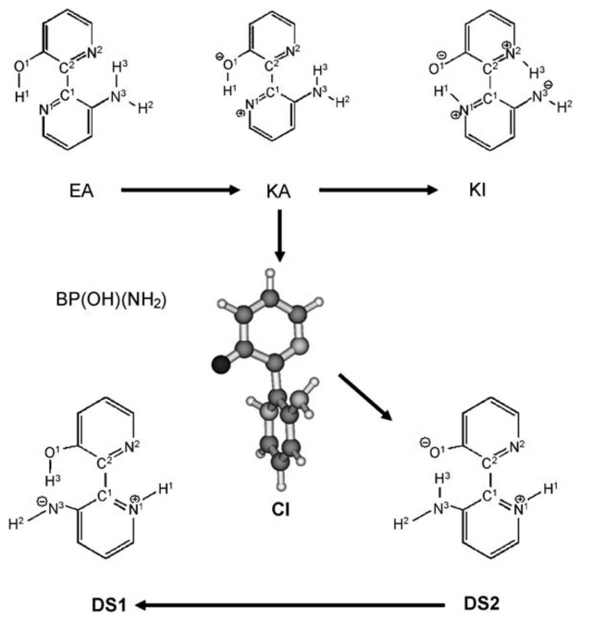

Figure 9. Schematic structures and atom-numbering of the geometries of the stationary points and the conical intersection region of BP(OH)-(NH_2) in S_0 and S_1 found along the O channel. The meaning of the bold letters is as described in Figure 8.

In the N channel (Figure 6) the KI* product is the most stable although the EI* structure is almost degenerate in energy. From this last structure, as in the previous cases, a conical intersection region can be accessed upon internal rotation of the two pyridine rings. The CI is clearly the lowest-energy structure in S_1 and, again, passage through it may lead to the dark states. Similarly to what was found for BP$(OH)_2$, only the DS1 structure (the one that has already transferred the proton) is stable in S_0. From this photochromic species the reverse photochemical path can be started by irradiation with light of 454 nm, which puts the system in the $\pi\pi^*$ S_1 state with quite a high oscillator strength of 0.263. The initially accessed geometry (FC structure) has enough energy to allow proton transfer leading to the now stable DS2* tautomer, which, in turn, is able to access again the conical intersection region and so revert back to the bright zone of the S_0 potential energy surface.

The O-channel path presents some peculiarities that are worth highlighting. In this case the KA* tautomer, obtained through a single proton transfer, is the most stable structure in the bright zone of the S_1 potential energy surface. KA* is, in fact, the most stable minimum-energy planar structure of BP(OH)(NH_2) in S_1 in such a way that the O-channel path is energetically favored over the N-channel path as discussed earlier.[36] As is the norm in all the systems analyzed so far, a conical intersection region can be accessed from KA* leading to the dark region of the ground electronic state. Now the proton transfer does not spontaneously occur and DS2 is the only stable form and the final photochromic species. From this point we can start the back-proton transfer by irradiation with 475 nm light, which puts the system in the $\pi\pi^*$ S_1 state with a high oscillator strength (0.276).

Once in the excited state, ESIPT might take place as DS1* is a stable species, even lower in energy than the optimized DS2* form. In any case, tautomerization in S_1 does not lead to any new photochemical path. Alternatively, internal rotation of the two pyridine rings in DS2* leads, energetically downhill, to the CI region from which, as usual, the whole photochemical cycle can be closed through a full 180° rotation, which again leads to the initial EA structure.

As in the previous cases, the AIM analysis was performed on the initial EA structure and the stable photochromic species in the N (DS1) and O channels (DS2). The results are shown in Table 3. An analysis of the data presented in Table 3 does not reveal any striking difference. In all cases the two intramolecular hydrogen bonds are well constituted and thus intramolecular proton transfer is feasible and internal rotation of the two pyridine rings is energetically costly. These two characteristics are essential in a bistable system, a required condition for a molecular photomemory device. Here, the choice of physical property that could be used to differentiate (read) the two stable forms of $BP(OH)(NH_2)$ is not as clear because the original EA structure is no longer symmetric (i.e., it does not possess an inversion center) and so it has a permanent dipole moment of 3.001 D, smaller than the calculated value of the two dark states: 3.607 (N channel) and 5.411 D (O channel), but not negligible. Hence a more careful look at the molecular properties of EA and the dark states would be necessary to find a property to discriminate the two photochromic forms. For example, an infrared (vibrational) absorption band found at very different wavelengths in the two forms would be enough for this purpose.

Table 3. Geometrical distances, electronic densities, and Laplacians at the bond critical points of the X−H···Y bonds of $BP(OH)(NH_2)$.[a]

Structure	Bond	r [Å]	ρ [e Å^{-3}]	$\nabla^2\rho$ [e Å^{-5}]
EA	O1−H1	1.009	0.314	−1.69
	H1···N1	1.629	0.0651	0.128
	N3−H3	1.018	0.332	−1.78
	H3···N2	1.903	0.0357	0.0988
N-channel DS1	N3−H1	1.041	0.309	−1.62
	H1···O1	1.610	0.0592	0.164
	N2−H3	1.031	0.329	−1.78
	H3···N1	1.878	0.0389	0.114
O-channel DS2	N3−H3	1.057	0.294	−1.50
	H3···O1	1.543	0.0704	0.171
	N1−H1	1.033	0.325	−1.76
	H1···N2	1.864	0.0403	0.114

[a] See Figures 7 and 9 for the atomic labeling.

Overall, the photochemistry of $BP(OH)(NH_2)$ is more complex than those of the preceding systems because in this case the asymmetry of the molecule increases the number of reaction paths but no great differences arise in the overall plot. In the absence of dynamic simulations and, in this case, any experimental data, it is hard to say whether the photochemistry of this molecule will differ from that of the two preceding isoelectronic systems. At first sight, the fluorescence quantum yield of $BP(OH)(NH_2)$ should not be high as the most stable EI* and KA* species, which result from single proton transfer, have no corresponding minimum-energy structure in S_0 and KI, the product of the full double proton transfer, is barely stable. Low fluorescence is an indication that the system may be accessing the conical intersection region, which opens the door to the formation of the photochromic species. Attainment of these, up to now, unknown isomeric species may depend on a subtle balance between the geometries and energies of the numerous stationary points and conical intersection regions located in both the ground and first singlet-excited electronic states such that it cannot be easily anticipated whether a given molecular system will be better suited to becoming an ideal photomemory device.

Conclusion

In the previous section the potential energy surfaces of the ground (S_0) and first singlet-excited (S_1) electronic states of three bipyridyl isoelectronic species have carefully been analyzed. In all the systems the energies of the tautomers corresponding to a single and double proton transfer and the transition states linking them have been calculated. Also, the presence of conical intersections between the S_0 and S_1 states reached upon internal rotation of the two pyridyl rings has been confirmed in the region of the single proton transfer and, most interesting, the existence of a whole family of "dark" states has been disclosed. These dark states can only be accessed upon irradiation with light of a given wavelength and they are predicted to be stable under normal conditions such that they may act as photochromic species. Radiation with light of a quite different wavelength would easily revert the process, transforming the photochromic species into the "original", which would be able to start the process again. As a whole, the photochemical properties of the three bipyridyl compounds meet the criteria of an ideal photomemory device as detailed in the Introduction. Comparison of the photocycle of an "ideal" photomemory device (Figure 1b) and the actual behavior of the three studied compounds (Figures 2, 4, 6, and 8) provides further proof of this.

In the light of the results presented in this paper, the most likely species to become a photomemory device is the $BP(NH_2)_2$ system as in this case, following the initial excitation, the path to the conical intersection seems the most likely one given that fluorescence is known to proceed with quite a low quantum yield ($\approx 10^{-5}$), and this can be envisaged from our theoretical results, as explained in the Results and Discussion. For $BP(OH)_2$, the most thoroughly studied system from an experimental point of view, the quantum yield of fluorescence is much higher (0.32) such that the internal conversion path through the conical intersection is a less likely process, again in accord with our theoretical calculations. However, the other conditions required for a photomemory device are fully accomplished by the two systems:

The photochromic species is sufficiently stable, there is a physical property (dipole moment) that enables the two forms to be easily discriminated, and light of a different wavelength can reverse the whole process. As for the "hybrid" BP(OH)(NH_2), no previous experimental work has been carried out on it and we only know from previous literature that it has been synthesized.[43] Its photochemistry is expected to be more complex as the asymmetry of the molecule allows for two proton transfer channels depending on whether the first transferred proton departs from a hydroxy or an amino group. A full comparison of our results has allowed us to predict a quantum yield for BP(OH)(NH_2) intermediate between those of $BP(OH)_2$ and $BP(NH_2)_2$. However, there is no way of further assessing the possibility of reaching the different photochromic species without performing an ambitious (and expensive) dynamics study that considers all the subtleties of the potential energy surfaces of S_0 and S_1 and their crossing regions. Work devoted to achieving this goal is in progress in our laboratory.

The very rich photochemistry of the bipyridyl compounds allows for a discussion of additional applications in the technological field. Even if, from now on, the discussion follows a more speculative track, it is worth mentioning the possibility of using the bipyridyl systems as molecular motors and/or rotors.[44,45] Given that the initial and photochromic forms in S_0 are interchanged through internal rotation, continuous irradiation using the two wavelengths that activate the interconversion would result in a continuous internal rotation of the molecule. That is, we have a molecule that is able to absorb radiation and transform the energy into mechanical (rotational) energy. To really have a molecular motor it would be necessary to additionally restrict the internal rotation so that it always proceeds in the same direction.[46] This could be accomplished, for instance, by the addition of a bulky, enantiomeric substituent on to the bipyridyl compound.

Another, up to now, unexplored field is the possibility of controlling the internal rotation of the bipyridyl systems through the surrounding media. As the initial species and its photochromic partner can only be interconnected through internal rotation, the full cycle is to be controlled by the rigidity of the external medium in which the full reaction takes place. That is, the ability to internally rotate the two (bulky) pyridyl rings may be severely restricted depending on the viscosity of the medium especially when sizeable substituents are introduced into the rings. It could be expected that the more hindered the internal rotation, the lower the difference between the $BP(OH)_2$ and $BP(NH_2)_2$ quantum yields. By changing the electronic properties of the substituents (apolar, polar, or even ionic) it could be possible to tune the system to be more sensitive to a specific property of the solvent. This would open the door to the use of these systems as molecular or nano viscometers, an idea that was foreseen several years ago.[47] The usefulness of bipyridyl derivatives as molecular rotors and/or viscometers relies on the predominance of the photochromic species as the final product after irradiation of the original compound. For this reason, the limited experimental data known up to now and our electronic results point to the $BP(NH_2)_2$ system as the most suited species to act not only as an ideal photomemory device but also as a molecular rotor and/or viscometer. In any case, we hope that the results and discussion presented in this paper may attract the scientific curiosity of the chemistry world so that the bipyridyl systems, mainly the diamino and hybrid systems, barely studied up to now, could be the subject of more ambitious work at the molecular level and confirm (or rule out) our tentatively proposed new applications.

Computational Details

Electronic density functional based methods were used to explore the topology of the ground (S_0) and first $\pi\pi^*$ singlet-excited (S_1) electronic states. Density functional theory (DFT) and time-dependent DFT (TDDFT)[48,49] optimizations were performed for the S_0 and S_1 states, respectively. TDDFT has successfully been used to study other related ESIPT systems.[49–51] The three-parameter hybrid functional of Becke with the correlation functional of Lee, Yang, and Parr (B3LYP)[52,53] was chosen. The Turbomole program (version 6.0),[54,55] which implements analytical gradients at the TDDFT level, was used to perform the TDDFT calculations.

Also an atoms-in-molecules (AIM) analysis was performed at the DFT level with the Gaussian 03 package.[56] As we stated in a previous paper,[57] the B3LYP functionals used in the Gaussian 03 and Turbomole packages differ very little in the relative stability of the calculated points, which implies a very small effect on our results. This small difference is a result of the use of a different form of the local correlation functional: The Gaussian 03 package uses the VWN(III) local correlation functional, whereas Turbomole uses VWN(V).[58]

Multireference complete active space self-consistent field (CASSCF)[59] calculations were performed with the MOLCAS program (Version 6.4).[60] The electronic energies of the S_0 and S_1 states were obtained by using a state-average with equal weights for both states and with an active space of 10 electrons and 10 molecular orbitals, which includes the five highest occupied and the five lowest unoccupied molecular orbitals. Note that this active space is probably not large enough to correctly describe the whole potential energy surface, but it has been used just to analyze the presence of conical intersections between the S_0 and S_1 states. A larger active space would be necessary to compare the different regions of the potential energy surface.

In all cases, to obtain a good description of the proton and charge transfer processes on the excited states, the 6-31G(d,p)[61,62] basis set was used for the hydrogen and carbon atoms whereas additional diffuse functions (6-31G+(d,p) basis set)[61,62] were added to the oxygen and nitrogen atoms.

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