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Excited-state intramolecular proton transfer (ESIPT) in 2-(2′-hydroxyphenyl)pyridine and some carbon-bridged derivatives

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Abstract

The absorption and emission properties of 2-(2′-hydroxyphenyl)pyridine (HPP), 10-hydroxy-5,6-dihydrobenzo[h]quinoline (HdihBQ) and 10-hydroxybenzo[h]quinoline (HBQ), are reported in non-polar, alcoholic and aqueous environments. Ground and excited state pK values are presented, and compared with those of related derivatives. The important role of intramolecular rotational mechanisms and structural flexibility in the behaviour of these systems is suggested by (1) the temperature dependence of the fluorescence and (2) the increase in the quantum yields of the tautomeric emission across the series HPP - HdihBQ - HBQ. The existence of conformers of HPP is proposed and their energy as a function of the torsional angle is estimated by quantum chemical calulations. It is concluded that two non-radiative channels operate in HPP tautomer, one connected to twisting and the other related to nπ^* deactivation. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Molecular systems possessing an intramolecular hydrogen bond have received considerable interest since the opening of this field of research by Weller [1,2]. In accordance with Förster's theory [3], excitation of such compounds can trigger the transfer of an acidic proton (from a hydroxyl or amino group) to an accepting function (nitrogen or carbonyl group). This process, excited state intramolecular proton transfer (ESIPT) occurs on a sub-picosecond time scale and yields an excited phototautomer of lower energy than the Franck-Condon precursor. In the ground state, the proton transferred species has higher energy than the normal form and reverse proton transfer takes place, regenerating the initial molecule. This mechanism, which occurs in a large number of systems, has recently reviewed [4–6] and has led to a wide range of applications such as photostabilisers [7,8], laser dyes [9], scintillators [10], solar collectors [11] and fluorescence probes [12].

In the present paper, we report on ESIPT in nitrogen heterocycles of the pyridine class, with a hydroxyl group as the proton donor (see Scheme 1). One of the simplest structures is represented by 2-(2′-hydroxyphenyl) pyridine (HPP), in which free rotation around the C_1-C_1' linkage is possible. In contrast, such twisting processes are inhibited in the bridged derivatives 10-hydroxy-5,6-dihydrobenzo[h]-quinoline (HdihBQ) and 10-hydroxybenzo[h]quinoline (HBQ), although a certain degree of flexibility may still be allowed in the former of these two. In terms of rigidity, HdihBQ can be regarded as an intermediate between HPP and fully aromatic, rigid HBQ molecule.
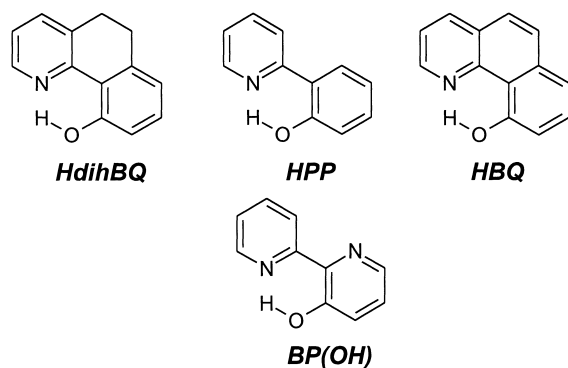
HPP has been studied by Kaczmarek et al. [13] who compared its spectroscopic properties with those of 2-(2′-hydroxyphenyl)-3-hydroxypyridine (HHPP), 2,2′-bipyridyl-3-ol (BP(OH)) and 2,2′-bipyridyl-3,3′-diol (BP(OH)$_2$). These workers found extremely weak fluorescence from the proton transferred tautomer of HPP in the region of

HdihBQ   **HPP**   **HBQ**

BP(OH)

Scheme 1.

540 nm in 3-methylpentane at 77 K. They proposed that strong coupling of the electronic energy with torsional motion and the proximity of $n\pi^*$ and $\pi\pi^*$ states contribute to the efficient radiationless decay in this group of compounds. Polyphenyl derivatives of HPP have been studied by Knyazhanskii et al. [14] who observed proton transfer fluorescence in iso-pentane (533 nm), and normal fluorescence and phosphorescence in ethanol (77 K). These authors propose that twisting of the benzene and heteroaromatic rings of the polyphenyl pyridines increase radiationless deactivation. ESIPT in HBQ was first reported by the group of Chou [15,16], and has also been studied by Sytnik and Del Valle [12]. The weak, red-shifted fluorescence observed in non-polar ($\lambda_{max}=623$ nm, $\Phi_f=5\times10^{-3}$), polar, alcoholic and aqueous solutions [17] was attributed to the proton transferred tautomer. To our knowledge, no spectroscopic work has been reported on HdihBQ to this date.

In this paper we report on our studies of the absorption and emission properties of HPP, HdihBQ and HBQ in non-polar, polar, alcoholic and aqueous environments. The photophysical properties of these molecules are discussed on the basis of intramolecular rotational mechanisms and structural flexibility. The results of quantum chemical calculations are compared with the experimental data.

2. Material and methods

2.1. Materials

2-(2′-Methoxypheny)pyridine (MPP), the methoxy derivative of 2-(2′-hydroxyphenyl)pyridine (HPP), was prepared by coupling 2-pyridyl copper with anisole according to the procedure of Malmberg and Nilson [18]. HBQ was purchased from TCI and used without further purification. A sample of HPP was obtained from the group of Prof. A. Grabowska [13]. A sample of HdihBQ was provided by Prof. W.Z. Antkowiak, Adam Mickiewicz University, Poznan, Poland. MdihBQ, the methoxy derivative, was prepared according to the procedure of Kubicki et al. [19].

2.2. Solvents

All solvents used were spectroscopic grade (Merck or Aldrich) and were used as supplied. Water was distilled and purified by ion exchange. All solvents were checked for residual fluorescence before use.

2.3. Instruments

Absorption spectra were recorded on a Hewlett-Packard HP8452A diode array spectrophotometer using 1 cm pathlength quartz cells. Corrected fluorescence spectra were recorded on a SPEX Fluoromax or an SLM Aminco AB2 spectrofluorimeter and fluorescence quantum yields were determined relative to quinine sulfate in 0.1 M perchloric acid ($\Phi_f=0.55$) [20]. Room temperature fluorescence lifetime measurements were undertaken at the Daresbury Synchrotron Radiation Source (in single bunch mode) as described eleswhere [21] and on a laser system at Imperial College, London. In the latter case, the excitation light (300 nm, 50 ps pulse length) was obtained by frequency doubling the 600 nm output of a dye laser (rhodamine 6G). Variable temperature fluorescence decay measurements were carried out using synchrotron radiation from BESSY (in single bunch mode) as the source of excitation. The equipment has been described previously [22]. In all cases, the time-correlated, single photon counting method [23] was used to accumulate fluorescence lifetime data. An iterative reconvolution program was used to analyse the decays and the χ^2 value together with the distribution of the residuals were examined to estimate the quality of the fit. Lifetimes down to approximately 0.1 numbers could be obtained using the BESSY and Daresbury synchrotrons and the laser system allowed us to analyse the decays down to approximately 10 ps. [1]H number spectra recorded in deuterated chloroform on a Brucker W250 instrument.

3. Results and discussion

3.1. Absorption Spectra

The UV absorption spectra of HPP, HdihBQ and HBQ are shown in Fig. 1 and the absorption maxima and extinction coefficients are given in Table 1. The extinction coefficients

Table 1
Absorption parameters for HPP, HdihBQ and HBQ. Extinction coefficient ε in $dm^3mol^{-1}cm^{-1}$

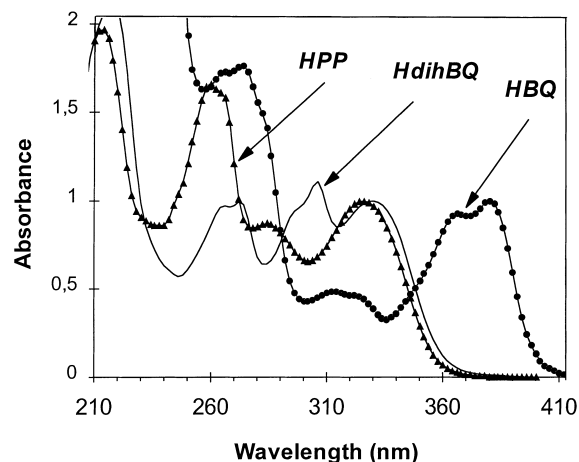|	Long wavelength band (nm) in MCH	Long wavelength band (nm) in ethanol	Extinction coefficient in ethanol
HPP	326	318	6600
HdihBQ	330	320	6600
HBQ	380	370	6000

Fig. 1. Absorption spectra of HPP, HdihBQ and HBQ in methylcyclohexane (MCH).

recorded for the various absorption bands are such that is is clear that all the absorption features given here relate to $\pi\pi^*$ transitions - we have not found any evidence for distinct $n\pi^*$ transitions and assume that these are hidden underneath the $\pi\pi^*$ transitions. The long wavelength $\pi\pi^*$ bands of HPP and HdihBQ are very similar in terms of shape, intensity and position suggesting that introducing a saturated bridge does not cause any significant increase in conjugation. This implies a planar conformation in HPP as expected from the presence of an intramolecular hydrogen bond. HBQ is not iso-π electronic with HPP and HdihBQ and possesses different absorption properties in that its absorption maxima are displaced to the red of the other two compounds. The extinction coefficients for the three compounds are all of the

order of 6000 dm^3 mol^{-1} (see Table 1) which indicates that the overall transition probability is not greatly altered upon bridging the HPP molecule to yield HdihBQ or extending the conjugation in HBQ. The absorption maximum was found to blue shift with increasing solvent polarity.

3.2. pK Data

Ground and excited state pK values were determined spectroscopically [24] for protonation (pK_1) and deprotonation (pK_2) of each compound. The results of these measurements are presented in Table 2 along with literature data on related unsubstituted and methoxy substituted compounds.

The pK values for protonation of pyridine and 2-aryl substituted pyridines (2-phenylpyridine, 3-phenylpyridine, 4-phenylpyridine and 2-(2′-methoxyphenyl)-pyridine (MPP)) all lie within 1 pK unit. This suggests a weak interaction between the 2-phenyl substituent and the pyridine ring, which is consistent with the conclusions of Katritzky and Simmons [27] and with the presence of a significant angle of twist between the phenyl and the pyridine rings in these compounds [25]. In contrast, the planar benzo[h]quinoline possesses a lower pK_1 value. The higher pK_1 value of 10-methoxybenzo[h]quinoline (MBQ) compared to MPP can also be rationalised in the same terms. The +M electron donating effect of the methoxy substituent is hardly felt in MPP since the two rings are at an angle to one another.

All these pyridines and quinolines are much stronger bases in the excited state as shown by the pK_1^* values in Table 2. This is in accord with the general observation of increased acidity/basicity of acidic and basic functions of

Table 2
Ground and excited state pK values for HPP, HdihBQ and related compounds

Compound	Protonation		Deprotonation	
	pK_1	pK_1^*	pK_2	pK_2^*
Pyridine [24]	5.19			
3-phenylpyridine [25]	4.8			
4-phenylpyridine [26]	5.3			
benzo[h]quinoline [17]	4.2	4.2[a]		
		13.2[b]		
2-phenylpyridine [25]	4.5	9.0±0.5		
9-azafluorene [26]	3.55	–		
10-methoxybenzo[h]quinoline (MBQ) [17]	7.5	13.8		
2-(2′-methoxyphenyl)pyridine (MPP)	4.6	14.4[b]		
10-methoxy-5,6-dihydrobenzo-[h]quinoline (MdihBQ)	≥7.5-			
10-hydroxybenzo[h]quinoline (HBQ)	3.7	7.0[b]	14.2 [17]	–
	3.8 [17]			
2-(2′-hydroxyphenyl)pyridine (HPP)	4.1	7.8[b]	10.2	7.1[b]
10-hydroxy-5,6-dihydrobenzo-[h]quinoline (HdihBQ)	4.4	8.3[b]	>12-13	–

Excited state pK values from[a] fluorescence titration,[b] Förster cycle.

molecules upon excitation. Increases in pK_1 of ≥ 4 pK units are routinely observed. It is noticeable that the excited state pK_1's of MPP and MBQ are of the same order (unlike the ground state situation) and this can be explained if MPP becomes more planar in the excited state such that the electron donating effect of the methoxy substituent can have its full effects. Similar behaviour has been postulated for some biphenyls [28]. The pK value for 10-methoxy-5,6-dihydrobenzo[h]quinoline (MdihBQ) has not been determined but this compound is protonated in pure ethanol [29], suggesting a pK_1 value at least as high as for MBQ.

On the basis of the above discussion, similar pK_1 values could be expected for HPP, HdihBQ and HBQ, which are all effectively planar molecules in their ground states. Any differences between their pK_1 values are proposed to be due to electronic effects introduced by the bridge between the two rings in HdihBQ and HBQ. In HdihBQ, the saturated bridge can be regarded as an alkyl substituent which acts as an electron donor via the inductive effect [30] and increases the electron density at the nitrogen, hence the higher pK compared to HPP. In HBQ, the extended conjugation introduced by the unsaturated bridge may introduce the further effect of lowering the electron density on the nitrogen by increasing the delocalisation of the π electrons, as reflected in the ground state pK_1 value.

The pK_2 of HPP, corresponding to deprotonation, was found to be much lower than that of HdihBQ and HBQ. In HPP, the molecule may help to stabilise the anion resulting from the deprotonaiton by twisting about the C_1-$C_1{}'$ bond thus allowing the negative charge on the oxygen to move away from the nitrogen lone pair. This electrostatic repulsion between the phenolate anion and the nitrogen lone pair is also present in HBQ and HdihBQ but the molecules are not able to undergo any substantial twisting as their structural movement is more restricted. In these two bridged molecules, formation of the anion is not as favourable as in HPP, hence their higher pK_2 values. These arguments neglect any influence that the strength of the intramolecular hydrogen bond could have on the pK values but number results suggest that the hydrogen bond is of similar strength in each of the three compounds (chemical shifts of the hydroxylic proton: δHPP 14:4 ppm, HdihBQ 14.0 ppm, HBQ 15.0 ppm [29]).

In the excited state, the heterocyclic nitrogen atoms in HPP, HdihBQ and HBQ all become more basic, as observed earlier for the unsubstituted or methoxy-substituted pyridines and quinolines. The pK_1^* values for HPP, HdihBQ and HBQ all lie in the region of 7–8 compared to values of 13–14 for benzo[h]quinoline, MBQ and MPP. One reason for this difference could be the choice of the different absorption energies used to calculate the excited state pK^* according to the Förster cycle. In HdihBQ the long wavelength band is shifted to the red by about 20–30 nm compared to MdihBQ. Such a shift is often attributed to the planar conformation imposed by the hydrogen bond. However, both HdihBQ and MdihBQ are planar and a 20 nm red shift is nevertheless still

observed. This spectral shift is likely to be related to the presence of a hydrogen bond which alters the electron distribution in the molecule. Semiempirical PM3 calculations show that a slightly more negative charge on the oxygen and a more positive charge on the nitrogen is observed when an intramolecular hydrogen bond is present [29]. The only pK_2^* value that we have been able to determine is for HPP where the expected decrease compared to the ground state is observed and it is gratifying to note that $pK_2^* < pK_1^*$ for this system, such that ESIPT is favoured. It should be noted that this pK_2^* value is higher than that found for some hydroxybiphenyls [28], which are of the order of 1–2.

3.3. Fluorescence measurements

The emission observed from HPP, HdihBQ and HBQ is weak under all the conditions (solvent and temperature) under which we have studied these system. Extremely weak, Stock shifted fluorescence was observed for HPP at 77 K in non-polar solvents (see Fig. 2) but we have not been able to detect fluorescence form this molecule at room temperature in non-polar solvents. In polar solvents, emission from the enol form of HPP is observed at room temperature but no emission from the proton transferred tautomer is observed. HdihBQ exhibits a very weak, red-shifted emission at room temperature in polar and non-polar solvents. Normal fluorescence from the enol species is weak or non-existent for HBQ and HdihBQ even in polar and protic solvents. The weak proton transfer fluorescence of HBQ has been previously reported and our results are in good agreement with the literature [12,15,16]. Fluorescence spectra of HPP, HdihBQ and HBQ are shown in Fig. 2 and the lifetime, quantum yields and emission maxima are presented in Table 3.

The introduction of a bridge in the HPP molecule appears to be an important factor in terms of fluorescence intensity
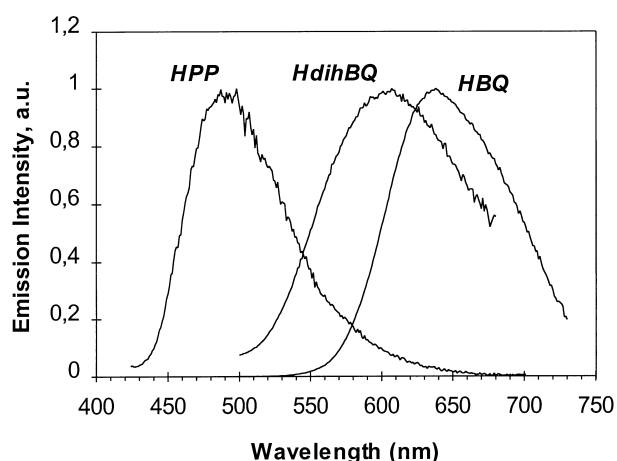

Fig. 2. Fluorescence spectra of HPP at 77 K, in methylcyclohexane: isopentane (3:1) and HdihBQ and HBQ methylcyclohexane at 298 K.

Table 3
Photophysical properties of HPP, HdihBQ and HBQ in non-polar solvents

	λ_{max}(nm)	Φ_f	τ(ns)	Stokes shift (cm^{-1})
HPP (77 K)	500	−[a]	1.9; 5.2	10 050
	540 [13]			12 150
HdihBQ (298 K)	605	<0.001	ca.0.01[b]	13 800
HBQ (298 K)	630	0.0057	0.35	10 400

[a]Fluorescence too weak for the quantum yield to be determined.
[b]Near the time resolution of the laser system.

which is observed from the tautomer. The effect of the bridge is presumably to prevent intramolecular twisting around the bond joining the phenolic and pyridine rings. In other weakly emitting compounds undergoing ESIPT (e.g. 2-(2′-hydroxyphenyl)benzothiazole (HPBT) [31], BP(OH) [11] and derivatives of HPP [14], a non-radiative deactivation channel was attributed to such a torsional mechanism. HdihBQ still possesses a certain degree of flexibility owing to the saturated bridge (as opposed to the unsaturated bridge in HBQ) and this may account for the weaker emission from this compound compared to HBQ. However, even the rigid HBQ molecule is only weakly fluorescent. Although HPP and HdihBQ have a similar long wavelength absorption band, they exhibit very different Stokes shifts. The Stokes shift is related to the shape of

the ESIPT potential, which is determined in particular by the translocation distance of the proton and by the distance between the oxygen and nitrogen atoms in conjunction with the associated vibrations [32,33]. These will be different for HPP and HdihBQ.

The emission of all the three systems was found to be temperature dependent but only HBQ and HdihBQ were studied in depth since they were emissive over the whole temperature range from ambient to 77 K whereas HPP was only fluorescent at 77 K. For HBQ, the fluorescence intensity and the lifetime increase by a factor of approximatively 4–5 from 298 K to 77 K (see Fig. 3), and a blue shift of 10–20 nm is observed upon solidification of the solvent. The emission of HdihBQ is 2–3 times more intense at 100 K than at ambient temperature but the weakness of the emission and the short decay times precluded lifetime measurements even at low temperature.

This temperature dependence is quite surprising given that both molecules are quite restricted (HBQ particularly so) in terms of the torsional movement they can undergo which might promote non-radiative deactivation. The changes are much smaller than those seen for HPBT [31] but the parallel increase in the two parameters, lifetime and quantum yield, in the case of HBQ indicates that the cause of these changes is a decrease in the efficiency of non-radiative decay. It would therefore appear that there may be two temperature dependent non-radiative decay paths in HPP
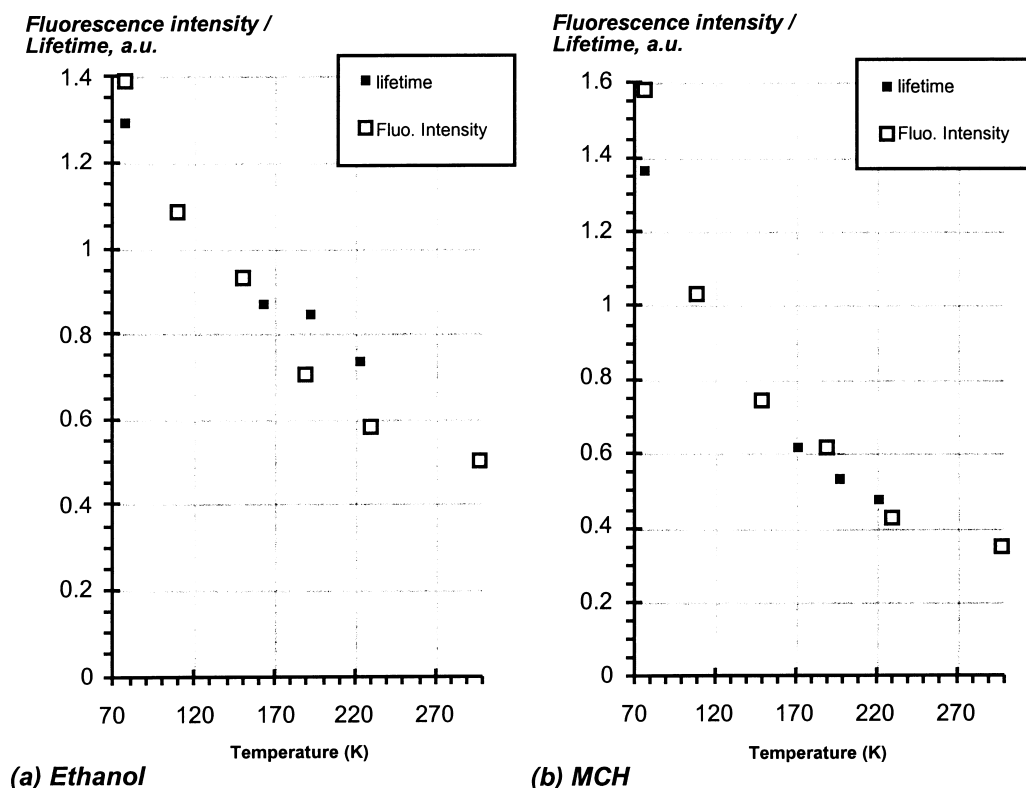

(a) Ethanol

(b) MCH

Fig. 3. Fluorescence lifetime and intensity for HBQ as a function of the temperature in (a) MCH and (b) ethanol, the fluorescence intensity is normalised to the value of the lifetime at 298 K.
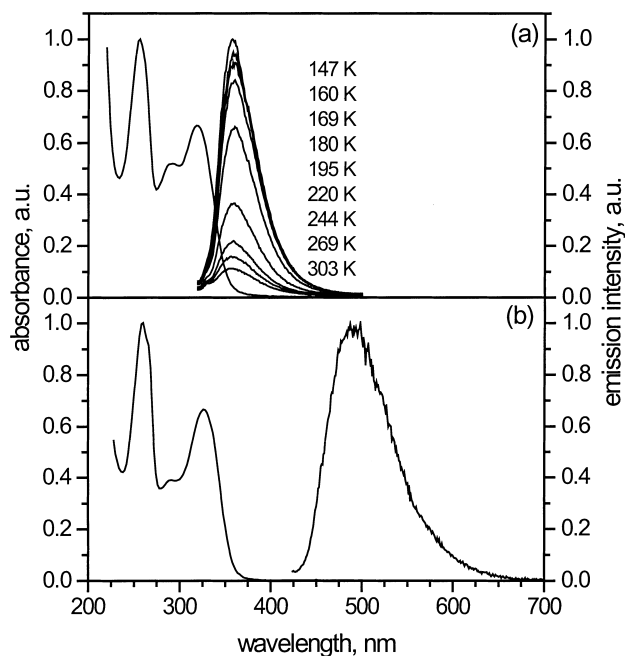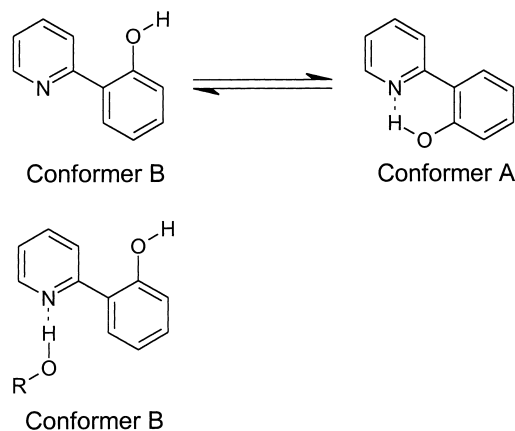
Fig. 4. Low-temperature fluorescence and excitation spectra of HPP in (a) ethanol (temperatures indicated) and (b) methylcyclohexane: iso-pentane (3:1) at 77 K.

Conformer B

Conformer A

Conformer B

Scheme 2.

B where the pyridine moiety has rotated through 180° (Scheme 2).

In aprotic solvents, conformer B will be less favoured than conformer A due to the absence of the intramolecular hydrogen bond. In BP (OH) conformer B will be even less favoured in aprotic solvents due to the proximity of the two nitrogen lone pairs. In HPP, this destabilisation is less and could lead to a small fraction of B population even in aprotic solvents. In ethanol, the OH group can be engaged in hydrogen-bonding with the solvent molecules, as well as the aza nitrogen. This disrupts the intra-molecular hydrogen bond. If both functions are hydrogen-bonded to a solvent molecule, this would introduce a steric interaction which would cause the two rings to twist with respect to one another. This could lead to a relative stabilisation of conformer B such that it becomes the only ground state species in the case of HPP in ethanol. This relative stabilisation is, however, not sufficient to lower the B conformer energetically below the A conformer in the case of BP (OH), due to the repulsion of the two aza nitrogens.

3.4. Quantum chemical calculations

In order to gain some insight into the relative stability of A and B conformers of HPP in the ground state, we carried out quantum chemical calculations using both the AM1 and PM3 parametrisation as contained in the AMPAC program package [34] and full geometry optimisation using the Newton algorithm with vibrational analysis. The energy difference between ground and excited states was calculated within CNDO/S [35] by using a large configuration inter-action (50 configurations).

The resulting ground state twist potentials with full geometrical optimisation of all other coordinates are shown in Fig. 5. Conformer A (cis-form) is not the global minimum in the AM1 framwork, but the most stable conformation is somewhat twisted (with a torsion angle of 45° between the two rings). In view of the above-mentioned experimental

and HdihBQ whilst HBQ is a rigid structure which cannot undergo intramolecular twisting analogous to HPBT. Kacz-marek et al. suggest that HPP may undergo non-radiative deactivation via an $n\pi^*$ excited state [13]. If such a process is endergonic then it could comprise the second temperature-dependent non-radiative decay channel together with the intramolecular twisting motion previously proposed for HPBT and other compounds [4–6].

It is very interesting to compare the fluorescence beha-viour of HPP in aprotic and protic solvents (Fig. 4). In the non-polar aprotic solvent methylcyclohexane: iso-pentane, the fluorescence is so weak at room temperature that is could not be observed. At 77 K, however, the red-shifted spectrum of the ESIPT state is observed. In ethanol, on the other hand, only short wavelength Franck-Condon fluorescence is obser-vable, at all temperatures investigated, and the typical increase of fluorescence intensity with decreasing tempera-ture is again observed.

The behaviour of HPP, namely enol fluorescence in protic and ESIPT fluorescence in aprotic solvents, is unusual and is in contrast to the behaviour of the closely related structure BP(OH) which shows ESIPT fluorescence in both protic and aprotic solvents [8,9].This observation may simply be explained by the fact that non-radiative decay is extremely efficient in the HPP tautomer under all conditions such that fluorescence is never able to compete. Alternatively, this effect may be due to protic solvation of the HPP nitrogen atom and OH group in ethanol which can disrupt the intramolecular H-bond present in the ground state in conformer A (cis-form) and allow population of conformer
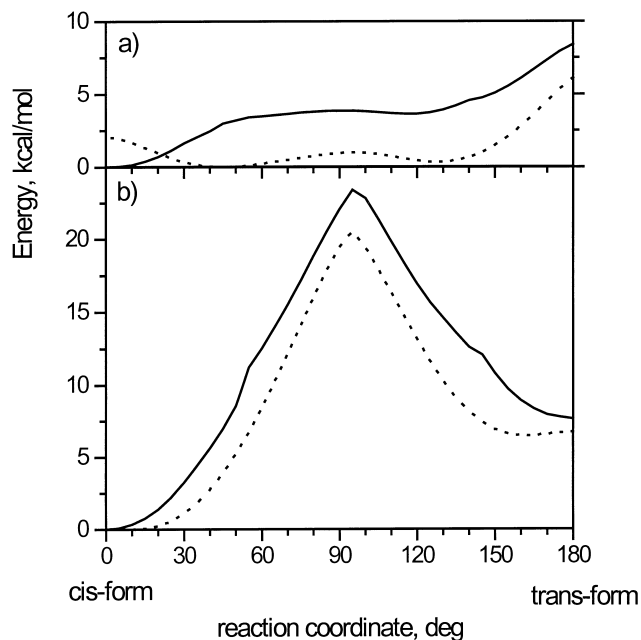
Fig. 5. HPP ground state twist potentials calculated in steps of 5° using AM1 (dashed line) and PM3 (solid line) with full optimisation at each point. (a) refers to the twisting of the enol OH form, (b) to the twisting of the keto NH form.

Fig. 6. Ground state twist potentials (full optimisation) for the tautomeric keto NH-species of HPP, calculated within the PM3 framwork. The excited state spectrum (by CNDO/S) for these ground state geometries is also shown for every point, with the S_1 state (filled circles) being of charge transfer character, and S_2 (triangles) of $n\pi^*$ character.

indications for a planar structure for HPP in the ground state we consider these results unreliable. It is possibly caused by the difficulties that the AM1 parameter set has with the description of hydrogen bonds [36]. Conformer B (trans-structure) is also found to be non-planar. The PM3 parametrisation, on the other hand, does not show the artifact of the non-planar cis-form. From the PM3 calculations, we conclude that the energy difference between the A and B conformers amounts to 15.2 kJ mol^{-1}. A similar calculation for BP(OH) yields a much larger energy difference between these two conformers (36.5 kJ mol^{-1}) in line with the above discussion.

We also carried out some excited-state calculations regarding the twist coordinate in the tautomeric NH-species, Fig. 6. In the ground state, the A conformer (cis-form) is the most stable, similar to the result observed for the enol structure in Fig. 5(a), but the barrier for interconversion to the B conformer is much higher. In the lowest excited singlet state, twisting turns out to be near-barrierless, within the theoretical approach used, i.e. by taking the PM3-optimised ground state energies for every point and adding the energy gaps calculated with CNDO/S-CI. In the planar conformations (cis and trans-forms), an $n\pi^*$ state is very close-lying in energy. These two features, a close-lying $n\pi^*$ state and barrierless twisting towards a 90° photochemical funnel can account for the experimental observations as discussed above: two distinct non-radiative channels in the ESIPT state, one connected (twisting coordinate in Fig. 6) and other one disconnected from twisting ($n\pi^*$ deactivation).
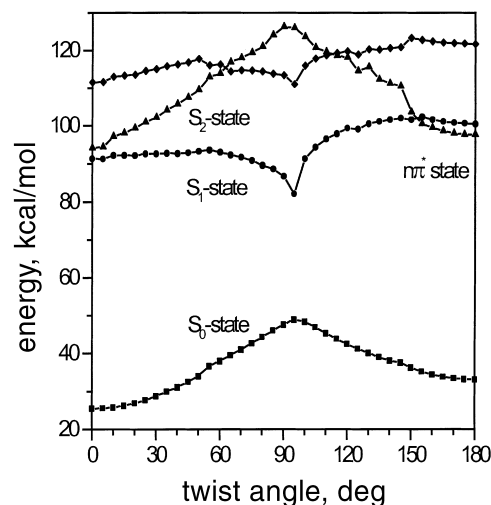
At 90° twist, S_1 and S_0 approach energetically reminiscent of the neighbourhood of a photochemical funnel [37,38] and suggesting the possibility for ultrafast non-radiative deactivation at this point. In fact, upon optimisation of this geometry in S_1, ground and excited states approach each other strongly. Fig. 7 shows the close lying S_1 and S_0 states for this twisted geometry of the BP(OH) tautomer as well as the fact that S_1 and T_1 approximately degenerate at 90°, hence the exchange integral is vanishing and the electronic nature is that of a biradical with an odd electron placed on each side of the twisted bond. Such a state was termed 'dot-dot' within the theory of biradicaloid states [37,39–41] and possesses weakly polar character. The corresponding ground state has the opposite electronic configuration [42], with a pair of electrons on one side ('hole-pair'-state) and a correspondingly larger dipole moment with reversed direction yielding a large change of dipole moment on excitaion.
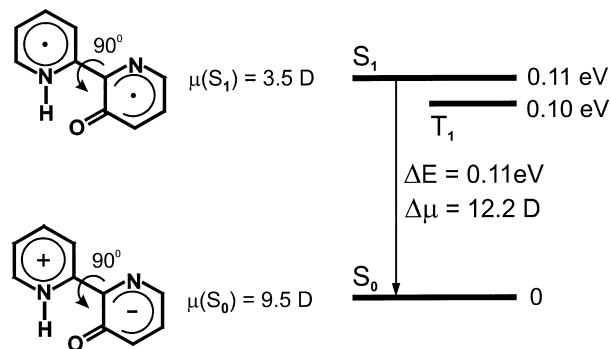

Fig. 7. Characterisation of ground and excited states of the NH-tautomer of BP(OH) at the biradicaloid geometry (90° twist) calculated with AM1 optimisation (C.I.=10) of S_1. Note the near degeneracy of S_1 and T_1 characteristic for the biradicaloid nature of the excited state.

These results are summarised in Fig. 7, where the calculated dipole moments, energy gaps and electronic structures for the tautomeric NH-species of BP(OH) are given at $90°$ twist.

4. Conclusion

The spectroscopic properties of a new proton transfer compound, HdihBQ, have been presented and its behaviour has been compared with the related HPP and HBQ molecules. HPP, HdihBQ and HBQ are all planar, and we propose that the differences in the pK values for protonation mainly reflect the nature of the $3,3'$-carbon bridge. The pK value for deprotonation of HPP is lower than that of HdihBQ and HBQ, possibly due to the possibility of stabilising the molecule by twisting, thereby moving the negative charge of the phenolate away from the pyridine lone pair. Excited state pK^* values are in agreement with the expected increase in acidity/basicity upon excitation, as proposed by the Förster cycle [3].

In non-polar solvents, HPP does not emit at ambient temperature but the tautomeric emission is restored upon bridging the molecules (as in HdihBQ and HBQ) or upon freezing the solvent. This suggests that deactivation in systems such as HPP is related to a twisting mechanism. Quantum chemical calculations support this conclusion and give evidence for a second non-radiative channel due to the proximity of nπ^* states. The proton transfer fluorescence from HBQ and HdihBQ is still rather weak for such molecules, where twisting is inhibited. For other proton transfer systems with nitrogen lone pairs, Stüber et al. [7] proposed that a small $S_1' - S_0'$ energy gap accelerates radiationless deactivation (energy gap law).

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