

Short Communication

Photochemical and photophysical behaviour of benzoylpyridines: remarks on the dual phosphorescence emission of benzoylpyridines at 77 K

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Study of the phosphorescence emission in neutral and acidic aqueous frozen solutions at 77 K of the three isomeric benzoylpyridines (2-BP, 3-BP and 4-BP), compared with benzophenone (B), gives further support to the theory that carbonyl compounds can exist in hydroxylic solvents both as free molecules and as hydrogen-bonded molecules [1 - 5]. This behaviour is of importance in determining the photophysical and photochemical properties of these molecules.

The phosphorescence spectra and lifetimes were measured by the techniques described previously [5], using samples of ketones purified by standard methods from the commercial products [6].

The two types of emission of BPs detected, in going from neutral to acidic solutions [6], correspond to the short-lived n, π^* α phosphorescence and to the longer-lived π, π^* β phosphorescence observed in acetic acid at 77 K for B and some substituted derivatives [5]. Phosphorescence studies in frozen water solutions of B led to the assignment of these emissions to solvent-free and hydrogen-bonded molecules respectively [4]. In contrast to observations in acetic acid, where the presence of α phosphorescence or β phosphorescence is mainly governed by the ketone concentration, the prevalence in water of one or the other type of emission, for both BPs and B, depends on the amount of the acid (or salt) added, α phosphorescence being the only emission that could be observed in the absence of additives. As in acetic acid, these emissions were characterized differently by the exciting and emitting wavelengths (shifted to the red for α phosphorescence) and lifetimes (shorter for α phosphorescence) and exhibited different vibronic structure (well structured for α phosphorescence and broader for β phosphorescence). Triplet energies for the two phosphorescence emissions of B and BPs in aqueous frozen solutions have been reported previously [6]. Singlet and triplet energies in various solvents were found to correlate with a set of σ parameters, proposed for the three positions of the heterocyclic nitrogen atom [7]. The triplet lifetimes determined in this work are presented in Table 1. A comparison amongst the triplet energies and the lifetimes of B

TABLE 1

Triplet lifetimes for α and β phosphorescences of B and BPs in aqueous frozen solutions at 77 K, and energy differences $\Delta\bar{\nu}_{\alpha-\beta}$ between α phosphorescence and β phosphorescence and σ parameters for the heterocyclic nitrogen atom

Compound	τ_{α} ($\times 10^{-3}$ s)	τ_{β} ($\times 10^{-3}$ s)	$\Delta\bar{\nu}_{\alpha-\beta}$ ($\times 10^3$ cm^{-1})	σ^a
B	3.9	85	1.8	0
2-BP	2.3	14	1.0	1.2
3-BP	3.6	33	1.4	0.3
4-BP	1.7	25	1.2	1.0

^aData taken from ref. 7.

and BPs shows that the heterocyclic nitrogen atom has the effect both of shortening the triplet lifetime and lowering the energy of the singlet and the triplet levels. The nitrogen-atom effect is stronger for acidic solutions than for neutral solutions for both the lifetimes and the energies. Figure 1 shows a reasonable fitting of the lifetimes to the proposed σ parameters, both for α phosphorescence ($\rho = -0.266$; $r = 0.885$) and β phosphorescence ($\rho = -0.535$; $r = 0.924$). A better correlation is shown, in the same figure, between τ_{β} and $\Delta\bar{\nu}_{\alpha-\beta}$ ($\rho = 0.999$; $r = 0.995$).

On the assumption that the solvent-solute interactions are not wholly different in fluid and in frozen solutions, we infer that the frozen solutions obtained by sudden cooling should provide information on the ratio of solvent-free and solvent-bonded molecules which exist at room temperature. Therefore we propose that, as for benzophenone [4], the solvent-free form is

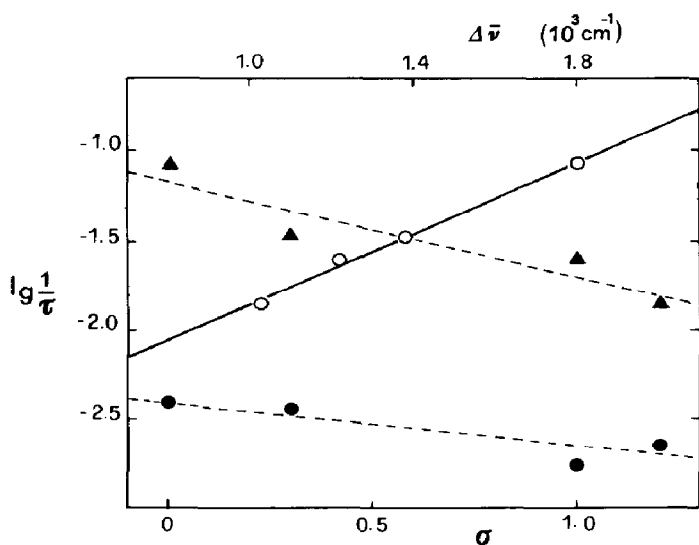


Fig. 1. Correlation diagram for the lifetimes of the phosphorescence emissions of B and BPs in frozen water solutions: ---, $\lg 1/\tau$ vs. σ parameters for α phosphorescence (\bullet) and β phosphorescence (\blacktriangle); —, $\lg 1/\tau$ of β phosphorescence vs. $\Delta\bar{\nu}_{\alpha-\beta}$ (\circ).

almost exclusively present in pure water whilst the solvent-bonded species is formed in the presence of additives. We believe that the single emission observed at room temperature [6] corresponds to the lower energy and shorter-lived emission observed at 77 K, although an anomalous red shift of the 0-0 transition (600 cm^{-1}) occurs on going from room temperature to liquid nitrogen temperature. However, an analogous effect was also observed in benzene and in acetic acid.

We believe that the energy differences between α phosphorescence and β phosphorescence observed in aqueous frozen solutions represent approximately the hydrogen-bond energies in the ground state. The positional effect of the heterocyclic nitrogen atom substantiates this hypothesis. It is seen in Table 1 that $\Delta\bar{\nu}_{\alpha-\beta}$ decreases with the increase in the electron-withdrawing ability of the nitrogen atom, which corresponds to a bond-energy change from 5 kcal mol^{-1} for B to 4 kcal mol^{-1} , 3.5 kcal mol^{-1} and 3 kcal mol^{-1} for 3-BP, 4-BP and 2-BP respectively. This decrease in hydrogen-bond energy is expected from the electron-withdrawing effect of the heterocyclic nitrogen atom. The decrease in charge density at the carbonyl group, produced by the heteroatom, is also the cause of the lifetimes of both α phosphorescence and β phosphorescence being shorter for BPs than for B. In fact, the n,π^* character of the α phosphorescence increases and the lifetime is shorter, whereas the π,π^* character of the β phosphorescence decreases and the lifetime is shorter. Generally, the electron-density shift produced upon excitation results in a change in the polar nature of the excited state, which implies different behaviour towards hydrogen bonding [8]. The dipole moment is expected to decrease upon n,π^* excitation and to increase upon π,π^* excitation. A decrease in dipole moment should cause a weakening of the hydrogen bond between the ketone and the hydroxylic solvent. In contrast, the increase in dipole moment upon π,π^* excitation should increase the hydrogen-bond strength. To gain more insight into the electron redistribution upon excitation for these molecules, a calculation of dipole moments in the lowest excited states has been carried out by the solvent-shift method, using the approximate equation

$$-\Delta\bar{\nu}_{1-2} = \frac{2\mu_g(\mu_e - \mu_g)}{hca^3} \Delta f_{1-2}(\epsilon, n) \quad (1)$$

proposed by Kawski and Gryczynski [9 - 11], where $\Delta\bar{\nu}_{1-2}$ is the shift of the emission or absorption bands between solvents of different dielectric constant ϵ and refractive index n , μ_g and μ_e are the dipole moments of the molecule in the ground state and in the excited state respectively, h is Planck's constant, c is the velocity of light, a is the Onsager cavity radius and $f(\epsilon, n)$ is a function of the dielectric constant and refractive index of the solvent given by the equation

$$f(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \quad (2)$$

Only room-temperature spectral shifts could be used because of the lack of refractive-index and dielectric-constant data for the frozen solvents. The dipole moments μ_S in the singlet and μ_T in the triplet n,π^* excited states are reported in Table 2 together with the ground state values μ_g taken from the literature [12]. They are all positive because the dipole does not switch direction in going from the ground to the excited state. The dipole moments were determined from the n,π^* absorption maxima and phosphorescence 0-0 transition shifts in methylcyclohexane ($f(\epsilon,n) = 0.00$), ethyl acetate ($f(\epsilon,n) = 0.49$) and acetonitrile ($f(\epsilon,n) = 0.86$), making use of the known values of μ_g [12]. Solvents were chosen which do not lead to specific interactions with the solute and allow room-temperature phosphorescence to be observed. The Onsager radius has been calculated from a structural model

TABLE 2

Dipole moments for B and BPs in the ground state (μ_g) and in the excited singlet (μ_S) and triplet (μ_T) states

<i>Compound</i>	μ_g^a (debyes)	μ_S (debyes)	μ_T (debyes)
B	2.98	1.80	2.6
2-BP	2.86	0.57	3.0
3-BP	2.94	1.29	2.9
4-BP	2.99	0.76	3.3

^aData taken from ref. 12.

for B ($a = 3.9 \text{ \AA}$) [13] and is assumed to have the same value for BPs. The agreement of the calculated values of μ for B with the values from the literature determined by Stark measurements on the crystal (1.79 debyes and 1.46 debyes for μ_S and μ_T respectively [14]) is surprisingly good, taking into account the uncertainty in the Onsager cavity radius and the approximate nature of the method used. For BPs, the values of μ_S decrease with the electron-withdrawing strength of the heterocyclic nitrogen atom, in contrast to the behaviour of the values of μ_g which are almost unaffected by the presence and position of the nitrogen atom. This trend shows a fairly good correlation with the values of σ ($\rho = -0.96$; $r = 0.986$). In determining the values of μ_T , the solvent shifts of the 0-0 phosphorescence bands were barely detectable because their magnitude was comparable with the uncertainty in the wavelength measurements ($\pm 1 \text{ nm}$). However, the slight increasing trend observed for BPs compared with B is real and might indicate a more heavy mixing of n,π^* with π,π^* configurations in the triplet manifold. From the absorption spectra [6], a decrease in energy difference between n,π^* and π,π^* levels in going from B to 3-, 4- and 2-BP has also been observed for the singlet state. Even though the exact energetic disposition of the $^3n,\pi^*$, and $^3\pi,\pi^*$ states remains unknown, they are expected to be even closer in the triplet manifold.

These findings are direct evidence that the change of electron distribution upon excitation is larger and more sensitive to the heteroatom in the singlet excited state than in the triplet and ground states. It should be noted, however, that a similarly low sensitivity of the triplet state to substituents, compared with the singlet state, has also been found for other derivatives of benzophenone [5].

The abnormally large blue shifts observed for n,π^* absorption in polar hydrogen-bonding solvents is probably the result of the cooperating effects of both electrostatic and hydrogen-bonding interactions. The individual contributions can be roughly discriminated by subtracting the electrostatic contribution (interpolated for water from the diagrams of $\Delta\bar{\nu}$ against $\Delta f(\epsilon, n)$) from the whole spectral shift [15]. Even though somewhat lower values for hydrogen-bond energies have been obtained (3.4 kcal mol⁻¹ for B and 3 kcal mol⁻¹, 2.6 kcal mol⁻¹ and 1.8 kcal mol⁻¹ for 2-BP, 3-BP and 4-BP respectively), the result is in qualitative agreement with that obtained from phosphorescence measurements; namely, a lowering of the hydrogen-bond strength occurs in the presence of the heterocyclic nitrogen atom.

Owing to the decrease in dipole moment upon singlet excitation, weakening or breaking of the hydrogen bond would occur in a polar protic solvent at room temperature, so that a large percentage of the molecules that cross to the triplet and phosphoresce are free. In contrast, however, hydrogen-bonded molecules, if present in the ground state at 77 K, are frozen up and phosphorescence emission originates from molecules in a polar hydrogen-bonding environment.

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