

Photochemical and Photophysical Behaviour of Benzoylpyridines. Part I. Triplet-Triplet Energy Transfer to Biacetyl

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Solvent and protonation effects on absorption and phosphorescence spectra of 2-, 3-, and 4-benzoylpyridines have been investigated. The lowest excited singlet and triplet states have been characterized as n,π^* in nature; the triplet state acquires considerable π,π^* character in acidic solution only. Triplet-triplet energy transfer from benzoylpyridines to biacetyl has been studied in benzene and aqueous neutral and acidic solutions. The results obtained are compared with those for benzophenone. Triplet yields and lifetimes of the three isomeric benzoylpyridines have been determined by their efficiency in sensitizing biacetyl phosphorescence in benzene solution and have been found to be somewhat lower than for benzophenone. The position of the heteroatom greatly affects the sensitizing power in aqueous solution, since the 2-isomer has been found not to sensitize at all. In acidic medium, there is a decrease in triplet lifetime of 3-benzoylpyridine, as found for benzophenone also, whilst the other isomers are inefficient sensitizers.

STUDY of the photosensitized phosphorescence of an acceptor allows information to be obtained on the properties of the lowest triplet state of the donor and of the processes by which this excited state is involved (interactions with the solvent and self-quenching processes).¹⁻³ In particular, it is important to emphasize that the excited state lifetime in solution at room temperature may be determined under the conditions under which photoreactions are carried out, whilst, instead, the most common method of obtaining τ values consists in measuring phosphorescence decay in rigid matrices at low temperature.

Using biacetyl as acceptor and an extensive series of benzophenone derivatives substituted in the 4- and 4,4'-positions as donors, this latter technique allowed us to study the effect of substituents on the lifetime and triplet yield of the aryl ketones in benzene.¹ The substituent group can influence the photoreactivity not only *via* the usual electrostatic effects but also by bringing about variation in the configuration of the excited states at lower energies¹ or by promoting new photochemical processes.²

A study of the photosensitization of biacetyl by benzophenone in aqueous media shows that a change in solvent, from benzene to water, increases the importance of self-quenching processes (which are negligible in benzene, at relatively low donor concentrations),⁴ whilst increase in acidity causes an increase in the rate of deactivation of the excited state, probably because of the formation of a complex with the hydroxonium ions.^{3,5}

The little information available on the spectroscopic and photochemical behaviour of the three isomeric benzoylpyridines (2-, 3-, and 4-BP) indicates, especially because of the similarity with the behaviour of benzophenone (Bp), that both the singlet and triplet lowest excited states are of n,π^* configuration.⁶⁻⁸

Measurements of absorption and emission spectra of the three isomeric BPs in various solvents have been performed with the aim of defining the energy and configuration of the excited states. We also wished to

observe the effects of introducing a heteroatom, of its position with respect to the carbonyl group, for comparison with Bp, and of protonation.

Experiments of sensitization of biacetyl phosphorescence have been carried out with the intention of obtaining further insight into the effect of structural changes on aromatic ketones and of investigating the possible influence of the n,π^* states of the nitrogen atom on the photo-chemical and -physical behaviour of these molecules.

Finally, it was of interest to see whether any generalization could be drawn concerning the photochemical reactivity of these molecules from information on their excited states.

EXPERIMENTAL

Benzophenone (Carlo Erba) and 4-benzoylpyridine (Aldrich) were recrystallized several times from water-ethanol; 2- and 3-benzoylpyridines (Aldrich) were recrystallized from light petroleum. Reagent grade solvents, n-hexane, benzene, and ethanol were purified by standard procedures. For measurements in aqueous solution, Britton buffers were employed down to pH 2 and HClO₄ solutions for lower pH values.

Absorption spectra were taken on a Unicam SP 500/2 single beam spectrophotometer. Phosphorescence spectra were recorded both at room and liquid nitrogen temperature on a Hitachi-Perkin-Elmer MPF-3 spectrofluorimeter, using an accessory for phosphorescence measurements for the experiments at low temperature.

The pK values were determined by u.v. absorption measurements in the wavelength region (310–330 nm) where the maximum spectral difference between the basic and acidic form is observed. The reported pK values are a mean of those obtained at five wavelengths at constant ionic strength (μ 0.1) in the pH interval 5–1. A Sargent PXB pH meter with a glass electrode was employed.

Sensitization measurements were performed in de-aerated solutions with light absorbed almost exclusively by the donor (Bp) and reading the intensities of the sensitized phosphorescence of biacetyl (Q) at the wavelength corresponding to the emission maximum of the quencher.

¹ G. Favaro, *Chem. Phys. Letters*, 1973, **21**, 401.

² G. Favaro, *Chem. Phys. Letters*, 1973, **23**, 592.

³ G. Favaro and G. Bufalini, *J. Phys. Chem.*, 1976, **80**, in the press.

⁴ L. A. Singer, R. E. Brown, and G. A. Davis, *J. Amer. Chem. Soc.*, 1973, **95**, 8638.

⁵ G. Favaro, *Chem. Phys. Letters*, 1975, **31**, 87.

⁶ D. A. Nelson and E. Hayon, *J. Phys. Chem.*, 1972, **22**, 3200.

⁷ P. Traynard and J. P. Bianchi, *Mol. Photochem.*, 1972, **4**, 223 and references therein.

⁸ J. P. Bianchi and A. R. Watkins, *Mol. Photochem.*, 1974, **6**, 133.

These intensities (P) were found to fit the Stern–Volmer equation (1) where τ is the lifetime of the donor triplet,

$$P^{-1} = K \left(1 + \frac{1}{k_t \tau [Q]} \right) \quad (1)$$

k_t is the rate constant for the energy transfer, and K is a constant inversely proportional to the donor triplet yield (ϕ_T),¹ also including the biacetyl triplet lifetime, the rate of light absorption, and an instrumental factor.

For measurements in benzene, the excitation was performed with 340 nm light and the intensities of the sensitized phosphorescence of biacetyl were read at 525 nm at varying biacetyl concentration in the range 10^{-3} – 10^{-6} M. Donor concentrations were of the order of 2×10^{-3} M to guarantee a constant absorption of 0.3. No concentration effect was observed by lowering the donor concentration. In such conditions, keeping all the instrumental factors constant, the maximum intensity values of phosphorescence sensitized by the different isomers may be compared. Assuming a unitary triplet yield for benzophenone,⁹ ϕ_T values

and 4-BP are shown in Table I, which also reports those of benzophenone for comparison. A property common to all the spectra is the presence of two distinct zones of absorption, the separation of which decreases with increase in solvent polarity. Absorption at longer wavelengths is characterized by low extinction coefficients ($\log \epsilon$ ca. 2.2) and that at shorter wavelengths by high extinction coefficients ($\log \epsilon$ ca. 4.2).

The spectra of all the isomers, in the various solvents, are very close to those of Bp, that of 3-BP in particular being most similar to Bp. If one considers that the heterocyclic nitrogen has similar effects ($-I$ and $-M$) as an electron-attracting group, the smaller spectral change observed for the *meta*-isomer indicates that the mesomeric effect prevails in the excited state. As for Bp, the absorption at higher wavelengths is assigned to the carbonyl n, π^* transition, on the basis of both the low τ value and the hypsochromic shift it undergoes on

TABLE I

Band maxima and extinction coefficients of the absorption spectra of benzophenone and benzoylpyridines in organic apolar and polar solvent and in aqueous solution at pH 7 and 1

Compound	Solvent			
	n-Hexane λ/nm ($\log \epsilon$)	Ethanol λ/nm ($\log \epsilon$)	Water	
			pH 7 λ/nm ($\log \epsilon$)	pH 1 λ/nm ($\log \epsilon$)
Bp	246 (4.32) 346 (2.06)	250 (4.30) 333 (2.21)	260 (4.25) 326sh (2.42)	260 (4.25) 326sh (2.42)
2-BP	264 (4.14) 360 (2.21)	265 (4.14) 349 (2.38)	267 (4.14) 335sh (2.53)	275 (4.13) 252sh (2.41)
3-BP	248 (4.21) 349 (2.07)	255 (4.28) 341 (2.20)	265 (4.11) 330sh (2.34)	266 (4.13) 338sh (2.30)
4-BP	252 (4.08) 347 (2.00)	258 (4.06) 338 (2.09)	265 (4.10) 335sh (2.27)	270 (4.03) 355sh (2.15)

for benzoylpyridines were evaluated from the ratios of the intercepts of the Stern–Volmer plots to that of benzophenone. The reported τ and ϕ_T values were averaged over three experimental runs.

For the measurements in aqueous solution, the excitation was performed with 320 nm light and the intensities of the sensitized biacetyl phosphorescence were read at 514 nm, varying biacetyl concentration in the range 4×10^{-6} – 4×10^{-8} M for 3-BP, and 2×10^{-5} – 5×10^{-3} M for 4-BP and 3-BPH⁺. A correction for the solvent background was always necessary. In the last two cases, where higher $[Q]$ were used, due to the very low lifetimes of the donors, the readings with $[Q] > 10^{-3}$ M also required a correction for directly excited biacetyl phosphorescence. Further increase in the concentration of the quencher ($[Q] > 5 \times 10^{-3}$ M) must be avoided since biacetyl triplet begins to be self-quenched.

For the experiments with 3-BP, whose own emission is fairly strong, the readings of the sensitized phosphorescence were corrected for the contribution of the long-wavelength tail of the emission of the donor.

RESULTS AND DISCUSSION

Spectroscopic Characterization.—Absorption spectra. The band maxima of the absorption spectra of 2-, 3-,

⁹ N. J. Turro, 'Molecular Photochemistry,' Benjamin, New York, 1965, p. 31.

¹⁰ P. J. Wagner and G. Capen, *Mol. Photochem.*, 1969, **1**, 173.

increase in solvent polarity. It is of interest to note that the n, π^* singlet is probably the excited state at lowest energy for the protonated molecules also, although the absorption band appears only as an ill defined shoulder, being almost covered by the more intense absorption at shorter wavelengths. The bathochromic shift with respect to the analogous band in Bp, produced by the introduction of the heteroatom, is also in agreement with an n, π^* assignment, considering the electron-attracting effect of the heterocyclic nitrogen. A similar shift has been observed in the three valerylpyridine isomers with respect to the valeryl ketone itself.¹⁰

The region at shorter wavelength and higher extinction coefficient includes the π, π^* transitions of benzoyl and pyridinecarbonyl groups, which undergo the predicted bathochromic shift with increase in solvent polarity. Compared with that of benzophenone, the absorption is found to higher λ for all three isomers and in all the solvents used. The introduction of a second heteroatom in di-4-pyridyl ketone leads to a more marked bathochromic shift,¹¹ whilst in valeryl ketone the heteroatom causes a hypsochromic shift on the π, π^* band.¹⁰ The stabilization of π, π^* states on introducing

¹¹ F. L. Minn, C. L. Trichilo, C. R. Hurt, and N. Filipescu, *J. Amer. Chem. Soc.*, 1970, **92**, 3600.

the nitrogen atom in BPs is probably due to a decrease in the repulsion between the two aromatic rings and hence to a greater planarity and overlap between the orbitals of the rings and those of the carbonyl group. This interpretation is only in partial agreement with the carbon-ring angles reported by Traynard and Blanchi,¹² which decreases in the order: 3-BP > Bp > 4-BP = 2-BP.

Emission spectra. As for many other carbonyl compounds, and especially benzophenone, the BPs are phosphorescent but not fluorescent. In addition, in common with benzophenone,^{3,13,14} they show the rather rare property of being phosphorescent even at room temperature in fluid solution.

The wavelengths of the maxima in the phosphorescence at 77 K of the three BP isomers in benzene, in a neutral aqueous solution and in acid (0.1M-HClO₄) are reported in Table 2.

In addition, although a quantitative measure of the phosphorescence lifetime has not been determined, from the minimum chopper velocity of the phosphorimeter necessary for observation of the emission, we estimate that the lifetime of phosphorescence in acid is *ca.* 10–20 times greater than that of non-protonated molecule. Taken together, these observations lead to the suggestion that the lowest triplet state acquires considerable π, π^* character. On the other hand, the effect of the protonated nitrogen on the BP spectra, compared to that of Bp, is that of lowering the energy of the triplet, as expected for the interaction of electron attractors with a n, π^* state. This effect is larger than that observed in neutral matrix. Anyway, the triplet energy level order remains the same: $E_T(\text{Bp}) > E_T(\text{3-BP}) > E_T(\text{4-BP}) > E_T(\text{2-BP})$. This trend is not in agreement with that calculated by Blanchi,¹⁶ which, instead, predicts higher triplet energy levels for benzoylpyridines

TABLE 2

Wavelengths of the maxima of the phosphorescence spectra of benzophenone and benzoylpyridines in benzene (77 K) and in neutral and acidic solution both at low and room temperature

Compound	Solvent					
	Benzene		Water			
	77 K		77 K		295 K	
	λ/nm	$10^{-3}\nu_{0-0}/\text{cm}^{-1}$	pH 7 λ/nm	pH 1 λ/nm	pH 7 λ/nm	pH 1 λ/nm
Bp	424	236	427.5	397	417	445
	457		461	423		
	492		497	447sh		
	535		540	475sh		
	578					
	578					
2-BP	436	229.5	439	420	417	445
	469		474	450		
	508		513	480sh		
	555		560			
	608					
	608					
3-BP	427	234	429	405	420	458
	458		462	432	447	
	494		499	460sh	476sh	
	537		543	500sh		
	584					
	584					
4-BP	434	230.5	437	415	450	
	467		470	444		
	504		509	470sh		
	548		553			
	600					
	600					

A characteristic common to the phosphorescence emissions in benzene and in neutral water solution is the presence of a well resolved vibrational progression with an interval of 1650 cm⁻¹, clearly attributable to the carbonyl stretching mode. The observation of this mode allows the emission to be assigned as the n, π^* triplet localized on the carbonyl group. The decrease in energy of the 0–0 transition with respect to benzophenone (ν_{0-0} is reported in the second column of Table 2, for benzene solution), which is larger in 2- and 4-BP, is in agreement with expectation.¹⁵

The spectra in acid matrix show less structure and give hypsochromic shifts compared with those in neutral

than for benzophenone. The agreement is better with the experimental triplet energies obtained by Blanchi and Watkins⁸ from phosphorescence spectra in butan-2-ol at 77 K.

The change in phosphorescence on going from neutral to acidic matrix may be imputed to a change of the molecule to give pyridinium cation (hence a different species with different spectroscopic characteristics). Nevertheless, comparison with benzophenone shows that this explanation is too over-simplified. In fact, the same spectroscopic variations have also been observed, with decrease in pH, in benzophenone and were attributed to the formation of a molecular complex, probably involving the carbonyl and H₃O⁺, in moderately strong acid medium.⁵

¹² P. Traynard and J. P. Blanchi, *Compt. rend.*, 1968, **267**, 1381.

¹³ M. B. Ledger and G. Porter, *J.C.S. Faraday I*, 1972, 539.

¹⁴ D. M. Rayner and P. A. H. Wyatt, *J.C.S. Faraday II*, 1974, 945.

¹⁵ D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301.

¹⁶ J. P. Blanchi, *J. Chim. phys.*, 1972, **69**, 1171.

The emission in the neutral fluid solution is observed only for the 3- and 4-BP isomers, whilst 3-BP only gives a very low emission in acid. The bands are broad and only in 3-BP at pH 7 is the emission partially resolved into three vibrational bands, as was observed for Bp itself.³

Photosensitization.—Measurements of the photosensitization of the phosphorescence of biacetyl by benzoylpyridines have been carried out in benzene and in aqueous medium at two pH values (7 and 1), so as to ensure the presence of either basic species or pyridinium cations. Appropriate pH values were chosen on the basis of the *pK* determinations for the three isomers, measured spectrophotometrically and shown in Table 3.

TABLE 3
Experimental *pK* values of BPs, compared with some literature values

Compound	<i>pK</i> ^a	<i>pK</i> ^b
2-BP	2.36 ± 0.05	2.15 ± 0.1
3-BP	3.00 ± 0.1	3.3 ± 0.2
4-BP	3.17 ± 0.05	3.6 ± 0.1

^a This work. ^b Ref. 6.

Comparison of the triplet energies of the three isomers, evaluated from the phosphorescence spectra, with that of biacetyl (E_T 19 000 and 19 500 cm⁻¹, in benzene and in water, respectively), shows that exothermic energy transfer can occur and hence allows us to adopt a diffusion value for the transfer constant (10¹⁰ mol⁻¹ dm³ s⁻¹, in benzene; 1.2 × 10⁹ mol⁻¹ dm³ s⁻¹, in water¹⁷).

Triplet yields and lifetimes in benzene. Table 4 shows

TABLE 4
Triplet lifetimes and yields of benzophenone and benzoylpyridines in benzene solution

Compound	10 ⁶ τ/s	φ _T
Bp	5.3 ± 0.6	1
2-BP	0.54 ± 0.07	0.7 ± 0.1
3-BP	1.3 ± 0.1	0.9 ₅ ± 0.1
4-BP	0.41 ± 0.04	0.7 ± 0.1

the results obtained in benzene for the three BPs compared to those for Bp. The lifetime of benzophenone is higher than that reported previously.¹ This is not surprising since it has been shown, by us¹ and by others,¹⁸ that the triplet lifetime of benzophenone in solution is strongly influenced by even the minimum traces of impurity in the solvent; therefore, to obtain comparable measurements, it is necessary to use solvent obtained from the same purified batch.

The data of Table 4 show that the BPs have very high triplet yields; in particular, φ_T is unity for 3-BP, as for Bp, within the limits of experimental error. In contrast, introduction of the heteroatom greatly lowers the lifetime, with respect to that of Bp, by about an order of magnitude for the isomers 2- and 4-BP, whilst the decrease is lower for 3-BP (τ ca. 0.25 that for Bp).

The suggestion put forward previously,¹ that the deactivation of the *n,π** carbonyl triplet in benzene occurs mostly *via* a chemical interaction with the solvent, where the excited carbonyl behaves like an electrophilic

reagent, seems confirmed by the results obtained for the BPs. The heterocyclic nitrogen atom performs a role, analogous to that of an electron-attracting substituent, lowering the charge density at the carbonyl oxygen and hence increasing the rate of the electrophilic interaction with the solvent. Although these experimental results accord well with those obtained previously,¹ it may be observed that they lead to conclusions which are the opposite to those arrived at theoretically by Traynard and Blanchi.^{7,12,16,19} Using the Parr-Pariser method, these authors calculated that the charge density on the carbonyl oxygen in the excited state increases from Bp to the BPs in the order: Bp < 4-BP < 3-BP < 2-BP, whilst a comparison of lifetimes in benzene together with the spectroscopic characteristics of the compounds would lead to 4-BP < 2-BP < 3-BP < Bp, in agreement with the prediction that the heterocyclic nitrogen exerts an electron-attracting effect on the excited carbonyl.

Lifetimes and self-quenching constants in water. In Britton buffers at pH 7, in which the BPs are present in the base form, only the 3- and 4-BP isomers transfer their excitation energy to biacetyl.

In acidic solution at pH 1, in which the pyridinium cationic forms (BPH⁺) are present, 3-BPH⁺ has fair sensitizing power, 2-BPH⁺ very little, and 4-BPH⁺ shows none. In this medium the very short triplet lifetime (10⁻⁷–10⁻⁸ s) requires high acceptor concentrations before energy transfer can be observed. This means that the corrections mentioned in the experimental part for the intensity of the direct emission of biacetyl must be applied. The filter effect and the self-quenching of biacetyl place an upper limit to the concentration of biacetyl utilizable ([Q] < 5 × 10⁻³M) and hence to the minimum value of τ which can be measured (τ > 10⁻⁸ s).

The lifetime of the BPs increases with decrease in concentration, as also observed previously for Bp.³ This behaviour is attributable to a self-quenching process which deactivates the donor triplet, in competition with the T₁ → S₀ intersystem crossing and, where this is present, with phosphorescence emission. The rate of deactivation of the triplet is thus given by equation (2) in which *k*_d, *k*_P, and *k*_{sq} are the kinetic constants for

$$r = (k_d + k_P + k_{sq}[\text{BP}]^2)[^3\text{BP}] \quad (2)$$

non-radiative deactivation, phosphorescence, and self-quenching, respectively.

At constant BP concentration, the experimental lifetime is related to the kinetic constants through equation (3). The true lifetime [τ_∞ = 1/(*k*_d + *k*_P)] may

$$1/\tau = k_d + k_P + k_{sq}[\text{BP}] \quad (3)$$

be found by extrapolating to infinite dilution (*i.e.* when the probability of a ³BP + BP encounter is zero) from the intercept of the straight line, 1/τ against [BP], carrying out a series of measurements at variable donor

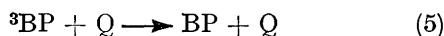
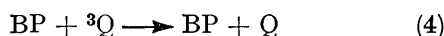
¹⁷ M. Almgren, *Mol. Photochem.*, 1972, **4**, 213.

¹⁸ J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, 1963, **85**, 528.

¹⁹ P. Traynard and J. P. Blanchi, *J. Chim. phys.*, 1972, **69**, 284.

concentration. The slope of this line gives the self-quenching constant directly.

The possible intervention of additional bimolecular processes leading to radiationless decay, such as (4) and (5) has also been taken into consideration.



The occurrence of process (4) can be checked by exciting biacetyl in the presence of BP and measuring the quenching of Q phosphorescence.² However, no quenching was detected for all the compounds examined, so that this process can be ruled out.

As far as process (5) is concerned, were a radiationless quenching competitive with the energy transfer, the measured lifetime should not correspond to the value given by equation (3). Nevertheless, neither of the experimental methods employed (phosphorescence sensitization of the acceptor or phosphorescence quenching of the donor) permits discrimination between this and

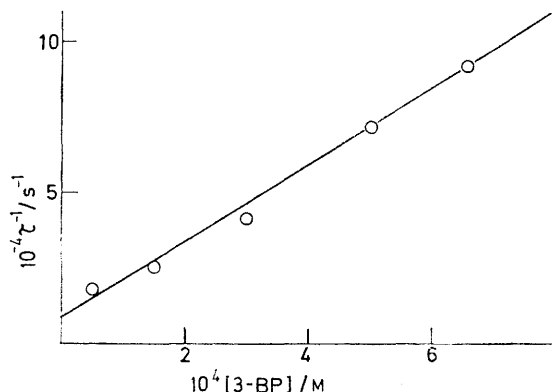
for the Figure which shows $1/\tau$ as a function of the concentration of 3-BP, from which extrapolation to infinite dilution gives $\tau_\infty 1.1 \times 10^{-4}$ s, while the slope of this line gives the self-quenching constant, $k_{sq} = 1.25 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

The lifetimes of the other compounds were measured from the biacetyl sensitized phosphorescence alone since the phosphorescence of the donor was either very weak (3-BPH⁺ and 4-BP) or not observable. The lifetime measured for the cation 3-BPH⁺ at pH 1 is lower by more than an order of magnitude than that of the base and is virtually independent of concentration changes, at least for the concentration range considered here. The differences observed are, in fact, of the same order as the experimental uncertainty ($\pm 10\%$) and hence the average of the values at the different concentrations (7.2×10^{-7} s) may be taken as the value of τ_∞ . Under these conditions, it is not possible to estimate the self-quenching constant. This does not necessarily mean that the acidic form is not able to undergo self-quenching processes, but that, given its short lifetime, much higher

TABLE 5
Triplet lifetime of benzoylpyridines in aqueous solutions as a function of concentration

3-BP			3-BPH ⁺		4-BP	
$10^4[\text{3-BP}]/\text{M}$	$10^5(\tau)_s/\text{s}$	$10^5(\tau)_q/\text{s}$	$10^4[\text{3-BPH}^+]/\text{M}$	$10^7(\tau)_s/\text{s}$	$10^4[\text{4-BP}]/\text{M}$	$10^7(\tau)_s/\text{s}$
6.6	1.0	1.2	3.28	6.9	6.85	7.0
5.0	1.4 ₅	1.3 ₅	2.0	7.1	3.95	7.6
3.0	2.6	2.2	1.0	7.1	2.26	19.8
1.5	5.0	3.0	0.31	7.7	0.54	19.2
0.5	6.0 ₅	5.2			0.39	22.7

the energy transfer process. However, direct τ measurements carried out for Bp by Rayner and Wyatt,¹⁴ showed good agreement with τ values obtained by the sensitization technique.³ For BPs also, direct measurements of τ will be the subject of further work.



Lifetime data for 3-BP at pH 7 treated according to equation (3)

The results of the measurements at various donor concentrations are shown in Table 5. For 3-BP, the lifetime in neutral solution was measured from both the sensitized biacetyl phosphorescence ($\tau)_s$ and the quenching of phosphorescence of 3-BP ($\tau)_q$. The values obtained by both methods are in good agreement with one another (Table 5). The average values have been used

concentrations (which are not possible for solubility reasons) would be required before the bimolecular process ${}^3\text{BPH}^+ + \text{BPH}^+$ becomes competitive with unimolecular deactivation (or with solvent deactivation). Nevertheless, it may be predicted that a k_{sq} for the encounter between two species having the same charge must be very low. For 4-BP at pH 7, the wide concentration range explored (3.9×10^{-5} – 6.8×10^{-4} M) allows the self-quenching constant to be evaluated, although only roughly, as $k_{sq} (1.9 \pm 0.5) \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, despite the fact that the lifetime extrapolated to infinite dilution is very short ($\tau_\infty 2.8 \times 10^{-6}$ s).

The results obtained for 2-BPH⁺ are not reported; the low reproducibility of each phosphorescence measurement, caused by the limiting conditions of instrument sensitivity because of the weak sensitizing power of this compound, does not allow good Stern–Volmer plots to be obtained, but only a rough estimate for τ (*ca.* 10^{-8} s). Nevertheless, it is important to underline that the photosensitizing power, absent in the neutral form, is established on protonation. Hurt and Filipescu²⁰ have, in fact, found that on irradiation in aqueous solution, 2-BP undergoes an intramolecular cyclisation process to give an indole derivative. The absence of phosphorescence emission at room temperature and the absence also of photosensitizing power for this isomer in neutral

²⁰ C. R. Hurt and N. Filipescu, *J. Amer. Chem. Soc.*, 1972, **94**, 3643.

aqueous solution are doubtlessly due to the competitive photochemical process. However, phosphorescence emission in aqueous rigid matrix shows that the emitting triplet is an n,π^* triplet localized on the carbonyl group for 2-BP.

TABLE 6

Triplet lifetimes extrapolated to infinite dilution (τ_∞) and self-quenching constants of benzophenone and benzoylpyridines in aqueous solution

Compound	Neutral solution		Acidic solution
	τ_∞/s	$k_{sq}/\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	τ_∞/s
Bp ^a	2.3×10^{-4}	1.7×10^8	9.8×10^{-8} ^b
2-BP	No sensitization observed		1×10^{-8} ^c
3-BP	1.1×10^{-4}	1.2×10^8	7.2×10^{-7} ^c
4-BP	2.8×10^{-6}	1.9×10^9	No sensitization observed

^a Ref. 3. ^b pH 1.35. ^c pH 1.0.

The results obtained in aqueous solution, listed in Table 6 together with those of benzophenone³ for comparison, clearly show that variation in the position of the heterocyclic nitrogen is much more important in water than in benzene, as is demonstrated by the particular photoreactivity of 2-BP and by the considerable decrease in triplet lifetime for 4-BP (about two orders of magnitude with respect to that of benzophenone). An analogous influence exerted by the positional isomerism of

nitrogen has been found in the acid-base properties of the corresponding ketyl radicals,⁶ which originate from the triplet state. On the other hand, measurements of lifetime by flash photolysis in perfluoromethylcyclohexane solution at room temperature⁸ show that the presence of the heterocyclic nitrogen atom causes an increase in the triplet deactivation rates of BPs also in this solvent. However, this effect is much larger for the 3-BP isomer, which result is precisely the opposite to that found here for benzene and aqueous solutions.

The decrease in lifetime in acidic solution cannot be entirely imputed to the protonation of the nitrogen atom alone, but, rather, to the particular solvation undergone by the carbonyl group in acid media, since benzophenone shows similar behaviour.³ It is important to underline that benzophenone cannot be used as a sensitizer in acid solution because of its short lifetime, whilst 3-BP, having a lifetime about an order of magnitude greater, acts as a sensitising agent even at pH 1.

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