PHOTOCHEMICAL AND PHOTOPHYSICAL BEHAVIOUR OF BENZOYLPYRIDINES
III: A PROPOSAL FOR σ VALUES OF BENZOYLPYRIDINES IN THEIR EXCITED STATES

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(Received August 15, 1980)

Summary

On the basis of the good linear relationships observed between absorption and phosphorescence emission spectral data for benzophenone and the three isomeric benzoylpyridines, a set of σ parameters is proposed for the three positions of the heterocyclic nitrogen atom. A comparison with some kinetic and spectroscopic data from the literature supports the reliability of the proposed parameters in predicting the effect of the heteroatom on the photochemical and photophysical behaviour of the excited state.

1. Introduction

The correlation and the prediction of the effect of substituent groups on reaction rates and equilibria by means of σ values have been extended in recent years to photochemical and photophysical processes of the excited molecules [1 - 9]. The interest in σ value correlations for photochemists comes from the possibility of obtaining information on the nature of the excited states involved in a photoprocess, since the sign and the magnitude of the angular coefficient (the ρ value) depend on the changes occurring in the site of the excited molecule involved in the photoprocess. However, the same photochemistry may arise from more than one excited state; therefore a study of the effect of substituents on photoreactions could lead to ambiguous conclusions.

In this paper we report some generalizations for the positional effect of the heterocyclic nitrogen atom in the three isomeric benzoylpyridines (BPs) (2-benzoylpyridine (2-BP), 3-benzoylpyridine (3-BP) and 4-benzoylpyridine (4-BP)), compared with benzophenone (B), obtained from an inspection of their absorption spectra at room temperature and of their luminescence spectra at liquid nitrogen temperature in various solvents.

Our interest in these molecules comes from previous studies on their behaviour as photosensitizers of organic as well as inorganic acceptors in polar and non-polar solvents [10, 11].

2. Experimental

B (Carlo Erba) and 4-BP (Aldrich) were recrystallized several times from water—ethanol; 2-BP and 3-BP (Aldrich) were recrystallized from light petroleum. Reagent grade solvents (n-hexane, benzene and ethanol) were purified by standard procedures. For measurements in aqueous solutions, Britton buffer was used for pH 7 and a 0.1 M $HClO_4$ solution was used for pH 1.

Absorption spectra were taken on a Unicam SP 500/2 spectrophotometer and a Perkin—Elmer Coleman 572 spectrophotometer. Phosphorescence spectra were recorded at liquid nitrogen temperature on a Hitachi–Perkin—Elmer MPF-3 spectrofluorimeter which was equipped with an accessory for phosphorescence measurements.

3. Results and discussion

The UV absorption spectra of the three isomeric BPs, like that of B, are characterized by two distinct zones of absorption. The high intensity absorption at shorter wavelengths (log $\epsilon \approx 4.2$) has been assigned to a π,π^* transition; the low intensity absorption at longer wavelengths (log $\epsilon \approx 2.2$) has been assigned to the carbonyl n,π^* transition [10]. In non-polar solvents (n-hexane, benzene) the n,π^* transition shows a partially resolved vibrational structure which is more marked for B and 3-BP. By increasing the polarity of the solvent, the bathochromic shift of the π,π^* transition and the hypsochromic shift of the n,π^* transition [12] combine to obscure the n,π^* transition which appears as a shoulder on the long-wavelength tail of the π,π^* transition, as shown in Fig. 1 for 2-BP.

Even though arylketones exhibit phosphorescence emission in many deaerated solvents at room temperature [10], we preferred in this correlation study to use low temperature phosphorescence spectra because of their greater sharpness. The emissions in polar (H_2O, pH 7) as well as in non-polar (benzene) solvents have been assigned to the n,π^* triplet localized on the carbonyl group, on the basis of both vibrational structure and lifetime [10]. In an acidic medium (aqueous solution, pH 1) the phosphorescence emission appears to be hypsochromically shifted and to be less structured, as shown in Fig. 2 for 2-BP, and it has been considered to acquire considerable π,π^* character [10]. Despite the broadening of the band, the 0—0 frequencies are well recognizable in all cases.

The edges of these phosphorescence emissions, plotted against the absorption maxima of the lowest n,π^* transition in benzene at room tem-
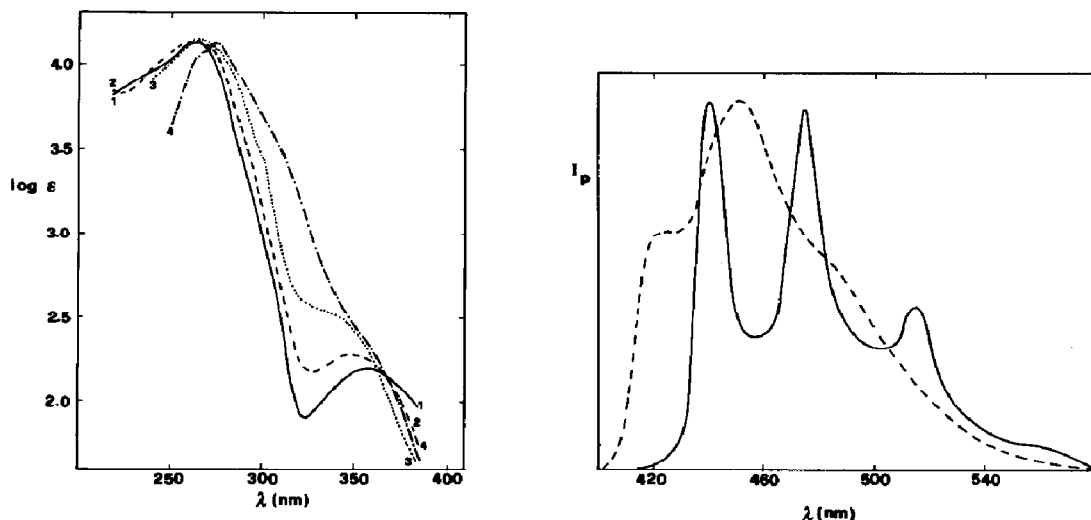
Fig. 1. The effect of the solvent on the absorption spectrum of 2-BP: curve 1, n-hexane; curve 2, ethanol; curve 3, water, pH 7; curve 4, 0.1 M aqueous solution, pH 1.

Fig. 2. Phosphorescence spectra of 2-BP in neutral (———) and in acidic (— — —) aqueous solution at liquid nitrogen temperature.

perature, were found to exhibit a fairly good linear relationship as shown by Fig. 3 and by the correlation coefficients reported in Table 1 ($r > 0.990$). The positive slopes indicate that the nitrogen effect is similar on both triplet and singlet energies. The ρ values, which are lower than unity for emissions in benzene ($\rho = 0.67$) and in neutral aqueous solution ($\rho = 0.66$) and are approximately equal, show that the nitrogen effect is less important for n,π^* triplet states than for singlet states and is the same for the triplet in both media. However, the ρ value (1.34) for the emission in an acidic medium indicates that the emitting triplet is more sensitive to the nitrogen position than is the n,π^* singlet.

Taking into account the fact that the best correlation is observed for benzene ($r = 0.9999$), we decided that this would be the best starting point for determining the σ values for the excited molecules. We found in the literature that σ values for all three positions of pyridine have been obtained from the electron distribution, calculated using the linear combination of atomic orbitals molecular orbital method, by assuming that the electron density increment induced by a substituent (the heterocyclic nitrogen atom in the present case) is proportional to the corresponding σ value [13, 14]. The calculated values have been compared with those derived from experimental data [15]. A reasonable agreement between the calculated and experimental values has been found only for the 4 position, as shown in Table 2. These experimental σ values have been used by Arnold [2] to insert the three BP isomers in a correlation diagram between the n,π^* triplet energy and the Hammett substituent constants for a large number of arylketones.
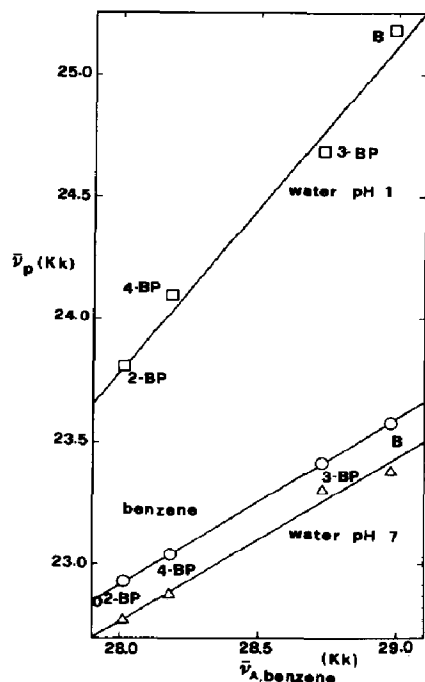
Fig. 3. Correlation plots for 0—0 frequencies of the phosphorescence emission ($\bar{\nu}_P$) in benzene and in aqueous solutions at liquid nitrogen temperature *vs.* the n,π^* absorption maxima ($\bar{\nu}_A$) in benzene at room temperature for B and BPs.

TABLE 1

Slopes ρ and correlation coefficients r for the plots given in Fig. 3

Solvent	Slope ρ	Correlation coefficient r
Benzene	0.67	0.9999
Water, pH 7	0.66	0.993
Water, pH 1	1.34	0.993

TABLE 2

σ values for the three positions of the heterocyclic nitrogen atom compared with calculated and experimental values from the literature

Nitrogen position	Literature value		This work
	σ_{calc} [a]	σ_{exp} [b]	σ
2	0.46	0.81	1.2
3	0.35	0.62	0.3
4	1.07	0.93	1.0

[a] Data taken from ref. 14.
[b] Data taken from ref. 15.
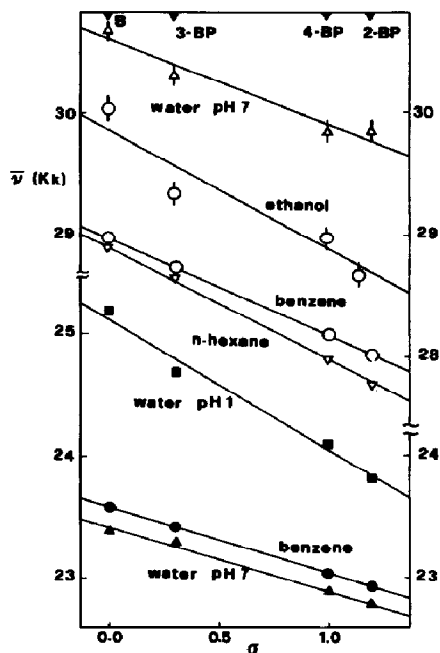
Fig. 4. Correlation diagrams for absorption (△, ○, ▽) and emission (▲, ●, ■, ▼) spectroscopic data of B and BPs.

TABLE 3

Slopes ρ and correlation coefficients r for the plots given in Fig. 4

Solvent	Absorption		Emission	
	Slope ρ	Correlation coefficient r	Slope ρ	Correlation coefficient r
Water, pH 1			− 1.07	0.991
Water, pH 7	− 0.68	0.975	− 0.53	0.994
Ethanol	− 0.90	0.953		
Benzene	− 0.80	0.9999	− 0.54	0.9999
n-Hexane	− 0.93	0.9995		

Again, a good fitting is shown by 4-BP, whilst 2-BP and 3-BP show appreciable deviations and the correlation becomes even worse if the calculated σ values rather than the experimental σ values are used. These considerations, together with the linear relationships observed, suggested that we should fix $\sigma = 1$ for 4-BP (by averaging the calculated (1.07 [14]) and the experimental (0.93 [15]) values from the literature) in the best least-squares line shown in Fig. 3 (benzene). The σ values for the other two isomers were interpolated. The values obtained are listed in Table 2, column 4.

Some absorption and emission spectroscopic data are plotted against these new σ values in Fig. 4 and the corresponding slopes ρ and correlation coefficients r of the least-squares lines are summarized in Table 3. The fre-

quencies for the absorption data used in the figure correspond to the maxima of the n,π^* transitions, well resolved in n-hexane and benzene and broad in ethanol, and to the long-wavelength shoulders in water. The emission data correspond to the short-wavelength edges of the phosphorescence spectra and, therefore, they represent the triplet energies. The linear correlations are excellent ($r > 0.990$) when the frequency readings are more precise (all the emission spectra and the absorption spectra in benzene and n-hexane), but are still satisfactory ($r > 0.950$) when the frequencies are read on broad absorption bands (ethanol) or shoulders (water). The negative slopes indicate that both the singlet and the triplet states are stabilized by decreasing the electron density at the carbonyl carbon. The ρ values for the absorption linear relationships in various solvents are very similar to each other, indicating that the nitrogen positional effect on the energy of the n,π^* singlet states is not much influenced by the medium. Comparison of the ρ values for the absorption and emission data (lower for emission except in an acidic medium) indicates that the singlet–triplet energy difference decreases with the electron density at the carbonyl carbon ($\rho = -0.3$, $r = 0.965$ for the correlation $\Delta\bar{\nu}_{S_1 - T_1}$ versus σ in benzene). The different extent of the nitrogen effect on singlet and triplet states may be attributed to a greater contribution of polar structures, with the negative charge on the heteroatom, in the excited singlet state than in the excited triplet state [16]. The ρ value for the plot of the emission data at pH 1, which is approximately twice the value in benzene and in aqueous neutral solution, indicates a greater stabilization of the triplet, in contrast with the expectation for a π,π^* state. This behaviour, which is also observed for the π,π^* absorption band, has been attributed previously to a greater planarity and to a greater overlap between the orbitals of the rings and those of the carbonyl group, because of a decrease in the repulsion between the two aromatic rings [10]. Also the variation of the triplet energy with the solvent ($\bar{\nu}_{benzene} - \bar{\nu}_{water,pH\ 7} = 200$ cm^{-1}), which is approximately constant for each compound, is contrary to expectation. An increase in solvent polarity should in fact raise the n,π^* triplet energy [12]. A possible explanation is that the emission in aqueous solution occurs in a solvent cage where ketone microcrystallites which are relatively free from solvent bonding are formed.

In order to establish the generality of the proposed σ values, some correlation diagrams for spectroscopic and kinetic data from the literature are shown in Fig. 5. The ρ values and the linear correlation coefficients are tabulated in Table 4. The fitting with our σ values is again fairly good. Comparison of the ρ values for triplet energies (in order to compare the ρ values all the energy data were converted to kilo Kayser (Kk) units) in a benzophenone host crystal at 1.4 K (Fig. 5, curve a [17]) and in methylcyclohexane at 77 K (Fig. 5, curve b [2]) with our values in benzene and neutral aqueous solution shows a very good agreement, confirming that the medium does not appreciably affect the effect of the heterocyclic nitrogen atom on the triplet energy. It should be noted that the ρ value which can be obtained from the Hammett plot of Arnold ($\rho = -0.5$ [2]), which includes a large
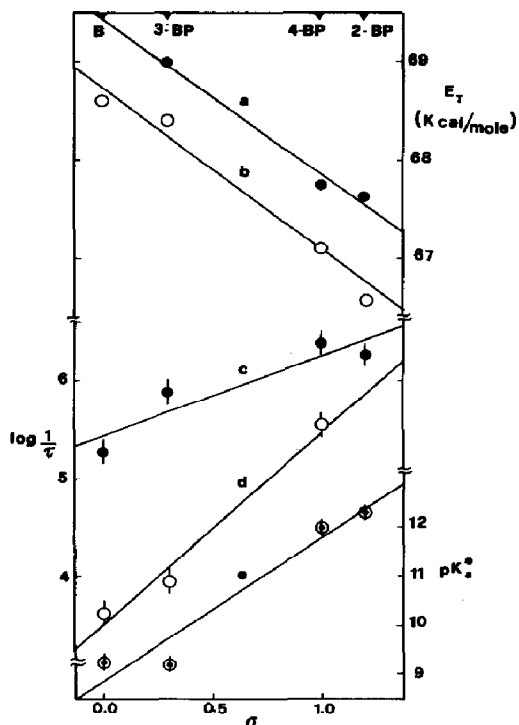
Fig. 5. Correlation diagrams for spectroscopic (E_T) and kinetic (log $1/\tau$, pK^*) data for B and BPs taken from the literature.

TABLE 4

Slopes ρ and correlation coefficients r for the plots given in Fig. 5

For E_T (Kk)		For $log \ 1/\tau^c$		For pK^{*f}	
Slope ρ	Correlation coefficient r	Slope ρ	Correlation coefficient r	Slope ρ	Correlation coefficient r
-0.55^a	0.990^a	0.80^d	0.925^d	2.90	0.971
-0.57^b	0.991^b	1.97^e	0.990^e		

[a]Data taken from ref. 17.
[b]Data taken from ref. 2.
[c]Data taken from ref. 10.
[d]In benzene.
[e]In water, pH 7.
[f]Data taken from refs. 18 and 19.

number of arylketones, is almost the same. These values may also be compared with $\rho = -0.4$, obtained by Saltiel et al. [4] for a plot of the triplet energies of aromatic ketones in CCl_4 at room temperature against Hammett's σ values.

The plots of the triplet lifetimes [10] against σ values (Fig. 5, curves c and d) may be compared with that previously obtained for nine aryl-ketones ($\rho = 1.34$, $r = 0.986$) in benzene solution at room temperature [5].

Considering the same solvent (benzene), the slope found for the BPs is lower (ρ = 0.8) even though it has the same sign; this substantiates the hypothesis of a deactivation through an n-type complex with the benzene solvent, where the excited carbonyl behaves like an electrophilic reagent.

At the bottom of Fig. 5, where the pK^* values of the ketyl radicals [18, 19] are plotted against σ values, the fitting is again satisfactory and the high ρ value obtained (2.9) indicates the great importance of the heterocyclic nitrogen atom in determining the acid–base properties of these ketyl radicals.

Other literature data for B and BPs, not reported in the figure, which show a satisfactory or reasonable fitting with the proposed parameters are triplet energies measured in ethanol [2] (ρ = -0.6, r = 0.959) and in 3-butanol [20] (ρ = -0.51, r = 0.878) at liquid nitrogen temperature and triplet energies measured in perfluoromethylcyclohexane [20] at room temperature (ρ = -0.63, r = 0.988). Similar ρ values for triplet energy correlations substantiate the hypothesis put forward in this work of the scarce influence of the medium on the substituent effect. However, the correlation does not hold for the photoreductive reactivity in isopropanol of B and BPs [21, 22]. This cannot be considered to invalidate the proposed parameters since the quantum yield for the disappearance of ketone by photoreduction can include subsequent processes, e.g. self-sensitization [22], which obscure the primary photoprocess.

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