

Short Communication

Photophysics of 2,2'-bipyridyl

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Studies of the electronic absorption spectra of nitrogen heterocyclic compounds have shown that these molecules have low lying (n, π^*) excited singlet states. The lowest singlet state of pyridine is almost certainly of (n, π^*) character and lies some 3600 cm^{-1} below the (π, π^*) singlet [1]. Absorption spectra of crystalline 2,2'-bipyridyl at low temperatures provide substantial evidence that the lowest excited singlet state is an (n, π^*) state [2], whilst a recent study [3] has shown that 1,10-phenanthroline possesses close lying (n, π^*) and (π, π^*) excited singlet states. This communication describes the photophysical properties of 2,2'-bipyridyl and locates the positions of the lowest excited singlet and triplet states in fluid solution.

Experimental

Biphenyl (Aldrich) and 2,2'-bipyridyl (BDH) were recrystallised from ethyl acetate and zone refined. Water was triple distilled and all other solvents were spectroscopic grade. General procedures were carried out as described previously [3] whilst all flash photolysis and fluorescence measurements were made with thoroughly outgassed solutions. Fluorescence quantum yields were calculated using biphenyl as a standard [4] and were measured with optically dilute samples. Phosphorescence was detected at 77 K after purging the solutions with oxygen-free nitrogen. The luminescence data were fully corrected for the spectral responses of the instrument and singlet state lifetimes were measured by the single photon counting technique.

Results and discussion

Biphenyl shows intense fluorescence with maxima at 305 and 315 nm that has been attributed to the lowest (π, π^*) excited singlet state [5]. In water, 2,2'-bipyridyl shows a fluorescence spectrum sufficiently similar to that of biphenyl for the fluorescent state to be identified as being of (π, π^*) character. However, the fluorescence spectrum of biphenyl is not affected

TABLE 1
Photophysical data for biphenyl and 2,2'-bipyridyl

Compound	Solvent	ϕ_F	τ_s (ns)	τ_p (s)	τ_t (μ s)	$10^{-3} \times k_d/\epsilon$ ($M^{-1} s^{-1}$)
Biphenyl	Cyclohexane	0.18	16.0	4.25	90	—
	Ethanol	0.14	14.4	4.00	80	—
2,2'-Bipyridyl	Cyclohexane	0.005	<1	1.02	86	11.0
	Ethanol	0.009	2.0	0.95	78	8.0
	Water	0.018	7.1	0.95	75	7.2

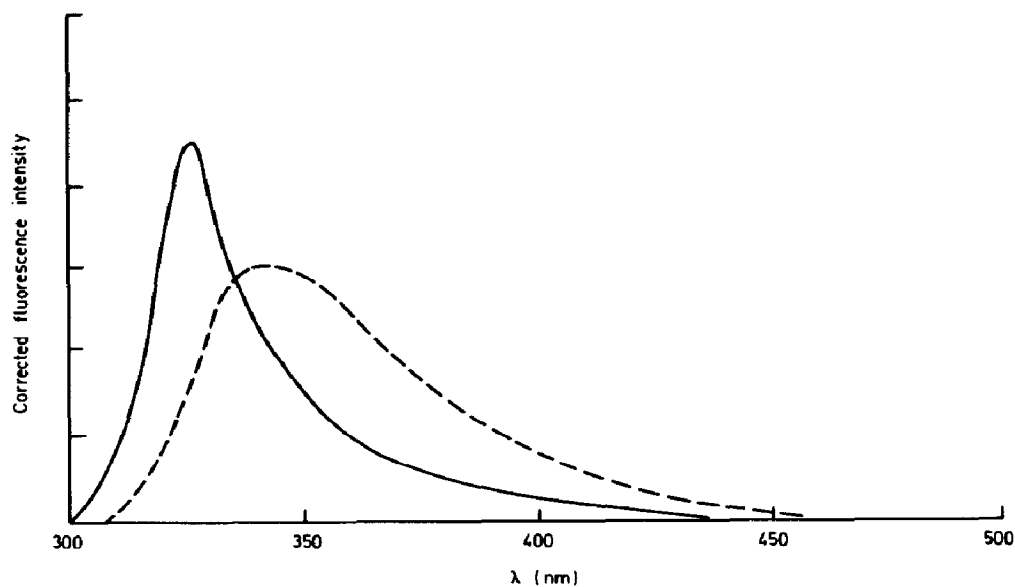


Figure 1. Fluorescence spectrum of 2,2'-bipyridyl in water (solid curve) and cyclohexane (broken curve).

by a change of solvent polarity whilst that of 2,2'-bipyridyl shows a marked dependence upon the nature of the solvent. Thus in non-polar solvents there is both a fairly large red shift and a loss of fine structure (Fig. 1) together with a substantial decrease in the fluorescence quantum yield ϕ_F and the singlet state lifetime τ_s (Table 1). These effects are characteristic of solvent-perturbed mixing of close lying (n, π^*) and (π, π^*) excited singlet states [6]. 2,2'-Bipyridyl shows intense phosphorescence at 77 K which was assigned to the (π, π^*) triplet state on account of the fairly long emission lifetime τ_p , the predominantly out-of-plane polarisation, the large external heavy atom effect and the small solvent shifts. It remains (π, π^*) when the solvent is changed from water to hydrocarbon so that the (n, π^*) triplet state must be situated at an energy which is too high to allow significant mixing with the phosphorescent state.

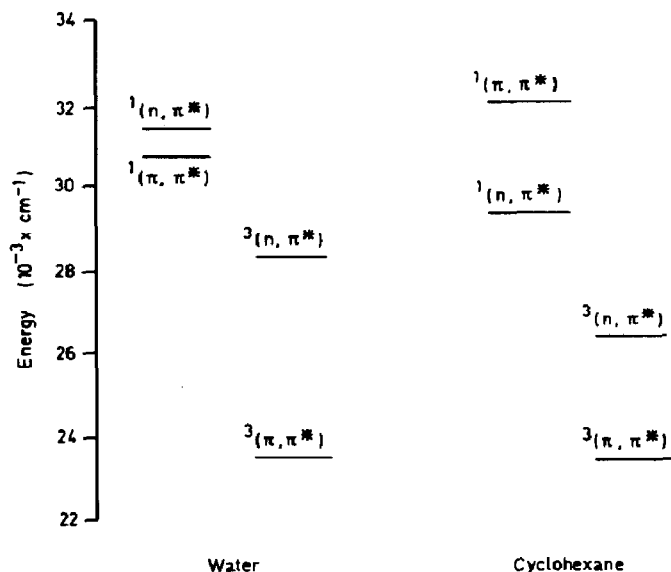


Fig. 2. Energy level diagram for the excited states of 2,2'-bipyridyl in water and cyclohexane.

Previous studies [7] have given an average (n, π^*) singlet-triplet splitting energy of about 3000 cm^{-1} for aza and diaza aromatic compounds and we assume that 2,2'-bipyridyl shows a similar value. Also, the energy of solvation of an (n, π^*) state by water is of the order of 2000 cm^{-1} [8]. An energy level diagram (Fig. 2) was constructed using these generalised values together with the luminescence data and shows that the triplet state remains (π, π^*) in all solvents. In hydrocarbon solvent the lowest singlet state is (n, π^*) so that weak fluorescence is observed. In water the lowest excited singlet state is (π, π^*) which is about 600 cm^{-1} below the (n, π^*) state. Since there is now an (n, π^*) triplet state positioned between the (π, π^*) singlet and triplet states, intersystem crossing is symmetry allowed and will be faster than with biphenyl. Hence the ϕ_F and τ_s values observed with 2,2'-bipyridyl are reduced considerably relative to those found with the parent hydrocarbon although in polar solvents the fluorescent state is (π, π^*) in both cases.

2,2'-Bipyridyl shows a strong triplet absorption spectrum with maxima at 355 and 370 nm. The triplet spectrum is identical to that of biphenyl [9], but with 2,2'-bipyridyl the flash spectroscopic records show the presence of a second longer lived species which has a similar spectrum to the triplet but which decays slowly with second order kinetics (Fig. 3). Triplet lifetimes τ_t and decay rate constants k_d/ϵ for the longer lived species are given in Table 1. In the presence of the triplet quenchers oxygen or penta-1,3-diene, the triplet absorption spectrum is not observed but the longer lived component remains unaffected. This latter species is formed within the flash duration rather than by a growing-in process so that it is formed from the singlet manifold. The longer lived component is observed in a range of dif-

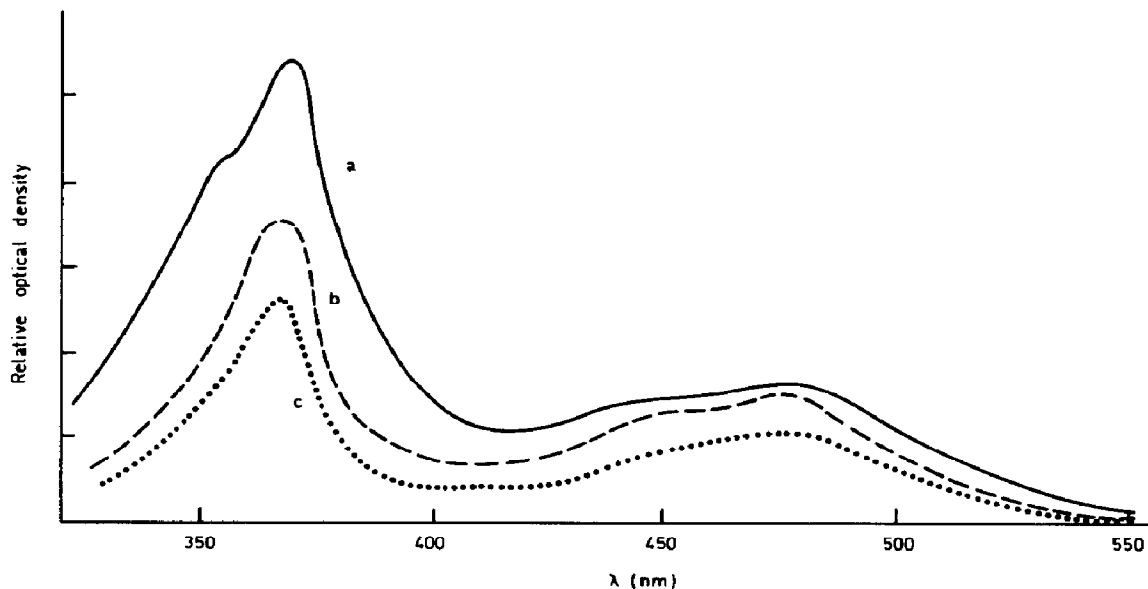
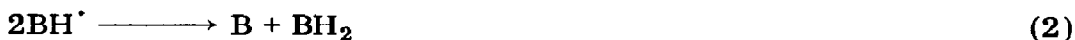


Fig. 3. Transient absorption spectrum obtained by flash spectroscopy for 2,2'-bipyridyl in cyclohexane; time delay (a) 15 μ s, (b) 200 μ s and (c) 2 ms.

ferent solvents but it is not found in perfluorocarbon solution suggesting that it is the radical BH^{\cdot} formed by hydrogen abstraction from the solvent:



In fact, steady state irradiation of 2,2'-bipyridyl in cyclohexane results in the formation of bicyclohexyl, whilst irradiation in tetrahydrofuran solution at 77 K within the cavity of an ESR spectrometer gives rise to a signal characteristic of an organic radical ($g = 2.0027$). The ESR signal is observed only at low temperature and decays rapidly when the excitation light is removed. In the flash photolysis records the radical decays by second order kinetics over at least three half-lives and probably involves either a disproportionation process



or a dimerisation process



Since the radical is formed by a singlet state reaction, it is tempting to propose that this is the (n, π^*) state. With carbonyl compounds it is well established that (n, π^*) excited states undergo efficient photoreduction whilst (π, π^*) states are relatively inert towards this type of reaction. Even in water, 2,2'-bipyridyl has an (n, π^*) singlet state positioned only about 600 cm^{-1} above the lowest energy (π, π^*) state, so that there will be a thermal population of the upper state of approximately 5% and inefficient radical formation does occur in aqueous solution.

In aqueous solution the radical BH^\cdot can participate in an acid-base equilibrium:



At a pH of 2 flash spectroscopy shows two overlapping long lived transient absorption bands. One band, with a maximum at 380 nm, is clearly the neutral radical BH^\cdot whilst the other band seems to be due to the protonated radical $\text{BH}_2^{\cdot+}$. The equilibrium can be followed by flash spectroscopy which gives a $\text{p}K$ of 4.2. Both BH^\cdot and $\text{BH}_2^{\cdot+}$ decay via a bimolecular process that leads to the formation of a faintly red coloured solution with absorption bands at 380, 495 and 510 nm. Several bipyridyl radical cations are known to form coloured dimers which have similar absorption spectra to those reported here. Thus, methyl viologen is reduced readily to the radical cation which undergoes dimerisation [10]. Also, N,N' -dimethyl-2,2'-bipyridyl bromide can be reduced with thiourea to give an unstable radical cation which decays to a dimer. Hence we tentatively propose that the preferred mode of decay for both $\text{BH}_2^{\cdot+}$ and BH^\cdot involves a dimerisation process.

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