^{13}C NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AND LIFETIME STUDIES OF THE SOLUTION PHOTOREACTIVITY OF 1,4-BIS(β-PYRIDYL-2-VINYL)BENZENE AND 2,5-DISTYRYLPYRAZINE

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Summary

The photoreactivity of 1,4-bis(β-pyridyl-2-vinyl)benzene and distyrylpyrazine has been investigated using lifetime, Shpol'skii and carbon-13 nuclear magnetic resonance (^{13}C NMR) techniques. Our study shows that long-lived emitting species exist in concentrated solutions indicating excited state aggregation that could lead to bimolecular processes in concentrated solutions. It is confirmed that the photoproducts do not emit in the spectral region studied by using the Shpol'skii technique.

^{13}C NMR has been performed only for concentrated solutions, revealing the formation of cis isomers in addition to the occurrence of the previously reported photochemical processes.

1. Introduction

The solution photoreactivity of 1,4-bis(β-pyridyl-2-vinyl)benzene (P2VB), 2,5-distyrylpyrazine (DSP) and some related diolefinic compounds has been investigated previously [1 - 4]. The discovery of the laser activity [5] of P2VB and DSP has led to an increase in activity towards a better understanding of their solution photoreactivity.

It is now known that the solution photoreactivity of P2VB and DSP is largely dependent upon the irradiation wavelength [1, 3, 4] and material concentration [6, 7].

Suzuki *et al.* [1] isolated the photoproduct obtained by prolonged (48 h) irradiation of concentrated (1.4×10^{-2} M in tetrahydrofuran) solutions of DSP ($\lambda_{ex} > 380$ nm) and P2VB ($\lambda_{ex} > 360$ nm). The photoproducts have been identified as photo-oligomers using molecular weight, ^{1}H NMR and UV-absorption methods. Such a remarkably long irradiation time, however, does not allow the various photochemical reaction stages and

processes previously revealed by kinetic studies [2, 4] to be adequately characterized.

In the present paper we report the lifetimes of the various emitting species formed in fresh and irradiated DSP and P2VB solutions of different concentrations. High resolution ^{13}C NMR and low temperature emission techniques have also been employed to identify the different photochemical products.

2. Experimental details

P2VB and DSP were prepared using the method of Hasegawa *et al.* [8]. The materials were purified as described previously [4].

Photo-irradiation was performed using a 200 W mercury arc combined with a cobalt glass filter with maximum transmission at 365 nm.

Low temperature emission measurements were carried out using the system that has been described in ref. 9. 10^{-6} M solutions in cyclohexane (AnalaR) were cooled to 77 K and gave quasi-linear emission (λ_{ex} = 365 nm).

Lifetime measurements were made using an Ortec single-photon counting device with a thyratron-gated spark lamp. A detailed description of the apparatus is given in ref. 10. Quartz cells of 1 mm path length were used to minimize reabsorption in the concentrated chloroform solutions (about 10^{-2} M).

^{13}C NMR spectra were recorded using a Bruker WM-200 Fourier transform NMR spectrometer. The following conditions were maintained: frequency used, 25.034 800 MHz; pulse width, 10 μs; repetition interval, 2 s; number of scans used, 25 000 at room temperature.

3. Results and discussion

3.1. Excited state lifetimes

Dilute chloroform solutions of DSP (about 10^{-5} M) give blue emission (λ_{ex} = 365 nm) but concentrated solutions (about 10^{-2} M) give greenish-blue emission. There is a significant shift in emission maxima owing to reabsorption in the concentrated solutions but excimer formation is also a possibility. Excimers have been detected in some other diolefinic compounds, *e.g.* diethyl *p*-phenylenediacrylate (*p*-PDAEt) [6] and *p*-phenylenediacrylic acid (*p*-PDA) [11]. The lifetimes of dilute and concentrated P2VB and DSP chloroform solutions are summarized in Table 1. In dilute DSP solutions a short-lived species with lifetime τ = 1.5 ± 0.2 ns is dominant both in fresh and in partially irradiated samples. In concentrated solutions, however, a longer-lived species with τ = 15 ± 1 ns having a significant weighting (about 30%) is observed. The longer-lived species is obviously due to excited state aggregation in concentrated solutions and is likely to undergo bimolecular photochemical reactions.

TABLE 1

Lifetime values of DSP and P2VB chloroform solutions (λ_{ex} = 365 nm)

Approximate concentration (M)	λ_{em} (nm)	Approximate weight percent	τ (ns)
DSP			
10^{-5}	440	100	1.4
10^{-5}	500	100	1.6
10^{-2}	450	70	1.6
10^{-2}	450	30	10.8
10^{-2}	520	70	1.6
10^{-2}	520	30	15.7
P2VB			
10^{-5}	410	100	0.6
10^{-3}	520	90	1.7
10^{-3}	520	10	12.5

The diolefinic homologue P2VB possesses similar properties. In dilute solutions a short-lived species with τ = 0.6 ± 0.1 ns is dominant whereas in concentrated solutions a longer-lived species with τ = 12.5 ns and about 10% weighting is detected.

Both short- and long-lived species contribute to the photochemical reactivity of DSP and P2VB and are believed to result in unimolecular and bimolecular processes such as photoisomerization and photo-oligomerization respectively.

The photoreactions of P2VB and DSP do not occur in frozen matrices. Thus irradiation of both P2VB and DSP in frozen ethanol (λ_{ex} = 365 nm) causes no virtual change in emission intensity. At 161 K the ethanol starts to melt, and there is a rapid decrease in emission intensity [12]. Figure 1(a) shows the typical behaviour of a 10^{-6} M ethanolic P2VB solution. This simple method could be used to determine the melting point of some matrices. The prohibited photoreactivity in frozen matrices indicates that the photoreaction is diffusion and/or rotation controlled.

The photoproducts do not emit (λ_{ex} = 365 nm) in the spectral range studied. This has been confirmed by applying the more sensitive Shpol'skii technique. The Shpol'skii spectrum of DSP in an *n*-tetradecane matrix at 4 K has been reported previously [13].

Similar spectra were obtained using a cyclohexane glass at 77 K as a Shpol'skii matrix for both DSP and P2VB. Figure 1(b) shows the Shpol'skii spectra of 10^{-6} M P2VB solutions in a cyclohexane glass at 77 K for fresh and irradiated (for 3 h at 300 K) samples. No new emission peaks appear and the main feature in the spectrum is the decrease in emission intensity owing to the consumption of P2VB trans–trans molecules.
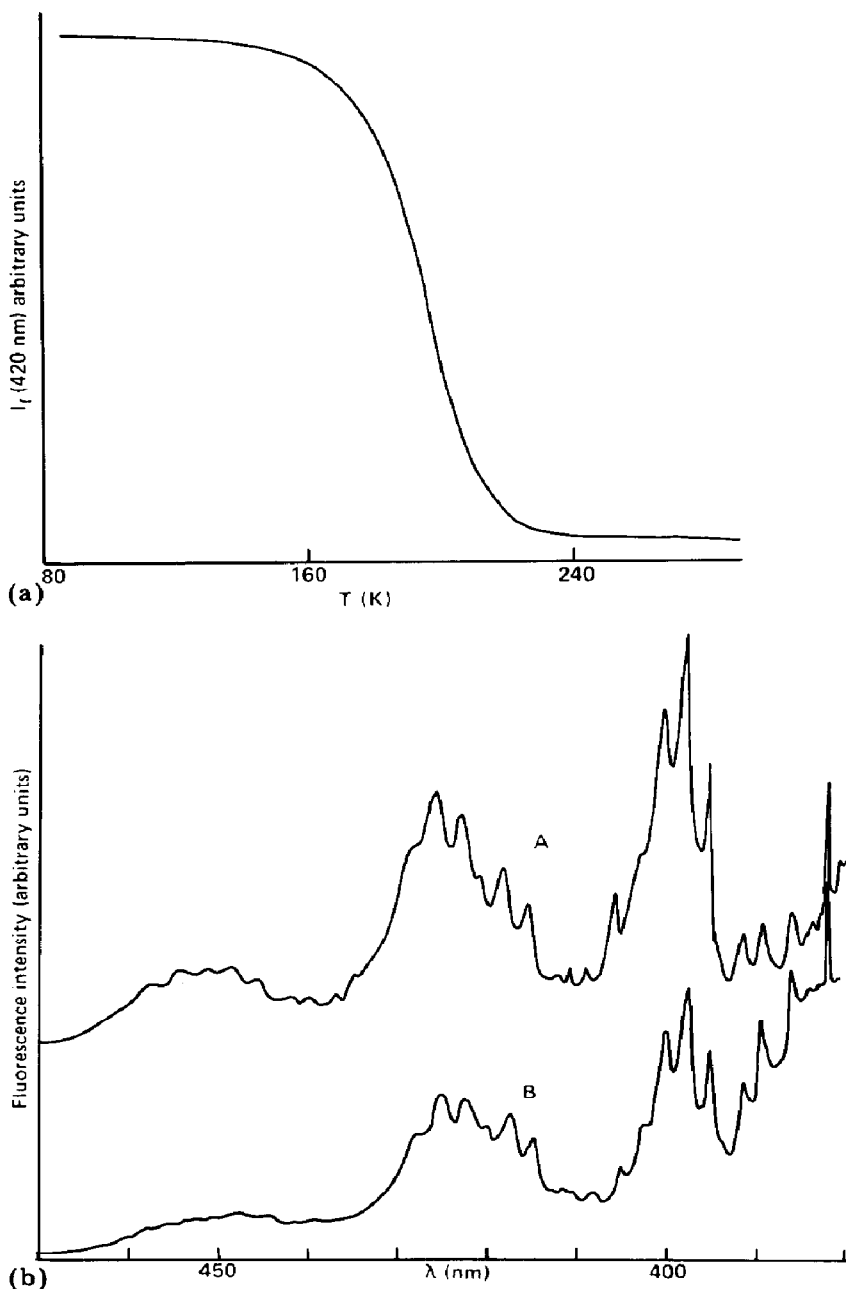
Fig. 1. (a) Changes in the emission maximum at 420 nm (λ_{ex} = 365 nm) of a 10^{-6} M ethanolic P2VB solution as a result of increasing the temperature. (b) Changes in the Shpol'skii spectrum of P2VB in cyclohexane at 77 K as a result of irradiation at 300 K for 3 h (λ_{ex} = 365 nm): curve A, fresh sample; curve B, irradiated sample.

3.2. ^{13}C NMR

Figure 2 shows the ^{13}C NMR spectra of saturated $CDCl_3$ solutions of DSP and P2VB before and after UV irradiation (λ_{ex} = 365 nm). The peaks at chemical shifts δ of 134.3 and 143.2 ppm are assigned to olefinic carbons

[14, 15]. Upon UV irradiation these peaks disappeared indicating the consumption of the olefinic bonds during the photochemical reaction. This supports the view that in concentrated solutions a four-centre-type addition occurs giving a higher molecular weight photoproduct. The resonance peaks at chemical shifts of 128.7, 127.1 and 124.0 ppm are assigned to the aromatic carbons [14] both in the pyrazine and in the phenyl moieties. These peaks clearly exist in both fresh and photo-irradiated samples.

In the ^{13}C NMR spectra of P2VB, the peaks at $\delta = 136.4$ and $\delta = 149.6$ ppm are assigned to olefinic carbons [14, 15]. Both peaks split upon UV irradiation giving peaks at 136.4, 136.6, 148.7 and 149.5 ppm, indicating a trans–cis isomerization around the olefinic double bonds [14]. There is a remarkable decrease in the heights of the peaks upon UV irradiation and a relatively weak set of peaks at $\delta = 45.3$, $\delta = 45.5$ and $\delta = 48.9$ ppm appears. This set of peaks is tentatively assigned to cyclobutane rings formed as a result of the addition of olefinic double bonds. A lot of peaks also ap-
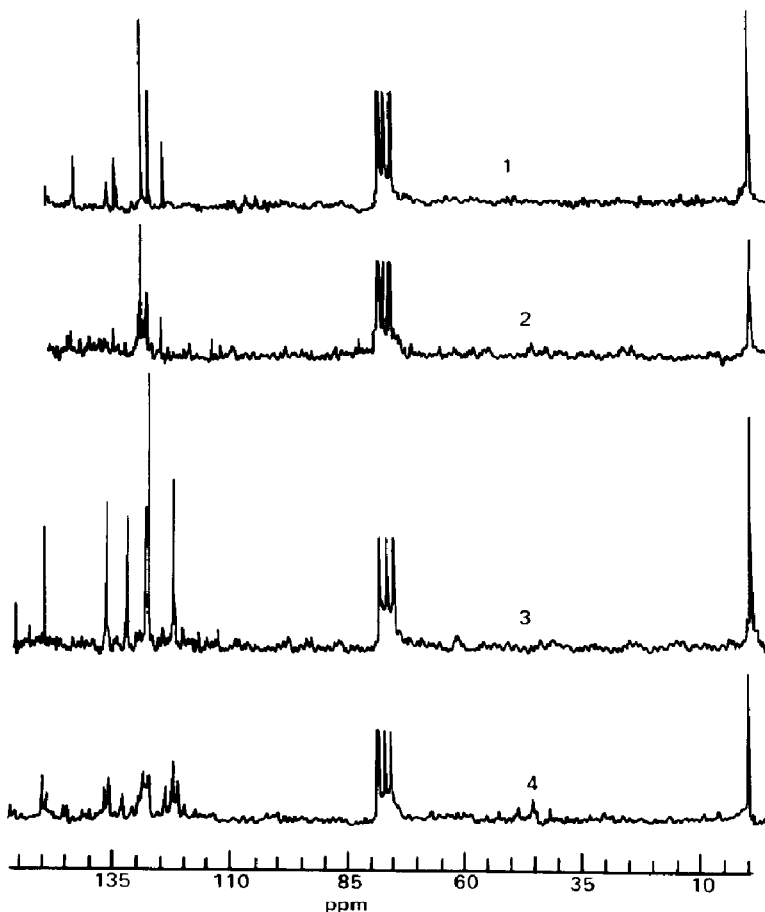

Fig. 2. ^{13}C NMR spectra: spectrum 1, fresh saturated DSP in $CDCl_3$; spectrum 2, DSP solution after irradiation for 2 h using 365 nm light; spectrum 3, fresh saturated P2VB in $CDCl_3$; spectrum 4, P2VB solution after irradiation for 2 h using 365 nm light.

peared in the region 120 - 140 ppm, indicating different anisotropic effects due to complicated topography.

4. General discussion and conclusion

Lifetime measurements reveal a relatively short excited state lifetime for both DSP (1.5 ns) and P2VB (0.6 ns) monomeric species. Any excited state association process must be diffusion limited and given that k_{diff} in chloroform is calculated as 1.84×10^{10} l mol^{-1} s^{-1} using the modified Debye equation [16], if excited state association is to compete with fluorescence decay, the critical material concentrations can be calculated as

$$[DSP]_c = \frac{[DSP]}{(1.84 \times 10^{10})(1.5 \times 10^{-9})} = 0.036 \text{ M}$$

and

$$[P2VB]_c = \frac{[P2VB]}{(1.84 \times 10^{10})(0.6 \times 10^{-9})} = 0.09 \text{ M}$$

The experimental concentrations that lead to excited state association, however, are lower than these values owing to solubility limitations and it is more likely that a ground state complex is formed. Since there is no significant change in the absorption spectra between dilute and concentrated DSP and P2VB solutions, the proposed ground state complex is thought to be of the loose type. The existence of a similar ground state complex has been proposed previously for p-PDAEt diolefin [6]. There is also a possibility of intersystem crossing (ISC) of a small fraction of singlet DSP and P2VB molecules to the first excited triplets which are capable of undergoing bimolecular reactions owing to their longer lifetime. The following scheme is proposed to account for the observed photophysical and photochemical processes in DSP and P2VB solutions.
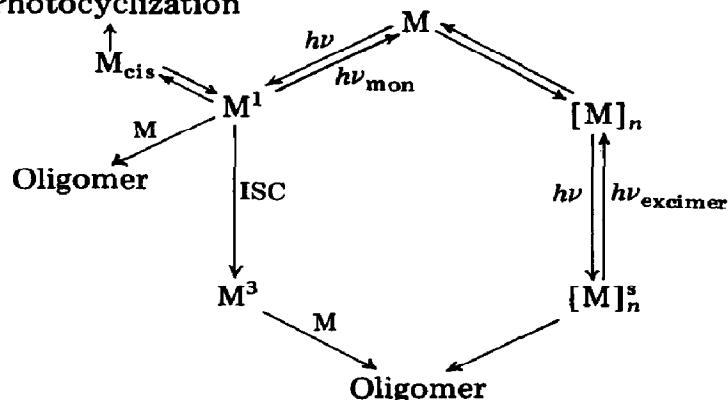
M, trans–trans monomer; M^1 and M^3, singlet and triplet excited molecules; M$_{cis}$, cis monomer; [M]$_n$, ground state aggregation; [M]$_n^s$, excited singlet state aggregation.

The resulting cis isomers are incapable of undergoing bimolecular photo-oligomerization and continued photoirradiation clearly causes a depletion of the trans isomer which undergoes the bimolecular photo-oligomerization reaction. This causes a shift in any established trans ⇌ cis equilibrium at the expense of the cis isomer. The photo-oligomer is thus obtained in a significant yield as reported previously (60% yield for DSP and 30% yield for P2VB in tetrahydrofuran solvent) [1].

It is more likely that both photoisomerization and photo-oligomerization proceed via a twisted configuration. The 90°-twisted form may represent the energy minimum. This is the case for simpler, non-conjugated, ethylene derivatives [17]. The cis isomers may also undergo photocyclization to phenanthrene-like structures.

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