EXCITED STATE REACTIVITY OF AZA-AROMATICS VIII: RELEVANCE OF THE EFFECTS OF PROTONATION, OXYGEN AND EXCITING WAVELENGTH ON FLUORESCENCE AND *trans → cis* PHOTOISOMERIZATION OF NAPHTHYLPYRIDYLETHYLENES IN AQUEOUS SOLUTION

G. BARTOCCI, G. FAVARO and G. G. ALOISI

Dipartimento di Chimica, Università di Perugia, 06100 Perugia (Italy)

Summary

The effects of pH, oxygen and exciting wavelength on the fluorescence and *trans → cis* photoisomerization of 1-(β-naphthyl),2-(4-pyridyl)-ethylene were investigated in aqueous solution. The results are compared with those obtained for the α isomer which is less sensitive to the experimental conditions.

The experimental findings are explained by assuming that the photoisomerization can proceed either from an excited singlet state (prevalent mechanism under high energy excitation) or from a triplet state (prevalent mechanism under low energy excitation); the fluorescent state is not involved in the photoreaction.

Spectroscopic evidence is provided for the existence of at least two conformers by low temperature measurements. The presence of these different conformations in solution can also explain the exciting wavelength effect.

1. Introduction

The physical properties and the reactivities of the excited states of naphthylpyridylethylenes have been the subject of previous studies [1 - 3]. Measurements of the fluorescence properties, such as quantum yields and lifetimes, have been performed for the six isomeric *trans*-1-naphthyl-2-pyridylethylenes (NPEs) in their basic and protonated forms [1]. The basicity in the first excited singlet state has been determined both by the Förster cycle and by fluorimetric titration. These studies have shown that NPEs exhibit similar fluorescence lifetimes (approximately 1 ns) but different fluorescence quantum yields in the basic and acidic forms and higher basicity in the excited state ($pK^* \approx 13$) than in the ground state ($pK \approx 5$). Relaxation times for the prototropic equilibrium

$$NPE^* + H_2O \; \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} \; NPEH^{+*} + OH^-$$
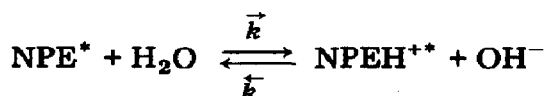
shorter than the mean lifetime of the excited state allow the equilibrium in the excited state to be established and lead to a fairly high percentage of protonated excited molecules in a pH range (approximately 8 - 11) where only the basic form is present in the ground state. This occurs to a greater extent for 1-(β-naphthyl),2-(4-pyridyl)-ethylene (β,4-NPE) than for the other isomers. For this reason β,4-NPE was chosen for studying the effect of pH on both the fluorescence quantum yields and the photoisomerization quantum yields, as previously carried out for 3-styrylpyridine (3-StP), with the aim of obtaining information on the excited state responsible for the isomerization [4, 5]. In parallel we also studied the α isomer (α,4-NPE), which has a longer relaxation time and therefore a lower equilibrium percentage.

Previous studies in non-polar organic solvents of direct and sensitized trans → cis photoisomerization of NPEs and of temperature and oxygen effects on the direct photoisomerization and the fluorescence have indicated that both singlet and triplet states are photoreactive, that the isomerization can occur in a state other than the fluorescent state and that internal conversion is not a negligible process [2].

The presence of a triplet pathway for β,4-NPE has also been shown by a study of the fluorescence and photoisomerization quenching by halides [3].

Further information on the photoreaction mechanism will be drawn from the results of this work.

2. Experimental

The compounds studied were trans-α,4-NPE and trans-β,4-NPE, prepared by standard methods for previous work [6]. Their purity was checked by gas chromatographic analysis; no trace of impurity was found.

Fluorescence and photoisomerization quantum yield measurements were carried out at room temperature (20 ± 2 °C). Fluorescence, absorption and fluorescence excitation spectra were also recorded at liquid nitrogen temperature using a Cary 17 spectrophotometer.

Fluorescence measurements were performed on a Hitachi Perkin—Elmer MPF-3 fluorescence spectrophotometer, equipped with an accessory for the spectrum correction using Rhodamine B as a quantum counter. For the determination of the fluorescence quantum yields ϕ_F, a solution of quinine sulphate in 0.1 N H_2SO_4 ($\phi_F = 0.55$ [7]) was used as the standard in the room temperature measurements and a solution of 9,10-diphenylanthracene in 3-methylpentane ($\phi_F = 1.0$ [8]) was used as the standard in the measurements at liquid nitrogen temperature. Refractive index corrections were made to adjust the quantum yield values for the various solvents used. The dependence of fluorescence on pH was followed in Britton buffer solu-

tions containing 10 vol.% ethanol. The ionic strength was kept constant (μ = 1) by adding Na_2SO_4 which has a negligible quenching power on the fluorescence. The solute concentrations were of the order of 10^{-6} M.

For the measurements of the *trans* → *cis* photoisomerization quantum yields ϕ_C, the solute concentrations were of the order of 10^{-5} M and the ethanol percentage was increased to 20 vol.% for solubility requirements. The study of the dependence of the photoisomerization quantum yields on pH was carried out in deaerated solution at an exciting wavelength of 336 nm. The ionic strength (μ = 1.6) was in this case buffered using $NaClO_4$.

The wavelength effect was followed in the presence and absence of oxygen. The excitation was performed using various wavelengths (290, 313, 336, 366 and 407 nm) isolated from a stabilized HBO 200 W high pressure mercury lamp by a Hilger–Watts D292 grating monochromator (reciprocal dispersion 66 Å mm^{-1}) or by Balzers interference filters (bandwidth at half-maximum of 10 nm). Deaerated and oxygen-saturated solutions were obtained by bubbling with pure nitrogen and oxygen respectively. The irradiations were carried out under conditions of total or partial absorption of the exciting light, using cells of path length 2, 4 and 10 cm, depending on the absorption coefficients of the NPEs at the exciting wavelength. Control experiments were performed to verify the absence of side reactions. The conversion percentages were held below 12% to avoid contribution from the *cis* → *trans* back reaction. The extent of the isomerization was measured by UV spectrophotometry in the region 300 - 360 nm, after suitable dilution, using a Unicam SP 500 spectrophotometer. Ferrioxalate actinometry [9] was used, monitoring the intensities of both the incident and the transmitted light when the absorption of the incident light was not complete.

The ϕ_C and ϕ_F values reported in the tables represent an averaged value of at least four independent runs. The mean deviation did not exceed 3% for the ϕ_C values and 5% for the ϕ_F values.

3. Results

3.1. pH effect

The trends with pH of the fluorescence I_F (λ = 510 nm) and of the *trans* → *cis* photoisomerization quantum yield ϕ_C for α,4-NPE and β,4-NPE are compared with the absorption trends in Fig. 1.

In the case of α,4-NPE the ϕ_C value appears to be independent of pH, because the reactivities of the neutral and cationic forms are almost the same. In contrast, the I_F curve shows two inflexion points which correspond to the ground state pK (5.2) and to the excited state pK^* (12.6) respectively. The percentage of molecules which attain the prototropic equilibrium in the excited state is 15% [1].

For β,4-NPE the trend of I_F with pH is qualitatively similar; the first inflexion point corresponds to the ground state pK (5.2) and the second to the excited state pK^* (13). The equilibrium percentage is 45% in this case
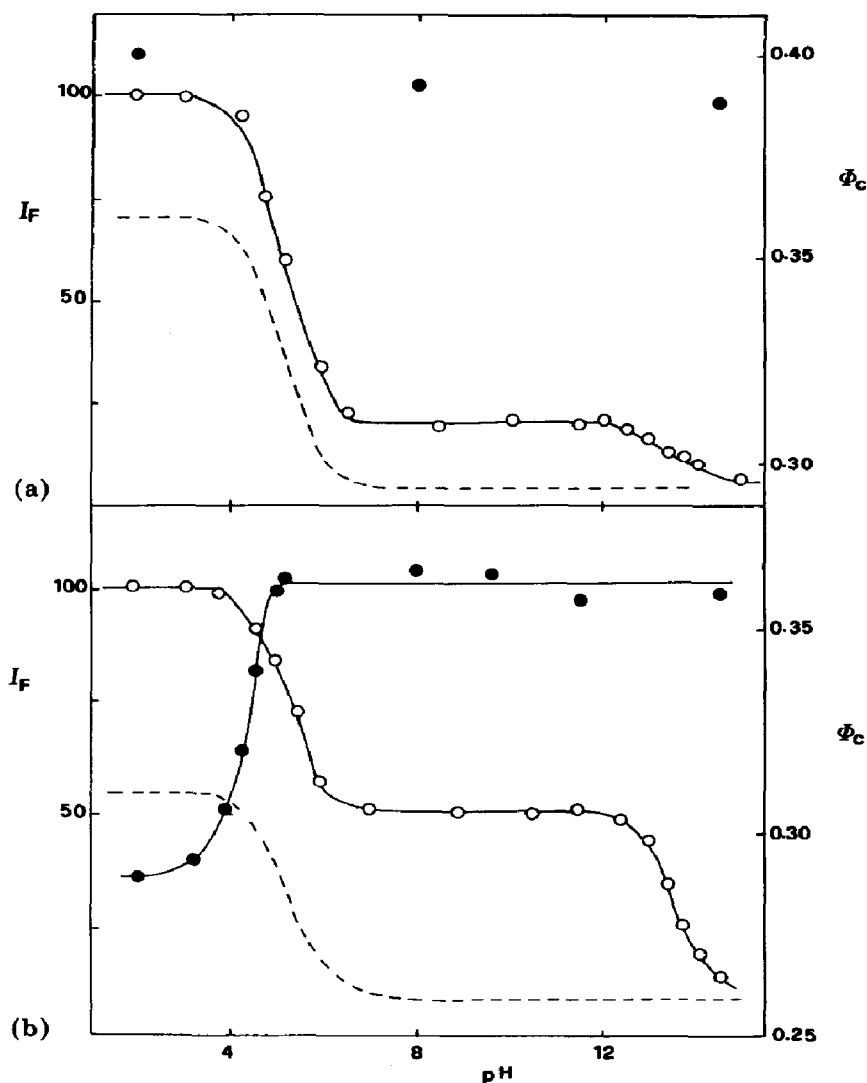
Fig. 1. The fluorescence intensity (○) and the photoisomerization quantum yield (●) for α,4-NPE (a) and β,4-NPE (b) as functions of pH. The broken lines represent the absorption trends.

[1]. The trend of ϕ_C with pH shows only one inflexion point which corresponds neither to the ground state pK nor to the excited state pK*, but is placed at about one pH unit (pH ≈ 4) below the ground state pK.

The behaviour of the NPEs therefore appears to be different from that of 3-StP, where the plots of both ϕ_C and ϕ_F versus pH exhibited two inflexion points (pK = 4.7; pK* = 12.5 [5]) and trends opposite to each other.

3.2. Oxygen effect

In order to examine the effect of oxygen, measurements of ϕ_C and ϕ_F were carried out for both compounds in deaerated ($\phi_{C,F}^{N_2}$), air-saturated ($\phi_{C,F}^{air}$) and oxygen-saturated ($\phi_{C,F}^{O_2}$) solutions.

From the results reported in Table 1, which were obtained by 336 nm light excitation, the ϕ_C and ϕ_F values of the α isomer appear to be almost not affected by oxygen. This can be explained in terms of a common excited state which is responsible for both reaction and fluorescence [2].

For the β isomer, however, the fluorescence is independent of oxygen whilst ϕ_C decreases for the basic form and increases for the protonated form with increasing oxygen concentration. The different behaviour of the fluorescence and reaction quantum yields with respect to the oxygen effect suggests that different excited states are likely to be responsible for fluorescence and isomerization.

3.3. Wavelength effect

With the aim of confirming this hypothesis, we determined whether there were any influences of the exciting wavelength on both the fluorescence and photoisomerization quantum yields for the β isomer. The results reported in Table 2 for the neutral and cationic forms show that an increase in the energy of the exciting light has an increasing effect on the ϕ_F values and a decreasing effect on the ϕ_C values. Special regard should be paid to the oxygen effect, which is relevant only under low energy exciting light and affects the ϕ_C values in opposite ways for the basic and acidic forms.

4. Discussion

In order to discuss these results we will take into account that, for the molecules under study, there are more excited states which can be involved in the photoisomerization mechanism.

Upon direct irradiation at the appropriate wavelengths a ground state NPE can be promoted to various electronically excited singlet states cor-

TABLE 1

Fluorescence and photoisomerization quantum yields of the neutral and cationic forms of α,4-NPE and β,4-NPE in deaerated, air-saturated and oxygen-saturated 80 vol.% water–20 vol.% ethanol solutions (exciting wavelength, 336 nm)

Compound	$\phi_F^{N_2}$	ϕ_F^{air}	$\phi_F^{O_2}$	$\phi_C^{N_2}$	ϕ_C^{air}	$\phi_C^{O_2}$
α,4-NPE	0.020	0.020	0.020	0.38	0.39	0.39
α,4-NPEH$^+$	0.037	0.037	0.037	0.40	0.40	0.40
β,4-NPE	0.068	0.068	0.068	0.36	0.32	0.26
β,4-NPEH$^+$	0.20	0.20	0.20	0.29	0.39	0.44

TABLE 2

Exciting wavelength effect on fluorescence and photoisomerization quantum yields for β,4-NPE in neutral (pH 14.2) and cationic (pH 2) forms in deaerated, air-saturated and oxygen-saturated 80 vol.% water–20 vol.% ethanol solutions

	Exciting wavelength (nm)				
	290	313	336	366	407
pH 14.2					
ϕ_F	0.11	0.090	0.068	0.053	
$\phi_C^{N_2}$	0.19	0.24	0.36	0.39	
ϕ_C^{air}	0.16	0.24	0.32	0.30	
$\phi_C^{O_2}$	0.17	0.23	0.26	0.31	
pH 2					
ϕ_F	0.25	0.26	0.20		0.18
$\phi_C^{N_2}$	0.18	0.26	0.29		0.28
ϕ_C^{air}	0.18	0.26	0.30		0.28
$\phi_C^{O_2}$	0.18	0.27	0.44		0.27

responding to stilbenic, pyridinic and naphthalenic excitation. The spectral assignments of these transitions were tentatively made using low temperature spectra (77 K) of β,4-NPE and of the parent hydrocarbon β-styrylnaphthalene (β,StN). The spectral position and the structure of the vibrational bands indicate the presence of the benzenic ($\lambda \approx 280$ nm, $\Delta\bar{\nu} = 1190$ cm^{-1}), stilbenic ($\lambda \approx 312$ nm, $\Delta\bar{\nu} = 1470$ cm^{-1}) and naphthalenic ($\lambda \approx 350$ nm, $\Delta\bar{\nu} = 560$ cm^{-1}) transitions[†] and a naphthalenic character in the emission spectrum of β,StN.

The low temperature fluorescence spectrum of β,4-NPE exhibits similar features. In the absorption spectrum the same absorption regions are well recognizable. There is no direct evidence of pyridinic π,π^* or n,π^* transitions, even though a marked broadening of the stilbenic band could indicate an overlapping of various transitions.

The presence of low-lying n,π^* states can play two important roles in the deactivation of the excited molecule, either (1) offering an alternative pathway to radiationless deactivation by internal conversion to the ground state or (2) promoting the intersystem crossing to the triplet. Even though it was impossible to study the sensitized reaction in aqueous solution, because of the low solubility of these compounds in water, the results obtained in benzene show that the isomerization can efficiently occur in the triplet state [2].

[†]The literature values are $\lambda \approx 240$ - 260 nm, $\Delta\bar{\nu} = 925$ cm^{-1} for benzene [10], $\lambda \approx 300$ nm, $\Delta\bar{\nu} = 1600$ cm^{-1} for stilbene [11] and $\lambda \approx 290$ - 320 nm, $\Delta\bar{\nu} = 428$ cm^{-1} for the lowest singlet transition of naphthalene [12].

The results of this work, as a whole, indicate that there is no possible relation (coupling or competition) between emission and photoreaction for the β isomer. Therefore it seems likely not only that the fluorescent and photoreactive states are different, but also that their population proceeds through different channels.

From a comparison of the spectral information with the photochemical data, it can be suggested that the naphthalenic fluorescent state is not implied in the reaction mechanism, whilst stilbenic and pyridinic excitations can be responsible for the isomerization.

Also on the basis of previous work [2, 3] we can assume that, for this class of molecules, the *trans* → *cis* photoisomerization proceeds, at least partially, through a triplet state, even when the n,π^* states are absent, since it occurs for the parent hydrocarbons α,StN and β,StN. Since the inter-system crossing (ISC) rate parameter is lower than the fluorescence rate parameter for the hydrocarbons [13], high ϕ_F and low ϕ_C values were found in n-hexane ($\phi_F = 0.69$ (α) and 0.74 (β); $\phi_C = 0.16$ (α) and 0.13 (β) [14]). In the same solvent α,NPE and β,NPE have higher ϕ_C values and lower ϕ_F values [2]. In aqueous solution the situation is quite similar, even though a greater radiationless deactivation route should be present since a further decrease in ϕ_F is not balanced by higher ϕ_C values. A greater contribution of triplet mechanism to the photoreaction should therefore be expected for the NPEs, whilst the lowest singlet should not contribute to the reaction. Experimental evidences are the following: (1) lower ϕ_F values for the NPEs than for the StNs were found in a rigid medium, (2) the curves of ϕ_F and ϕ_C *versus* pH exhibit different trends and (3) the fluorescence of β,4-NPE is unaffected by oxygen, in contrast with the behaviour of the reaction quantum yield.

(1) Fluorescence quantum yields in 3-methylpentane at 77 K are 0.77 and 0.62 for β,StN and β,4-NPE respectively. Because of the large S_1–S_0 energy gap in the planar form, the $S_1 \rightarrow S_0$ internal conversion is negligible [7]. Moreover, because the rotation is hindered ($\phi_C = 0$) in the rigid matrix at liquid nitrogen temperature, $\phi_{ISC} = 1 - \phi_F$. It can be concluded that a larger fraction of molecules reaches the triplet state for β,4-NPE than for β,StN.

(2) The observed trends of ϕ_F and ϕ_C with pH show that the measured pK^* refers to an excited state which is not the reactive state. The inflexion point observed in the ϕ_C curve of β,4-NPE could be due to the triplet state pK^* or, probably, to an overlapping of ground and triplet state pKs. A smaller difference between ground and triplet state pKs than between ground and excited singlet state pKs is not unusual for the nitrogen heterocycles, because of a greater contribution of polar structures with a negative charge on the heteroatom in the excited singlet state than of those in the triplet state [15].

(3) The interaction of oxygen with an excited state molecule should be efficient only when the lifetime of that state is relatively long. This is the case for the singlet state of β,4-NPE in n-hexane ($\tau = 8.5$ ns [2]) in which the oxygen is also more soluble than in water, but not in aqueous solution ($\tau = 0.9$ ns [1]) where the fluorescence is unaffected by oxygen, at least up to

the saturation concentration. Considering the solubility of oxygen in aqueous–ethanol solutions (approximately 10^{-3} M [16]), only excited states with a lifetime longer than 10^{-8} s could be quenched by oxygen. Therefore an oxygen effect, if any, could affect only the triplet state. For β,4-NPE in alkaline solution, quenching of ϕ_C by oxygen is observed when the excitation is performed in the high wavelength region (see Table 2). For β,4-NPEH$^+$ the situation is even more peculiar since the effect of oxygen, which enhances the ϕ_C value, operates only in a restricted wavelength range; above and below this range the ϕ_C value can be considered to be constant with increasing oxygen concentration. With regard to this exciting wavelength effect on the β derivative, we believe that, under excitation by high energy light, the reaction mainly proceeds through a common twisted singlet intermediate, the precursor of which is the directly excited stilbenic state, as proposed by Orlandi and Siebrand [17] for stilbene. Under such conditions the contribution of the triplet to the photoreaction is small and, therefore, no oxygen effect can be observed on ϕ_C. By decreasing the energy of the exciting light a different reaction pathway prevails, probably implying the pyridinic n,π^* states which favour intersystem crossing to the reactive triplet. Therefore the photoreaction quantum yield increases and the oxygen effect becomes relevant. A reliable interpretation of the opposite oxygen effects on the neutral and cationic species can be proposed by considering that oxygen can affect the $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ processes to different extents. For the neutral form the interaction with oxygen favours $T_1 \rightarrow S_0$ intersystem crossing which lowers the yield of the triplet reaction. However, for β,4-NPEH$^+$ oxygen increases the isomerization yield by induced $S_1 \rightarrow T_1$ intersystem crossing; this effect is similar to that produced on the same molecule by inorganic anions [3].

A further contribution to the understanding of the photoreaction mechanism, which can be considered either as an additional or as an alternative hypothesis, comes from the assumption that two conformational isomers can exist in solution, as this has often been found for similar molecules [18, 19]. Even though no direct evidence for conformers can be drawn from the comparison of the absorption and fluorescence excitation spectra at room temperature, the existence of distinct conformations can be inferred from low temperature spectra. This experimental result refers only to the neutral form of β,4-NPE because of the difficulty of obtaining the acidic form in a transparent glassy solvent. In Fig. 2 the fluorescence spectra in 3-methylpentane at 77 K, obtained by exciting at two different wavelengths (λ_{exct} = 281 and 339 nm), are reported together with the emission excitation spectra (λ_{em} = 380 and 450 nm) and the absorption spectrum. Even though the fluorescence emissions are rather similar, but not identical, to each other, a clear-cut difference appears in the absorption and emission excitation spectra. Similar features, even though less marked, were also observed in a polar matrix (ether–isopentane–ethanol). The differences observed at low temperature cannot be appreciated at room temperature because of the broadness of the spectra. However, no change in the position of the conformational equilibrium
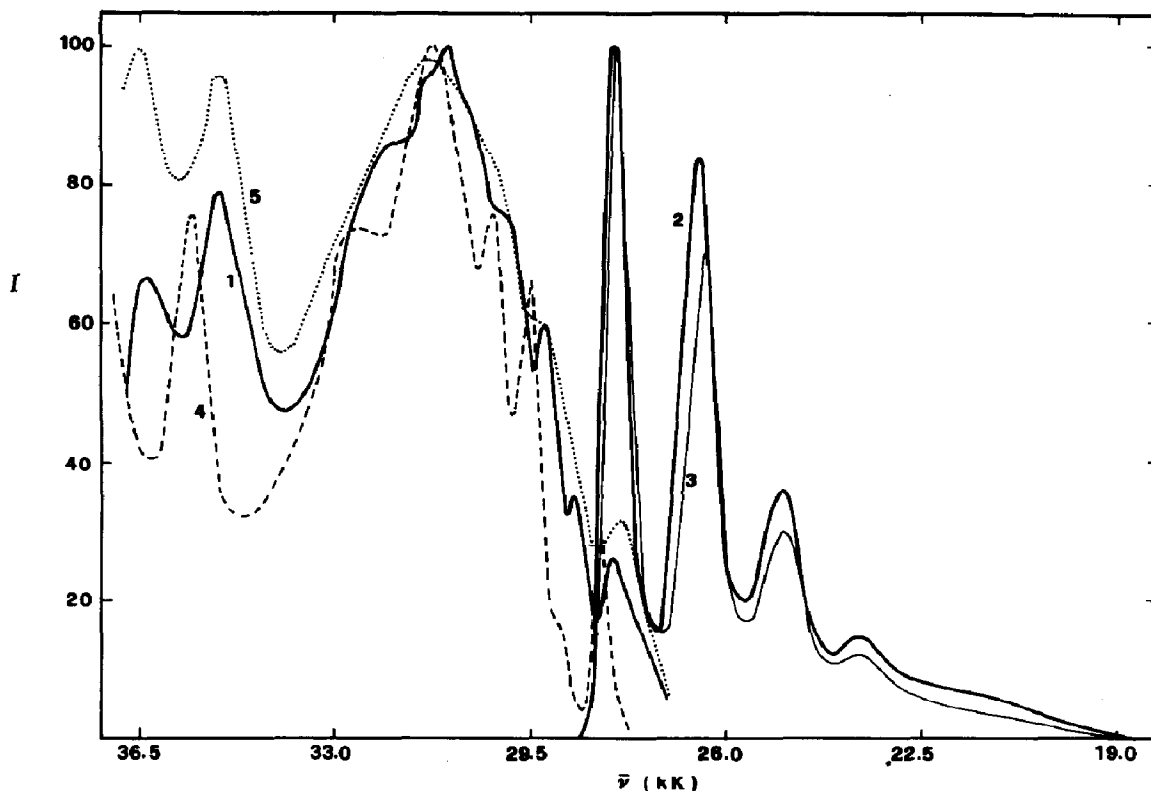
Fig. 2. Absorption and corrected emission spectra of β,4-NPE in 3-methylpentane at 77 K, normalized to the maximum. Absorption: curve 1; fluorescence emission: curve 2 (λ_{exct} = 281 nm), curve 3 (λ_{exct} = 339 nm); fluorescence excitation: curve 4 (λ_{em} = 380 nm), curve 5 (λ_{em} = 450 nm).

should occur on sudden cooling to 77 K of the room temperature solutions. Since excitation is spread over both conformers, variations in relative absorbance of the conformers and different deactivation routes of the excited states can satisfactorily explain the dependence on the exciting wavelength of the ϕ_F and ϕ_C values.

Further work is in progress with the aim of giving a complete characterization of the conformers by exploring the effects of solvent polarity and temperature on the conformational equilibrium.

Acknowledgment

References

1 G. Favaro, F. Masetti, U. Mazzucato and P. Bortolus, *J. Phys. Chem.*, **79** (1975) 2785.
2 P. Bortolus, F. Masetti and G. Galiazzo, *J. Photochem.*, **5** (1976) 479.

3 G. Bartocci, U. Mazzucato and G. Favaro, *J. Photochem.*, *11* (1979) 79.
4 G. Favaro, U. Mazzucato and F. Masetti, *J. Phys. Chem.*, 77 (1973) 601.
5 G. Bartocci, P. Bortolus and U. Mazzucato, *J. Phys. Chem.*, 77 (1973) 605.
6 G. Galiazzo, P. Bortolus and F. Masetti, *J. Chem. Soc., Perkin Trans. II*, (1975) 1712.
7 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970.
8 W. W. Mantulin and J. R. Huber, *Photochem. Photobiol.*, *17* (1973) 139.
9 G. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, *235* (1956) 18.
10 G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. 3, Van Nostrand, New York, 1966, p. 555.
11 R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, *16* (1962) 2326.
12 H. McConnell and D. S. McClure, *J. Chem. Phys.*, *21* (1953) 1296.
13 J. B. Birks, *Chem. Phys. Lett.*, *38* (1976) 437.
14 P. Bortolus and G. Galiazzo, *J. Photochem.*, *2* (1973) 361.
15 G. Jackson and G. Porter, *Proc. R. Soc. London, Ser. A*, *260* (1961) 13.
16 R. W. Cargill, *J. Chem. Soc., Faraday Trans. I*, *72* (1976) 2296.
17 G. Orlandi and W. Siebrand, *Chem. Phys. Lett.*, *30* (1975) 352.
18 E. Haas, G. Fischer and E. Fischer, *J. Phys. Chem.*, *82* (1978) 1638.
19 Yu. B. Scheek, N. P. Kovalenko and M. V. Alfimov, *J. Lumin.*, *15* (1977) 157.