Synthesis, Electronic Spectra, and Photoisomerization of Naphthylpyridylethylenes

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The synthesis and spectral characterization of the isomeric naphthylpyridylethylenes (NPEs) are reported. It can be deduced from the u.v. spectra that the 2-pyridyl compounds display a smaller deviation from planarity than the other isomers. *trans*-NPEs have higher photoreactivity and give a lower yield of radiative deactivation than the parent hydrocarbons. The differences are particularly remarkable for the 2- and 4-pyridyl isomers. These differences are tentatively explained on the basis of variable involvement of n,π^* states in the deactivation pathways of excited NPEs.

For some years we have been interested in the photophysical and photochemical properties of aza-analogues of stilbenes. Fluorescence,[1] *cis–trans*-photoisomerization (direct and sensitized by triplet energy donors [2]), photocyclization,[3] and excited state acid–base equilibria [4] have been extensively investigated, in particular for the three isomeric styrylpyridines (STPs). These molecules display photochemical behaviour noticeably different from that of stilbene, probably due to the involvement of n,π^* states in the deactivating pathways of the excited molecules. In the absence of triplet donor sensitizers, geometric interconversion seems to occur mainly in the singlet manifold even though no definitive conclusions can be reached.[2]

To obtain further insight on the mechanism of *cis–trans*-photoisomerization, Hammond [5] studied the photochemistry of β-styrylnaphthalene (β-STN). This study was at first extended by us to α-STN and its 4′-Cl and 4′-Br derivatives.[6] The triplet state seems responsible for the direct isomerization of these compounds.[6,7]

We have extended our investigation to the photochemical and photophysical behaviour of the aza-analogues of STNs, the twelve isomeric naphthylpyridylethylenes (NPEs) to obtain insight on the role played by the n,π^* states introduced by the heterocyclic nitrogen on the radiative and radiationless deactivation of the excited STNs.

In this paper the synthesis, absorption, and fluorescence spectra of the isomeric NPEs are reported. Preliminary results of the study of the luminescence and photoisomerization quantum yields are also reported.

EXPERIMENTAL

The 2- and 4-pyridyl isomers were prepared by Shaw condensation [8] of α- (or β-)naphthaldehyde and 2- (or 4-)picoline. The 3-pyridyl isomers were prepared by decarboxylation of the corresponding pyridylnaphthylacrylic acid obtained by Perkin condensation of α- (or β-)naphthaldehyde with sodium salts of pyridine-3-acetic acid. This is necessary because the charge density is greater in the *meta*- than in the *ortho*- and *para*-positions of the pyridine ring making proton detachment from the reactive methyl group too difficult.

We report, as an example of the two procedures followed, the preparation of α-naphthyl-2-pyridyl-(α,2-NPE) and β-naphthyl-3-pyridyl-(β,3-NPE)ethylene.

Preparation of α-Naphthyl-2-pyridylethylene.—α-Naphthaldehyde (15.6 g, 0.1 mol) and of 2-picoline (9.5 g, 0.1 mol) in acetic anhydride (72 g, 0.7 mol) were refluxed for 48 h. The reaction mixture was then treated with twice the volume of water to hydrolyse the excess of acetic anhydride, neutralized with NaOH, and extracted with $CHCl_3$ (100 ml, in three portions). The extracts were shaken with an aqueous saturated solution of sodium hydrogen sulphite in order to remove unchanged aldehyde and the chloroform solution was then dried over K_2CO_3 and distilled. After the removal of chloroform, the residue was distilled under reduced pressure (0.5 mmHg) and the distillate was purified by column chromatography on alumina using the eluotropic series: light petroleum, light petroleum–benzene, benzene. The *cis*-form is eluted first.

Preparation of β-Naphthyl-3-pyridylethylene.—Sodium pyridine-3-acetate (15.9 g, 0.1 mol) (prepared by neutralizing pyridine-3-acetic acid dissolved in EtOH with NaOH) and β-naphthaldehyde (15.6 g, 0.1 mol) in acetic anhydride (72 g, 0.7 mol) were refluxed for 48 h. The mixture was treated with an excess of water to hydrolyse the excess of acetic anhydride and left for three days. The precipitate was filtered, washed with a small quantity of cold water, and dried on P_2O_5. It consisted of pure 2-(3-pyridyl)-3-(β-naphthyl)acrylic acid which could be decarboxylated to the corresponding naphthylpyridylethylene by heating in boiling quinoline in the presence of copper chromite as catalyst.[9] The filtrate was neutralized with NaOH and extracted with $CHCl_3$, the extracts were shaken with an aqueous saturated solution of sodium hydrogen sulphite to remove unchanged aldehyde, and the chloroform solution was dried over K_2CO_3 and distilled. After the removal of chloroform, the residue was distilled under reduced pressure (0.5 mmHg) and the distillate, consisting of a mixture of *trans*- and *cis*-isomers, was purified by column chromatography.

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As may be seen from the data in Table 1, in the case of the synthesis of α,4-NPE and β,2-NPE, only traces of the *cis*-isomers could be isolated. In these cases, the *cis*-isomers were obtained by photochemical isomerization of the *trans*-compounds by the following procedure. *trans*-Isomer (1 g) was dissolved in benzene (3 l) and irradiated for 12 h at 15° with an immersion high pressure mercury lamp (Hanovia; 1 200/PL 357) whose emission was filtered through Pyrex. After the removal of benzene by distillation under reduced pressure, the residue, consisting of a *trans–cis*-mixture containing *ca.* 80% of *cis*-isomer, was purified by column chromatography following the procedure previously described.

TABLE 1

Physical and analytical data for NPEs

Compound	M.p. (°C)	Yield [a] (%)	Found (%) [b] C	H	N
α,2-NPE *trans*	39—40	54	87.9	5.75	5.9
cis	Liquid	6	88.1	5.7	5.9
α,3-NPE *trans*	Liquid	16	87.25	5.8	6.25
cis	Liquid	24	88.2	5.5	6.0
α,4-NPE *trans*	82—83	78	87.8	5.6	5.85
cis	Liquid	Trace	88.1	5.5	6.0
β,2-NPE *trans*	123—124	40	88.45	5.7	6.05
cis	Liquid	Trace	87.9	5.5	6.1
β,3-NPE *trans*	118—119	12	88.15	5.75	6.2
cis	Liquid	18	88.0	5.75	6.05
β,4-NPE *trans*	158—160	36	88.25	5.75	6.0
cis	Liquid	4	88.0	5.4	6.2

[a] Data for α,3- and β,3-NPE refer to the products isolated from the reaction mixture (see Experimental section). [b] $C_{17}H_{13}N$ requires C, 88.3; H, 5.65; N, 6.05%.

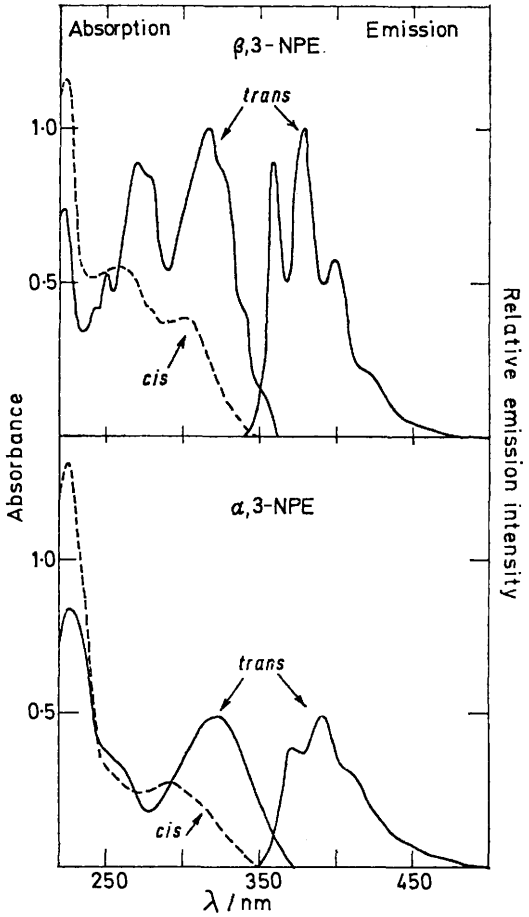
Elemental analysis, yields, and m.p.s (determined on a Kofler hot stage apparatus) of the NPEs are collected in Table 1. Their purity was checked by t.l.c. and g.l.c. analysis; no detectable impurity was found in the *trans*-isomers, while *cis*-isomers contain a small quantity ($\leqslant 1\%$) of the *trans*-isomer. The attribution of *cis*- or *trans*-configuration was made on the basis of u.v. and i.r. absorption spectra, in particular the absence of the 965 cm^{-1} band in the *cis*-isomers (out of plane deformation of ethylene CH).

Spectral and Quantum Yield Measurements.—The absorption spectra were measured using single-beam Unicam SP 500/2 and double beam Perkin-Elmer 356 spectrophotometers. Fluorescence spectra were obtained by a Perkin-Elmer MPF-3 spectrofluorimeter with an accessory for spectra correction using Rhodamine B as a quantum counter. Fluorescence quantum yields in deaerated n-hexane (Carlo Erba RS spectrophotometric grade) were obtained relative to 2-(1-naphthyl)-5-phenyl-1,3,4-oxadiazole(α-NPD) in cyclohexane (ϕ_f 0.58 [10]). Refractive index corrections were made to adjust for the different solvents used.

The photoisomerization quantum yields were determined by an irradiation system which uses a xenon XBO 150 W stabilized lamp coupled with a narrow band Balzers interference filter peaked at 310 nm. Irradiations were performed in solutions deaerated by bubbling pure nitrogen under conditions of total absorption of the incident light (c_{NPE} 2.10^{-4}M). After suitable dilution, the conversion percentages (never exceeding 10%) were determined by u.v. spectrophotometry in the region 310—350 nm. Preliminary control experiments showed the absence of any important side photoreactions under our experimental conditions: in all cases, good *cis–trans*-isosbestic points were obtained up to more than 50% conversion. Ferrioxalate actinometry was used to monitor the intensity of the exciting light.[11]

RESULTS AND DISCUSSION

The Figure shows the absorption and fluorescence spectra of *trans*- and *cis*-forms of α,3-NPE and β,3-NPE. The u.v. spectral data of STNs and NPEs are collected in Table 2.



Absorption spectra of *cis*- and *trans*-α,3 and -β,3-NPE in n-hexane (c 3 × 10^{-5}M). Corrected fluorescence spectra of *trans*-isomers, normalized to corresponding absorption long wavelength bands

The u.v. absorption spectra of NPEs closely resemble those of the corresponding hydrocarbons indicating the basic π,π^* nature of the transitions involved. This nature is also confirmed by the high intensity of the bands and by their red shift in polar solvent.[12] No signs of n,π^* transitions were found in the spectra of any compound as they are probably buried in the high intensity π,π^* bands.

The spectra of *trans*-styrylnaphthalenes have been extensively discussed by Wettermark *et al.*[13] on the basis of Pariser–Parr–Pople computations. The first (320—325 nm) and the second (265—280 nm) maxima have

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[10] J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley, London, 1970, p. 136.

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[12] F. Masetti, P. Bortolus, and G. Galiazzo, to be published.

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been associated, respectively, with the *p* and β bands (in Clar's notation [14]) of the aromatic hydrocarbons. On the basis of the absence of the vibrational fine structure and of a reduction of the intensity of the longest wavelength band, Wettermark concluded that α-STN shows a deviation from planarity due to steric interference of the *peri*-hydrogen in the naphthyl group with the hydrogen of the ethylene double bond.[13] On the basis of similar interference, the differences in the spectrum of α- and β-phenylnaphthalenes were also explained.[15]

TABLE 2

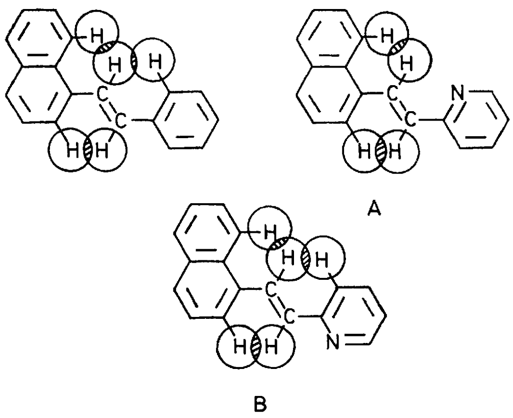
U.v. spectral data of STNs and NPEs in n-hexane

Compound		$\lambda_{max.}$/nm (log ε/dm^3 mol^{-1} cm^{-1})
α-STN	*trans*	231 (4.525), 260,[a] 267 (4.165), 320 (4.310)
	cis	260,[a] 300 (4.000)
α,2-NPE	*trans*	232 (4.495), 250,[a] 329 (4.360)
	cis	224 (4.675), 290 (3.985)
α,3-NPE	*trans*	227 (4.450), 255,[a] 322 (4,218)
	cis	225 (4.640), 289 (3.960)
α,4-NPE	*trans*	229 (4.510), 250,[a] 324 (4.270)
	cis	225 (4.630), 290 (3.950)
β-STN	*trans*	225 (4.420), 238,[a] 251 (4.175), 271 (4.475), 280 (4.500), 304,[a] 316 (4.590), 330 (4.460), 350[a]
	cis	225 (4.675), 245 (4.285), 265 (4.255), 300 (4.135)
β,2-NPE	*trans*	222 (4.380), 242,[a] 250 (4.260), 262,[a] 271 (4.470), 280 (4.350), 294,[a] 310,[a] 324 (4.560), 340,[a] 354 (3.860)
	cis	223 (4.655), 248,[a] 267 (4.190), 304 (4.130)
β,3-NPE	*trans*	223 (4.392), 242,[a] 250 (4.234), 270 (4.473), 278,[a] 316 (4.522), 328,[a] 340,[a] 352[a]
	cis	223 (4.585), 256 (4.270), 280,[a] 300 (4.100)
β,4-NPE	*trans*	223 (4.420), 238,[a] 250 (4.205), 261,[a] 270 (4.485), 280 (4.525), 305,[a] 316 (4.585), 328,[a] 348,[a] 354,[a]
	cis	224 (4.765), 250,[a] 269 (4.020), 278,[a] 291 (3.920), 304 (3.882)

[a] Inflections.

Given the similarity of the absorption spectra of *trans*-NPEs and STNs, the attribution of the bands proposed by Wettermark for the spectra of styrylnaphthalenes also seems reliable for the bands of NPEs.

It is noteworthy that the longest wavelength band of α,2-NPE is bathochromically shifted with respect to that of the corresponding hydrocarbon and that its absorption coefficients are higher. This should reflect a minor deviation from planarity of the NPE with respect to the corresponding hydrocarbon.[16] The less hindered planar conformations of *trans*-α-STN [13] and α,2-NPE are shown in the Scheme. The greater planarity of the aza-aromatic compound is a consequence of lower steric crowding which is probably due to the preferential conformation A of the molecule in solution. The preferential conformation A has been suggested for *trans*-2-styrylpyridine by Sorriso and Lumbroso [17] on the basis of the value of the dipole moment of the molecule and by Coletta *et al.* on the basis of n.m.r. chemical shifts.[18] A preferred conformation of type A should be assumed by the less crowded β,2-NPE which, in fact, has $\lambda_{max.}$ of longer wavelength than that of the other β-isomers.



SCHEME

The long wavelength band of the *cis*-isomers is hypsochromically and hypochromically shifted with respect to the corresponding band of the *trans*-isomer; a loss of vibrational structure is also generally observed. These phenomena, shown by most of the *cis*-isomers, are due to a deviation from the planar configuration of the molecule as a consequence of the interference of the *o*-hydrogens of the aromatic rings.[19]

Styrylnaphthalenes are known to fluoresce in the *trans*-form,[5,6] while the crowded *cis*-isomers are not fluorescent at room temperature.[20] *trans*-NPEs have fluorescence spectra quite similar to that of the corresponding hydrocarbons while their fluorescence quantum yields are generally much lower. Table 3 gives the fluorescence maxima of *trans*-STNs and -NPEs. As for absorption, the β-naphthyl derivatives show a fine structure in the fluorescence spectra greater than that of the α-naphthyl-derivatives (see Figure). The spectra shift towards higher wavelengths on going from non-polar to polar solvent.[12] This, as well as the fact that the fluorescence spectra are a mirror-image of the absorption spectra, indicate the π,π* nature of the emitting state. Dilute solutions of *cis*-isomers show only weak fluorescence due to *trans*-impurity.[20]

TABLE 3

Fluorescence maxima of *trans*-isomers of STNs and NPEs in n-hexane

Compound	$\lambda_{max.}$/nm
α-STN	370, 389, 410[a]
α,2-NPE	374, 390, 410[a]
α,3-NPE	372, 391, 410[a]
α,4-NPE	372, 391, 410[a]
β-STN	359, 379, 399, 420,[a] 450[a]
β,2-NPE	358, 378, 398, 420,[a] 450[a]
β,3-NPE	359, 379, 399, 421,[a] 450[a]
β,4-NPE	359, 379, 399, 421,[a] 450[a]

[a] Inflections.

Table 4 collects the fluorescence and *trans*→*cis*-photo-

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TABLE 4

Fluorescence (ϕ_f) of *trans*→*cis*-photoisomerization (ϕ_t) quantum yields of NPEs and STNs in deaerated n-hexane solutions

Compound	ϕ_f	ϕ_t
α-STN [a]	0.69	0.16
α,2-NPE	0.046	0.42
α,3-NPE	0.43	0.24
α,4-NPE	0.057	0.58_5
β-STN [a]	0.75	0.13_3
β,2-NPE	0.065	0.26_7
β,3-NPE	0.51	0.15
β,4-NPE	0.26	0.24

[a] From ref. 6.

isomerization quantum yields of *trans*-NPEs in n-hexane solution together with the corresponding values of STNs for comparison. From these data it is possible to see that the introduction of a heterocyclic nitrogen strongly affects the photochemical and photophysical behaviour of STNs. The presence of nitrogen decreases, in some cases noticeably, the radiative deactivation yield and increases the yield of the photochemical process. The extent of the variations strongly depends on the nitrogen position; the fluorescence efficiency decreases much more for the 2- and 4- than for the 3-pyridyl isomer. Correspondingly, for the 3-pyridyl isomer, the increase in the *trans*→*cis*-photoisomerization quantum yield is less than for the 2- and 4-pyridyl compounds. Briefly, the 3-pyridyl isomers have radiative and radiationless parameters of the excited state similar to that of the parent hydrocarbon. This peculiar behaviour has already been found with other classes of stilbene-like compounds containing nitrogen *e.g.* styrylpyridines [2] and dipyridylethylenes.[21] On the basis of theoretical calculations [22] this behaviour has been attributed to the presence of low-lying, non-fluorescent n,π^* states which could be easily reached by internal conversion for the 2- and 4-pyridyl isomers, but not available for the 3-pyridyl isomer because the heteroatom is located at a near node in the π and π^* M.O. This theoretical prediction also seems to explain the different photophysical and photochemical behaviour of α,3-NPE and β,3-NPE with respect to that of all the other isomeric NPEs. However, theoretical calculations and experimental work (on the effects of temperature, oxygen, solvent polarity, protonation, viscosity on isomerization, and fluorescence quantum yields) are in progress with the aim of obtaining information on the relative position of n,π^* and π,π^* states in NPEs and on the excited state (singlet or triplet) responsible for the isomerization.

We thank Professor U. Mazzucato for criticism of the manuscript and Mr. A. Bertòn for elemental analysis. This work was partially supported by the C.N.R.

[5/511 *Received, 17th March,* 1975]

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