

DIRECT AND ANTHRAQUINONE SENSITIZED *trans* → *cis* PHOTO-ISOMERIZATION OF NAPHTHYL-PYRIDYL-ETHYLENES

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Summary

Direct and anthraquinone sensitized *trans* → *cis* photoisomerization of naphthyl-pyridyl-ethylenes has been investigated. Oxygen and temperature effect on fluorescence and direct photoisomerization quantum yields have also been studied. The nitrogen positional isomerism affects the photophysical and photochemical parameters in different ways. From the results it may be deduced that both singlet and triplet excited states are involved in the direct photoisomerization and that radiationless deactivation is not a negligible process.

Introduction

There is in the recent literature an increasing interest in photochemical [1] and photophysical [2] behaviour of heteroaromatic nitrogen compounds.

The study of photophysical and photochemical behaviour of styryl-pyridines [3] and dipyridylethylenes [4] in solvents of different polarity has shown an interesting correlation between the changes of *trans* → *cis* (Φ_t) photoisomerization and fluorescence (Φ_f) quantum yields of the *trans* isomers. These studies emphasize the importance of n, π^* states in the deactivation pathways of these excited aza-aromatics even if no definitive conclusion on the excited state responsible for the photoisomerization process could be deduced.

We have studied recently the photochemistry and fluorescence of the two positional isomers of *trans*-styrylnaphthalenes [5]. For these compounds a triplet mechanism for the photoisomerization process was deduced on the

basis of the different influence of oxygen on fluorescence and photoisomerization yields (the oxygen quenches the fluorescence and increases the photoisomerization yield) and of the comparison between the direct and the photosensitized process. Moreover, the quantum yield of *trans* \rightarrow *cis* photoisomerization of β -styrylnaphthalene (β -StN) increases with its concentration; no concentration effect was detected in the photoisomerization of α -StN.

The effect of the introduction of a nitrogen in the molecular skeleton might, owing to a probable involvement of n,π^* states in the deactivation pathways, modify, remarkably too, the photophysical and photochemical behaviour of StNs. To obtain information on this role of n,π^* states, the photochemistry and fluorescence of *trans* naphthyl-pyridyl-ethylenes (NPEs) have now been investigated in n-hexane with the aim, also, of having insight into the excited state responsible for the photoisomerization.

Experimental

Nomenclature, synthesis, purification and u.v. spectral characteristics of NPEs are reported in a previous paper [6].

n-Hexane (RS Carlo Erba) and anthraquinone (RP Carlo Erba) were used without further purification. Benzene (RS Carlo Erba) was stirred over concentrated H_2SO_4 for three days, washed with sodium bicarbonate solution and then washed several times with water. The benzene was dried over anhydrous MgSO_4 and then distilled. The middle portion was used.

The light source was a stabilized high pressure xenon lamp, Osram XBO 150, from which the exciting wavelengths (310 nm and 409 nm for the direct and the sensitized isomerization, respectively) were isolated by narrow band Balzers interference filters. Ferrioxalate actinometry was used [7].

Direct *trans* \rightarrow *cis* photoisomerizations were performed in n-hexane in conditions of total absorption of the incident light ($c_{\text{NPE}} \approx 10^{-4} \text{ M}$). Anthraquinone sensitized photoisomerizations were performed in de-aerated benzene solutions containing $5.5 \times 10^{-3} \text{ M}$ anthraquinone and 10^{-2} M naphthyl-pyridyl-ethylene (this olefin concentration ensures a practically complete capture of the sensitizer triplets [5]).

When the quantum yields were determined in de-aerated solutions, the oxygen was removed by bubbling with pure nitrogen.

The conversion percentages, which never exceeded 10%, were determined by u.v. spectrophotometry after suitable dilution; single beam Hitachi-Perkin-Elmer 128 and double beam Perkin Elmer 356 spectrophotometers were used. Control experiments showed the absence of any important side photoreaction in both de-aerated and air saturated solutions. Two examples of the variation of the absorption spectrum of *trans* isomer with increasing irradiation time are reported in Figs. 1 and 2 for α ,2-NPE and β ,2-NPE isomers. Sensitized quantum yield values are corrected for the back reaction [8]. No correction was made on the values for the direct process; however, since the stationary states (although not precisely determined)

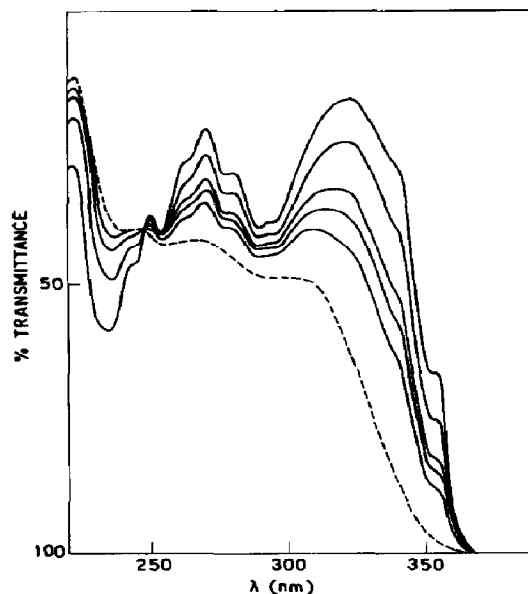
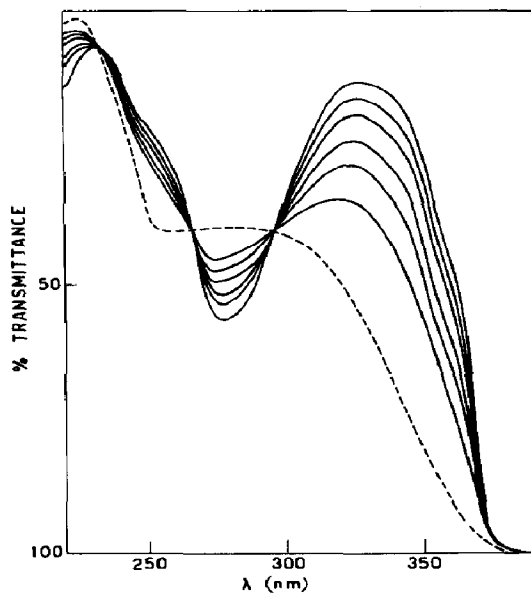


Fig. 1. Spectral changes of a n-hexane solution of $\alpha,2$ -NPE irradiated at 310 nm for increasing times; - - - -, spectrum of the *cis* isomer.

Fig. 2. Spectral changes of a n-hexane solution of $\beta,2$ -NPE irradiated at 310 nm for increasing times; - - - -, spectrum of the *cis* isomer.

contain *cis* percentages greater than those for the sensitized process and the irradiations were carried to low conversions, correction should raise quantum efficiencies by no more than 5%. Sensitized photostationary state compositions were reached from both sides. Analysis was either by u.v. spectrophotometry and gas chromatography (a Perkin-Elmer model F 11 equipped with flame ionization detector was used; column SE 30 5% on Chromosorb G).

Fluorescence measurements were made by a Perkin-Elmer MPF-3 with an accessory for spectra corrections; some spectra were checked on a Turner 210 absolute spectrofluorimeter; good agreement was found between the fluorescence quantum yields obtained with the two instruments. Fluorescence quantum yields were obtained relative to α -NPD in cyclohexane ($\Phi_f = 0.58$ [9]); refractive index corrections were made to adjust for the different solvents used. Fluorescence lifetimes were measured by the pulse sampling technique using an apparatus with resolution time of about 1 ns described elsewhere [10].

Results and discussion

The deactivation of the excited states of *trans* NPEs in dilute solutions occurs with fluorescence emission (no phosphorescence is detectable even at low temperatures) and geometrical isomerization. This latter phenomenon can occur on direct excitation and by a triplet energy donor's sensitized process.

TABLE 1

Anthraquinone sensitized *trans* → *cis* isomerization of naphthyl-pyridyl-ethylenes in de-aerated benzene solution

Compound	Φ_t	Stationary state (% <i>cis</i>)
α , 2-NPE	0.38	45
α , 3-NPE	0.48	57
α , 4-NPE	0.48	53
β , 2-NPE	0.50	54
β , 3-NPE	0.45	52
β , 4-NPE	0.49	56.5

The quantum yields of anthraquinone sensitized photoisomerization of *trans* NPEs are collected in Table 1 together with the *cis* percentages at the photostationary state. The Φ_t values experimentally found are in good agreement with those calculated by multiplying the *cis* percentages at the photostationary composition by 0.9 (Φ_{ISC} of anthraquinone [8]). This confirms that the anthraquinone sensitized isomerization of NPEs occurs following the general mechanism of the isomerization of olefinic compounds photosensitized by high triplet energy donors [11]; according to this mechanism, *trans* and *cis* triplets of the olefins, populated by energy transfer from the sensitizer, decay rapidly and efficiently to a common twisted form of lower energy which deactivates giving the two geometrical isomers. The quantum yields are practically the same for the isomeric NPEs and very similar to that of the corresponding hydrocarbon [5] (only the α ,2-isomer has a lower value) indicating that the presence and the positional isomerism of the nitrogen scarcely affects the triplet reactivity.

In Table 2 are collected the *trans* → *cis* photoisomerization (Φ_t) and fluorescence (Φ_f) quantum yields in de-aerated and air saturated n-hexane solutions and the fluorescence lifetimes in de-aerated solutions of NPEs. No concentration effect on Φ_t was found in the range 10^{-4} - 10^{-3} M. Styrylnaphthalenes are characterized by a very high radiative deactivation yield and a quite low isomerization yield in de-aerated solutions. Introduction of a nitrogen in the benzenic ring lowers the fluorescence yield, particularly when the heteroatom is in positions 2- and 4- (*ortho* and *para* positions) with respect to the ethylenic bond. Correspondingly, the yield of the photochemical process increases; once again the effect is more pronounced for 2- and 4- isomers and for the α than the β ones. This positional isomerism effect of the nitrogen on Φ_f and Φ_t parallels that found in the isomeric styrylpyridines in which the isomer containing the nitrogen in the *meta* position with respect to the ethylenic double bond has photochemical behaviour more similar to that of the parent hydrocarbon, the stilbene [3, 12].

As found for StNs [5] and for dinaphthyl-ethylenes [13], the dissolved oxygen differently affects the deactivation pathways of the lowest NPE's

TABLE 2

Trans → *cis* photoisomerization and fluorescence quantum yields in air-saturated and de-aerated n-hexane solutions and fluorescence lifetimes in de-aerated *trans*-naphthylpyridyl-ethylenes

Compound	Air-saturated		De-aerated		τ (ns)
	Φ_t	Φ_f	Φ_t	Φ_f	
α -StN ^a	0.23 ₃	0.60	0.16	0.69	—
α , 2-NPE	0.42	0.04 ₅	0.42	0.04 ₅	1.8
α , 3-NPE	0.24	0.36	0.24	0.43	2.2
α , 4-NPE	0.56	0.05 ₅	0.57	0.057	1.7
β -StN ^a	0.27 ₄	0.25	0.13 ₃	0.74	—
β , 2-NPE	0.36 ₅	0.05 ₇	0.27	0.06 ₅	5.0
β , 3-NPE	0.34	0.23 ₅	0.15	0.51	9.5
β , 4-NPE	0.40 ₅	0.16 ₅	0.26	0.26	8.5

^aFrom ref. [5].

excited singlet state; it generally decreases the fluorescence yield and increases the photoisomerization yield. The extent of the effect is greater for the β isomers than the α ones. As the fluorescence is concerned, this is probably related to the longer lifetimes of the β isomers than the α ones, but other factors, related to the molecular structure, must be operative; in fact, the oxygen effect on the fluorescence of the isomer β ,2-NPE is proportionally lower than that on α ,3-NPE, although the lifetime of the latter isomer is about one-half of that of β ,2-NPE. The most consistent explanation of the opposite effect of the dissolved oxygen on Φ_t and Φ_f seems to be, in this case too, an oxygen induced ISC [5, 14] to the triplet state of NPEs in which the isomerization can occur as demonstrated by the anthraquinone sensitized experiments.

In Table 3 are reported the fluorescence and photoisomerization quantum yields of NPEs in de-aerated n-hexane solutions at 20° and 62 °C. It may be seen that by increasing the temperature, the photoreaction yield increases and the fluorescence yield decreases; the two phenomena match quite well ($\Delta\Phi_t \approx \Delta\Phi_f$). A similar behaviour has been already found for stilbene at low temperatures [15] and, more recently, for styrylnaphthalenes and dinaphthyl-ethylenes [16] in the same range of temperatures explored by us. The positive temperature effect on photoisomerization was attributed to the existence of energy barriers in the geometrical conversion pathway. If the photoisomerization process occurs in the singlet state, the energy barrier should be located between the lowest spectroscopic singlet state and a twisted singlet state which decays with isomerization. If only the triplet state is involved in the photochemical process, the temperature effect could be explained as due to an activated intersystem crossing; if one assumes that the radiationless decay $S_1 \xrightarrow{\text{ISC}} S_0$ is negligible (this hypothesis is widely accepted for the aromatic hydrocarbons [17]), the ISC yield of the process

TABLE 3

Temperature effect on fluorescence and *trans* → *cis* photoisomerization quantum yields of NPEs in de-aerated n-hexane solutions

Compound	Φ_f		Φ_t	
	20 °C	62 °C	20 °C	62 °C
α , 2-NPE	0.045	0.019	0.42	0.46
α , 3-NPE	0.43	0.29	0.24	0.42
α , 4-NPE	0.057	0.024	0.58 ₅	0.62 ₂
β , 2-NPE	0.06 ₅	0.02 ₅	0.26 ₇	0.29 ₅
β , 3-NPE	0.51	0.35 ₂	0.15	0.29 ₅
β , 4-NPE	0.26	0.13 ₃	0.26	0.42

$S_1 \xrightarrow{\text{ISC}} T_1$ at a given temperature is $\Phi_{ISC}^{62^\circ C} = (1 - \Phi_f^{62^\circ C})$. The increase of the conversion yield with the temperature should therefore be obtained by multiplying the increase of Φ_{ISC} ($\Delta\Phi_{ISC}$) by the yield of the corresponding sensitized process. Table 4 collects the variations of Φ_{ISC} , $\Delta\Phi_{ISC} = (\Phi_{ISC}^{62^\circ C} - \Phi_{ISC}^{20^\circ C})$, calculated according to the above assumption and the expected increase of the photochemical process yield for the various isomers together with the variations experimentally found. In all cases, the increase found is greater than that calculated; so, on the basis of the above assumption, the hypothesis of a temperature enhanced ISC as the only responsible for the increase of the photochemical process yield should be disregarded.

However, the hypothesis that the radiationless deactivation $S_1 \xrightarrow{\text{IC}} S_0$ is negligible does not seem reliable in the case of NPEs. In fact, with the reasonable assumption that the decrease of the fluorescence yield of NPEs in oxygen containing solutions is due to an enhanced ISC, one could calculate the increase of the photoisomerization yield of a given isomer by multiplying $\Delta\Phi_{ISC} = \Delta\Phi_f$ (difference in fluorescence yields in nitrogen saturated and air saturated solutions) by the yield of the sensitized process. For all the β isomers, in particular for β ,2- and β ,4-, the increase of the yield experimentally found is greater than that calculated. A consistent explanation is that the radiationless deactivation is an important pathway of the excited singlet state of NPEs and the presence of the oxygen forces a fraction of the molecules to decay without emission into another deactivation channel (inter-system crossing $S_1 \xrightarrow{\text{ISC}} T_1$). Note that, if consistent internal conversion is operative in the case of the α isomers also, the increase of the isomerization yield with the temperature can be compatible with an increase of inter-system crossing.

Radiationless deactivation yields (Φ_{IC}) of singlet NPEs are obtainable in the following two extreme cases: (1) the isomerization occurs exclusively in the singlet state; (2) the isomerization occurs exclusively in the triplet state. Following the first hypothesis ($\Phi_t + \Phi_f = 1 - \Phi_{IC}$). In the second case

TABLE 4

Variations of intersystem crossing yield calculated on the basis of temperature effect on Φ_t , expected increases of Φ_t and $\Delta\Phi_t$ experimentally found

Compound	$\Delta\Phi_{ISC}$	$\Delta\Phi_t$ (expected)	$\Delta\Phi_t$ (found)
α , 2-NPE	0.027	0.01	0.04
α , 3-NPE	0.14	0.067	0.13
α , 4-NPE	0.033	0.016	0.037
β , 2-NPE	0.04	0.02	0.03
β , 3-NPE	0.16	0.072	0.145
β , 4-NPE	0.127	0.062	0.16

$$(1 - \Phi_{IC}) = \Phi_t + \frac{(\Phi_t)_{dir.} \times (\Phi_{ISC})_{sens.}}{(\Phi_t)_{sens.}}$$

where $(\Phi_t)_{dir.}$, $(\Phi_{ISC})_{sens.}$ and $(\Phi_t)_{sens.}$ are the quantum yields of the direct photoisomerization, of the intersystem crossing of the sensitizer and of the photosensitized isomerization, respectively. The values of $(1 - \Phi_{IC})$ calculated on the basis of the second hypothesis for the experiments carried out at 20 and 62 °C in de-aerated solutions and at 20 °C in air-saturated solutions are collected in Table 5; the values calculated following the first hypothesis are obtainable from Tables 2 and 3. On the basis of the data of Table 5, one must conclude that for α isomers the triplet state cannot be the only responsible for the direct isomerization because the value of $(1 - \Phi_{IC})$ is generally greater than one; so, for these isomers, a substantial fraction of the isomerization process (if not the whole process) must occur in the singlet state. For β ,3- and β ,4-isomers, at high temperature and in air-saturated solutions, there is not appreciable internal conversion; only for β ,2- this process has appreciable yield. Calculations by means of the first hypothesis give values of Φ_{IC} ranging from 0.3 to 0.7. It is probable that the real values are intermediate between those calculated as above; the determination of the right value of Φ_{IC} is strictly related to the identification of the excited state involved in the photoisomerization. From the data at our disposal, one can deduce that both the singlet (see *e.g.* data for α isomers) and triplet state (see anthraquinone sensitized experiments and oxygen effect on photoisomerization) are photoreactive, that the fluorescent state is not the photoreactive state or that the isomerization can occur in an excited state different from the fluorescent state (see temperature and oxygen effects on fluorescence and photoisomerization) and finally, that internal conversion is not a negligible process.

For *trans* styrylnaphthalenes, fluorescence and *trans* \rightarrow *cis* isomerization are the only deactivation paths of the excited molecule [16] and some evidence has been obtained that the triplet state is responsible for the isomerization [5, 18, 19]. Therefore, as already found for styrylpyridines, the

TABLE 5

Calculated values of $(\Phi_{ISC} + \Phi_f)$ assuming that the isomerization occurs exclusively in the triplet state

Compound	De-aerated solution		Air-saturated solution
	20 °C	62 °C	20 °C
α , 2-NPE	1.05	1.12	1.05
α , 3-NPE	0.88	1.09	0.81
α , 4-NPE	1.17	1.21	1.12
β , 2-NPE	0.55	0.56	0.72
β , 3-NPE	0.81	0.95	0.92
β , 4-NPE	0.76	0.91	0.92

introduction of a heterocyclic nitrogen strongly affects the photochemical and photophysical deactivation paths of StNs. The differences in photochemical behaviour of stilbene and StPs have been attributed to the presence of low lying n, π^* states spectroscopically hidden. Also in the spectra of NPEs there is no evidence of n, π^* states; n, π^* transitions, owing to their very low oscillator strengths, are probably buried in the high intensity π, π^* bands. In some StPs and dipyrindyl-ethylenes, low lying n, π^* singlet states are responsible for the photoreduction and photoaddition reactions in hydrogen atom donors' solvents [4] and radiationless deactivation in hydrocarbon solvents. The presence of low lying n, π^* states responsible for the radiationless deactivation of NPEs is a suggestive hypothesis which, however, contrasts with the high fluorescence yields of these compounds; moreover, the results of molecular orbital calculations [20] indicate that the n, π^* singlet state is above the π, π^* state for all the isomeric NPEs.

More definitive conclusions about the contribution of the singlet and the triplet state to the isomerization process and on the role of n, π^* states in the deactivation pathways of NPEs are expected from the results of the study of azulene quenching on fluorescence and photoisomerization and solvent effects on photoreactivity of NPEs which is in progress.

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