

## DIRECT AND ANTHRAQUINONE SENSITIZED *CIS-TRANS* PHOTOISOMERIZATION OF $\alpha$ AND $\beta$ STYRYLNAPHTHALENES

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### SUMMARY

Direct and anthraquinone sensitized *cis-trans* photoisomerization of  $\alpha$ - and  $\beta$ -styrylnaphthalene (StN) and of 4-Cl and 4-Br derivatives of  $\alpha$ -StN have been investigated. Unlike  $\alpha$ -StN and its derivatives, the quantum yield for  $\beta$ -StN in direct isomerization is concentration dependent; this dependence is attributed to an excitation energy redistribution induced by energy transfer between an excited StN and a StN in the ground state. For all isomers, the direct photoisomerization quantum yields are greater in air-saturated than in de-aerated solutions (the opposite behaviour has been observed for fluorescence quantum yields); this oxygen effect is attributed to an increased population of the lowest StN triplet state caused by  $O_2(^3\Sigma_g^-)$  quenching of the StN singlet state. From these observations and from a comparison between direct and sensitized quantum yields, it is concluded that the lowest StN triplet state is involved in the direct isomerization.

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### INTRODUCTION

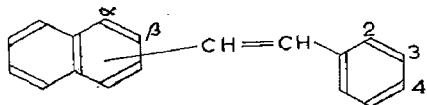
It is well known that the mechanism of direct *cis-trans* photoisomerization of ethylenic compounds, in particular of stilbene and its derivatives, is still a subject of lively controversy<sup>1-4</sup>. No definitive evidence of the involvement of the triplet or the singlet excited state has yet been found. To gain further insight into the photoreaction mechanism, the study was extended to the photoisomerization of  $\beta$ -styrylnaphthalene ( $\beta$ -StN)<sup>5,6</sup>; some features of the interesting results reported seemed to deserve further investigation and induced us to enlarge the study to  $\alpha$ -styrylnaphthalene ( $\alpha$ -StN) and some of its halogen derivatives. In particular, we have studied the concentration dependence of the quantum yield for *trans*  $\rightarrow$  *cis* isomerization of  $\alpha$ - and  $\beta$ -StN, the anthraquinone photosensitized *trans*  $\rightarrow$  *cis*

and *cis* → *trans* isomerization of the two isomers and  $\alpha$ -StN halogen derivatives and fluorescence quantum yields of all these molecules to obtain information on the effect of  $\alpha$  and  $\beta$  isomerism and heavy atoms on photochemical and photo-physical processes. Experimental results may be interpreted as evidence for a triplet mechanism of the direct photoreaction.

## EXPERIMENTAL

### Compound preparation

The styrylnaphthalenes were obtained by decarboxylation, catalyzed by



Cu chromite in boiling quinoline, of the corresponding phenylnaphthyl acrylic acids prepared by the Perkin synthesis from  $\alpha$  (or  $\beta$ ) naphthaldehyde and sodium salts of phenylacetic (or *p*-halogen substituted) acids<sup>7</sup>. The reaction mixture was acidified with 6 *N* HCl in order to eliminate the quinoline and extracted with benzene; the benzenic extracts were dried on Na<sub>2</sub>SO<sub>4</sub> and distilled. After the removal of benzene, the residue was distilled under reduced pressure (0.5 Torr); the residual quinoline distilled first at  $\approx 70^\circ\text{C}$ , the three fractions distilling above  $120^\circ\text{C}$  being collected. The first was nearly pure *cis* isomer; the second was a mixture of *cis* and *trans* isomers and the third was nearly pure *trans* isomer. The crude *trans* and *cis* isomers so obtained (overall yield  $\approx 40\%$ ) were purified by column chromatography on alumina using petroleum ether (which mainly elutes the *cis* isomer) and a mixture of petroleum ether/ethyl ether (1:1 v/v) (which elutes the *trans* isomer) as eluents. The purity of the compounds was tested by thin-layer and gas chromatographic analysis (Fractovap GI Carlo Erba, equipped with ionization detector, column 8 ft., 1/8 in. 5% SE 30 on Chromosorb G); the *cis* isomers contained a small quantity of the *trans* isomers, which never exceeded 2%. The elemental analysis (with the theoretical percentages in parenthesis), melting points (determined on a Kofler hot stage apparatus) and u.v. of the long wavelength band spectral data in *n*-hexane for the compounds synthesized, are as shown in Table 1.

### Photoisomerization

Benzene (RP), thiophene free, and *n*-hexane (RS Carlo Erba) were used as solvents. Anthraquinone (RP Carlo Erba) was used without purification.

The exciting source was a 150 W high pressure xenon lamp (Osram XBO). The interference filters were peaked at 313 nm (Balzers) for the direct isomerizations (for irradiation of diluted solutions the light intensity was reduced by a grey filter) and at 404 nm (Schott and Gen. Mainz), for the sensitized isomerizations.

TABLE I  
PARAMETERS FOR COMPOUNDS SYNTHESIZED

Compound	Analyses (%)		Cl/Br	M.p. (°C)	$\lambda_{\max}$ (nm)	log $\epsilon$
	C	H				
<i>trans</i> - $\alpha$ -StN	93.97 (93.86)	6.14 (6.14)	—	76	320	4.315
<i>cis</i> - $\alpha$ -StN	93.00 (93.86)	6.19 (6.14)	—	liq.	298	4.000
<i>trans</i> - $\beta$ -StN	94.14 (93.86)	5.94 (6.14)	—	147-148	316	4.595
<i>cis</i> - $\beta$ -StN	94.33 (93.86)	6.13 (6.14)	—	liq.	301	4.135
<i>trans</i> -4-Cl- $\alpha$ -StN	81.35 (81.66)	5.01 (4.95)	13.46 (13.39)	102-103	325	4.362
<i>cis</i> -4-Cl- $\alpha$ -StN	81.92 (81.66)	5.42 (4.95)	13.53 (13.39)	liq.	300	4.000
<i>trans</i> -4-Br- $\alpha$ -StN	69.98 (69.90)	4.41 (4.20)	26.38 (25.90)	110-111	325	4.395
<i>cis</i> -4-Br- $\beta$ -StN	70.29 (69.90)	4.45 (4.20)	25.46 (25.90)	56-57	300	4.022

The irradiations were performed in conditions of total absorption of incident light, in the case of the direct isomerizations. The sensitized isomerizations were carried out in de-aerated solutions with a fixed anthraquinone concentration ( $7.8 \times 10^{-3} M$ ) which, in the 10 mm cells used, transmitted about 30% of the 404 nm incident light. Where the quantum yields were determined in de-aerated solutions, the oxygen was removed by bubbling with pure nitrogen.

Ferrioxalate actinometry<sup>8</sup> was used. In the case of sensitized isomerizations the transmitted light was also monitored by actinometry.

The conversion percentages, which never exceeded 10%, were determined by u.v. spectrophotometry in the region of 310–340 nm after suitable dilution; single beam Unicam SP500/2 and Optica CF 4 DR double beam spectrophotometers were used. Preliminary experiments showed that, in all cases, good *cis-trans* isobestic points were obtained up to 50% conversion. The values reported for photoisomerization quantum yields are a mean of 4–5 independent experiments; those for sensitized reactions are corrected for the contribution of the back reaction by the formula of Lamola and Hammond<sup>9</sup>, using the experimental photostationary compositions.

Sensitized photostationary compositions were at first roughly obtained by irradiating solutions containing anthraquinone and the pure *cis* or *trans* isomer; the photostationary state was then reached from both sides by irradiation of a *cis-trans* mixture of composition near to the photoequilibrium.

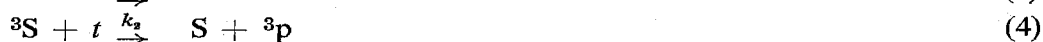
### Fluorescence

Fluorescence measurements were made by a Perkin-Elmer MPF 3 spectrofluorimeter; the  $\Phi_f$  values were determined in dilute solutions ( $\lambda_{exc}$ . 313 nm, OD  $\simeq$  0.03) using a cyclohexane solution of  $\alpha$ -NPD ( $\Phi_f = 0.58^{10}$ ) as a standard. Oxygen was removed by bubbling in pure nitrogen. The values of  $\Phi_f$  reported are a mean of at least 5 experiments which were reproducible to  $\pm 5\%$ .

## RESULTS AND DISCUSSION

### Photosensitized isomerizations

Our data on the sensitized isomerizations of StN are consistent with the following reaction scheme<sup>11</sup>:



where S = sensitizer, *t* = *trans* isomer, *c* = *cis* isomer and  $^3p$  = common olefin triplet or equilibrating triplets. By applying the approximation of the steady state to  $^3S$  and  $^3p$  and neglecting step (5) when the photoisomerization *trans*  $\rightarrow$  *cis* is concerned (the photoreaction was followed only in the first stages) one obtains the following expression for the sensitized *trans*  $\rightarrow$  *cis* process:

$$\frac{1}{\Phi_{t \rightarrow c}} = \frac{k_1}{k_2} \times \frac{k_4 + k_5}{k_4 \Phi_{ISC} [t]} + \frac{k_4 + k_5}{k_4 \Phi_{ISC}} \quad (8)$$

Likewise, in the case of *cis*  $\rightarrow$  *trans* process, neglecting step (4), one obtains:

$$\frac{1}{\Phi_{c \rightarrow t}} = \frac{k_1}{k_3} \times \frac{k_4 + k_5}{k_5 \Phi_{ISC} [c]} + \frac{k_4 + k_5}{k_5 \Phi_{ISC}} \quad (8')$$

At high acceptor concentrations, the above expressions can be written in a simplified form, which represents the "maximum" photosensitized quantum yields:

$$\frac{1}{\Phi_{t \rightarrow c}} = \frac{1}{\Phi_{ISC}} \times \frac{k_4 + k_5}{k_4} \quad (9)$$

and 
$$\frac{1}{\Phi_{c \rightarrow t}} = \frac{1}{\Phi_{ISC}} \times \frac{k_4 + k_5}{k_5} \quad (9')$$

The plot  $1/\Phi$  vs.  $1/[A]$  ( $[A]$  is the concentration of the olefin in the *cis* or *trans* form) should be a broken line whose arms are represented by eqns. (8) and (9) for low and high concentrations of acceptor, respectively. In Fig. 1 we report, as an example, the plot of  $1/\Phi$  vs.  $1/[A]$  for the isomerization of *trans*- $\alpha$ -StN; similar plots were obtained for the other compounds. The "maximum" quantum yields are collected in Table 2; it can be seen that the sum  $\Phi_{t \rightarrow c} + \Phi_{c \rightarrow t}$ , which

TABLE 2

"MAXIMUM" EXPERIMENTAL QUANTUM YIELDS FOR ANTHRAQUINONE SENSITIZED *trans*  $\rightarrow$  *cis* AND *cis*  $\rightarrow$  *trans* PHOTOPROCESSES IN BENZENE SOLUTION

Compound	$\Phi_{t \rightarrow c}$	$\Phi_{c \rightarrow t}$
$\beta$ -StN	0.46 <sub>5</sub>	0.44
$\alpha$ -StN	0.41 <sub>5</sub>	0.47 <sub>5</sub>
4-Cl- $\alpha$ -StN	0.45	0.46
4-Br- $\alpha$ -StN	0.47	0.42

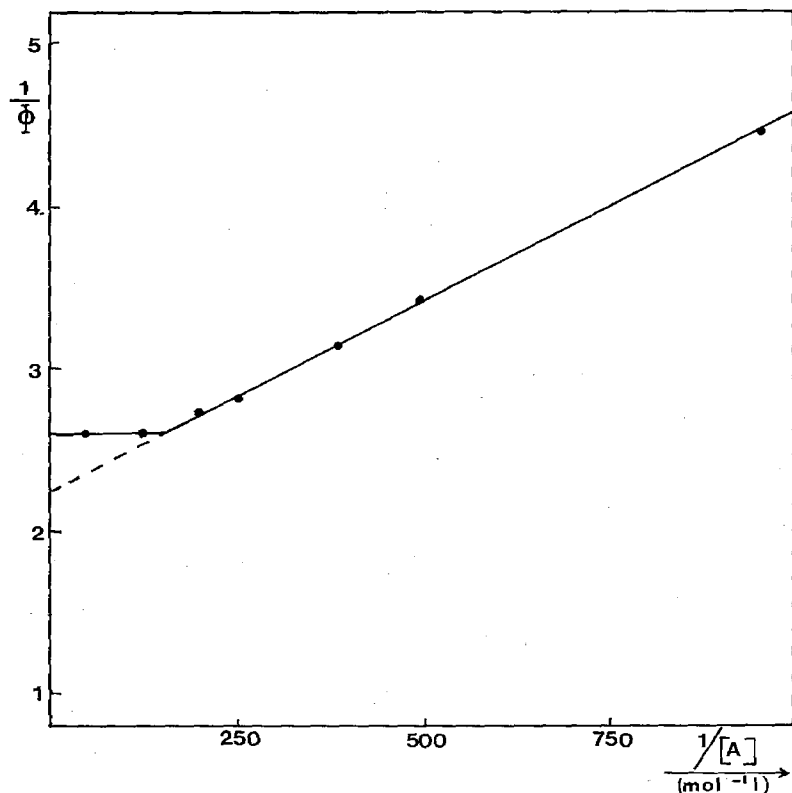


Fig. 1. Plot of  $1/\Phi$  vs.  $1/[A]$  for the anthraquinone sensitized *trans*  $\rightarrow$  *cis* photoisomerization of  $\alpha$ -StN.

should give the value of  $\Phi_{ISC}$  for anthraquinone, is  $\approx 0.9$  for all compounds listed, in excellent agreement with the literature value<sup>9</sup>. The data indicate a similar reactivity of the triplet of StN; on the other hand, the 4-Cl and 4-Br derivatives of  $\alpha$ -StN have  $\Phi_{t \rightarrow c}$  a little higher than the parent compound, indicating that the heavy atom increases  $k_4$  more than  $k_5$ .

#### Direct photoisomerization

The *trans*  $\rightarrow$  *cis* isomerization and fluorescence quantum yields in air saturated and de-aerated solutions of n-hexane are collected in Table 3 (the concentration of StN in the photoreaction experiments was about  $1.5 \times 10^{-4} M$ ). It is to be noted that all StNs show a very high radiative deactivation yield in comparison with stilbene; this fact is responsible for their much lower isomerization quantum yield with respect to stilbene. Oxygen affects differently reaction and emission, increasing the yield of the photochemical process and decreasing that of the photophysical one. The increase of  $\Phi_t$  in the presence of oxygen is remarkable and could be attributed to an increased population of the lowest triplet of StNs. There is, in fact, experimental evidence<sup>12-14</sup> that for some aromatic hydrocarbons

TABLE 3

PHOTOISOMERIZATION *trans* → *cis* ([StN] ≈ 1.5 × 10<sup>-4</sup> M) AND FLUORESCENCE QUANTUM YIELDS IN AIR SATURATED AND DE-AERATED N-HEXANE SOLUTIONS

Compound	Air saturated		De-aerated	
	$\Phi_{t \rightarrow c}$	$\Phi_f$	$\Phi_{t \rightarrow c}$	$\Phi_f$
$\beta$ -StN	0.27 <sub>4</sub>	0.25	0.13 <sub>3</sub>	0.74
$\alpha$ -StN	0.23 <sub>3</sub>	0.60	0.16	0.69
4-Cl- $\alpha$ -StN	0.19 <sub>5</sub>	0.69	0.13 <sub>5</sub>	0.76
4-Br- $\alpha$ -StN	0.23	0.44 <sub>5</sub>	0.21 <sub>5</sub>	0.47

the lowest excited triplet state is produced by the quenching of their singlet excited state by O<sub>2</sub> (<sup>3</sup>Σ<sup>-g</sup>). In our case, as a result of the interaction between S<sub>1</sub> and O<sub>2</sub> (<sup>3</sup>Σ<sup>-g</sup>), the enhancement of styrylnaphthalene intersystem crossing seems to be due to a direct intermolecular exchange interaction<sup>15,16</sup> or to the inhomogeneous field of O<sub>2</sub> (<sup>3</sup>Σ<sup>-g</sup>)<sup>17,18</sup> rather than to a charge transfer mechanism as recently proposed<sup>14</sup> for some aromatic compounds. The latter has been proposed on the basis of the fact that oxygen and diethylaniline have a similar quenching effect on S<sub>1</sub> both leading to an increased population of T<sub>1</sub> level. In the present case, however, oxygen and amines have a different behaviour; in fact, amines quench very efficiently not only the fluorescence of StNs, with formation of a heteroexcimer, but they also quench the photoreaction, practically to the same extent.

The effect of halogens is interesting. While chlorine has little influence on both fluorescence and photoreaction yields, bromine substitution noticeably affects the fluorescence yield although it leaves the photoisomerization yield unchanged. The reduced  $\Phi_f$  for this latter compound could be ascribed to an enhanced intersystem crossing to a triplet state due to a greater spin-orbit coupling induced by the heavy atom.

Comparison of direct and sensitized quantum yields makes it possible to calculate the "maximum"  $\Phi_{ISC}$  of StNs from:

$$\frac{\Phi_{dir}}{\Phi_{sens}} = \frac{(\Phi_{ISC})_{acc}}{(\Phi_{ISC})_{sens}}$$

on the hypothesis that all the direct isomerization occurs in the triplet state<sup>1,19</sup>. The values obtained are 0.34<sub>5</sub>, 0.27 and 0.41 for  $\alpha$ -StN and its 4-Cl-, and 4-Br-derivatives, respectively, using the values of direct isomerization quantum yields in de-aerated solutions, or 0.50<sub>5</sub>, 0.39 and 0.42, using the values for direct isomerization in air saturated solutions. The sums of  $\Phi_{ISC} + \Phi_f$  are 1.03<sub>5</sub>, 1.03 and 0.88 in de-aerated, and 1.10<sub>4</sub>, 1.08 and 0.86<sub>5</sub> in air saturated n-hexane. The agreement between fluorescence and photoreaction could be indicative of the implication of the triplet state in the photoisomerization process.

TABLE 4

DIRECT *trans* → *cis* PHOTOISOMERIZATION QUANTUM YIELDS OF  $\beta$ -StN AT 313 NM IN N-HEXANE SOLUTION

Concentration $M$ (mol/l)	$\Phi_{\text{de-aerated}}$	$\Phi_{\text{air-saturated}}$
$3.4 \times 10^{-5}$	0.095	0.21 <sub>3</sub>
$1.5 \times 10^{-4}$	0.13 <sub>3</sub>	0.27 <sub>4</sub>
$9.5 \times 10^{-4}$	0.21 <sub>3</sub>	0.28 <sub>6</sub>
$3.1 \times 10^{-3}$	0.31	0.30 <sub>5</sub>
$6.2 \times 10^{-3}$	0.40	0.39 <sub>5</sub>

TABLE 5

DIRECT *trans* → *cis* PHOTOISOMERIZATION QUANTUM YIELDS OF  $\beta$ -StN AT 313 NM IN BENZENE SOLUTION

Concentration $M$ (mol/l)	$\Phi_{\text{de-aerated}}$	$\Phi_{\text{air-saturated}}$
$1.6 \times 10^{-4}$	0.077	0.18
$1.0 \times 10^{-3}$	0.12 <sub>5</sub>	0.20 <sub>3</sub>
$3.2 \times 10^{-3}$	0.17 <sub>2</sub>	0.23 <sub>6</sub>
$6.3 \times 10^{-3}$	0.22 <sub>8</sub>	0.27 <sub>3</sub>
$1.0 \times 10^{-2}$	0.28	0.30
$2.2 \times 10^{-2}$	0.34	0.38 <sub>5</sub>
$4.2 \times 10^{-2}$	0.38 <sub>2</sub>	0.41 <sub>6</sub>
$6.4 \times 10^{-2}$	0.42 <sub>5</sub>	0.43 <sub>5</sub>

The behaviour of  $\beta$ -StN is particularly interesting; Tables 4 and 5 collect the *trans* → *cis* quantum yields in n-hexane and benzene both in air saturated and in de-aerated solutions. The Tables show a noticeable dependence of photoisomerization yield on  $\beta$ -StN concentration in both solvents, in de-aerated and in air saturated solutions\*; the increase of photoisomerization with increasing concentration is accompanied by a decrease of fluorescence quantum yield. No dimer formation was shown by thin-layer and gas chromatography, even in more concentrated solutions. On the contrary, no dependence of photoisomerization yields on concentration for  $\alpha$ -StN and its derivatives was found in the range  $1.5 \times 10^{-4} M$ – $3.0 \times 10^{-3} M$ . Tentatively, we assign the increase of the photoisomerization yield to an energy transfer between an excited  $\beta$ -StN and a  $\beta$ -StN in the ground state, which should occur through an excimer formation; this could lead to a redistribution of energy more favourable to the isomerization. This hypothesis is not in

\*The oxygen and concentration effect on  $\Phi_t$  of  $\beta$ -StN have been checked under slightly different experimental conditions (cyclohexane as solvent; fixed absorbance in cells 0.1, 1 and 10 mm thickness; de-aerated solution flushed with argon) at Professor Fischer's Laboratory, Rehovot, Israel. His results are in fair to good agreement with those of Tables 3 and 4. We are indebted to Professor Fischer for these useful checks and information.



disagreement with the results of Fischer and Stegemeyer<sup>6,20</sup> who found a temperature dependence of  $\Phi_t$  of  $\beta$ -StN, attributed to a "substantial energy barrier between the excited states involved in the photoisomerization". The excimer formation was detected in poly(vinyl- $\alpha$ - and  $\beta$ -naphthalenes)<sup>21,22</sup> systems which are quite similar to that presently studied. In our case, a dependence of fluorescence spectrum, at the long wavelength side, on  $\beta$ -StN concentration has been found. In Fig. 2 the fluorescence intensity ratios  $I_{\lambda}/I_{\max}$ , in benzene solution at three StN concentrations are reported; it appears that in more concentrated solutions the ratios at longer wavelengths are larger probably because of the increase in the excimer emission.

As regards the excited state involved in photoisomerization, these results do not allow us to distinguish conclusively between the two conflicting, singlet or triplet, mechanisms invoked in the case of the photoisomerization of stilbene, even though they seem to indicate the triplet pathway as the more probable.

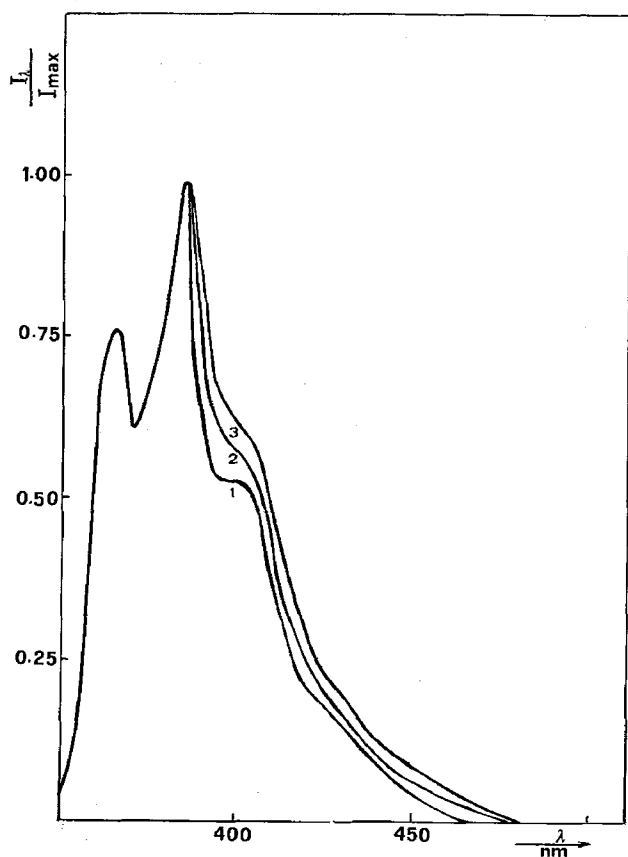


Fig. 2 Intensity ratios  $I_{\lambda}/I_{\max}$  vs.  $\lambda$  for the emission of  $\beta$ -StN in benzene solution. [StN]: (1)  $5.5 \times 10^{-4}$  mol/l; (2)  $4.5 \times 10^{-3}$  mol/l; (3)  $7.0 \times 10^{-2}$  mol/l.

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