DIRECT AND SENSITIZED *CIS–TRANS* PHOTOISOMERIZATION OF 2-STYRYLTHIOPHENE

L. L. COSTANZO, S. PISTARÂ and G. CONDORELLI

Istituto di Chimica Generale, Università di Catania, 95125 Catania (Italy)

G. SCARLATA

Istituto di Chimica Industriale, Università di Catania, 95125 Catania (Italy)

Summary

Direct and sensitized *cis–trans* photoisomerization of 2-styrylthiophene has been investigated. From the results it can be deduced that with both direct and sensitized isomerization the same mechanism is operating, a triplet state, twisted at 90 ° with respect to both isomers, being the probable common intermediate.

Introduction

The *cis–trans* photoisomerization of olefins has been the subject of extensive investigation. In particular the stilbenes have been studied more frequently than any other pair of isomers. However, although there is general agreement that sensitized isomerization occurs at the triplet level [1], there is disagreement about the way in which direct photoisomerization occurs. In fact experimental and theoretical results have been interpreted as evidence for both singlet and triplet mechanisms [2 - 6].

To gain further insight into the photoisomerization mechanism the study was extended to stilbene analogues in which a phenyl ring was substituted by naphthalene [7, 8], pyridine [9 - 13] or the thioamidic group [14]. The interesting results reported encouraged us to enlarge the investigation to other ethylene derivatives containing a heterocyclic ring. These compounds are attractive both from a theoretical point of view, because of the information that can be obtained about the reaction mechanism, and from a practical point of view, since the compounds have a potential biological activity connected with the molecule geometry [15 - 17]. The *trans* isomers are obtained more easily than the *cis* isomers; the latter isomers may thus be obtained simply by the photochemical method.

The present work was undertaken in order to investigate the photoisomerization mechanism of 2-styrylthiophene, the catalysed thermal isomerization of which has been studied by one of the authors [18].

Experimental

Materials

Trans- and *cis*-2-styrylthiophene were prepared by the Wittig reaction from benzyltriphenylphosphonium chloride and 2-thiophenecarboxaldehyde in the presence of sodium ethoxide in ethanol. Isomer separation was carried out by column chromatography [19]. Cyclohexane, benzene and ethanol were of spectroscopic grade and were used without further purification. Triphenylene (Fluka) and benzophenone (Baker) were suitable for "sensitizer use".

Apparatus

Radiations of 254, 313, 333, 365 and 436 nm were obtained using the irradiation equipment previously described [20]. The intensity of the incident light, measured by a ferric oxalate actinometer, was of the order 10^{-7}-10^{-8} einstein min^{-1}.

Spectrophotometric measurements were carried out with an Optica CF4NI spectrophotometer with all compartments thermostated at 25 °C.

Luminescence measurements were performed with a Hitachi Perkin–Elmer MPF 3L spectrofluorimeter thermostated at 25 °C. A Hitachi phosphorescence attachment supplied with this instrument was used to obtain low temperature luminescence measurements on samples in ethanol glass, which were contained in cylindrical tubes.

Procedures

In the direct isomerization experiments 10^{-5} - 10^{-4} M solutions of the pure *trans* isomer or of a mixture at $\approx 90\%$ of the *cis* isomer were irradiated in standard spectrophotometric cells after deoxygenation. The reaction was followed by measuring the spectral changes at regular intervals in a suitable region of the isomer absorption (320 nm). Quantum yields were calculated (Zimmerman's method) by the kinetics of the isomerization and by the composition of the photostationary state attained from both directions.

In the sensitized photoisomerization experiments the solutions were irradiated in spectrophotometric cells which were deoxygenated with a stream of very pure nitrogen and were sealed. Triphenylene and benzophenone were used as sensitizers. In the experiments with triphenylene mixture of the sensitizer (0.5×10^{-3} M) and the substrate ($(0.35 - 0.1) \times 10^{-4}$ M) in cyclohexane were irradiated at 254 nm and the photoisomerization was followed at 333 nm. The triphenylene fluorescence was observed at room temperature under the same experimental conditions with exciting light of 254 nm. In the experiments with benzophenone, mixtures of the sensitizer (0.45×10^{-2} M) and the substrate ($(0.3 - 0.15) \times 10^{-4}$ M) in benzene were irradiated at 365 nm and followed at 313 nm. The benzophenone phosphorescence was observed at room temperature in the same conditions with exciting light of 365 nm. The phosphorescence intensity was obtained from the experimental readings at 455 nm, the maximum of the uncorrected spectrum.

In the conditions described, the best possible experimentally, we considered the light to be entirely absorbed by sensitizers. In calculating the quantum yields, the observed ratios of the two isomers at various irradiation times were corrected for the back reaction contribution [21].

Results and discussion

The UV spectra of the two isomers in various solvents are reported in Table 1. There are two main absorption zones due to $\pi-\pi^*$ transitions: the first, at about 340 and 295 nm respectively for *trans* and *cis* isomers, shifts towards longer wavelengths compared with that of stilbene; the second, at about 235 nm, is not affected by the presence of the heterocyclic ring and is in the same spectral region as the parent stilbene [19].

TABLE 1

UV spectra of 2-styrylthiophene in various solvents

trans		cis	
λ_{max} (nm)	log ϵ	λ_{max} (nm)	log ϵ
Cyclohexane			
(340)[a]	4.24	295	3.965
320	4.46	(270)	3.889
(270)	3.776	237	3.97
233	3.88		
Ethanol			
(340)	4.267	290	3.96
320	4.487	265	3.829
(270)	3.774	237	3.9
Benzene			
(345)	4.15	300	3.87
325	4.425		

[a]( ) indicates a shoulder.

Only the *trans* isomer shows fluorescence and phosphorescence (Fig. 1). The energies of the lowest singlet and triplet states are calculated from the shortest wavelength bands of these emissions ($E_S = 75.3$ kcal mol^{-1}, $E_T = 42$ kcal mol^{-1}). The lack of planarity in the *cis* form prevents luminescence of this isomer.

Under direct irradiation *trans*-2-styrylthiophene shows a gradual variation of the spectrum (Fig. 2) until it reaches a stationary state which is a function of the exciting wavelength. The process is not thermally reversible, but can retrocede when irradiated with the appropriate light wavelength. It is evident
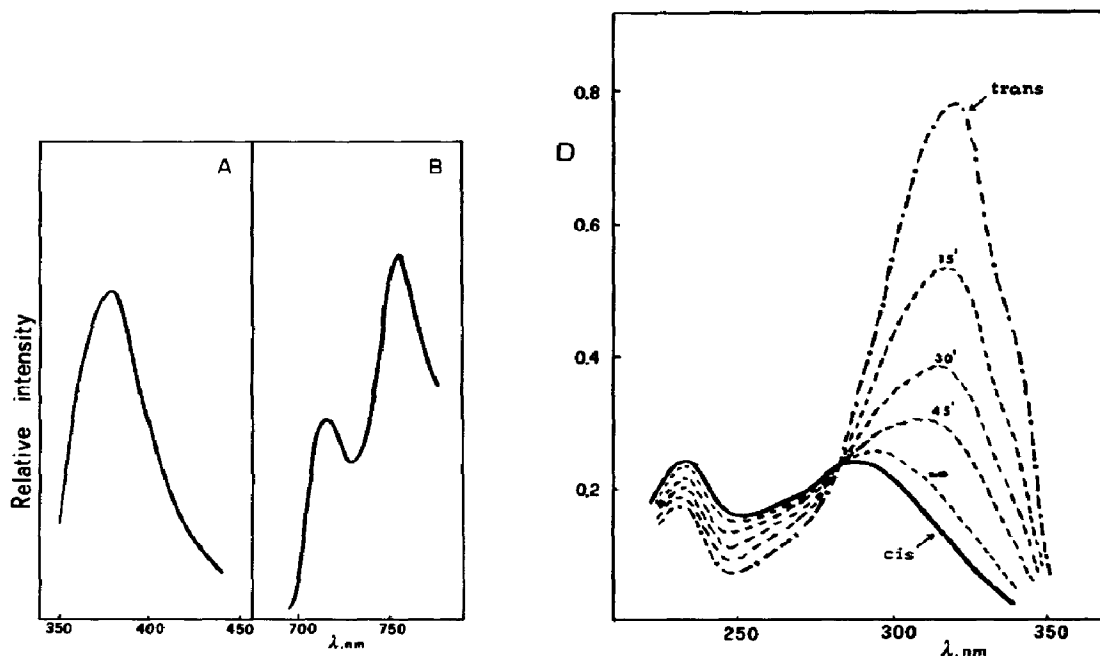
Fig. 1. Emission spectra of *trans*-2-styrylthiophene in ethanol at temperatures (A) 293 K and (B) 77 K.

Fig. 2. Spectral changes of the 2-styrylthiophene in cyclohexane under 333 nm irradiation. The numbers on the curves give the irradiation time in minutes.

that the photochemical reaction is identical for all wavelengths and is not accompanied by side reactions. The spectrophotometric data demonstrate that a photochemically reversible *trans–cis* photoisomerization occurs:
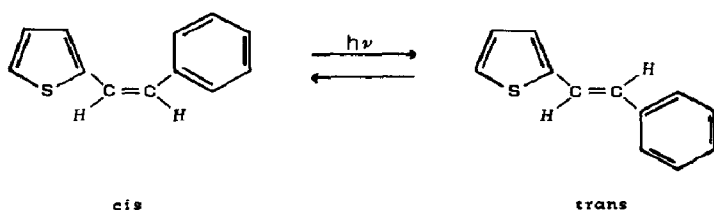
The quantum yields for photoisomerization by exciting light of wavelengths 365, 333, 313 and 254 nm in various solvents are summarized in Table 2. It is evident that the quantum yields are almost independent of the solvent nature and are affected by the wavelength of the exciting light. In the range 10^{-4} - 10^{-5} M the concentration has no influence. No experiments were done at higher concentrations since concurrent dimerization reactions can occur [22].

Photoisomerization can be induced by triphenylene (E_S = 82 kcal mol^{-1}, E_T = 67 kcal mol^{-1}) and benzophenone (E_T = 69 kcal mol^{-1}).

Preliminary experiments were carried out under the same conditions as those of photoisomerization in order to establish which states were excited.

TABLE 2

Quantum yields[a] for direct *cis–trans* photoisomerization of
2-styrylthiophene in various solvents

λ_{exc} (nm)		Ethanol	Cyclohexane	Benzene
254	φ_{t-c}	0.44	0.44	
	φ_{c-t}	0.22	0.20	
313	φ_{t-c}	0.33	0.32	0.31
	φ_{c-t}	0.15	0.14	0.19
333	φ_{t-c}	0.20	0.20	0.22
	φ_{c-t}	0.09	0.09	0.13

[a]Error, ± 0.01.

Both *trans-* and *cis*-styrylthiophenes were found to quench the fluorescence
intensity of triphenylene. With the *trans* isomer a simultaneous changeover of
the fluorescence of the donor to that of the acceptor occurs as the concentra-
tion is increased. The energy transfer resulting in the quenching of the fluor-
escence of one species and the sensitization of that of the other implies singlet
states. For this type of transfer radiative or non-radiative processes can be
operating. In the present case the former must be unimportant owing to the
absence of overlap between the donor emission and acceptor absorption. The
system appears to be unsuitable for the quantitative study of a non-radiative
process, because measurements of the sensitized fluorescence and concurrent
quenching are not possible owing to the overlap of donor–acceptor emissions
during the changeover.

Benzophenone phosphorescence intensity is progressively quenched by
adding various concentrations of the *trans* and *cis* substrate acceptor. A plot
of P_0/P *versus* [styrylthiophene] produces a straight line (Fig. 3); from its
slope and from the value of the benzophenone triplet lifetime (1.9×10^{-6} s)
the rate constant for the quenching is calculated to be $K_q = 10^{10}$ M^{-1} s^{-1}.
This shows the efficiency of benzophenone as a triplet sensitizer for both
isomers. In the experiments with triphenylene and benzophenone the same
photostationary state was reached, whether the starting isomer was *trans* or
cis (percentage *cis* = 0.55 $\pm$ 0.01, percentage *trans* = 0.45 $\pm$ 0.01). The appar-
ent initial quantum yields increase with the acceptor concentration. The plots
of $1/\varphi_{app}$ *versus* $1/$[styrylthiophene] give good straight lines (Fig. 4). At high
acceptor concentration, when $1/$[styrylthiophene] $\rightarrow 0$, the intercept value is
obtained from which the limit quantum yields were calculated:

for benzophenone $\Phi_{t-c} = 0.46 \pm 0.01$ $\Phi_{c-t} = 0.37 \pm 0.01$

for triphenylene $\Phi_{t-c} = 0.44 \pm 0.01$ $\Phi_{c-t} = 0.33 \pm 0.01$

It can be seen that the quantum yields for the isomerization sensitized by
triphenylene are less than those for the isomerization sensitized by benzo-
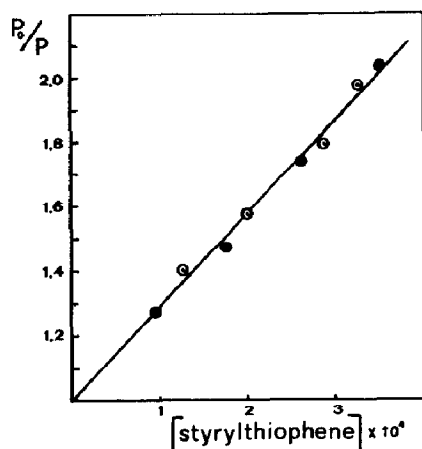phenone by a factor almost equal to the intersystem crossing (ISC) quantum

302

Fig. 3. Stern–Volmer plot for the quenching of the benzophenone phosphorescence by *trans* (○) and *cis* (●) styrylthiophene. Temperature, 293 K.
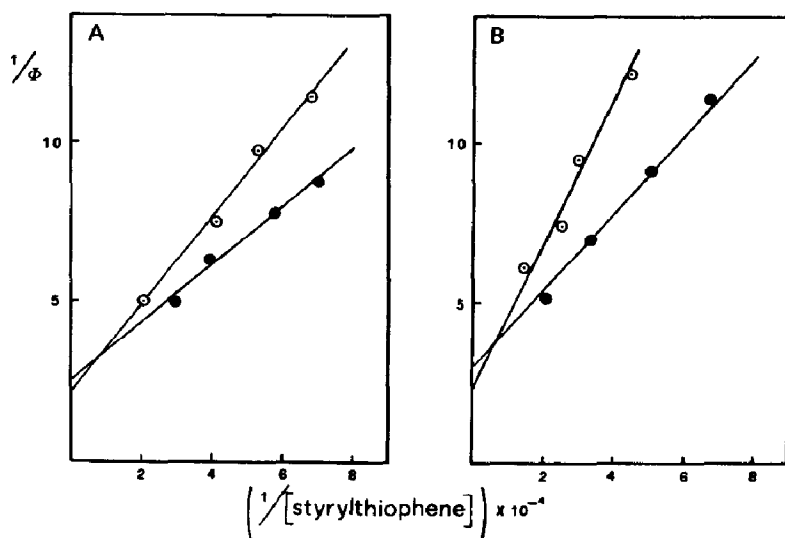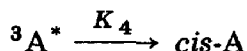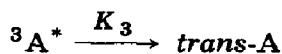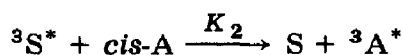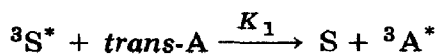

Fig. 4. The isomerization of styrylthiophene photosensitized by (A) benzophenone and (B) triphenylene: ○ *trans–cis*; ● *cis–trans*.

yields (Φ_{ISC} is 1 and 0.95 respectively for benzophenone and triphenylene). The ratios of the intercepts to slopes give the sensitization constants τK_q. For benzophenone $\tau K_q = 14.625$, which confirms that triplet energy transfer controlled by diffusion occurs; for triphenylene $\tau K_q = 11.500$, which is intermediate between the values expected for singlet [23] and triplet [24] sensitization controlled by diffusion. This result shows that both singlet and triplet energy transfer are operating.

The experimental results of the sensitized photoisomerization agree with a mechanism involving energy transfer to both isomers which leads to the formation of a common excited state, probably a π–π^* state twisted at 90 °, from which decay to the ground state occurs. An abbreviated scheme is as follows (the contribution of singlet sensitization by triphenylene is neglected):

$$^3S^* + trans\text{-A} \xrightarrow{K_1} S + {}^3A^*$$

$$^3S^* + cis\text{-A} \xrightarrow{K_2} S + {}^3A^*$$

$$^3A^* \xrightarrow{K_3} trans\text{-A}$$

$$^3A^* \xrightarrow{K_4} cis\text{-A}$$

where S is the sensitizer, $^3S^*$ is the excited triplet, A is the acceptor (styryl-thiophene) and $^3A^*$ is the excited triplet.

At the stationary state the mechanism predicts that

$$\frac{[cis\text{-A}]}{[trans\text{-A}]} = \frac{K_4 K_1}{K_3 K_2}$$

where the decay ratio K_4/K_3 is equal to Φ_{t-c}/Φ_{c-t} and the excitation ratio K_1/K_2 is unity for a high energy sensitizer. In our case the energy transfer is controlled by diffusion and $K_1 = K_2$. The experimental result that

$$\frac{\Phi_{t-c}}{\Phi_{c-t}} = \frac{[cis\text{-A}]}{[trans\text{-A}]}$$

demonstrates that the proposed mechanism is correct.

Comparison of the results for the sensitized and direct reactions provides an explanation for the mechanism of the direct photoisomerization. If excitation by direct absorption of light was followed by quantitative crossing to the triplet state, the decay ratio should be the same for both the sensitized and direct processes. Since the excitation ratio for direct irradiation is precisely the ratio of the molar extinction coefficients for the two isomers, the photostationary state relationship becomes $[cis]/[trans] = \epsilon_t K_4/\epsilon_c K_3$. This relationship does not hold for styrylthiophene because the value of K_4/K_3 predicted was about 1.2, whereas it was about 1.6 in benzene and 2.2 in ethanol and cyclohexane. However, the closeness of the results obtained from the direct (at 254 nm) and sensitized reactions and the analogy of the singlet and triplet sensitization by triphenylene rules out the possibility that the direct reaction involves isomerization of the excited singlets themselves either while they are excited or during the act of internal conversion (IC) to ground singlets. Better, the observed discrepancy between the values of K_4/K_3 can be an indication that crossing from singlets to the triplet does not occur quantitatively nor with the same efficiency, the isomerization occurring only in those molecules that become triplets.

The pattern of the variation of the quantum yields with wavelength is consistent with this interpretation. By excitation to a higher singlet, the molecule undergoes ISC to a higher triplet state from which it decays to the twisted triplet; if both these processes occur with high efficiency, as supported by the lack of fluorescence for excitation at 254 nm, the highest value of the isomerization quantum yield is explained. By excitation in the first excited singlet, the ISC competes with IC and fluorescence for the trans isomer and this causes the observed decrease of quantum yields.

References

1 G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, J. Am. Chem. Soc., 86 (1964) 3197.
2 J. Saltiel and E. D. Megarity, J. Am. Chem. Soc., 94 (1972) 2742.
3 J. Saltiel and J. T. D'Agostino, J. Am. Chem. Soc., 94 (1972) 6445.
4 F. D. Lewis, J. C. Dalton and N. J. Turro, Mol. Photochem., 2 (1970) 67.
5 F. Momicchioli, M. C. Bruni, I. Baraldi and G. R. Corradini, J. Chem. Soc. Faraday Trans. 2, 70 (1974) 1325.
6 G. Orlandi and W. Siebrand, Chem. Phys. Lett., 30 (1975) 352.
7 G. S. Hammond, S. C. Shim and S. P. Van, Mol. Photochem., 1 (1969) 89.
8 P. Bortolus and G. Galiazzo, J. Photochem., 2 (1974) 361.
9 P. Bortolus, G. Gauzzo, U. Mazzucato and G. Galiazzo, Z. Phys. Chem., 51 (1966) 264; 63 (1969) 29.
10 G. Favaro, F. Masetti and U. Mazzucato, Z. Phys. Chem., 66 (1969) 206.
11 D. G. Whitten and M. T. McCall, J. Am. Chem. Soc., 91 (1969) 5097.
12 L. Pederson, D. G. Whitten and M. T. McCall, Chem. Phys. Lett., 3 (1969) 569.
13 P. Bortolus, F. Masetti and G. Galiazzo, J. Photochem., 5 (1976) 479.
14 G. Condorelli, L. L. Costanzo and S. Giuffrida, Mol. Photochem., 5 (1973) 443.
15 Ng. Ph. Buu-Hoï and Ng. Hoan, Rec. Trav. Chim. Pays-Bas, 67 (1948) 309.
16 Ng. Ph. Buu-Hoï, Ng. Hoan and D. Lavit, J. Chem. Soc., (1950) 2130.
17 G. W. Steinkopf, Die Chemie des Thiophens, Steinkopff, Leipzig, 1941, p. 29.
18 G. Scarlata and M. Torre, J. Heterocycl. Chem., 13 (1976) 1193.
19 A. Arcoria, S. Fisichella, G. Scarlata and M. Torre, J. Heterocycl. Chem., 10 (1973) 643.
20 G. Condorelli, L. L. Costanzo, S. Pistarà and S. Giuffrida, Z. Phys. Chem., Neue Folge, 90 (1974) 58.
21 A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43 (1965) 2129.
22 B. S. Green and L. Heller, J. Org. Chem., 39 (1974) 197.
23 A. B. Smith and W. C. Agosta, Chem. Commun. (1970) 466.
24 W. G. Herkstroeter and G. S. Hammond, J. Am. Chem. Soc., 88 (1966) 4769.