DIRECT AND SENSITIZED *cis–trans* PHOTOISOMERIZATION OF α-PHENYL-β-(2-THIENYL)-ACRYLONITRILE

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Summary

The direct and benzil-sensitized *cis–trans* photoisomerization of α-phenyl-β-(2-thienyl)-acrylonitrile in solution was studied. On the basis of the different effects of the quencher (azulene), it was concluded that the pathways of the direct and sensitized processes do not involve crossing. Singlet states were mainly responsible for the direct isomerization because intersystem crossing was ineffective. Benzil sensitization occurred with different energy transfer constants for the two isomers, the *trans* isomer being the better acceptor. Of the *trans* and *cis* triplet states implied in sensitized isomerization, only the *trans* triplet was quenched by azulene, its lifetime being in the range 10^{-7} - 10^{-8} s.

1. Introduction

In our photochemical investigations of geometric isomerization we have previously studied [1] 2-styrylthiophene photoisomerization and have concluded that the same triplet mechanism is operative in both the direct irradiation and the energy transfer processes. This interpretation, in contrast with the hypothesis more generally proposed for stilbene [2, 3], emphasized the importance of the substituents bonded to the ethylenic group in the determination of the photoisomerization mechanism.

In order to obtain more information about the substituent effect we examined the photochemistry of α-phenyl-β-(2-thienyl)-acrylonitrile (PTA) which is a derivative of 2-styrylthiophene. In this compound the substitution of a hydrogen atom in the ethylenic bridge by the CN group increases the conjugation and modifies the relative energies of the excited states, making the compound interesting from the point of view of photochemical investigation.

2. Experimental details

2.1. Materials

trans-PTA was synthesized [4] from 2-thiophenecarbaldehyde and phenylacetonitrile in ethanol (melting point, 92 °C).

cis-PTA was prepared by the method described previously [5] or by irradiating a concentrated solution of trans-PTA with an immersion mercury vapour lamp (Hanovia 450 W) fitted with a uranium filter, and the compound was isolated by alumina column chromatography using benzene as the eluant. The compound was recrystallized using xylene (boiling point, 157 °C at 0.3 mmHg). The UV spectra of the two isomers in ethanol showed absorption bands characteristic of $\pi\pi^*$ transitions at 343 nm (ϵ = 25 500), 290 nm (ϵ = 5800) and 236 nm (ϵ = 8000) for trans-PTA and at 320 nm (ϵ = 19 500), 290 nm (ϵ = 11 400) and 245 nm (ϵ = 5300) for cis-PTA.

2.2. Apparatus and procedure

The experimental equipment for irradiation, for measuring the incident light and for obtaining the spectra were the same as those described previously [6].

The PTA was irradiated both in the solid state and in solution. In the former case PTA powder was placed between two thin quartz sheets and irradiated at 436, 405 and 365 nm. The photochemical reaction was monitored by reflectance spectroscopy. After irradiation the powder was dissolved in ethanol and the usual spectrophotometric analysis was carried out. When the PTA was irradiated in solution, ethanol and benzene were used as the solvents and the photoisomerization was monitored by the usual spectrophotometric methods. The irradiation was carried out at 436, 405, 365, 313 and 254 nm. The quantum yields were calculated from the initial rate of the reaction or by Zimmerman's method depending on which was more convenient. In the investigations of the quenching of the direct reaction, samples of PTA and azulene were irradiated at 365 nm. The relative concentrations of the PTA ((3 - 5) $\times 10^{-3}$ M) and the quencher (10^{-2} M) were such that most of the light was absorbed by the PTA. In all cases the light intensity was corrected for the fraction absorbed by the azulene.

In the sensitization experiments samples of PTA (10^{-5} - 10^{-3} M) and benzil (6 $\times 10^{-3}$ M) were irradiated at 405 nm. In the investigations of the quenching of the sensitized reaction, samples containing PTA and azulene ((0.5 - 4) $\times 10^{-3}$ M) in the concentration ratio 1:1 together with the sensitizer (2 $\times 10^{-2}$ M) were irradiated at 405 nm.

Benzil phosphorescence was observed at ambient temperature by excitation at 405 nm. The emission intensity was obtained from readings at 554 nm which is the maximum of the uncorrected spectrum. The phosphorescence quenching was carried out at a quencher concentration of (0.2 - 2) $\times 10^{-5}$ M.

3. Results

3.1. Direct irradiation

Preliminary experiments showed that irradiation of *trans*-PTA resulted in two different processes depending on whether the compound was irradiated in solution or in the solid state.

Irradiation of PTA in solution produced *cis* $\rightleftarrows$ *trans* isomerization without side reactions (Fig. 1).
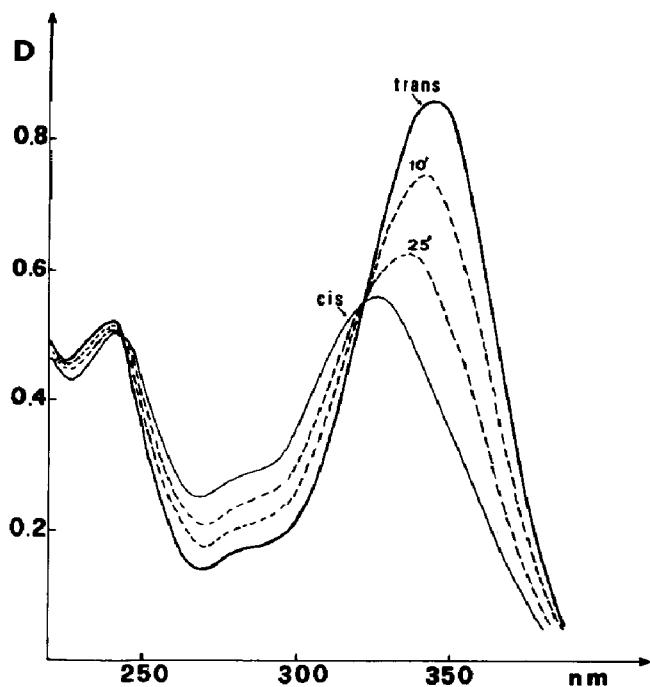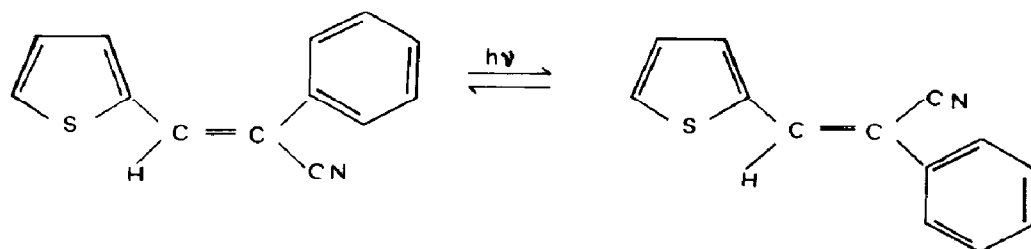

Fig. 1. Spectral changes produced by irradiating a solution of PTA in ethanol at 333 nm.

The same photostationary state was attained by both isomers. The quantum yields were independent of the initial concentration, in the range 10^{-2} - 10^{-5} M, of the solvent used (ethanol or benzene) and of the irradiation wavelength. The following values were obtained for the quantum yields:

$$\varphi_{t-c} = 0.38 \pm 0.02 \qquad \varphi_{c-t} = 0.22 \pm 0.02$$

In order to investigate the participation of the triplet state we carried out experiments to examine the quenching of the excited state and the heavy atom effect. It was found that irradiation of solutions of PTA containing azulene (10^{-2} M) leads to photoisomerization with the same quantum yields as observed with PTA alone. Experiments carried out in solutions saturated with xenon showed clearly that heavy atoms do not affect the photoisomerization process.

Irradiation of *trans*-PTA in the solid state at wavelengths below 405 nm produced reversible *trans* $\rightleftarrows$ *cis* photoisomerization, whereas at wavelengths above 405 nm photodimerization occurred. The photoproduct was identified as the dimer

Th—CH————C(CN)—Ph
Ph—C(CN)——CH—Th
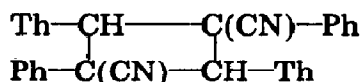
by comparison of the UV spectrophotometry, nuclear magnetic resonance (NMR) and mass spectral analysis data with those for *trans*-PTA (Table 1). On irradiation of the dimer at 254 nm, the *trans* isomer was recovered both in the solid state and in solution (φ = 0.22 for solutions in ethanol) (Fig. 2).

TABLE 1

Characteristic data for PTA and the photoproduced dimer

	UV (ethanol)		NMR $\delta(DMSO\text{-}d_6)^a$ (ppm)	Mass molecular peak	Melting point (°C)
	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1}			
trans-PTA	343	25500	8.45	211	92
Dimer	240	15600	6.15	422	235

^{a}DMSO-d$_6$, fully deuterated dimethyl sulphoxide.

In the case of the *cis* isomer, excitation at all wavelengths produced only *cis* → *trans* photoisomerization both in the solid state and in solution.

3.2. Sensitized photoisomerization

Reversible photoisomerization of PTA can be induced by benzil. Preliminary investigations of the quenching of benzil phosphorescence by both isomers were carried out. The linearity of the Stern–Volmer plots of P_0/P *versus* [PTA] suggests that the quenching is due to energy transfer (Fig. 3). The following quenching constants k_q were obtained from the slopes of the plots and from the benzil triplet lifetime (τ = 5.88 $\times 10^{-5}$ s): k_q = 1.9 $\times 10^9$ for *trans*-PTA and k_q = 1 $\times 10^9$ for *cis*-PTA.

These values, which are very close to those expected for a diffusion-controlled process, show that the *trans* isomer is the better acceptor and that the energy transfer to the *cis* isomer occurs with a lower efficiency, probably because of its triplet energy or geometric form. The initial quantum yields of
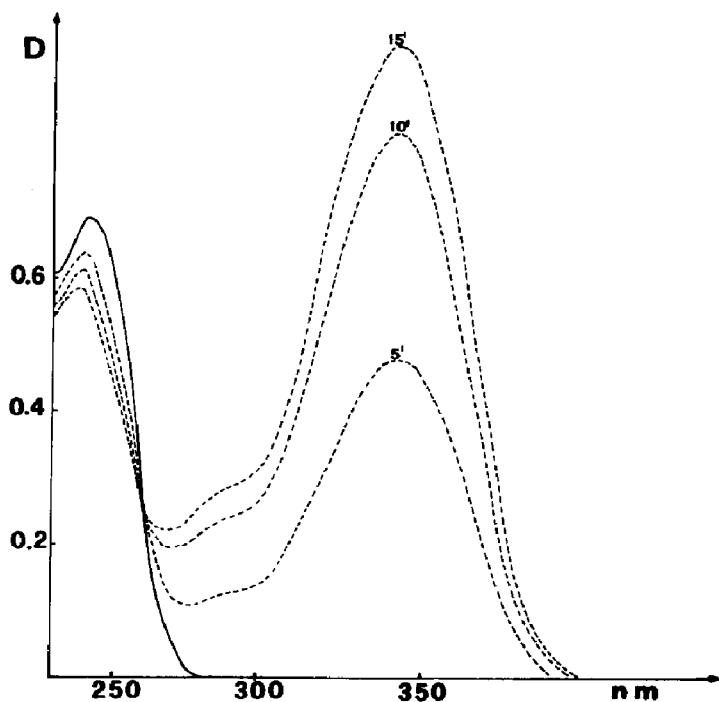
Fig. 2. Spectral changes (– – –) produced by irradiating a solution of PTA dimer (——) in ethanol at 254 nm.
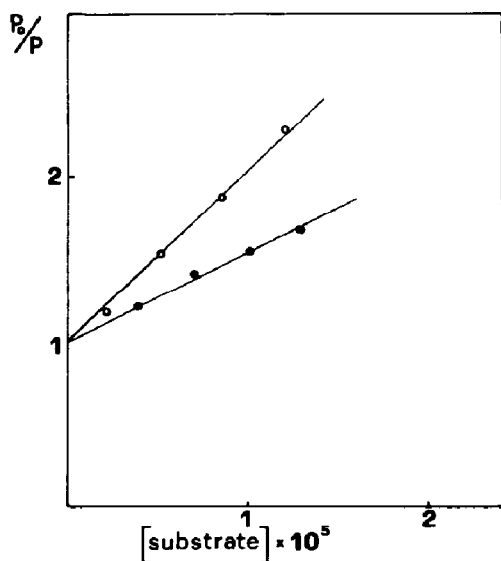

Fig. 3. Stern—Volmer plots for the quenching of benzil phosphorescence by *trans*-PTA (○) and *cis*-PTA (●).

the sensitized photoisomerization increase with the PTA concentration below 10^{-4} M. The plots of $1/\Phi_{aD}$ *versus* $1/[\text{PTA}]$ gave good straight lines from which the limiting quantum yields and the sensitization constants k_s

were calculated. The following values were obtained: Φ_{t-c} = 0.5 and k_s = 1.8 $\times 10^9$ for the *trans* isomer; Φ_{c-t} = 0.44 and k_s = 1 $\times 10^9$ for the *cis* isomer. In this calculation we took into account the intersystem crossing efficiency of benzil (η = 0.89).

Almost constant quantum yields were obtained at PTA concentrations in the range 10^{-4} - 10^{-3} M. The values found experimentally were Φ_{t-c} = 0.45 $\pm$ 0.02 and Φ_{c-t} = 0.39 $\pm$ 0.02, and the photostationary state was formed by 33% of the *trans* isomer and 67% of the *cis* isomer. It should be noted that the ratio of photostationary state concentrations (0.5) is not the same as the ratio of the quantum yields (0.85). This disparity is in agreement with the differences between the rate constants for quenching of the sensitizer phosphorescence and for energy transfer found for the two isomers and supports the contention that the *trans* isomer is a better triplet acceptor than the *cis* isomer is.

In order to obtain information about the quenchability of the triplet states involved in the process, sensitized isomerization in the presence of azulene was investigated. The PTA concentration was in the range 10^{-3} - 10^{-4} M with a constant quantum yield and the [PTA] : [azulene] ratio was fixed at 1:1. It was found that the initial quantum yield of the *trans* → *cis* isomerization decreased as the quencher concentration increased and that the ratio $\Phi_{t-c}/\Phi_{t-c}{}^q$ was a linear function of the azulene concentration (Fig. 4). The plot of $\Phi_{t-c}/\Phi_{t-c}{}^q$ *versus* [azulene] has a slope of 186 and an intercept of 2.52.
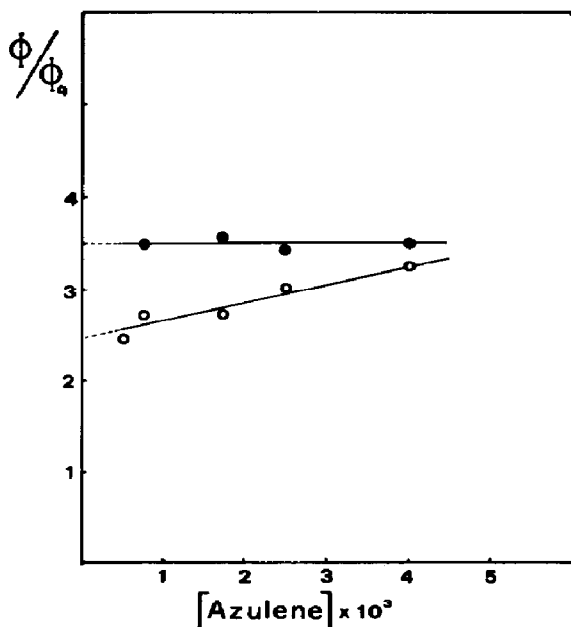

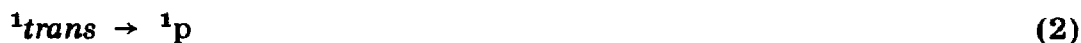Fig. 4. The effect of azulene on the sensitized photoisomerization of *trans*-PTA (○) and *cis*-PTA (●).

Under the same experimental conditions the quantum yield Φ_{c-t}^{a} of the *cis* → *trans* isomerization was reduced by the addition of azulene to a constant value of 0.11.

4. Discussion

Some proposals regarding the isomerization mechanism of PTA can be made. The fact that the quantum yields are independent of the irradiation wavelength suggests that the precursor state of isomerization is a common state attained via relaxation of the lower excited *trans* or *cis* states which are either populated directly or else reached with unitary efficiency from higher states. This common state, which probably has perpendicular geometry (^{1}p), can be assumed to be the minimum of the potential energy surface of the lower excited singlets of the two isomers from which the molecule decays to the ground *trans* or *cis* forms via the distorted state ^{0}p.

Azulene has no effect on the direct process although it is an efficient quencher in the sensitized process. This difference in behaviour confirms that the triplet state does not participate in direct isomerization which proceeds only via singlet states. The triplet exclusion can be attributed to the low efficiency of singlet–triplet intersystem crossing because the excited molecule undergoes fast radiationless decay to the common distorted state responsible for isomerization. This hypothesis is in accordance with the lack of phosphorescence and with the marked decrease observed in the fluorescence yield compared with that of the unsubstituted parent [7].

The following isomerization scheme based on the experimental results describes the direct isomerization pathways:

$$trans \xrightarrow{h\nu} {}^1trans \tag{1}$$

$$^1trans \rightarrow {}^1p \tag{2}$$

$$cis \xrightarrow{h\nu} {}^1cis \tag{3}$$

$$^1cis \rightarrow {}^1p \tag{4}$$

$$^1p \rightarrow {}^0p \rightarrow trans + cis \tag{5}$$

The following simplified reaction scheme, where S is the sensitizer, is proposed for sensitized isomerization:

$$^3S + trans \rightarrow S + {}^3trans \tag{6}$$

$$^3trans \rightarrow {}^3p \tag{7}$$

$$^3S + cis \rightarrow S + {}^3cis \tag{8}$$

$$^3cis \rightarrow {}^3p \tag{9}$$

$$^3p \rightarrow {}^0p \rightarrow trans + cis \tag{10}$$

In the presence of azulene (Q) the isomerization scheme becomes

$$^3S + Q \rightarrow S + Q \tag{11}$$

$$^3trans + Q \rightarrow trans + Q \tag{12}$$

$$^3cis + Q \rightarrow cis + Q \tag{13}$$

It has been noted [8, 9] that the ratio of the limiting quantum yield Φ in the absence of azulene to the limiting quantum yield Φ^q in its presence must obey the relation

$$\frac{\Phi_{t-c}}{\Phi_{t-c}{}^q} = 1 + \frac{K_{11}[Q]}{K_6[trans]} + \left(1 + \frac{K_{11}[Q]}{K_6[trans]}\right) \tau_{^3trans} K_{12}[Q]$$

and

$$\frac{\Phi_{c-t}}{\Phi_{c-t}{}^q} = 1 + \frac{K_{11}[Q]}{K_8[cis]} + \left(1 + \frac{K_{11}[Q]}{K_8[cis]}\right) \tau_{^3cis} K_{13}[Q]$$

Under our experimental conditions both [Q]/[trans] and [Q]/[cis] were constant and equal to unity. Therefore a linear relation between Φ/Φ^q and [Q] is expected with intercept $1 + K_{11}[Q]/K_{6(8)}[PTA]$ and slope $1 + K_{11}[Q]/K_{6(8)}[PTA]$.

We found that in the trans → cis isomerization the plot of Φ/Φ^q versus [Q] was a straight line of slope 186 and intercept 2.52. The intercept value of 2.52 indicates that the constant for energy transfer from the sensitizer to the quencher is higher than that for energy transfer from the sensitizer to the trans isomer. The product $\tau_{^3trans} K_{12}[Q]$ is obtained from the slope-to-intercept ratio. Given that $K_{12} \approx 10^9$, the lifetime of ^3trans becomes about 0.7×10^{-7}. In the case of cis → trans isomerization the ratio remains constant as the azulene concentration is increased, i.e. a straight line of intercept 3.54 and of slope almost zero is obtained. The higher intercept value obtained for cis → trans isomerization confirms that the cis isomer is a poorer energy acceptor than the trans isomer, i.e. K_8 is less than K_6. The value of the slope shows that the product $\tau_{^3cis} K_{13}$ is almost zero and hence that these two values are smaller than those for the corresponding trans isomer.

It should be noted that the observed behaviour of PTA differs from that of stilbene [2]. In stilbene the state quenched by azulene is a ^3p distorted state which interacts with the quencher to give only a trans molecule in the ground state.

Finally, the effect of the wavelength on the photoreaction (isomerization or dimerization) in the solid state can be explained by the hypothesis that irradiation at longer wavelengths populates excited states which lie at lower energies than the state responsible for photoisomerization. Therefore the excited molecule does not contain sufficient energy to produce distortion. A trivial explanation that the dimer formed at wavelengths lower than 400 nm reabsorbs the irradiation and transforms to the trans isomer does not

appear to be a reliable alternative hypothesis because of the features of the absorption spectrum.

The differences in the photochemical behaviour of the two isomers, the *trans* isomer undergoing isomerization and dimerization and the *cis* isomer undergoing isomerization only, confirms the role of the crystal lattice in determining the fate of the excited molecule [10].

Acknowledgment

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