

Short Communication

Azulene effect on the *cis-trans* photoisomerization of 3-styrylquinoline

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The influence of triplet quenchers on the photochemical *cis-trans* isomerization of olefins is a very useful tool for mechanistic investigation [1 - 5]. We have recently applied this technique to azastilbenes. The photochemistry of these compounds is particularly interesting since it was shown that the introduction of a nitrogen atom in the ring strongly affects the properties of the excited states [6 - 8]. In this paper we expose our results on the effect of azulene, a well known triplet quencher [1], on the direct and sensitized *cis-trans* photoisomerization of 3-styrylquinoline. It will be shown that both processes occur *via* a triplet mechanism.

Experimental

3-Styrylquinoline (3-StQ) was prepared by a Wittig synthesis involving the reaction of benzyl-triphenyl-phosphonium bromide and 3-quinoline aldehyde in the presence of sodium ethylate. In this way both geometrical isomers were obtained, as revealed by t.l.c. The separation of the two isomers was accomplished by column chromatography on alumina with petroleum ether (*cis*-isomer) and benzene (*trans*-isomer) as eluents. The total yield was about 60%, *trans*-StQ was purified by recrystallization from n-hexane (m.p. 98 - 99 °C) and the *cis*-isomer by vacuum distillation. The purity of both isomers was checked by gas chromatographic analysis. Absorption maxima in n-hexane: *cis*-isomer λ_{\max} 225, 265, 295 (sh) nm (ϵ_{\max} 32,400, 16,200, 11,600); *trans*-isomer λ_{\max} 225, 280, 315 nm (ϵ_{\max} 23,000, 28,000, 33,000).

Benzene (Uvasol Merck) was purified by standard procedure and azulene was purchased from Fluka. Anthraquinone (Carlo Erba) was used as a triplet donor sensitizer.

Irradiations were performed in benzene at $25^\circ \pm 0.1^\circ \text{C}$. Removal of oxygen from the solutions was achieved by bubbling pure nitrogen. The

light source was a stabilized Osram HBO 200 W high-pressure mercury lamp equipped with Balzers interference filters to isolate the excitation wavelengths. Ferrioxalate actinometry was employed. Spectrophotometric measurements after prolonged irradiation of air-saturated and oxygen-free solutions revealed that neither anthraquinone nor azulene undergo appreciable photodecomposition. The total 3-StQ concentration in the irradiation experiments was $\sim 5 \times 10^{-3} M$, and the percentage of the two isomers was determined by g.l.c. (1/8 in. column, 5% SE 30 on Chromosorb G). For the determination of quantum yields of direct *trans* \rightarrow *cis* photoisomerization (Φ_t) the fractional conversion was maintained at 10% or less, in order to minimize the effect of the back reaction. In the photosensitized isomerization, photostationary compositions ($[t]/[c]_s$) were approached from both sides. In the direct photoisomerization, owing to the concomitant photocyclization of the *cis* isomer, the irradiation times were minimized by using *trans*-*cis* mixtures which bracketed the expected photostationary states.

Fluorescence quantum yields (Φ_F) were determined in benzene with a Perkin-Elmer MPF 2A spectrofluorimeter; α -NPD in deoxygenated cyclohexane ($\Phi_F = 0.58$) [9] was used as standard, allowance being made for refractive index difference with respect to benzene.

Results and Discussion

A first indication that the effect of azulene on the direct photoisomerization is not due to a singlet quenching comes from the comparison of the Stern-Volmer plots in Fig. 1; azulene quenches the fluorescence of *trans*-3-StQ (the *cis*-isomer does not fluoresce in our experimental conditions) but the effect is small compared with that on Φ_t .

The plots of ($[t]/[c]_s$) vs. [azulene] are shown in Fig. 2, and the intercept (i) and the slope/intercept ratios (s/i) from these plots are reported in Table 1. The photostationary composition in both direct and sensitized photoisomerization as well as the values of Φ_t (0.17) and Φ_F (0.33) are the same in deaerated and in air-saturated solutions. The presence of oxygen is also without effect on the slopes of the ($[t]/[c]_s$) vs. [azulene] plots.

The effect of azulene on the photosensitized isomerization is similar to that found for stilbene (slope/intercept = $120 M^{-1}$ for the benzophenone-sensitized photoisomerization in benzene at 30 °C) [5] and can be attributed to an excitation transfer from the phantom triplet of 3-StQ to azulene, which leads to the preferred formation of the *trans*-3-StQ.

If both direct and sensitized photoisomerization occur in the triplet state, identical values of the slope/intercept ratios for the ($[t]/[c]_s$) vs. [azulene] plots should be obtained [2]. The data in Table 1 indicated that this is indeed the case. It should be noted that in the direct photoisomerization of stilbene (for which a singlet mechanism was inferred), the azulene

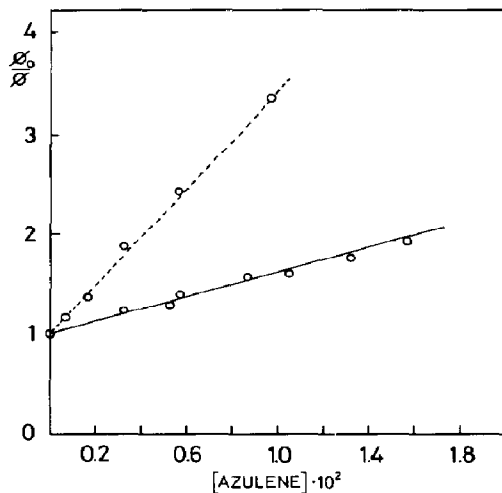


Fig. 1. Effect of azulene on the fluorescence (—) and on the *trans* \rightarrow *cis* photoisomerization (---) quantum yields. Irradiation at 366 nm (at this wavelength the absorption of azulene is negligible).

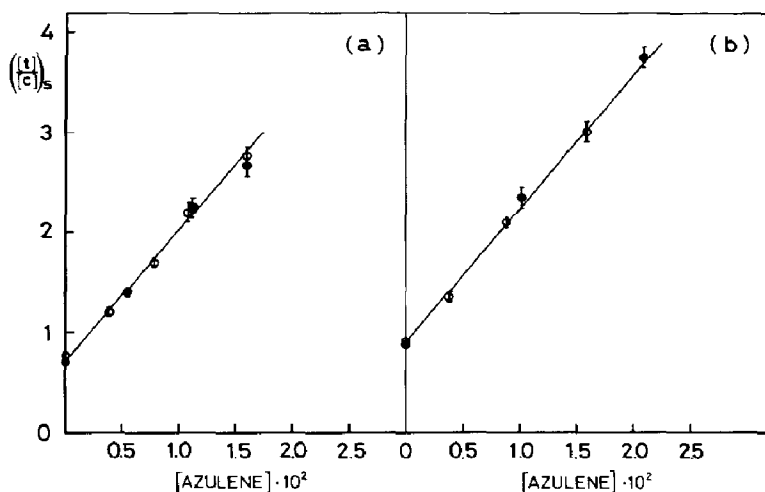


Fig. 2. Effect of azulene on the photostationary states in the *cis-trans* photoisomerization of 3-StQ. (a) Direct photoisomerization, irradiation at 313 nm; (b) anthraquinone-photosensitized isomerization, irradiation at 400 nm. \circ , Deaerated solutions; \bullet , air saturated solutions.

effect on the photostationary composition is very small compared with that on the sensitized one [10].

Oxygen is without effect on the photostationary composition. Such behaviour was also observed in the direct photoisomerization of nitrostilbenes [4] and in the sensitized photoisomerization of stilbene [5], and was explained by assuming that oxygen quenches the "phantom" triplet, without affecting its decay ratio [5]. If this interpretation is correct, the slopes of the azulene plots should be lowered in the presence of oxygen,

TABLE 1

Intercepts and slope to
intercept ratios of the plots
in Fig. 2.

	<i>i</i>	<i>s/i</i>
Direct	0.75	165
Sensitized	0.90	150

because of its competitive quenching. This effect was observed in the photosensitized isomerization of stilbene [5], but is absent in both direct and sensitized photoisomerization of 3-StQ. This result is rather surprising, oxygen being known as a very efficient triplet quencher [5]. Flash-photolysis measurements for the direct observation of transients and for the determination of their lifetime are in progress.

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