

## MECHANISM OF PHOTOCHEMICAL REACTIONS OF ARYLVINYLENETHIOAMIDES II: THE PHOTOISOMERIZATION OF $\alpha$ -THIENYLVINYLENE-THIOAMIDE

L. L. COSTANZO, S. GIUFFRIDA and S. PISTARÀ

*Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, 95125 Catania (Italy)*

G. CONDORELLI

*Cattedra di Chimica Generale ed Inorganica, Facoltà di Farmacia, Università di Catania, 95125 Catania (Italy)*

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### Summary

The *cis-trans* photoisomerization of  $\alpha$ -thienylvinylethioamide in benzene solution displayed some interesting features. The quantum yields  $\varphi_{t \rightarrow c}^q$  and  $\varphi_{c \rightarrow t}^q$  of the *trans*  $\rightarrow$  *cis* isomerization and the *cis*  $\rightarrow$  *trans* isomerization respectively showed different dependences on the azulene concentration. Smaller  $\varphi_{t \rightarrow c}^q$  values and higher  $\varphi_{c \rightarrow t}^q$  values were found when the azulene concentration was increased. The photostationary state changed according to the quantum yield variation. A mechanism for *cis-trans* photoisomerization via the triplet state as an intermediate that is quenched by azulene is presented. The results of benzophenone sensitization experiments supported the proposed model.

### 1. Introduction

The most recent theoretical [1 - 3] and experimental [4 - 8] studies of *cis-trans* isomerization about the ethylenic bond indicate that this process can occur (i) via twisting of the excited singlet states into one distorted singlet state ( $^1p$ ) or (ii) via intersystem crossing of the excited singlet states into triplet states and subsequent twisting into one distorted state of the same multiplicity ( $^3p$ ). The molecule decays from the  $^1p$  and  $^3p$  states to the ground *trans* or *cis* isomers either directly or through a  $^0p$  state. Whether this rotation takes place in the excited singlet state or in the triplet state depends mainly on the form of the potential energy, which is a function of the torsional angle, and on the efficiency of intersystem crossing and hence on the nature of the substituents bonded to the ethylenic group.

Since most of the investigations reported have concerned stilbene, stilbene derivatives and stilbene aza analogues, we considered it useful to extend our study to another type of compound, the arylvinylethioamides. These compounds are interesting both theoretically in view of the contribution they can make to the general problem of the photoisomerization mechanism and practically in that they are known to have a bactericidal effect [9].

Our earlier investigations [10] of the photochemical behaviour of thiocinnamamide suggested that the triplet state does not participate in the photoisomerization process of this compound. In the present work we report an investigation of the photoisomerization of  $\alpha$ -thienylvinylethioamide ( $C_4H_4S-CH=CH-CSNH_2$ ) (TVA).

## 2. Experimental details

### 2.1. Preparation and characterization of *trans* and *cis* $\alpha$ -thienylvinylethioamide

*trans*-TVA (melting point, 136 - 137 °C) was prepared in absolute ethanol from thioacetamide and thienyl aldehyde [8]. *cis*-TVA was prepared by irradiating benzene solutions of the *trans* isomer with a mercury immersion vapour lamp (Hanovia 450 W) fitted with a uranium filter. A mixture that was rich in the *cis* isomer (melting point, 96 - 97 °C) was obtained, and this was isolated using a silica gel column with a 60:40 diethyl ether:petroleum ether mixture as the eluant.

The *cis* configuration was assigned on the basis of a comparative analysis of the UV, IR and nuclear magnetic resonance (NMR) spectra of the two isomers. The UV and visible spectra of the *trans* isomer, recorded in benzene, showed a shoulder at about 460 nm ( $\epsilon = 315$ ) which was attributable to an  $n-\pi^*$  transition overlapped by the nearest  $\pi-\pi^*$  band; they also showed a three-band  $\pi-\pi^*$  system with peaks centred at 360 nm ( $\epsilon = 13\ 000$ ), 330 nm ( $\epsilon = 15\ 600$ ) and 320 nm ( $\epsilon = 16\ 100$ ) that were attributable to conjugated thioamidic, ethylenic and thienylic groups respectively. In the *cis* isomer spectra there was a shoulder at about 405 nm ( $\epsilon = 910$ ), which was due to an  $n-\pi^*$  transition, and a  $\pi-\pi^*$  band at about 295 nm ( $\epsilon = 12\ 900$ ). A marked hypochromic and hypsochromic effect was observed which indicated a decrease of the conjugation because of an increase in the steric hindrance of the molecule in the *cis* configuration. The bands in the IR spectra at 1000 - 1600  $cm^{-1}$ , where NCS group and thienylic ring stretching vibrations occur, were shifted to higher frequencies for the *cis* isomer, in agreement with the probable vibration hindrance in that configuration. The splitting of the  $NH_2$  group bending bands at about 850  $cm^{-1}$  in the *cis* isomer spectra confirmed this configuration. Ethylenic protons appeared as an AB system at  $\delta = 6.7$  ppm and  $\delta = 8$  ppm ( $J_{AB} = 15$  Hz) in the NMR spectrum of the *trans* isomer, whereas in the *cis* isomer spectrum they appeared at  $\delta = 6.1$  ppm and  $\delta = 6.6$  ppm ( $J_{AB} = 12$  Hz).

## 2.2. Apparatus

Standard equipment was used for the irradiation. A low pressure mercury vapour lamp (Hanau Q 400) equipped with an interference filter (Schott) was used to produce radiation of wavelengths 313, 333, 365, 405 and 436 nm. The intensity of the incident light was measured using a ferric oxalate actinometer and was of the order of  $10^{-7}$  -  $10^{-8}$  einstein  $\text{min}^{-1}$ .

Spectrophotometric measurements were carried out using an Optica CF4NI spectrophotometer with the cell compartment thermostatted at 25 °C. IR spectra were obtained on a Perkin-Elmer model 257 spectrophotometer using the KBr pellet technique. The NMR spectra of the samples in  $\text{CDCl}_3$  solutions were obtained on a Varian EM 360 instrument. Tetramethyl silane was used as an internal standard.

## 2.3. Procedure

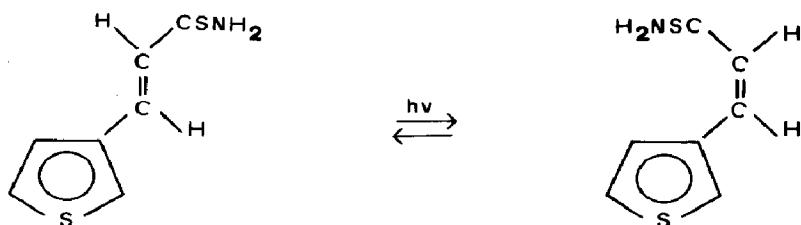
In the direct photoisomerization experiments benzene solutions containing pure isomer in the concentration range  $(0.5 - 3.5) \times 10^{-4}$  M were irradiated in standard spectrophotometric cells. The photochemical reaction was followed spectrophotometrically in suitable absorption regions. The quantum yields were calculated from the initial rate of the reaction or by Zimmerman's method. Since the same results were obtained regardless of whether the experiments were carried out on deaerated or non-deaerated samples, we used non-deaerated samples.

In the experiments carried out with the quencher the following conditions were chosen: [*trans*-TVA],  $1 \times 10^{-4}$  M; [*cis*-TVA],  $2.5 \times 10^{-4}$  M; [azulene],  $(0 - 4.4) \times 10^{-2}$  M;  $\lambda_{\text{exc}} = 405$  nm. These conditions ensured that as much light as possible was absorbed by the TVA. When necessary, the light intensity value used in the quantum yield calculations was corrected for the fraction absorbed by the azulene.

In the sensitized photoisomerization experiments samples of benzophenone and TVA were irradiated at 333 nm after deoxygenation with a stream of very pure nitrogen. The concentrations of the sensitizer and the TVA were as follows: [benzophenone] = 0.2 M; [*trans*-TVA],  $(0.5 - 2.5) \times 10^{-4}$  M; [*cis*-TVA],  $(1.5 - 4.5) \times 10^{-4}$  M. In these conditions the light was completely absorbed by the sensitizer. The quantum yields were calculated from the conversion (less than 10%) during the initial stages of the reaction.

## 3. Results

Under direct irradiation TVA underwent *cis*  $\rightleftharpoons$  *trans* isomerization:



The spectrum of the irradiated solution shows a gradual variation (Fig. 1) until it reaches a stationary state which is a function of the exciting wavelength. The process is not thermally reversible but it can be altered by irradiation with light of a suitable wavelength. The constant isosbestic point and the chromatographic analysis indicated that only one product was formed by irradiation; no side reactions were detected.

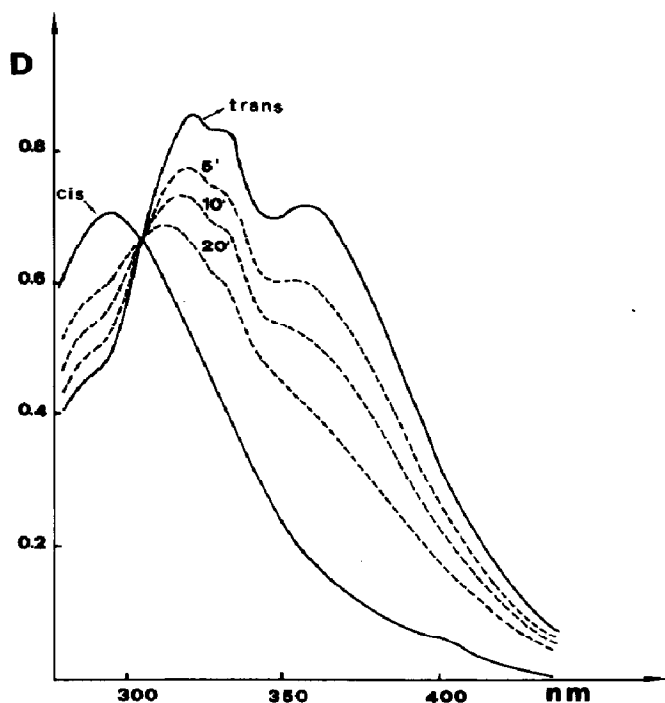


Fig. 1. Changes in the spectrum of TVA in benzene produced by irradiation at 365 nm.

The photochemical isomerization was investigated as a function of the irradiating wavelength, the TVA concentration and the presence of the triplet quencher (azulene). It was found that the quantum yields were independent of the irradiating wavelengths and the initial TVA concentration. The following values were obtained:

$$\varphi_{t-c} = 0.34 \pm 0.02 \quad \varphi_{c-t} = 0.30 \pm 0.02$$

At all wavelengths the photoequilibrium state was close to that predicted by the relation

$$\frac{[\text{trans-TVA}]}{[\text{cis-TVA}]} = \frac{\epsilon_c \varphi_{c-t}}{\epsilon_t \varphi_{t-c}}$$

The quantum yield values and the photoequilibrium composition were the same in deaerated and non-deaerated samples.

In the presence of azulene (Q) the photoisomerization kinetics were altered as follows. As the concentration of azulene increased, the *trans* → *cis* quantum yields decreased whereas the *cis* → *trans* quantum yields in-

creased (Fig. 2); it was also observed that, as the quantum yields changed, the photoequilibrium composition became richer in the *trans* isomer. The

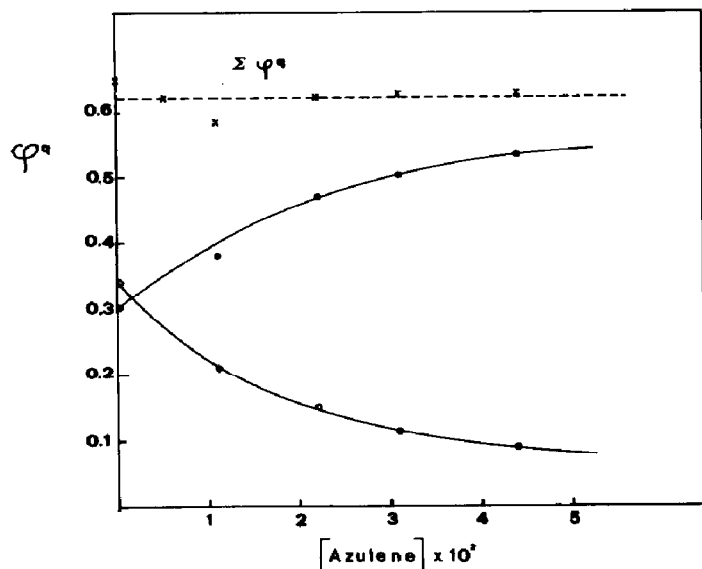


Fig. 2. Quantum yields for *trans* → *cis* (○) and *cis* → *trans* (●) isomerization of TVA and the total quantum yield (x) as a function of the azulene concentration ( $\lambda_{\text{exc}} = 405 \text{ nm}$ ).

sum of the quantum yields approximated to a constant value with an error of less than 10% (Fig. 2). The reciprocal of the *trans* → *cis* quantum yield was a linear function of the quencher concentration:

$$\frac{1}{\varphi_{t-c}^q} = a + b[Q]$$

i.e.  $\varphi_{t-c}^q$  tended towards zero as the quencher concentration increased (Fig. 3).

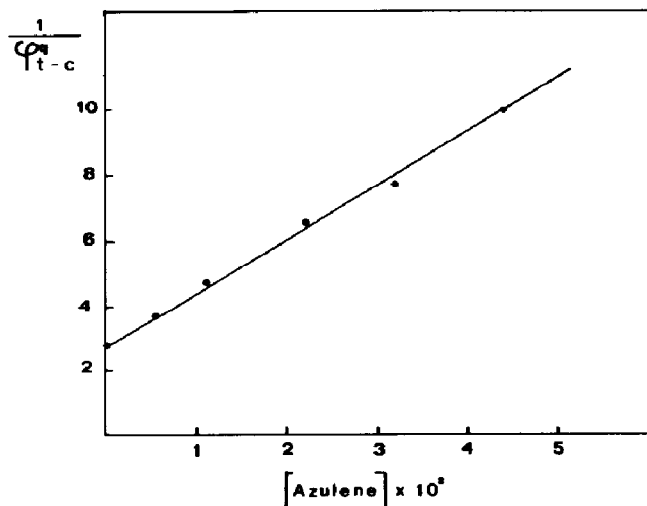


Fig. 3.  $1/\varphi_{t-c}^q$  as a function of the azulene concentration.

Sensitized photoisomerization of both isomers can be induced by benzophenone which was the best sensitizer for achieving pure sensitization conditions. The results showed that the apparent initial quantum yields of the isomerization increase as the TVA concentration increases. Plots of  $1/\Phi_{\text{app}}$  versus  $1/[\text{TVA}]$  gave good straight lines, and the limit quantum yields were calculated from the intercepts of these lines. The values obtained were  $\Phi_{t-c} = 0.48$  and  $\Phi_{c-t} = 0.45$ . The ratios of the intercepts to the slopes gave the sensitization constant  $\tau k_s$ , where  $\tau = 1.9 \times 10^{-6}$  s is the lifetime of benzophenone. The values of  $k_s$  for the *trans* and the *cis* isomers are  $1.5 \times 10^9$  and  $1.9 \times 10^9$  respectively. The composition of the photo-stationary state was, within experimental error, that expected for the relation

$$\frac{[\textit{trans-TVA}]}{[\textit{cis-TVA}]} = \frac{\Phi_{c-t}}{\Phi_{t-c}}$$

The combined use of the sensitizer and the quencher does not give correctly interpretable results because of the impossibility of achieving experimental conditions suitable for such a study. In fact the relative spectral characteristics of benzophenone and TVA do not allow an appropriately high TVA concentration to be attained without the occurrence of a concomitant direct isomerization.

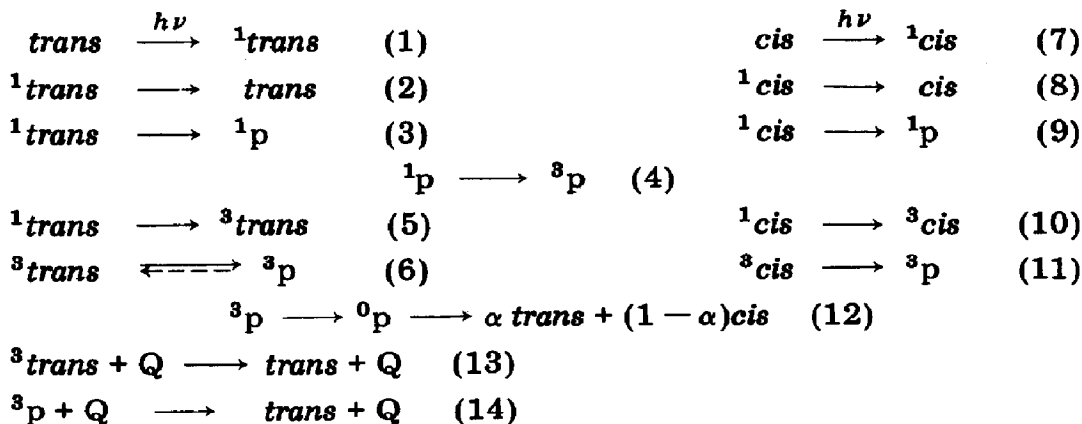
#### 4. Discussion

The overall results can be interpreted by the scheme in Fig. 4. When the *trans* molecule has attained the lowest singlet state for direct irradiation (1) or for decay from higher states it takes the following pathways: (2) internal conversion to the ground *trans* isomer, (3) relaxation to the minimum ( $^1p$ ) of the potential energy surface with concomitant twisting and (4) subsequent intersystem crossing to the  $^3p$  state or (5) intersystem crossing to  $^3\textit{trans}$  and (6) relaxation to  $^3p$ . Pathways (3), (4) and (5), (6) lead to population of the distorted state  $^3p$  from which the molecule undergoes intersystem crossing to  $^0p$  (the distorted form of the ground state) and subsequent decay to the ground *trans* and *cis* isomers according to the ratio  $\alpha/(1 - \alpha)$  (0.45 - 0.48) obtained in the sensitized experiments. The  $^1\textit{cis}$  molecule populates the  $^3p$  state through pathways (9), (4) and (10), (11) by an analogous mechanism. Because the sum of the sensitized quantum yields is almost unity, direct decays from the  $^3\textit{trans}$  and  $^3\textit{cis}$  states to the ground state are excluded.

At present there is no evidence as to whether both methods of attaining  $^3p$  (via  $^1p$  or via  $^3\textit{trans}$  and  $^3\textit{cis}$ ) are operative or whether only one of them is.

The effect of azulene on the photoisomerization of TVA is interpreted on the basis of the hypothesis that the quencher interacts only with triplet states because the spectral features of TVA and azulene are not such as to





By making the usual assumption of a stationary state, the following relations can be obtained from eqns. (1) - (14) for the effect of the quencher on the isomerization process:

$$\frac{\varphi_{t-c}}{\varphi_{t-c}^a} = 1 + K[\text{Q}] \quad (15)$$

$$\frac{\varphi_{c-t}^a}{\varphi_{t-c}^a} = \frac{\varphi_{c-t}}{\varphi_{t-c}} \left( 1 + \frac{K}{\alpha} [\text{Q}] \right) \quad (16)$$

$$\frac{[\text{trans-TVA}]_a}{[\text{cis-TVA}]_a} = \frac{\epsilon_c \varphi_{c-t}}{\epsilon_t \varphi_{t-c}} \left( 1 + \frac{K}{\alpha} [\text{Q}] \right) \quad (17)$$

where

$$K = \frac{k_{13} k_{-6}}{k_{12} k_6}$$

for hypothesis (1) and

$$K = \frac{k_{14}}{k_{12}}$$

for hypothesis (2).

The experimental values of  $\varphi_{t-c}/\varphi_{t-c}^a$ ,  $[\text{trans-TVA}]_a/[\text{cis-TVA}]_a$  and  $\varphi_{c-t}^a/\varphi_{t-c}^a$  are plotted against [azulene] in Figs. 5(a), 5(b) and 5(c) respectively. Good straight lines are obtained which confirm that the experimental data fit eqns. (15) - (17). The value of the slope-to-intercept ratio for Fig. 5(a) is 50, whereas those for Figs. 5(b) and 5(c) are each 106. The value of 0.47 for  $\alpha$  calculated from these data is almost equal to the experimental value (0.45).

The excellent agreement of the experimental results with the theoretical predictions strongly supports the validity of the proposed model.



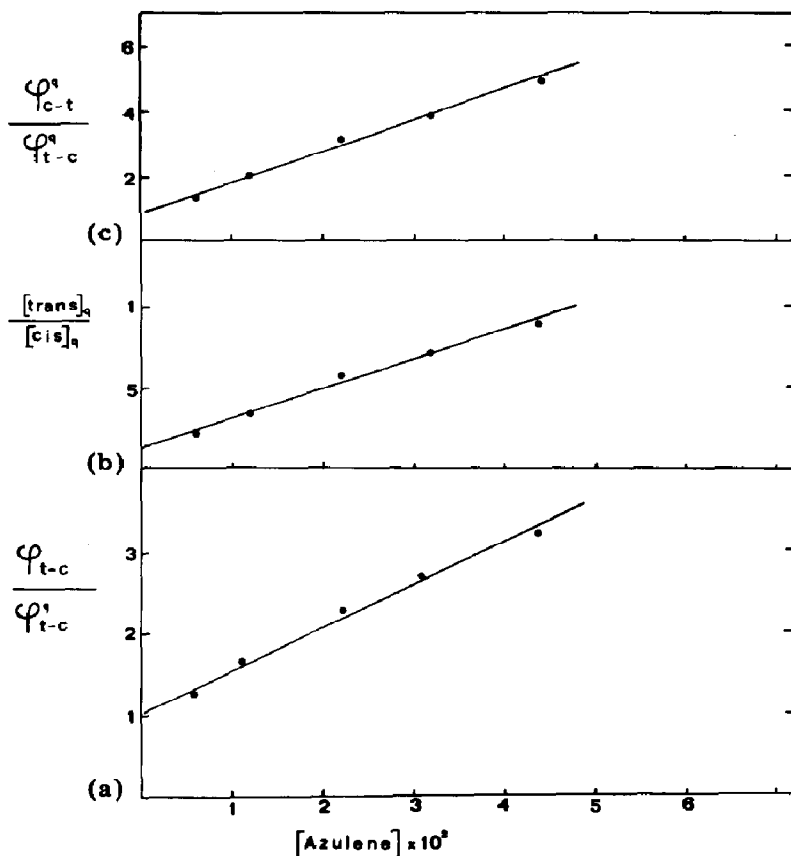


Fig. 5. The effect of azulene on the direct isomerization of TVA.

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