MECHANISM OF PHOTOCHEMICAL REACTIONS OF ARYLVINYLENETHIOAMIDES III: THE PHOTOISOMERIZATION OF 2-NAPHTHYLVINYLENETHIOAMIDE

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(Received April 12, 1983)

Summary

The *cis–trans* photoisomerization of 2-naphthylvinylenethioamide was investigated in ethanol and benzene solutions at various excitation wavelengths. The quantum yields varied in an irregular manner with the excitation wavelength; this unusual result was attributed to the existence of rotamers, each decaying with its own characteristics. The *trans* → *cis* quantum yield decreased with increasing quencher concentration in the presence of azulene, whereas the *cis* → *trans* yield increased. The sum of the two quantum yields was constant. Benzophenone sensitized the photoisomerization such that the same quantum yield (0.5) was obtained for the *trans* → *cis* and the *cis* → *trans* processes. The results were interpreted on the basis of an isomerization scheme in which the process proceeded through a triplet state directly quenched to the *trans* isomer by azulene.

1. Introduction

Our earlier investigations of the photochemical behaviour of arylvinylenethioamides provided evidence for the role of the aryl ring in the photoisomerization mechanism. In the two cases previously studied, we found that direct photoisomerization occurred via singlet states for thiocinnamide [1] and via triplet states for α-thienylvinylenethioamide [2]. To contribute to a better understanding of the photoisomerization mechanism in compounds of this type we performed a photochemical investigation of 2-naphthylvinylenethioamide (NVTA) and the results are reported in this paper.

2. Experimental details

2.1. *Preparation and characterization of trans- and cis-2-naphthylvinylene-thioamide*

trans-NVTA (melting point, 215 - 217 °C) was prepared in absolute ethanol from thioacetamide and naphthylaldehyde [3]. *cis*-NVTA (melting point, 126 - 128 °C) was prepared by irradiating solutions of the *trans* isomer in benzene with a mercury immersion vapour lamp (Hanovia 450 W) fitted with a uranium glass filter. The *cis* isomer was isolated from the irradiated solutions using silica gel column chromatography with a 60:40 diethyl ether:petroleum ether mixture as eluent. The *cis* configuration was assigned on the basis of a comparative analysis of the IR and nuclear magnetic resonance (NMR) spectra of the two isomers.

The IR data are as follows: *trans* isomer, 850 cm^{-1} (ν_{NH} bending) and 1240 - 1260 cm^{-1} ($\nu_{C=S}$ stretching); *cis* isomer, 860 - 870 cm^{-1} (ν_{NH} bending) and 1270 - 1280 cm^{-1} ($\nu_{C=S}$ stretching). The splitting of the bending band of NH and the shift to higher frequencies of the stretching vibration of C=S in the *cis* isomer are in agreement with the enhanced steric hindrance in that configuration.

The NMR data (obtained in dimethyl sulphoxide at 60 MHz) are as follows: *trans* isomer, $\delta = 7.1$ - 8.1 ppm (multiplet; 8 H) and $\delta = 7.0$ ppm (doublet; 1 H; $J = 14$ Hz); *cis* isomer, $\delta = 7.3$ - 8.1 ppm (multiplet; 8 H) and $\delta = 6.35$ ppm (doublet; 1 H; $J = 5$ Hz). The shift to a lower δ value and the decrease in the coupling constant found in the *cis* isomer confirmed the configuration.

Further support for the two different geometric configurations was obtained from the UV and visible spectra recorded in benzene and ethanol. The spectra of the *trans* isomer showed a shoulder due to an n,π^* transition at 450 nm ($\epsilon = 280$) (extinction coefficients are given in decimetres cubed reciprocal mole centimetres) in benzene and a three-band π,π^* system with the following absorption maxima (in nanometres): 360, 348 ($\epsilon = 14\,000$ and $\epsilon = 15\,000$), and 317, 307 ($\epsilon = 19\,500$ and $\epsilon = 18\,000$) in benzene; 358, 342 ($\epsilon = 14\,000$ and $\epsilon = 15\,500$), 313, 305 ($\epsilon = 22\,500$ and $\epsilon = 21\,500$) and 278, 269 ($\epsilon = 23\,000$ and $\epsilon = 22\,500$) in ethanol. A shoulder was observed at 254 nm ($\epsilon = 17\,500$). In the spectra of the *cis* isomer the n,π^* shoulder was more prominent in benzene at 400 nm ($\epsilon = 800$). All the π,π^* bands were shifted to higher frequencies with the following maxima: 308, 298 ($\epsilon = 16\,000$ and $\epsilon = 15\,000$) in benzene; 304, 292 ($\epsilon = 16\,000$ and $\epsilon = 16\,500$) and 264, 258 ($\epsilon = 22\,000$ and $\epsilon = 22\,500$) in ethanol. The spectra were in accord with the enhanced steric hindrance of the *cis* isomer and the consequent loss of planarity and decrease in conjugation.

2.2. *Apparatus and procedure*

The apparatus used for irradiation, for measuring the incident light and for obtaining the spectra was the same as that described previously [2].

The direct photoisomerization was carried out using solutions of pure isomer in benzene and ethanol deaerated with nitrogen. The experimental conditions were as follows: [NVTA] = 10^{-3} - 0.5×10^{-4} M; excitation wavelengths λ_{exc} of 254, 313, 333, 365 and 436 nm. The quantum yields were calculated from the initial rate of the reaction or by Zimmerman's method. The quencher experiments were carried out in benzene solutions under the following conditions: [trans-NVTA] = 0.6×10^{-3} M; [cis-NVTA] = 10^{-3} M; [azulene] = $(1.5 - 10) \times 10^{-2}$ M; λ_{exc} = 405 nm. The conditions were chosen to ensure that as small a fraction of the light as possible was absorbed by the azulene. However, the data were corrected as necessary for the azulene absorption.

The sensitized photoisomerization experiments were performed in benzene solutions under the following conditions: [trans-NVTA] = $(0.1 - 0.3) \times 10^{-3}$ M; [cis-NVTA] = $(0.2 - 0.6) \times 10^{-3}$ M; [benzophenone] = 0.4 M, λ_{exc} = 333 nm. These conditions were chosen to achieve pure sensitization as far as possible. The quantum yields were calculated from the conversions (less than 10%) taking place during the initial stages of the reaction.

All the photochemical kinetics were followed spectrophotometrically in a suitable region of the spectrum.

3. Results

Irradiation of the NVTA solutions at all wavelengths resulted in a gradual variation in the spectrum until a photostationary state, dependent on the excitation wavelength, was attained (Fig. 1). The constant isosbestic
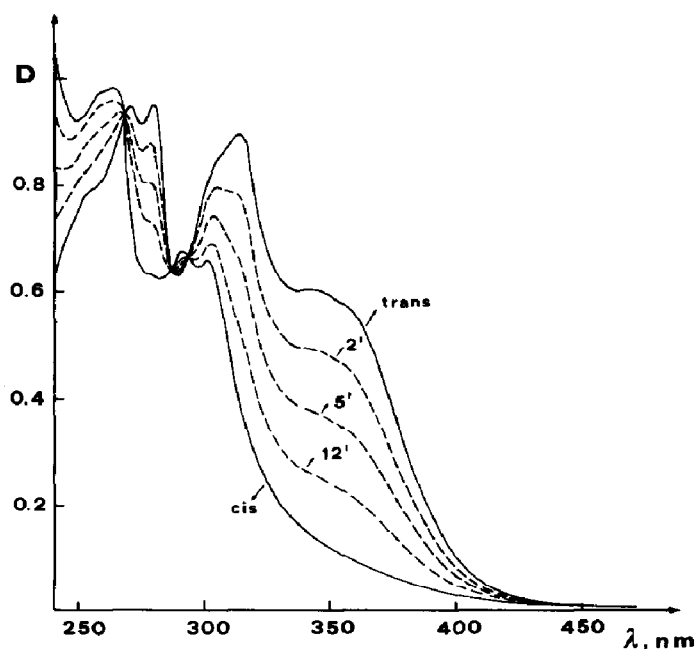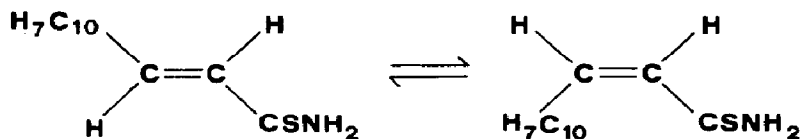

Fig. 1. Changes in the spectrum of trans-NVTA in ethanol produced by irradiation at 365 nm.

points showed that there were no side reactions. The species formed photochemically was isolated by chromatography and was identified as a geometrical isomer of the initial compound. Therefore the photochemical reaction was a cis $\rightleftarrows$ trans isomerization:

The quantum yields varied with the irradiation wavelength as shown in Table 1. In all cases the relation

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

was obtained. The kinetics were monitored in deaerated solutions; however, the same results were obtained for non-deaerated solutions. Some experiments were carried out using oxygen-saturated samples. In these conditions the photochemical kinetics were altered because the cis isomer underwent reaction with oxygen and an unidentified compound was formed. In the range considered the NVTA concentration did not influence the quantum yields.

To demonstrate the role of a triplet state in the process, deaerated solutions of NVTA in benzene were irradiated at 405 nm in the presence of various concentrations of azulene as triplet quencher. The choice of this excitation wavelength was particularly appropriate because the fluorescence of the substrate and of azulene is negligible and because the φ_{t-c} and φ_{c-t} isomerization yields are equal. It was found that as the quencher concentration increased the trans $\rightarrow$ cis quantum yield $\varphi_{t-c}{}^a$ decreased, whereas the cis $\rightarrow$ trans yield $\varphi_{c-t}{}^a$ increased; accordingly the photoequilibrium state

TABLE 1

Quantum yields of direct trans–cis photoisomerization at various excitation wavelengths

λ_{exc} (nm)	Benzene		Ethanol	
	φ_{t-c}	φ_{c-t}	φ_{t-c}	φ_{c-t}
254	—	—	0.19 ± 0.01	0.17 ± 0.01
313	0.285 ± 0.005	0.38 ± 0.03	0.40 ± 0.01	0.480 ± 0.005
333	0.490 ± 0.005	0.37 ± 0.01	0.485 ± 0.005	0.50 ± 0.01
365	0.375 ± 0.005	0.42 ± 0.01	0.38 ± 0.02	0.32 ± 0.01
405	0.380 ± 0.005	0.385 ± 0.005	0.47 ± 0.02	0.43 ± 0.01
436	0.38 ± 0.01	0.46 ± 0.01	0.39 ± 0.01	0.44 ± 0.01

TABLE 2

Quantum yields of *trans–cis* photoisomerization at various azulene concentrations

[Azulene] × 10^2	φ_{t-c}^{q}	φ_{c-t}^{q}	$\Sigma\varphi$
0	0.38	0.38	0.76
2.15	0.26	0.46	0.72
2.81	0.22	0.48	0.70
4.30	0.20	0.55	0.75
5.85	0.17	0.57	0.74
7.65	0.15	0.60	0.75
10.43	0.13	0.62	0.75

$[trans]^{q}/[cis]^{q}$ became richer in the *trans* isomer. The results are reported in Table 2. It is important to note that the sum of the quantum yields is approximately constant at about 0.74.

Benzophenone sensitized the *cis–trans* isomerization of NVTA without significant side reactions under the experimental conditions chosen. The limiting quantum yields calculated from intercepts of the linear plots of $1/\Phi_{dp}$ *versus* $1/[NVTA]$ were $\Phi_{t-c} = \Phi_{c-t} = 0.50 \pm 0.01$. The composition of the photostationary state (50% *cis*-NVTA) agreed with the quantum yield values. The sensitization constants τK_s (where the lifetime τ of the benzophenone triplet is 1.9×10^{-6} s) calculated from the ratios of the intercepts to the slopes of these straight lines gave K_s values very close to those expected for a diffusion-controlled process (3.2×10^9 l mol^{-1} s^{-1} and 4×10^9 l mol^{-1} s^{-1} for the *trans* and the *cis* isomers respectively).

The effect of the quencher on the sensitized photoisomerization has not yet been investigated because the relative spectroscopic properties of the sensitizer, the substrate and the quencher make it difficult to achieve suitable experimental conditions for this study and for quantitative evaluation. Attempts to employ benzil as a sensitizer were unsuccessful because secondary reactions of both isomers were detectable.

4. Discussion

The results obtained show the following. The quantum yields of the direct process fluctuate in an irregular manner with the excitation wavelength. This behaviour is unusual and in particular was not observed in the photochemistry of the analogous arylvinylenethioamides. However, it seems that this anomaly is quite common in compounds containing the naphthalene ring [4, 5]. Because the observed variation is not monotonic, it is not possible to justify it on the basis of competitive decay rates (internal conversion or intersystem crossing) of various excited states. In addition the preliminary

results of a fluorescence investigation show that the fluorescence quantum yields change in a regular manner with the excitation wavelength, decreasing to almost zero at 365 nm. This trend is neither analogous to nor complementary with that observed in photoisomerization; therefore it is reasonable to conclude that the two observations cannot be directly correlated.

We believe that the irregular variation in the photoisomerization quantum yields can be attributed to the existence of the rotamers that have been observed in our current fluorescence investigation. An analogous explanation has been invoked in other investigations of the photochemistry of naphthalene derivatives [4, 5]. The atypical trend of the photoisomerization quantum yields of NVTA may be due to the relatively small shift in the absorption spectra of the rotamers; a different percentage of rotamers can be excited at each irradiation wavelength. If each rotamer has its own decay characteristics, the quantum yields will vary with the wavelength even if each rotamer has the same quantum yield at all wavelengths. This assumption allows us to give a simplified interpretation of the results of the photoisomerization of NVTA.

The data obtained in the presence of the sensitizer and in the presence of azulene show some significant characteristics.

The *trans* → *cis* and *cis* → *trans* quantum yields Φ of the benzophenone-sensitized photoisomerization were equal and this supports the hypothesis that a triplet intermediate, which decays with the same probability to the *trans* and *cis* isomer, was formed during energy transfer.
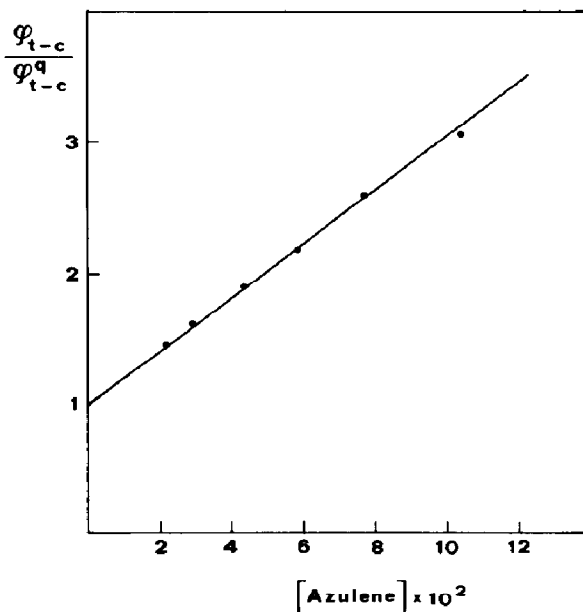

Fig. 2. Dependence of $\varphi_{t-c}/\varphi_{t-c}^q$ on the azulene concentration.
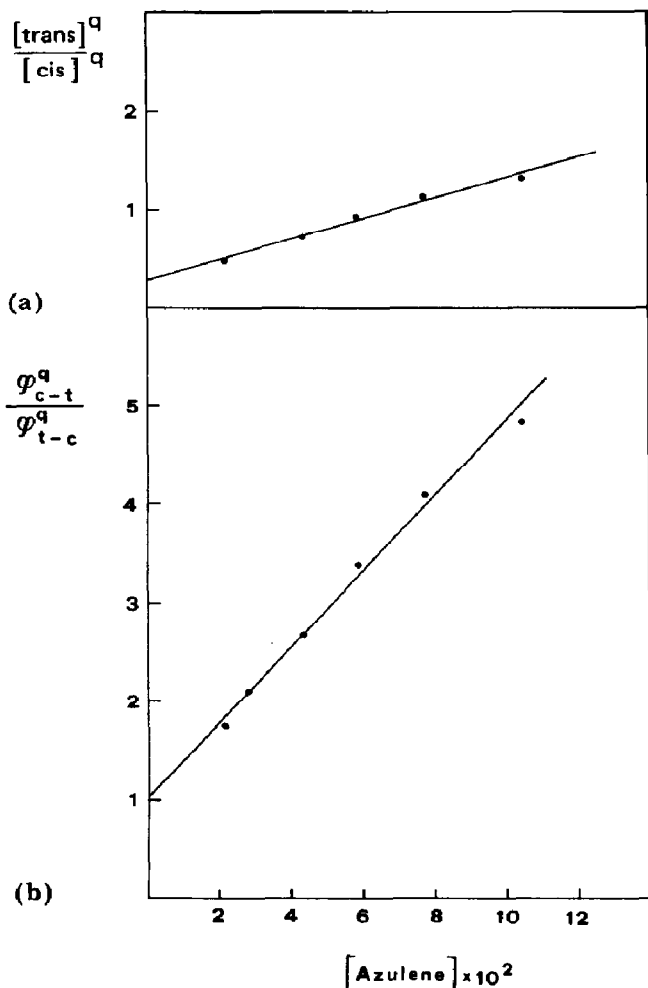
Fig. 3. Dependence of (a) $[trans]^q/[cis]^q$ and (b) $\varphi_{c-t}{}^q/\varphi_{t-c}{}^q$ on the azulene concentration.

The plot of $\varphi_{t-c}/\varphi_{t-c}{}^q$ against the azulene concentration (Fig. 2) gave a good straight line with a slope of 20.

The plots of $\varphi_{c-t}{}^q/\varphi_{t-c}{}^q$ and $[trans]^q/[cis]^q$ against the azulene concentration (Fig. 3) were good straight lines. The ratio of slope to intercept was 40 in each case, *i.e.* a factor of 2 greater than the slope of the plot in Fig. 2.

The sum of $\varphi_{t-c}{}^q$ and $\varphi_{c-t}{}^q$ was constant with a value close to the ratio φ/Φ which was about 0.76.

These results are consistent with a photoisomerization mechanism analogous to that proposed for α-thienylvinylenethioamide [2] which can be represented by the following scheme:

$$trans \xrightarrow{h\nu} {}^1trans \qquad (1)$$

$${}^1trans \longrightarrow trans + h\nu \qquad (2)$$

$${}^1trans \longrightarrow {}^3trans \qquad (3)$$

$${}^1trans \longrightarrow {}^1p \qquad (4)$$

$${}^1trans \longrightarrow trans \qquad (5)$$

$${}^3trans \longrightarrow {}^3p \qquad (6)$$

$$cis \xrightarrow{h\nu} {}^1cis \qquad (7)$$

$${}^1cis \longrightarrow cis + h\nu \qquad (8)$$

$${}^1cis \longrightarrow {}^3cis \qquad (9)$$

$${}^1cis \longrightarrow {}^1p \qquad (10)$$

$${}^1cis \longrightarrow cis \qquad (11)$$

$${}^3cis \longrightarrow {}^3p \qquad (12)$$

$${}^1p \longrightarrow {}^3p \qquad (13)$$

$${}^3p \longrightarrow {}^0p \longrightarrow \alpha trans + (1 - \alpha)cis \qquad (14)$$

The excited singlet ${}^1trans$ or ${}^1cis$ states may fluoresce (eqns. (2) and (8)), decay to the lowest triplet ${}^3trans$ or ${}^3cis$ states (eqns. (3) and (9)), decay to a twisted perpendicular excited singlet state ${}^1p$ (eqns. (4) and (10)) or undergo a radiationless transition to the *trans* or *cis* ground state (eqns. (5) and (11)). In view of the low value of Φ_F (of the order of 10^{-3}) fluorescence is not significant. We were unable to evaluate the importance of decay pathways (5) and (11), but the efficiency η of ${}^3p$ formation, which is given by the ratio φ/Φ, is high ($\eta = 0.76$ for both isomers). The sum of the quantum yields Φ is unity, indicating that the ${}^3trans$ and ${}^3cis$ states decay exclusively to the ${}^3p$ state (eqns. (6) and (12)) which converts to *trans* and *cis* with equal probability (eqn. (14) with $\alpha = 0.5$) via a ${}^0p$ state. The energy difference between the ${}^3p$ and the ${}^0p$ states is probably much smaller than that between the ${}^3p$ and the *trans* or *cis* ground states.

The effect of azulene can be explained in terms of this mechanism by assuming (i) that the ${}^3trans$ state is in thermal equilibrium with the ${}^3p$ state

$${}^3trans \rightleftharpoons {}^3p \qquad (15)$$

and can be quenched to *trans* by azulene

$${}^3trans + Q \longrightarrow trans + Q \qquad (16)$$

or (ii) that the ${}^3p$ state is quenched only to *trans* by azulene

$${}^3p + Q \longrightarrow trans + Q \qquad (17)$$

As noted above the ratio $\varphi_{t-c}/\varphi_{t-c}{}^q$ of the quantum yield of the *trans* $\rightarrow$ *cis* isomerization in the absence of azulene to that in its presence shows a linear dependence on the quencher concentration (Fig. 2), indicating that only one intermediate along the *trans* $\rightarrow$ *cis* route was quenched. The slope K of this Stern–Volmer plot

$$\frac{\varphi_{t-c}}{\varphi_{t-c}{}^q} = 1 + K[Q] \qquad (18)$$

should be given by $K_q\tau$ where K_q is the rate constant for the quenching reaction and $1/\tau$ is the rate constant for the decay of the excited state in the

absence of azulene. $K_q \tau$ was equal to 20 in this case. When pathways (15) and (16) are operative

$$K_q = \frac{K_{16}K_{-15}}{K_{15}}$$

and the τ value of ^3trans cannot be calculated. When pathway (17) is operative and $K_q = K_{16} \approx 10^9$ is assumed τ is of the order of 10^{-8} s or less which is reasonable for a twisted triplet state.

Unfortunately no quenching measurements could be performed on the singlet states because of the low values of Φ_F. In addition, no data for the combined effect of the quencher and the sensitizer are available at present and consequently we have no unequivocal evidence that azulene quenches only the triplet state and does not affect the singlet state.

However, the excellent agreement between the experimental results and those expected on the basis of the above scheme supported our interpretation. In fact, when the usual assumption of a stationary state [6 - 9] is made, the following relations can be obtained from the proposed scheme:

$$\frac{\varphi_{c-t}{}^q}{\varphi_{t-c}{}^q} = \frac{\varphi_{c-t}}{\varphi_{t-c}} \left(1 + \frac{K}{\alpha}[Q]\right) \tag{19}$$

$$\frac{[trans]^q}{[cis]^q} = \frac{\epsilon_c \varphi_{c-t}}{\epsilon_t \varphi_{t-c}} \left(1 + \frac{K}{\alpha}[Q]\right) \tag{20}$$

The experimental values of the slope-to-intercept ratios of eqns. (19) and (20) are the same and differ from the slope of eqn. (18) by a factor of $1/\alpha$. From sensitization experiments we expected α to have a value of 0.5 and this was found.

In addition we have

$$\varphi_{t-c}{}^q = \eta' \frac{1 - \alpha}{1 + K[Q]} \tag{21}$$

$$\varphi_{c-t}{}^q = \eta'' \alpha \frac{1 + K[Q]/\alpha}{1 + K[Q]} = \eta'' \frac{\alpha + K[Q]}{1 + K[Q]} \tag{22}$$

where η' and η'' are the efficiency of ^3p formation from ^1trans and ^1cis respectively. When $K[Q]$ is much greater than unity $\varphi_{t-c}{}^q$ tends to zero and $\alpha + K[Q] \approx 1 + K[Q] \approx K[Q]$ so that $\varphi_{c-t}{}^q$ approaches η''. The experimental values of φ^q do not reach these limits because the azulene concentration is not high enough. However, the value of $\Sigma\varphi^q$ obtained from eqns. (21) and (22) is very significant. In fact, since we found $\eta' = \eta'' = \eta$, the sum $\Phi_{t-c}{}^q + \Phi_{c-t}{}^q$ is equal to η.

The good agreement of the expected value of η (0.76) with that found (about 0.74) provides further support for the hypothesis that the cis–trans photoisomerization of NVTA occurs only through the triplet pathway and that the participation of the singlet excited states is negligible or absent.

Finally it should be noted that, because the solvents have little influence on the photochemical kinetics, the ground and excited states are equally solvated.

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