

STUDY OF THE *TRANS*→*CIS* PHOTOISOMERIZATION OF 4-NITRO-4'-DIMETHYLAMINOSTILBENE IN TOLUENE SOLUTIONS

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ABSTRACT

The direct *trans*→*cis* photoisomerization of 4-nitro-4'-dimethylaminostilbene (NDMAS) in toluene solutions and the role of triplet states have been studied by standard techniques and laser flash photolysis, respectively. The quantum yields of *trans*→*cis* photoisomerization ($\phi_{t \rightarrow c}$), of fluorescence (ϕ_f) and of triplet formation (ϕ_T) as well as the triplet lifetime (τ) have been measured as functions of temperature (−80 to 100°C). Different activation energies, obtained from ϕ_f and $\phi_{t \rightarrow c}$ measurements, indicate the presence of two consecutive thermally activated steps. None of the hitherto published mechanisms for *trans*→*cis* photoisomerization account for this result. The *trans*→*cis* photoisomerization pathway is tentatively assigned to the sequence $t^* \xrightarrow{\Delta} A^* \xrightarrow{\Delta} p^* \rightarrow {}^1p \rightarrow (1 - \beta)c$. The steps marked with Δ are thermally activated steps, A^* is an excited *trans* state and p^* is an excited twisted state which decays to the twisted ground state (1p) which in turn deactivates to the *cis* and *trans* forms.

INTRODUCTION

The mechanism of *trans*→*cis* photoisomerization changes from a singlet pathway at room temperature for stilbene [1, 2] and 4-cyanostilbenes [3, 4] to a triplet pathway for 4-nitrostilbenes [5–10]. Bromo substitution in the 4-position leads to a significant contribution from an upper excited triplet mechanism [11] which is different from the lowest triplet mechanism in the case of 4-nitrostilbenes. Substitution of 4-nitrostilbene by a dialkylamino group in the 4'-position leads to the appearance of a strong intramolecular charge-transfer interaction between the electron-donating and-accepting groups via the conjugated π electrons [12–22]. Does the introduction of a strong intramolecular charge-transfer interaction also change the mechanism of *cis*→*trans* photoisomerization? An attempt to answer this question, which may have some relevance for the photochemistry of dyes containing C=C double bonds, is made in this paper.

The absorption and fluorescence properties of *trans*-4-nitro-4'-dimethylaminostilbene (*trans*-NDMAS) and its unusually large solvatochromism have been investigated by Lippert et al. [12–15] and by Liptay [16]. Lippert was the first to determine the dipole moments for *trans*-NDMAS in the first excited singlet state and the ground state [14–18]. From previous work it is known that the quantum yield of *trans*→*cis* photoisomerization ($\phi_{t \rightarrow c}$)

generally decreases significantly on increasing the polarity of the solvent [19, 20] and increases markedly on increasing the temperature [20]. Formation of the lowest triplet state after laser pulse excitation of *trans*-NDMAS has been reported recently [5, 8]. Whether or not the observed triplet is involved in the *trans*→*cis* photoisomerization is an open question. For 4-nitro-4'-methoxystilbene (NMS), another molecule with intramolecular charge-transfer characteristics, a triplet mechanism has been established [5–10]. On the other hand, a singlet mechanism has been suggested for the *trans*→*cis* photoisomerization of 4-cyano-4'-methoxy-(CMS) and 4-cyano-4'-dimethyl-amino-stilbene (CDMAS) [3, 4].

In this work results from temperature-dependent fluorescence and *trans*→*cis* photoisomerization as well as triplet yield (ϕ_T) and lifetime measurements (τ) of NDMAS are presented. Toluene was chosen since in this solvent the effect of temperature on some photochemical properties, especially on $\phi_{t \rightarrow c}$ is unusually large. The results indicate surprisingly that two consecutive activation barriers are involved in the *trans*→*cis* photoisomerization which occurs by twisting in excited states.

EXPERIMENTAL

Fluorescence and photostationary irradiation measurements were carried out as described previously [6–9]. ϕ_f and $\phi_{t \rightarrow c}$ were determined by standard techniques [4, 11, 23]. The laser flash photolysis set-up was the same as that reported recently [4–11]. Laser pulses at 353 nm (~ 10 ns) were produced by the third harmonic of a neodymium laser [4, 7] and laser pulses at 450 nm (~ 20 ns) were produced by a dye laser (Coumarin 2 in methanol), which was pumped by the 308-nm line of an excimer laser (EMG 200, Lambda Physik). Ferrocene (Merck) was recrystallized, azulene (Aldrich) used as received and *trans*-NDMAS was the same as in previous work [19]. Toluene (Merck) was either used as commercially available or further purified by fractional distillation; identical results were obtained in both cases.

RESULTS

For NDMAS in toluene solutions at room temperature $\phi_{t \rightarrow c}$ is low whereas $\phi_{c \rightarrow t}$ is substantial (Table 1) [20]. In previous work it has been shown that $\phi_{t \rightarrow c}$ and $\phi_{c \rightarrow t}$ for NDMAS in cyclohexane and benzene solutions are almost independent of the wavelength of irradiation ($\lambda_{irr} = 313$ – 436 nm) [19]. No deviation from Lambert–Beer's law was found for the absorption spectrum of *trans*-NDMAS in toluene solutions (range = 1×10^{-5} – 5×10^{-4} M); this is strong evidence against a possible formation of ground-state dimers. In non-polar solvents at lower temperatures, however, aggregation followed by precipitation has been reported [20].

On irradiation of the *trans* isomer at 436 nm, the position of the photostationary state at room temperature was found to be independent of

TABLE 1

Quantum yields of *cis*⇌*trans* photoisomerization, fluorescence and intersystem crossing for NDMAS in toluene solutions^a

<i>t</i> (°C)	$\phi_{t \rightarrow c}$	$\phi_{c \rightarrow t}$	(% <i>cis</i>) _s	ϕ_f	ϕ_T^b
100	0.37 (0.38) ^e	(0.52)	70, 55 ^c	0.26 ^d	0.09
25	0.035 (0.04)	(0.55)	17, 10 ^c	0.54 0.53 ^d	0.05
-25	≤ 0.002		≤ 1	0.6 ^d	0.04

^aIn deoxygenated solutions; $\lambda_{exc} = 436$ nm unless otherwise indicated. ^b $\lambda_{exc} = 353$ nm; within experimental error the same temperature dependence was observed on excitation at 450 nm. ^c $\lambda_{exc} = 366$ nm. ^d $\lambda_{exc} = 410$ nm. ^eValues in parentheses are taken from ref. 20.

[NDMAS] (1×10^{-5} — 5×10^{-4} M); this indicates that *trans*→*cis* photoisomerization is not influenced by the concentration. A precedence for such a concentration effect has been reported for $\phi_{c \rightarrow t}$ of NMS [24].

On going from 25 to 100°C, $\phi_{t \rightarrow c}$ increases by a factor of ten (Fig. 1), whereas $\phi_{c \rightarrow t}$ is essentially temperature-independent (Table 1) [20] suggesting that no thermally activated step is involved in the *cis*→*trans* pathway. As a consequence, the position of the photostationary state is shifted from 17% *cis* at 25°C to 70% *cis* at 95°C ($\lambda_{irr} = 436$ nm). At temperatures below -25°C the percentage of *cis* in the photostationary state [(% *cis*)_s] is smaller than 1, corresponding to $\phi_{t \rightarrow c} \leq 0.002$. From the linear region of the plot of $\log \phi_{t \rightarrow c}$ versus T^{-1} (below 45°C) an activation energy

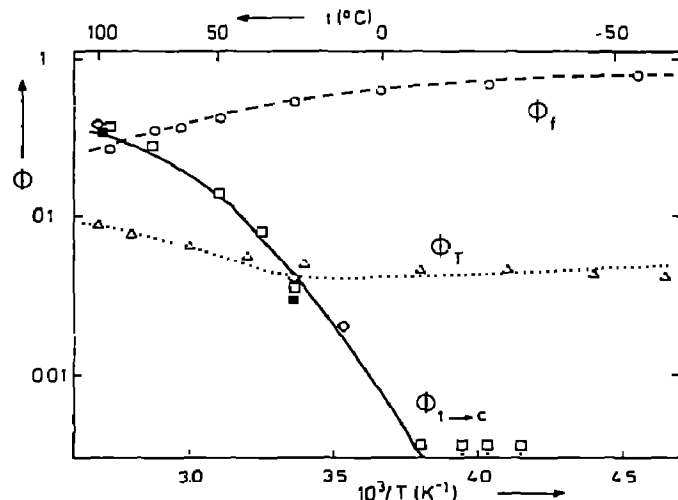


Fig. 1. Semilogarithmic plots of ϕ_f (dashed line, circles; $\lambda_{exc} = 410$ nm), $\phi_{t \rightarrow c}$ (full lines, open squares; $\lambda_{irr} = 436$ nm; full squares, $\lambda_{irr} = 366$ nm) and ϕ_T (dotted lines, triangles; $\lambda_{exc} = 353$ nm) versus T^{-1} in toluene solutions; values for $\phi_{t \rightarrow c}$ (\diamond) were taken from ref. 20; all curves are calculated (see text).

($E_{t \rightarrow c}$) of $10.5 \text{ kcal mol}^{-1}$ was calculated. The question arises as to which step in the *trans*→*cis* photoisomerization the thermally activated step should be assigned? (A thermally activated step is hereafter simply called an activated step.)

An answer to this question may be obtained from the temperature dependences of ϕ_f , ϕ_T and τ . Lippert et al. have shown that the absorption and emission maxima of *trans*-NDMAS exhibit significant temperature dependences [13]. On going from -80 to 100°C , the absorption and emission maxima in toluene solutions are blue-shifted by 800 and 1500 cm^{-1} , respectively. Therefore, care was taken to correct the ϕ_T and ϕ_f values for temperature-dependent changes in the optical densities (at λ_{exc}). Within experimental error, ϕ_f was found to be independent of λ_{exc} (366 – 436 nm). Therefore, temperature-dependent ϕ_f values were obtained by using $\lambda_{exc} = 410 \text{ nm}$, since at this wavelength the molar extinction coefficient is almost independent of temperature. Owing to the fluorescence lifetime of 2 – 3 ns (cf. refs. 13, 22), oxygen quenches ϕ_f . For example, a 35% reduction in ϕ_f was observed in oxygen-saturated solutions at 25°C relative to degassed toluene solutions. The temperature dependence of ϕ_f (Fig. 1) was analyzed in terms of eqn. (1)

$$\phi_f^{-1} = 1 + \frac{k_0}{k_f} + \frac{A_\nu}{k_f} e^{-E_\nu/RT} \quad (1)$$

Here, A_ν and E_ν are the pre-exponential factor and the activation energy of the activated step competing with fluorescence respectively, k_f is the radiative rate constant and k_0 summarizes the rate constants of the non-activated radiationless steps. Values of $E_\nu = 4.0 \text{ kcal mol}^{-1}$, $A_\nu/k_f = 530$ and $k_0/k_f = 0.2$ were obtained from the curve of Fig. 1.

In order to determine the yield (ϕ_T) and lifetime (τ) of the lowest triplet state, laser flash photolysis measurements were performed ($\lambda_{exc} = 353$ and 450 nm). The observed triplet of *trans*-NDMAS in fluid solutions has been recently assigned to the *trans* configuration ($^3t^*$) [8]. ϕ_T was obtained from the optical densities of the triplet absorption after the laser pulse and after disappearance of the fluorescence signal. At room temperature a maximum ϕ_T value of 0.1 was estimated in toluene ($\lambda_{max} = 800 \text{ nm}$) relative to cyclohexane ($\lambda_{max} = 730 \text{ nm}$), assuming $\phi_T = 1$ in cyclohexane and the same extinction coefficient for triplet absorption (at λ_{max}) in both solvents. If, in accordance with $\phi_{t \rightarrow c} = 0.25$ [19, 20], a more realistic value of $\phi_T = 0.5$ for NDMAS in cyclohexane is anticipated, ϕ_T in toluene solutions at room temperature reduces to 0.05 . At lower temperatures ϕ_T remains almost constant and increases by a factor of less than two on going from 25 to 95°C (Fig. 1).

The first-order rate constant for triplet decay ($k_{obs} = \tau^{-1}$) follows an Arrhenius dependence between -80 and 100°C (Fig. 2). The activation energy $E_\tau = 4.0 \text{ kcal mol}^{-1}$ and the pre-exponential factor $A_\tau = 4.5 \times 10^8 \text{ s}^{-1}$ for NDMAS are larger than for NMS in toluene solutions ($E_\tau = 1.6 \text{ kcal mol}^{-1}$, $A_\tau = 1.1 \times 10^8 \text{ s}^{-1}$ [7]). On addition of quenchers [$Q = \text{ferrocene (Fe)}$]

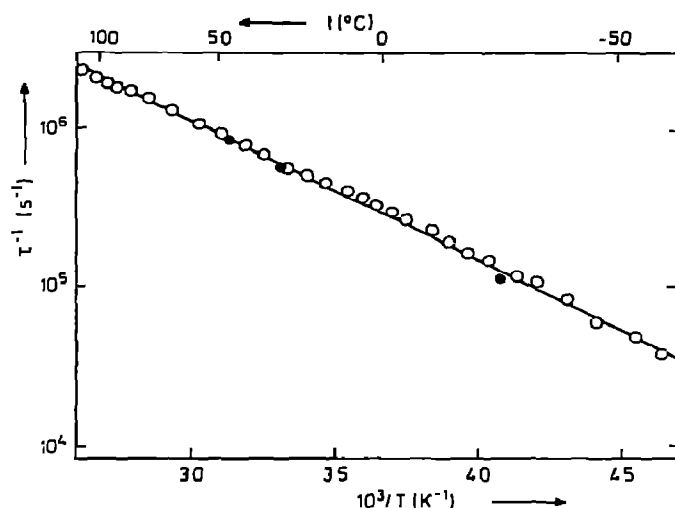


Fig. 2. Semilogarithmic plot of τ^{-1} versus T^{-1} in deoxygenated toluene solutions (\circ , $\lambda_{\text{exc}} = 450 \text{ nm}$; \bullet , $\lambda_{\text{exc}} = 353 \text{ nm}$).

and azulene (Az)] at 25 and 95°C the pseudo first-order decay rate constants showed linear dependences on $[Q]$ as predicted from eqn. (2)

$$k_{\text{obs}} = \tau^{-1} + s_Q [Q] \quad (2)$$

The slopes (s_Q) of these plots are close to the diffusion-controlled limit (Table 2). The slope/intercept ratios (τs_Q) differ from Stern—Volmer constants of $K_{\text{Az}} = 300 \text{ M}^{-1}$ and $K_{\text{Fc}} = 200 \text{ M}^{-1}$, obtained from quenching measurements of $\phi_{t \rightarrow c}$ by azulene and ferrocene, respectively. These quenching measurements were carried out at 95°C since $\phi_{t \rightarrow c}$ is too small at room temperature (see below).

TABLE 2

Triplet lifetimes and rate constants for triplet quenching by ferrocene and azulene^a

Quencher	t (°C)	τ^b (μs)	$s_Q \times 10^{-9}$ ($\text{M}^{-1} \text{s}^{-1}$)	$\tau s_Q \times 10^{-3}$ (M^{-1})
None	100	0.50		
	25	1.8		
	−50	20		
Azulene	95		12	6.0
	25		7.0	13
Ferrocene	95		12.2	6.1
	25		7.6	14

^aIn deoxygenated solutions; $\lambda_{\text{exc}} = 353 \text{ nm}$. ^bWithin experimental error the same values were obtained for $\lambda_{\text{exc}} = 450 \text{ nm}$.

DISCUSSION

The *trans*→*cis* photoisomerization of stilbene derivatives has been reported to occur by twisting about the C=C double bond in the first excited singlet state [1, 4, 11], in an upper excited triplet state [11] or in the lowest triplet state [5–10, 23]. To a first approximation, the activated step, which determines the temperature dependence of $\phi_{t \rightarrow c}$, may in the case of NDMAS be assigned to (1) intersystem crossing, (2) twisting in the lowest triplet or (3) twisting in an excited singlet (Fig. 3).

(1) For NMS in toluene solutions it has been shown that an activated intersystem crossing step ($^1t^* \xrightarrow{\Delta} ^3t^{*'} \rightarrow ^3t^*$) competes with fluorescence ($E_\nu = 5.5 \text{ kcal mol}^{-1}$ †). The *trans*→*cis* photoisomerization occurs via the pathway $^1t^* \xrightarrow{\Delta} ^3t^{*'} \rightarrow ^3t^* \rightleftharpoons ^3p^* \rightarrow ^1p \rightarrow (1 - \alpha)^1c$. If this scheme also applies for NDMAS and if no further activated step is involved in the *trans*→*cis* photoisomerization route, the same activation energy would be expected for ϕ_f and $\phi_{t \rightarrow c}$. Clearly, this scheme cannot be applied for NDMAS in toluene solutions since E_ν is much smaller than $E_{t \rightarrow c}$ (Table 3).

(2) An alternative route is an activated intersystem crossing to the lowest triplet ($^1t^* \xrightarrow{\Delta} ^3t^{*'} \rightarrow ^3t^*$) and an activated twisting step in the triplet state ($^3t^* \xrightarrow{\Delta} ^3p^*$) followed by the sequence $^3p^* \rightarrow ^1p \rightarrow \alpha^1t + (1 - \alpha)^1c$ in competition with non-activated intersystem crossing from the *trans* triplet ($^3t^* \rightarrow ^1t$). In this case, which has been postulated by Fischer and co-workers [20], the temperature dependences of $\phi_{t \rightarrow c}$ and τ should originate predominantly from the same activation barrier ($E_{t \rightarrow c} = E_\tau$). However, $E_{t \rightarrow c}$ is 2.5 times greater than E_τ (Table 3). Furthermore, at temperatures (below 0°C) where the

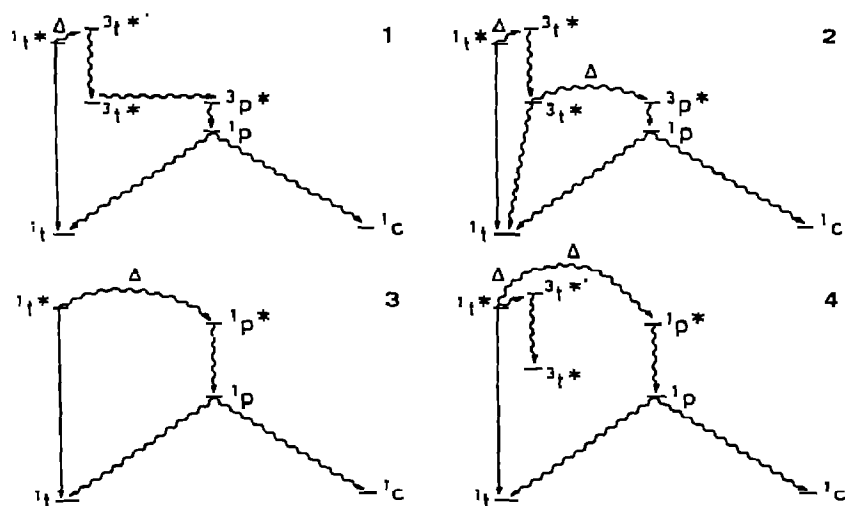


Fig. 3. Possible schemes for *trans*→*cis* photoisomerization of stilbenes (see text).

† A reexamination of the temperature dependence of ϕ_f for NMS in toluene solutions [23] gave $E_\nu = 5.5 \text{ kcal mol}^{-1}$, $A_\nu/k_f = 1.5 \times 10^6$, and $A_\nu \sim 3.2 \times 10^{14} \text{ s}^{-1}$.

TABLE 3

Activation energies and pre-exponential factors from temperature dependences of ϕ_f , $\phi_{t \rightarrow c}$ and τ^a

Temperature dependence	E (kcal mol ⁻¹)	A, k	Eqn. used in evaluation
ϕ_f	$E_\nu = 4.0$	$A_\nu/k_f \approx 530$ $k_o/k_f = 0.2$	(1)
$\phi_{t \rightarrow c}$	$E_{t \rightarrow c} \approx 10.5$ $E_s = 10$	$A_s/k_s = 2.0 \times 10^7$	(3), $E_i = 0^b$ (3), $E_i = E_\nu$
τ	$E_\tau = 4.0$	$A_\tau = 4.5 \times 10^8 \text{ s}^{-1}$	$k_{\text{obs}} = A_\tau e^{-E_\tau/RT}$
ϕ_T		$k_o'/k_f = 0.06$ $k_s/k_s = 8$	(4)

^aData are obtained from Fig. 1 (ϕ_f , $\phi_{t \rightarrow c}$ and ϕ_T) and Fig. 2 (τ). ^bFrom the linear region of the plot of $\ln \phi_{t \rightarrow c}$ versus T^{-1} below 45°C.

activation barrier $E_{t \rightarrow c}$ is no longer overcome, τ is expected to be essentially independent of temperature because the observed triplet should only be deactivated by the step $^3t^* \rightarrow ^1t$. However, the plot of $\log \tau^{-1}$ versus T^{-1} is linear and no bend was found between -80 and 100°C (Fig. 2). This conclusion also holds if the existence of a $^3t^* \xrightleftharpoons[k_2]{k_1} ^3p^*$ equilibrium [7] is assumed at high temperatures. Extension of scheme (2) by introducing a $^3t^* \rightleftharpoons ^3p^*$ equilibrium still does not agree with the results.

For schemes (1) and (2) quenching measurements of $\phi_{t \rightarrow c}$ and τ by azulene (ferrocene) should give almost the same Stern-Volmer constants. However, at 95°C slope/intercept ratios from the former measurements ($K_{Az} = 300 \text{ M}^{-1}$) are much lower than those obtained from the latter ($\tau s_{Az} = 6 \times 10^3 \text{ M}^{-1}$). This result and the temperature dependences of ϕ_f , $\phi_{t \rightarrow c}$, ϕ_T and τ exclude a major contribution from a pathway via the lowest triplet state to the *trans*→*cis* photoisomerization.

(3) If the activated step is assigned to twisting in the first excited singlet state into the twisted singlet configuration ($^1t^* \xrightleftharpoons[k_2]{k_1} ^1p^*$) the same activation energy would be expected for the temperature dependences of $\phi_{t \rightarrow c}$ and ϕ_f ($E_{t \rightarrow c} = E_\nu$). This has been shown to be the case for stilbene, 4-cyanostilbenes (e.g. CDMAS) and for 4-halostilbenes at high temperatures [1-4, 11]. However, for NDMAS in toluene solutions the activation energies $E_{t \rightarrow c}$ and E_ν differ by a factor of 2.5.

(4) This mechanism is a combination of mechanisms (1)-(3). Similar to (1) and (2), an activated intersystem crossing step competing with fluorescence ($^1t^* \xrightleftharpoons[k_2]{k_1} ^3t^* \rightarrow ^3t^*$) is assumed. As in (3), an activated internal conversion step [twisting in an excited singlet ($^1t^* \xrightleftharpoons[k_2]{k_1} ^1p^*$)] is assumed. The temperature dependence of ϕ_f should reflect the two activated steps in competition with the radiative decay of $^1t^*$. However, the observed decrease in ϕ_f on increasing the temperature is too small to account for the dominance of the step $^1t^* \xrightleftharpoons[k_2]{k_1} ^1p^*$ at high temperatures, as expected from the temper-

ature dependence of $\phi_{t \rightarrow c}$. This also holds if, in addition to the described steps, $^1t^*$ decays by non-activated channels, e.g. internal conversion ($^1t^* \rightarrow ^1t$) and/or intersystem crossing ($^1t^* \rightarrow ^3t^*$). However, contribution from the non-activated radiationless steps is suggested to be rather small since $\phi_f = 0.26$ and $\phi_{t \rightarrow c} = 0.37$ at 100°C (Table 1).

(5) Since the hitherto proposed mechanisms for *trans*→*cis* photoisomerization [schemes (1)–(4)] fail to describe the *trans*→*cis* photoisomerization of NDMAS in toluene solutions, a new mechanism is introduced which proposes the intermediacy of a further excited *trans* state (A^*), an excited twisted state (p^*) and two consecutive activated steps. In scheme (5) the following sequence for the *trans*→*cis* isomerization is postulated: $^1t^* \xrightarrow{\Delta} A^* \xrightarrow{\Delta} p^* \rightarrow ^1p \rightarrow (1 - \beta)^1c$ (Fig. 4).

The first activated step ($^1t^* \xrightarrow{\Delta} A^*$, k_1) competes with the fluorescence (k_f) and a non-activated radiationless decay (k_0). The second activated step ($A^* \xrightarrow{\Delta} p^*$, k_3) which represents the isomerization step, competes only with a radiationless decay (k_2). Therefore the activation energy of the fluorescence is different from that for *trans*→*cis* photoisomerization ($E_\nu < E_{t \rightarrow c}$). The temperature dependences of ϕ_f and $\phi_{t \rightarrow c}$ according to this scheme are given by eqns. (1) and (3), respectively

$$\phi_{t \rightarrow c}^{-1} = \left(1 + \frac{k_f + k_0}{A_1} e^{E_1/RT} \right) \left(1 + \frac{k_2}{A_3} e^{E_3/RT} \right) \left(\frac{1}{1 - \beta} \right) \quad (3)$$

Here A_3 and E_3 are the pre-exponential factor and the activation energy of the step $A^* \xrightarrow{\Delta} p^*$ respectively, $E_1 = E_\nu$, $A_1 = A_\nu$ and β is the fraction of p^* decaying to 1t . Since E_1 is significantly smaller than $E_{t \rightarrow c}$, the temperature dependence of $\phi_{t \rightarrow c}$ is mainly determined by the second factor in eqn. (3). Using eqn. (3), $E_3 = 10 \text{ kcal mol}^{-1}$ and $k_2/A_3 = 2.0 \times 10^{-7}$ and assuming

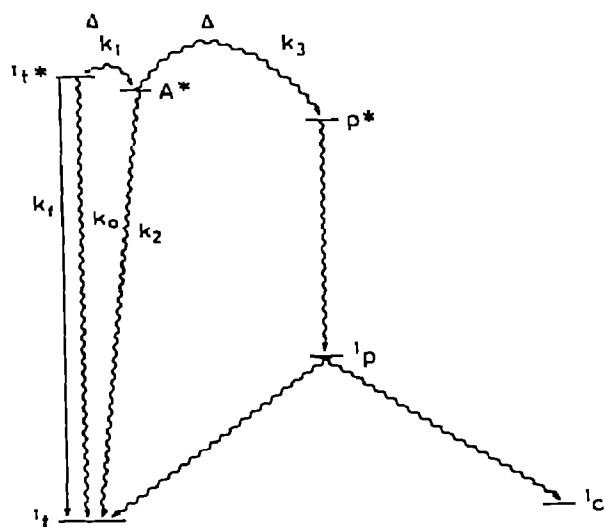


Fig. 4. Scheme proposed for *trans*→*cis* photoisomerization of NDMAS in toluene solutions assuming the minimum of necessary states involved.

$\beta = 0.5$ the calculated curve in Fig. 1 fits reasonably well with the experimental points. The results show that $\phi_{t \rightarrow c}$ is predominantly reduced at lower temperatures by the non-activated step $A^* \rightarrow {}^1t$. The ratio $k_2/A_3 \sim 10^{-7}$ indicates that A^* should have a lifetime of ≤ 100 ns at temperatures below 25°C if a value of $A_3 \geq 10^{14} \text{ s}^{-1}$ is assumed. Owing to the strong fluorescence the search for A^* by absorption spectroscopy has remained unsuccessful. It should be noted that the proposed scheme (Fig. 4), especially the postulation of the state A^* is based only on kinetic and not on structural arguments. At the present time it is not known whether or not A^* and p^* are excited singlet or upper excited triplet states.

The new mechanism (double activated mechanism) outlined above is suggested to be the dominant isomerization route since ϕ_T is too small ($\phi_T \leq 0.09$ whereas $\phi_{t \rightarrow c}$ is ≥ 0.35 above 80°C). Therefore, the contribution from a pathway via the lowest triplet state to the *trans*→*cis* photoisomerization is of minor importance. A small contribution from the triplet route at high temperatures is indicated by the effect of azulene on $\phi_{t \rightarrow c}$. If, on the one hand, only ${}^1t^*$ is quenched by azulene a Stern–Volmer constant of $< 100 \text{ M}^{-1}$ for $\phi_{t \rightarrow c}$ is estimated from fluorescence quenching measurements. If, on the other hand, only the observed triplet is quenched by azulene a Stern–Volmer constant $\tau s_{Az} = 6000 \text{ M}^{-1}$ is expected for $\phi_{t \rightarrow c}$. Experimentally, a Stern–Volmer constant $K_{Az} = 300 \text{ M}^{-1}$ was observed from quenching measurements of $\phi_{t \rightarrow c}$. This result may be explained by a 5% contribution from the quenching of ${}^3t^*$. Therefore, the contribution from the triplet pathway should not exceed 10% and may be even smaller if A^* is also quenched by azulene.

If, by analogy to NMS [6, 7], a ${}^3t^* \rightleftharpoons {}^3p^*$ equilibrium is also assumed for NDMAS, the temperature dependence of the triplet lifetime is mainly determined by a shift of the ${}^3t^* \rightleftharpoons {}^3p^*$ equilibrium to the *trans* side on decreasing the temperature. For NDMAS this shift is stronger and correspondingly the triplet lifetime (see Fig. 2) is larger than for NMS [7]. A stronger intramolecular charge-transfer interaction for NDMAS as compared to NMS may account for this difference. Formation of the lowest triplet may occur from p^* (k_4) as well as from ${}^1t^*$ (k_0'). The latter step is proposed since ϕ_T is almost temperature independent below room temperature. The step $p^{*k_4} \rightarrow {}^3p^* \rightleftharpoons {}^3t^*$ in competition with the step $p^{*k_5} \rightarrow {}^1p$ is assumed to account for the increase in ϕ_T on increasing the temperature. According to this hypothesis ϕ_T is the sum of the two components given in eqn. (4)

$$\phi_T = \frac{k_0'}{k_f} \phi_f + \frac{\phi_{t \rightarrow c}}{1 - \beta} \frac{k_4}{k_4 + k_5} \quad (4)$$

Using eqn. (4), the temperature dependences of ϕ_f [eqn. (1)] and $\phi_{t \rightarrow c}$ [eqn. (3)] and the data listed in Table 3, the calculated curve for ϕ_T in Fig. 1 fits with the experimental points.

Below room temperature the contribution from the lowest triplet pathway to the *trans*→*cis* photoisomerization appears to be small. From sensitized

cis-trans photoisomerization measurements in benzene solutions at room temperature a value of $\alpha' = 0.74$ for the fraction of triplet decaying to 1t has been reported [9]. Assuming $\alpha' = 0.74$ in toluene solutions, a contribution to $\phi_{t \rightarrow c}$ of approximately 0.01 may be estimated. Since at temperatures lower than 0°C, $\phi_{t \rightarrow c}$ drops off significantly while ϕ_T remains constant (Fig. 1), α' may be temperature dependent, thereby reducing $\phi_{t \rightarrow c}$.

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