Fluorescence of Trans-4-Cyano-4′-dimethylaminostilbene; No Evidence for a TICT State

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Dedicated to Professor Günther O. Schenck on the occasion of his 70th birthday

The fluorescence properties of trans-4-cyano-4′-dimethylaminostilbene (trans-**1**) and a rigid analogue, in which the dimethylaminophenyl group is replaced by an indoline ring, trans-1-(4-cyanophenyl)-2-(5-[2,3-dihydro]N-methylindolyl)ethylene (trans-**2**) were studied in 20 solvents. The quantum yields of fluorescence (Φ_f) and of trans→cis photoisomerization ($\Phi_{t\to c}$) as well as the fluorescence maximum ($\tilde{\nu}_f$) and the bandwidth ($\Delta\tilde{\nu}_f$) were examined. The activation energies (range: 3.5 – 7.8 kcal/mol) obtained from Φ_f and $\Phi_{t\to c}$ measurements are nearly the same for **1** and **2** in a given solvent. Φ_f, $\tilde{\nu}_f$ and $\Delta\tilde{\nu}_f$ as a function of solvent polarity and temperature show similar trends for **1** and **2**. No dual emission was observed for either of the cyanostilbenes. These findings indicate that a twisted intramolecular charge transfer (TICT) state is not involved in the relaxation process of the first excited trans singlet state ($^1t^*$). The main deactivation pathway of $^1t^*$ competing with fluorescence is trans→cis photoisomerization by twisting about the C=C double bond in the first excited singlet state for both.

1. Introduction

Aromatic systems with cyano and dialkylamino groups 4-substituted on a benzene ring, e.g. 4-cyano-N,N-dimethylaniline (dimethylaminobenzonitrile, DAB), show dual fluorescence emission [1 – 8]. Grabowski et al. have shown that the origin of the long wavelength fluorescence component is to be attributed to a twisted intramolecular charge transfer (TICT) state in which the dimethylamino group is perpendicular to the phenyl ring [2]. The emission properties of trans-stilbenes, substituted in the 4 and 4′ positions by electron donating and accepting groups, also depend markedly on intramolecular charge transfer interaction [9 – 20]. The question arises therefore whether or not a TICT state is also involved in the deactivation of trans-4-cyano-4′-dimethylaminostilbene (trans-**1**) which may be regarded as an extended DAB-structure. The answer to this question is of importance for the interpretation of experimental data concerning the mechanism of cis-trans photoisomerization of substituted stilbenes.

In the present work we have studied the fluorescence properties of trans-**1** and an analogue, in which a methylamino group is incorporated in a stiff dihydroindole ring (trans-**2**). The two cyanostilbenes differ by virtue of the fact that in **1** the dimethylamino group can undergo a twisting motion about the single bond to the phenyl ring relatively freely, while this is impossible in **2**. Comparative fluorescence studies of DAB and rigid analogues (DAB-system) were decisive for the characterization of a TICT state [1 – 6]. The spectral characteristics of trans-**1** and trans-**2** as well as the quantum yields of fluorescence and trans→cis photoisomerization (Φ_f and $\Phi_{t\to c}$, respectively) are very similar in a broad range of solvents. The absence of dual emission and near parallelism of the temperature dependences of Φ_f, $\Phi_{t\to c}$, the emission maximum and the half-bandwidth ($\tilde{\nu}_f$ and $\Delta\tilde{\nu}_f$, respectively) for both cyanostilbenes speak against involvement of a TICT state.

2. Experimental

Apparatus and Procedures

For irradiation a 1000 W high-pressure xenon-mercury lamp and a monochromator (Schoeffel) and for recording the absorption spectra a spectrophotometer (Perkin-Elmer 554) were used. $\Phi_{t\to c}$ was determined by analysis of the absorption spectra as described elsewhere [17] and by employing the ferrioxalate and the aberchrome 540 actinometers [21, 22]. Emission spectra were recorded on a spectrofluorimeter (Spex-Fluorolog) equipped with

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a photon-counting detection system using a red sensitive photomultiplier (RCA C31034) and a unit which corrects the spectral sensitivity of the photomultiplier and the lamp [23]. Φ_f was determined using 9,10-diphenylanthracene in air-saturated ethanol ($\Phi_f = 0.68$ and 1.0 at 25 and −196 °C, respectively [24]) as fluorescence standard and with the same absorption at λ_{exc}. Temperature dependent emission spectra were also recorded on another spectrofluorimeter (Perkin Elmer, MPF 2A) as described elsewhere [16, 17].

Care was taken to reduce the error in Φ_f due to trans→cis photoisomerization during the fluorescence measurements. The samples were handled under red light and fresh solutions were irradiated for the shortest time possible. For each fluorescence measurement the absorption spectra were measured prior to and after irradiation. Generally, less than 5% trans was converted to cis. No corrections for the refractive index of the solvent were made. The fluorescence spectra were recorded in argon- or air-saturated solutions; in the latter case Φ_f values at room temperature were corrected for oxygen-free solutions by using the experimentally determined Φ_f/Φ_f^{ox} ratio. For $\Phi_{t\to c}$ measurements the samples were deoxygenated by purging with argon.

Materials

Trans isomers of **1** and **2** were synthesized according to the procedure of Pfeiffer [25]. For **2**,1-methyl-5-formyl-2,3-dihydroindole [26] was used as the aldehyde reactant. The reaction product was purified by column chromatography or preparative thin-layer chromatography on silica gel employing a mixture of chloroform and toluene (9:1) as eluant. The main fraction was recrystallized from dioxane to yield yellow needles: mp 183−184 °C; IR(KBr) 3020, 2920, 2840, 2220, 1608, 1580, 1570 cm^{-1}; NMR($CDCl_3$): δ 2.80 (s, 3H), 2.86−3.53 (m 4H), 6.38−7.65 (m, 9H); UV(dioxane) λ_a 388 nm (ε 35300); mass spectrum *m/e* 260 (H^+); Anal. for $C_{18}H_{16}N_2$; calculated: C, 83.04; H, 6.19; N, 10.76; found: C, 83.09; H, 6.17; N, 10.8. Purity of trans-**1**, as determined by HPLC in a mixture of acetonitrile and water (4:1) and monitored at 366 and 390 nm was 99.4 and 99.0%, respectively. Corresponding values of 98.4 and 98.7% were obtained for trans-**2**. By GC the purity of both trans isomers was found to be close to 99%.

9,10-Diphenylanthracene (EGA) was used as supplied. The solvents (Merck) were of highest quality commercially available; Uvasol (e.g. 2,2-dimethylbutane: n-pentane (8:3, DMB-nP), toluene, and acetonitrile) or z.A. n-Pentane, 2-methyltetrahydrofurane (MTHF), benzene, dimethylformamide, n-butanol, and ethanol were purified by fractional distillation. Tetrahydrofuran (THF) was purified on an activated alumina column. MTHF was checked for its peroxide content by the potassium iodide-acetone method prior to use.

3. Results

Spectra

The absorption and fluorescence emission spectra of trans-**1** and trans-**2** in n-pentane, acetonitrile and 2-methyltetrahydrofurane (MTHF) solutions at room temperature are shown in Figs. 1 and 2. The absorption and corrected fluorescence excitation spectra coincide in these cases. All spectra are unstructured except for fluorescence emission spectra in non-polar solvents. The ground state absorption spectra of the two trans isomers in a given solvent are rather similar (Table 1). On increasing the solvent polarity the absorption maximum (λ_a) is displaced to slightly longer wavelengths, e.g. from 375 nm in n-pentane to 390 nm in dimethylformamide for **1** and from 378 to 395 nm

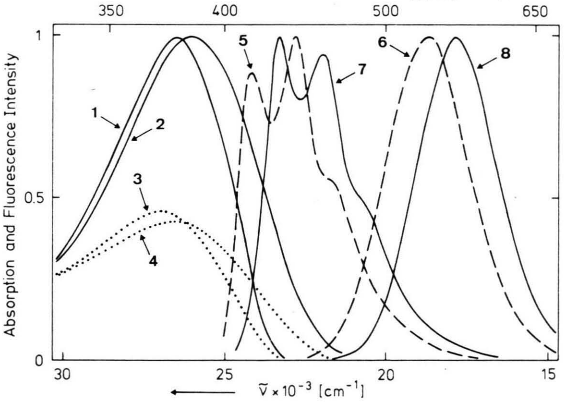

Fig. 1. Absorption spectra of trans-**2** in n-pentane (1, $\varepsilon = 39\,000$) and acetonitrile (2, $\varepsilon = 35\,000$) before irradiation (full lines) and in the photostationary state (dotted lines, 3 and 4, respectively); fluorescence emission spectra of trans-**1** in n-pentane (5) and acetonitrile (6) and of trans-**2** in n-pentane (7) and acetonitrile (8) at room temperature $\lambda_{irr} = 366$ nm).

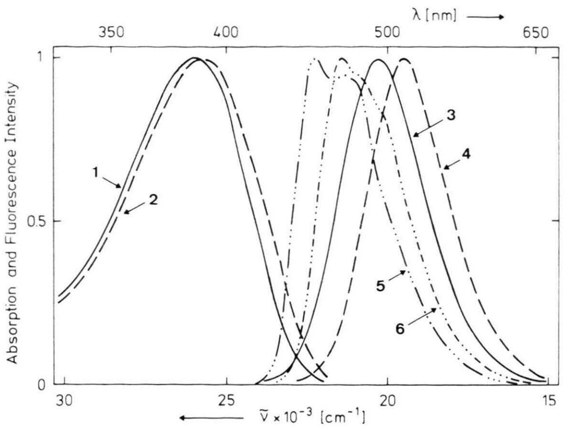

Fig. 2. Absorption spectra in MTHF of trans-**1** (1, $\varepsilon = 36\,000$) and trans-**2** (2, $\varepsilon = 34\,000$) at 25 °C and fluorescence emission spectra of trans-**1** (3) and trans-**2** (4) at 25 °C and of trans-**1** (5) and trans-**2** (6) at −196 °C.

for **2**, respectively. The half-bandwidth of the absorption spectrum is larger for **2** than for **1** and increases with increasing solvent polarity, e.g. from 4300 to 4800 cm^{-1} for **1** in n-pentane and ethanol, respectively and from 4500 to 5200 cm^{-1} for **2** in these solvents.

The fluorescence emission spectra in a given solvent are also very similar and the maximum (λ_f) is displaced to longer wavelengths (15−30 nm) for trans-**2** as compared to trans-**1** (Table 1). In several solvents (e.g. toluene, MTHF, and ethanol) it was found that variation of λ_{exc} between 313 and ~436 nm does not change the emission spectrum of either compounds. Values for $\Delta\tilde{\nu}_f$ are essentially independent of solvent polarity (range ±10%); for trans-**2** $\Delta\tilde{\nu}_f$ is about 3000 cm^{-1} and slightly larger (~3200 cm^{-1}) for trans-**1**.

Because of intramolecular charge transfer between the dialkylamino group and the cyanophenyl group the energy of the emitting state decreases on increasing the solvent polarity. In all solvents examined the Stokes shift ($\tilde{\nu}_a - \tilde{\nu}_f$) is larger for trans-**2** than for trans-**1** since for trans-**2** the red shift in λ_f is larger than in λ_a. Using the empirical Dimroth parameter $E_T(30)$ as a measure of the solvent polarity [27], a plot of $\tilde{\nu}_a - \tilde{\nu}_f$ versus $E_T(30)$ is shown in Figure 3. Although there is some scatter the Stokes shift increases linearly with increasing $E_T(30)$ values. However, in highly polar solvents ($E_T(30) \geqq 50$ kcal/mol) deviations from linearity are significant. The slopes are very similar for the cyanostilbenes.

Table 1. Absorption and fluorescence maxima for trans isomers of **1** and **2**[a].

No	Solvent	$E_T(30)$[b] (kcal/mol)	λ_a **1** (nm)	**2**	λ_f[c] **1** (nm)	**2**
1	n-Pentane		375 (375)[d]	378 (379)	412, 438	429, 455
2	Cyclohexane	31.2	380	382	418, 442	434, 460
3	Tetrachloroethylene	31.9	386	389	431, 456	450, 477
4	m-Xylene	33.3	386	390	460	482
5	Toluene	33.9	386 (388)	390 (392)	464	485
6	Benzene	34.5	387	391	465	487
7	Diethylether	34.6	380	383	466	490
8	Dioxane	36.0	386 (387)	387 (390)	475	497
9	MTHF	36.5	384 (385)	388 (389)	491	513
10	THF	37.4	385	387	499	514
11	Acetic acid ethyl ester	38.1	384	388	495	510
12	Chloroform	39.1	390	392	492	516
13	Dichloromethane	41.1	388	392	506	530
14	GT	41.6	388	390	507	530
15	Acetone	42.2	386	388	523	548
16	Dimethylformamide	43.8	390	395	536	565
17	Acetonitrile	46.0	383	386	532	561
18	n-Butanol	50.2	385	389	511	538
19	Ethanol	51.8	385	386	524	552
20	Formamide	56.6	389	385	557	587

[a] At 24° ± 2 °C in air-saturated solutions.
[b] Taken from [27].
[c] Corrected fluorescence emission maximum, $\lambda_{exc} = 366$ nm.
[d] Values in parentheses refer to the corrected fluorescence excitation maximum, λ_f as indicated.

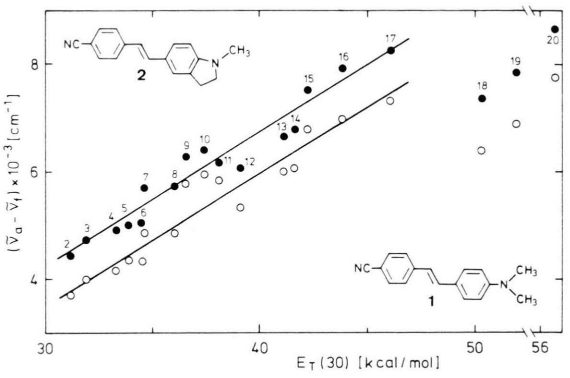

Fig. 3. Stokes shift as a function of $E_T(30)$ at room temperature for trans-**1** and trans-**2** (open and full circles, respectively) using data from Table 1.

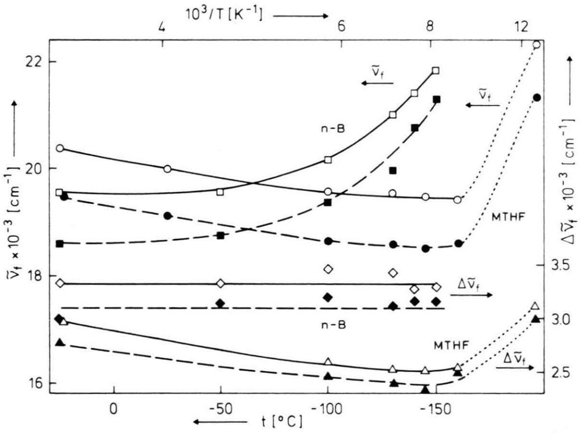

Fig. 4. Temperature dependence of $\tilde{\nu}_f$ in MTHF and n-butanol (n-B) (circles and squares, respectively) and of $\Delta\tilde{\nu}_f$ in MTHF and n-butanol (triangles and ◇, ◆, respectively) for trans-**1** and trans-**2** (open and full symbols, respectively, $\lambda_{exc} = 390$ nm).

In order to probe for possible new emission and/or relaxation channels of the excited singlet state the effects of temperature on Φ_f, $\tilde{\nu}_f$ and $\Delta\tilde{\nu}_f$ were studied. The temperature dependences of $\tilde{\nu}_f$ and $\Delta\tilde{\nu}_f$ are shown in Fig. 4 for trans-**1** and trans-**2** in MTHF and n-butanol. Although the temperature effects depend on the solvent they are very similar for both cyanostilbenes. On decreasing the temperature $\tilde{\nu}_f$ increases in n-butanol and decreases in MTHF reaching a minimum at about −160 °C and then increases on further cooling. The marked increase of $\tilde{\nu}_f$ in rigid media is caused by the inhibition of solvent reorientation. In n-butanol $\Delta\tilde{\nu}_f$ is essentially temperature independent while in MTHF $\tilde{\nu}_f$ shows a minimum around −150 °C. The overall change of $\Delta\tilde{\nu}_f$ in MTHF is about 20% and the trend is very similar for both. No indication of a second emission at longer wavelengths (up to 850 nm) was found in these cases at lower temperatures and in the other solvents at room temperature.

Quantum yield of fluorescence

Φ_f values in various solvents at room temperature are listed in Table 2. In the main, Φ_f shows a trend to larger values for **2** as compared to **1**. For both cyanostilbenes Φ_f increases with increasing $E_T(30)$ (e.g. from 0.025 to 0.22 for **2** in n-pentane and acetonitrile, respectively). In polar solvents quenching of fluorescence by oxygen was observed. For example, Φ_f decreases by about 20% for trans-**2** in acetonitrile, on going from argon-saturated to oxygen-saturated solutions. In toluene this ratio (Φ_f/Φ_f^{ox}) is reduced to $\lesssim 1.05$ (Table 2).

The temperature dependence of Φ_f in MTHF is very similar for trans-**1** and trans-**2** (Figure 5). On

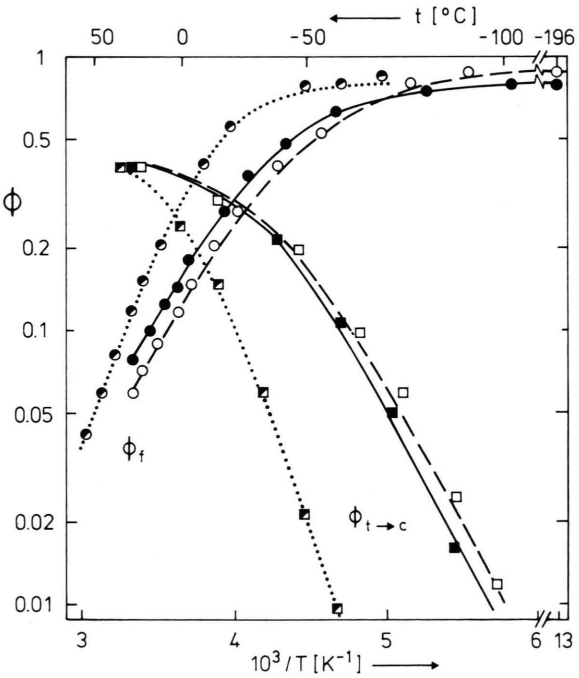

Fig. 5. Semilogarithmic plots of Φ_f (circles) and $\Phi_{t\to c}$ (squares) versus T^{-1} in MTHF for trans-**1** and trans-**2** (open and full symbols, respectively) and Φ_f and $\Phi_{t\to c}$ (semi-filled symbols) for trans-**2** in GT.

decreasing the temperature Φ_f increases and reaches a value close to unity below −100 °C. High Φ_f values observed also in other rigid media (Table 2) indicate that the rate constant for radiationless decay to the trans ground state (k_0) is small at low temperatures ($k_0 \ll k_f$). The experimental points can be fitted to a calculated curve assuming that one activated step competes with fluorescence.

$$\Phi_f = \frac{k_f}{k_f + k_0 + A_f e^{-E_f/RT}}\,. \qquad (1)$$

Values of $E_f = 4.8$ kcal/mol and $A_f/k_f = 4.4 \times 10^4$ for trans-**1** and comparable values for trans-**2** were calculated from experimental results in MTHF (Figure 5). Using $k_f = 4 \times 10^8\ \mathrm{s}^{-1}$ [17] gives a pre-exponential factor of $A_f \sim 2 \times 10^{13}\ \mathrm{s}^{-1}$ as expected for twisting about the C=C double bond. E_f values range from 3.5 to 7.5 kcal/mol (Table 3). For trans-**2** E_f is slightly larger in a given solvent, e.g. in a mixture of methylcyclohexane (MCH) and toluene (1:1), toluene, glycerol triacetate (GT), acetonitrile, n-butanol, and ethanol. This is probably due to the lower energy of the emitting state of **2** as compared with **1**. In GT E_f is mainly determined by the effect of viscosity which has also been reported for other stilbenes [9, 17]. The activation energy is determined by a number factors (e.g. dipole moments of excited configurations, viscosity, avoided crossing). Since potential energy surfaces have not been calculated this subject was not examined further.

Attempts to measure the temperature dependence of Φ_f also in a non-polar solvent failed because the fluorescence spectrum of both cyanostilbenes (concentration $\leqq 3 \times 10^{-5}$ M) changes at lower temperatures (see Table 3). This effect is not due to a dual emission but to a drastic change in the absorption spectrum which is similar for trans-**1** and trans-**2**. This points to precipitation or aggregation which has been reported by Fischer for other stilbenes [28]. In MCH-toluene (1:1), a weakly polar solvent mixture, this phenomenon did not occur.

Quantum yield of trans → cis photoisomerization

Values for $\Phi_{t\to c}$ at room temperature are similar and substantial for both cyanostilbenes in most

Table 2. Quantum yields of fluorescence and trans → cis photoisomerization [a].

Solvent	Φ_f		$\Phi_{t\to c}$		(%cis)$_s$	
	1	2	1	2	1	2
n-Pentane	0.02	0.025	0.45	0.45	80	75
Cyclohexane	0.03	0.03				
m-Xylene	0.03	0.04				
Toluene	0.03	0.05	0.45	0.45	75	73
					50 [b]	52 [b]
					86 [c]	86 [c]
Diethylether	0.05	0.06				
Dioxane	0.06	0.07	0.4	0.4	77	75
MTHF	0.06	0.08	0.4	0.4	76	74
	[0.9] [d]	[0.9]				
Chloroform	0.05	0.08				
Dichloromethane	0.06	0.08				
GT	0.07	0.12	0.4	0.4	74	72
	[0.9]	[0.8]				
Dimethylformamide	0.13 (1.1) [e]	0.25 (1.2)	0.4	0.35	70	60
					50 [b]	50 [b]
Acetonitrile	0.13 (1.1)	0.22 (1.2)	0.4	0.35	75	67
n-Butanol	0.05	0.08				
Ethanol	0.07	0.10	0.5	0.45	80	70
	[0.9]	[0.9]				

[a] At 24 ± 2 °C; values for Φ_f were corrected for deoxygenated solutions and values for $\Phi_{t\to c}$ were measured in argon-saturated solutions, $\lambda_{exc} = 366$ nm unless otherwise indicated.

[b] $\lambda_{irr} = 313$ nm.

[c] $\lambda_{irr} = 405$ nm.

[d] Values in square brackets refer to −196 °C for MTHF and ethanol and to −75 °C for GT.

[e] Values in parentheses refer to Φ_f/Φ_f^{ox}.

Table 3. Activation energy from Φ_f and $\Phi_{t\to c}$ measurements [a].

Compound	Solvent	Temp. Range (°C)	$A_f/k_f \times 10^{-4}$	E_f (kcal/mol)	E_t (kcal/mol)
1	MCH-MCP[b]	−196		[d]	
2	MCH-MCP	−196		[d]	
1	DMB-nP[c]	< − 50		[d]	
2	DMB-nP	< −100		[d]	
1	MCH-Toluene	25 ... −140	1.8	3.8	4.0
2	MCH-Toluene	25 ... −140	1.5	4.0	4.2
1	Toluene	80 ... − 90	1.8	3.8	4.0
2	Toluene	80 ... − 90	1.5	4.0	4.2
1	MTHF	25 ... −196	4.4	4.8	4.8
2	MTHF	25 ... −196	4.7	5.0	5.1
1	GT	80 ... − 75	150	7.0	7.5
2	GT	80 ... − 75	200	7.5	7.8
1	Acetonitrile	70 ... − 70	4	5.3	5.3
2	Acetonitrile	70 ... − 70	5	5.7	~6
1	n-Butanol	70 ... −150	0.7	3.5	4.0
2	n-Butanol	70 ... −150	0.7	3.8	4.2
1	Ethanol	70 ... −196	0.8	3.8	4.0
2	Ethanol	70 ... −196	0.7	4.0	4.4

[a] In argon-saturated solutions, $\lambda_{exc} = \lambda_{irr} = 366$ nm.

[b] methylcyclohexane: methylcyclopentane (1:1).

[c] 2,2-dimethylbutane: n-pentane (8:3).

[d] No E_f value obtainable since formation of a new species at low temperatures is indicated from absorption and emission spectra.

solvents (Table 2). The percentage of cis in the photostationary state ((% cis)$_s$) depends on λ_{irr} and on the solvent. In polar solvents $\Phi_{t\to c}$ and (% cis)$_s$ tend to be smaller than in non-polar solvents. One possible explanation may be the markedly higher Φ_f values in polar solvents which go along with a reduction in $\Phi_{t\to c}$.

The temperature dependence of $\Phi_{t\to c}$ in MTHF is similar for **1** and **2** (Figure 5.). The experimental points can be fitted by assuming that the cis isomer is reached only via an activated step (activation energy: E_t). If this step competes with fluorescence and if it is the only activated step in the trans→cis pathway E_t should equal E_f. Assuming that trans and cis isomers are populated 50% each after the activated step (i.e. $\beta = 0.5$) the temperature dependence of $\Phi_{t\to c}$ is given by

$$\Phi_{t\to c} = (1-\beta) \times \frac{e^{-E_t/RT}}{B + e^{-E_t/RT}}\,, \tag{2}$$

where B is a constant ($B = (k_f + k_0)/A_f$ if $E_f = E_t$).

Agreement between experimental points and calculated curves using values for $(k_f + k_0)/A_f$ from Φ_f-measurements was found for both compounds in several solvents at temperatures below 25 °C (cf. Table 3).

4. Discussion

In this paper we attempt to understand the nature of radiationless decay processes in dialkylaminocyanostilbenes. At least three radiationless energy dissipation processes should be considered for trans-**1** and trans-**2**: i) twisting about the C=C double bond, ii) radiationless decay without a geometric change, and iii) twisting about single bonds. The first process leading to trans→cis photoisomerization has recently been studied for several cyanostilbenes [15–17], the second process has been observed in rigid media and may also contribute in fluid solutions [9, 17] and the third process involves a conformational change. This may occur by rotation about the bond between the dimethylamino group and the phenyl ring or about the bond between the dimethylaminophenyl group and the double bond. Either one of these changes may lead to a TICT state as hitherto described for DAB [2].

For DAB a TICT state (a^*) is clearly involved in the decay of the initially populated excited singlet state (b^*) in polar media as documented by a number of investigations [1–8]. One of its characteristic properties is dual emission from a^* and b^* which depends on temperature and solvent polarity. If the dialkylamino group is forced into near rigidity by incorporation in an indoline ring fluorescence occurs only from b^*. Dual emission and a TICT state have also been found for 4-diethylaminobenzoic acid ethyl ester [29]. Additional systems in which involvement of a TICT state has been discussed are: 4-(9-anthryl)-N,N-dimethylanilines (ADA-system) [30–32], a series of N-aryl carbazoles (pyrroles) [33], N,N-dialkyl-4-(1,3,5-triazinyl)-anilines (DTA-system) [34], 4-N,N-dialkylaminobenzylidenemalonitriles (DBM-system) [35, 36], and (phenylamino)naphthalenesulfonates [37].

Absorption and Fluorescence Emission Properties

On the basis of the results obtained from absorption and emission spectra of trans-**1** and trans-**2** at room temperature we suggest that the electron distribution in the Franck-Condon excited singlet state ($^1t^{*\prime}$) and in the solvent relaxed singlet state ($^1t^*$) is similar for both. For **1** the Stokes shift has previously been examined in terms of a Bilot-Kawski relationship [19]. Values of $\mu_g = 7$ and $\mu_e \sim 22$ Debye calculated with this method agree with those obtained by other methods [10, 19, 20].

Evidence for a TICT state in the ADA-system was obtained from an analysis of the effect of temperature on $\Delta\tilde{\nu}_f$ and $\tilde{\nu}_f$ in n-butanol [31]. On varying the temperature $\Delta\tilde{\nu}_f$ shows a maximum (increaseslightly from $\sim 4500\ \mathrm{cm}^{-1}$ at 25 °C to $6000\ \mathrm{cm}^{-1}$ at about -90 °C and decreases to $\sim 3000\ \mathrm{cm}^{-1}$ at -170 °C). This was linked to the observation of non-separated fluorescence from two emitting states [31, 32]. In our system however, $\Delta\tilde{\nu}_f$ is constant within $\pm 5\%$ (Figure 4). Changes in $\tilde{\nu}_f$ are also substantially smaller for **1** ($2300\ \mathrm{cm}^{-1}$) and **2** ($2800\ \mathrm{cm}^{-1}$) than for the ADA-system ($\sim 5200\ \mathrm{cm}^{-1}$). As a solvent of lower polarity MTHF was chosen which also has a wider accessible temperature range. No significant difference in the temperature dependences of $\Delta\tilde{\nu}_f$ and $\tilde{\nu}_f$ was found for the two cyanostilbenes. Larger $\Delta\tilde{\nu}_f$ values for **1** may be due to rotation of the dimethylamino group in **1**. Smaller $\tilde{\nu}_f$ values for **2** in the temperature range between 25 and -196 °C reflect the larger dipole moment of $^1t^*$ for **2**. From results in 20 solvents at room temperature (Table 1) and in solvents at low temperatures (Table 3) no indication for dual emission was found for trans-**1** and trans-**2**.

Quantum Yield of Fluorescence

For aromatic systems in which two portions of the molecule have substantial torsional freedom with respect to one another, Φ_f is generally smaller than in the corresponding rigid system. Pertinent examples are trans-stilbene versus indeno[2,1-a]indene ($\Phi_f \sim 0.05$ and 0.94, respectively) [38] and biphenyl versus fluorene ($\Phi_f \sim 0.18$ and 0.8, respectively) [39]. In view of this a marked increase in Φ_f would be expected on going from the flexible to the more rigid cyanostilbene. However, this was not found; values of Φ_f at room temperature are quite similar in solvents of low polarity and in polar solvents less than a factor of 2 higher for **2** than for **1** (Table 2). This suggests common radiationless deactivation channels for both (see below).

Φ_f values of the cyanostilbenes may also be compared with those in the DBM-system [35, 36] and with two coumarins one of which has a “free” dialkylamino group and the other an amino group which is forced into planarity [40]. For the flexible coumarin Φ_f is smaller (e.g. by a factor of about 3 in cyclohexane and ethanol-water) than for the rigid analogue. For the DBM-system Φ_f values in the 10^{-3} range have been reported and Φ_f increases (e.g. by a factor of up to 4) on going from the flexible to the constrained molecule [35, 36]. For these systems as well as for the pyrroles and the DTA-system participation of a TICT state was adduced indirectly (no dual emission observed).

Further information about a possible involvement of a TICT state in **1** can be obtained from an analysis of the temperature dependence of Φ_f as shown by Grabowski et al. for the DAB-system [2–4]. A minimum in a plot of $\log \Phi_f$ versus T^{-1} for the (short-wavelength) emission from b^* and a decrease of Φ_f on decreasing the temperature for the (long-wavelength) emission from a^* substantiate the model in which a^* (TICT state) is separated from b^* by an activation barrier and in equilibrium with it [2, 29]. In contrast Φ_f in our system increases monotonously on decreasing the temperature (without a minimum). For 3-methoxy-4-cyanodimethylaminobenzene in MTHF (temperature range: 25 to -50 °C) an activation energy of ~ 2 kcal /mol has been reported for the step $b^* \overset{\Delta}{\rightarrow} a^*$ [2, 4]. Larger activation energies (~ 5 kcal/mol in MTHF) were obtained for the cyanostilbenes (Table 3). In acetonitrile this difference in activation energies is even larger. In contrast to the DAB-system the two cyanostilbenes have a very similar temperature dependence of Φ_f (Figure 5). This is strong evidence against involvement of a TICT state for **1**. In the

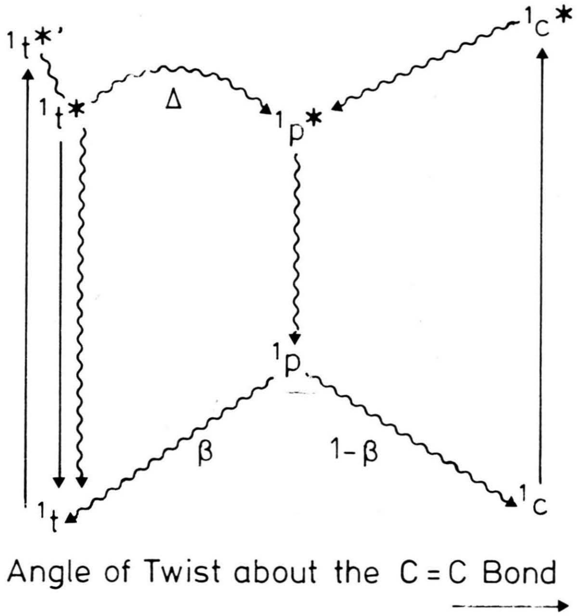

Fig. 6. Scheme for deactivation of **1** and **2** after excitation.

DBM-system in MTHF activation energies of 1.3 and 1.2 − 1.7 kcal/mol have been reported for the compounds with a "free" and a "rigid" dialkylamino group, respectively [35, 36]. However, the relaxation process has not been assigned unambiguously since a possible isomerization route by twisting about the C=C double bond has not been considered.

Deactivation Channels for the Excited Trans Isomer

Very similar effects of solvent polarity on the Stokes shift and on Φ_f as well as similar effects of temperature (and viscosity) on $\tilde{\nu}_f$, $\Delta\tilde{\nu}_f$ and Φ_f were observed for **1** and **2** (Figs. 1 − 5 and Tables 1 − 3). From these results no indication was found for a substantially different behaviour of the flexible as compared to the rigid cyanostilbene. Therefore, we conclude that twisting of the dialkylamino group (about the C−N bond) is not involved in the decay process of ${}^1t^*$. The question remains whether or not twisting of either the dimethylaminophenyl group or the N-methyldihydroindolyl group (about a C−C single bond) contributes effectively to the radiationless decay of ${}^1t^*$. This process can be excluded since the result $E_f \approx E_t$ (Table 3) speaks against twisting about a single bond as an important decay channel. Furthermore, since the sum of Φ_f and $\Phi_{t\to c}/(1-\beta)$ is close to unity (in the range 25 to − 196 °C), (Fig. 5 and Table 2) twisting processes about single bonds cannot make a substantial contribution.

Thus, for **1** and **2**, in contrast to other systems (e.g. DAB), trans → cis photoisomerization is the dominant deactivation step of ${}^1t^*$ competing with fluorescence. After excitation of the trans isomer (${}^1t$) to the excited Franck Condon state (${}^1t^{*\prime}$) solvent solute interaction in fluid solution leads to the relaxed ${}^1t^*$ state which interconverts (in the first excited singlet state) to the twisted configuration ${}^1p^*$. As previously suggested for **1** other deactivation pathways than fluorescence and the step ${}^1t^* \xrightarrow{\Delta} {}^1p^*$ are of minor importance [17]. The same conclusion may be reached for **2** since the temperature dependences of Φ_f and $\Phi_{t\to c}$ are very similar for both compounds (Figure 5). Non-activated internal conversion and intersystem crossing as negligible pathways are also indicated by Φ_f values close to unity in rigid media (Table 2).

A scheme accounting for cis ⇄ trans photoisomerization in fluid media is shown in Figure 6. After twisting in the excited singlet state (${}^1t^* \xrightarrow{\Delta} {}^1p^*$) the cis isomer (${}^1c$) is reached by internal conversion at the twisted configuration (${}^1p^* \to {}^1p$) and further twisting in the ground state. Cis → trans photoisomerization occurs also by twisting in the excited singlet state (${}^1c^* \to {}^1p^*$) followed by the step ${}^1p^* \to {}^1p$ and further twisting in the ground state. No indication for emission from ${}^1c^*$ was found by exciting cis rich solutions at room temperature. A short lifetime of ${}^1c^*$, i.e. rapid twisting from ${}^1c^*$ to ${}^1p^*$, is in agreement with findings for other cis-stilbenes [9, 12]. From known $\Phi_{c\to t}$ values for **1** [17] and similar photostationary states for **1** and **2** (Table 2) we conclude that cis → trans photoisomerization is the dominant route for deactivation of ${}^1c^*$ for both.

Viewing **1** and **2** as an extended DAB-system the question arises why a TICT state is not involved here. It may well be that charge transfer from the electron donor to the acceptor is unfavourable since the distance between the dimethylamino group and the cyanophenyl ring is greater for the stilbenes than for DAB. The significance of the Coulomb term is made apparent in a model for the energetic requirements for a TICT state [41].

5. Summary

The effects of solvent polarity and temperature on the fluorescence emission characteristics ($\Delta\tilde{\nu}$, $\tilde{\nu}_f$, and

Φ_f) of trans-4-cyano-4′-dimethylaminostilbene and a rigid analogue are very similar. Based on these results and on the absence of dual emission it is concluded that a TICT state does not play a noticeable role in the relaxation processes of the trans isomers after excitation. Similar activation energies obtained from the temperature dependences of Φ_f and $\Phi_{t\to c}$ ($E_f \approx E_t$) support the conclusion that the main relaxation pathway competing with fluorescence is trans→cis photoisomerization via the sequence: ${}^1t^{*\prime} \to {}^1t^* \xrightarrow{\Delta} {}^1p^* \to {}^1p \to (1-\beta)\,{}^1c$. In fluid media, twisting about the C=C double bond via an activation barrier (${}^1t^* \xrightarrow{\Delta} {}^1p^*$) controls Φ_f while rotation of the dimethylamino group or of the dimethylaminophenyl group about a single bond can play a minor role only.

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