# Trans $\rightarrow$ Cls Photolsomerization, Fluorescence, and Relaxation Phenomena of trans-4-Nitro-4'-(dialkylamino)stilbenes and Analogues with a Nonrotatable Amino **Group**<sup>†</sup>

### Henry Gruen<sup>‡</sup> and Helmut Görner\*

Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim an der Ruhr, Federal Republic of Germany (Received: January 9, 1989; In Final Form: April 26, 1989)

The steady-state fluorescence properties of five 4-nitro-4'-aminostilbenes (4-nitro-4'-aminostilbene (1); 4-nitro-4'-(dimethylamino)stilbene (2); 4-nitro-4'-(diethylamino)stilbene (3); and 1-(4-nitrophenyl)-2-(2,3-dihydro-N-R-indol-5-yl)ethylene, R = H(4) and  $R = CH_3(5)$  were studied in various solvents and as a function of temperature. The quantum yield of fluorescence for the trans isomer  $(\Phi_t)$ , the Stokes shift, and the quantum yield of trans  $\rightarrow$  cis photoisomerization  $(\Phi_{t\rightarrow c})$  depend markedly on the nature of the solvent. When the polarity is increased, the Stokes shift increases,  $\Phi_{t \rightarrow c}$  decreases strongly, and  $\Phi_f$  at first rises and then also decreases strongly. The five trans isomers show similar effects of solvent polarity and, generally, only small differences for a given solvent. This shows that the reduction in  $\Phi_{t\rightarrow c}$  in solvents of moderate and higher polarity is not caused by deactivation of the first excited trans singlet state (1t\*) via rotation of the dialkylamino group since in 4 and 5 it cannot rotate whereas in 1-3 it can. Activation energies in *m*-xylene, toluene, and dioxane, obtained from  $\Phi_{t\rightarrow c}$ (range: 7-13 kcal/mol) and from  $\Phi_f$  measurements (3-4 kcal/mol), differ significantly. It is concluded that the substantial decrease of  $\Phi_{t\rightarrow c}$  on going from nonpolar to slightly polar solvents is due (i) to relaxation to the trans ground state of a transold excited state ( $A^*$ ) that is not identical with the solvent-relaxed spectroscopic <sup>1</sup>t<sup>\*</sup> state and (ii) to the presence of an energy barrier along the pathway of trans  $\rightarrow$  cis photoisomerization (following the step  $^{1}t^{*} \rightarrow A^{*}$ ), which cannot be overcome in more polar solvents.

#### Introduction

It has recently been shown that the direct cis  $\rightleftharpoons$  trans photoisomerization of 4-cyano-4'-(dimethylamino)stilbene (CDMAS) occurs by twisting about the central double bond in singlet states.<sup>1</sup> The quantum yields of fluorescence for the trans isomer, and of trans  $\rightarrow$  cis and cis  $\rightarrow$  trans photoisomerization ( $\Phi_{f}, \Phi_{t\rightarrow c}$ , and  $\Phi_{c \rightarrow t}$ , respectively) are substantial for CDMAS at room temperature and are little influenced by the polarity of the solvent.<sup>2</sup> Steady-state<sup>2</sup> and time-resolved<sup>3</sup> measurements did not indicate the involvement of a fluorescing twisted intramolecular chargetransfer (TICT) state. On the other hand, relaxation of excited trans-CDMAS via a TICT state has recently been proposed.4,5

When the cyano group is replaced by the nitro group,  $\Phi_{t\to c}$  decreases drastically with increasing solvent polarity.  $^{6-11}$ trans-4-Nitro-4'-(dimethylamino)stilbene (trans-2), the nitro analogue of trans-CDMAS, has been the subject of numerous investigations.<sup>6-18</sup> Over 30 years ago, Lippert and his group demonstrated that the large dipole moment of trans-2 in the excited singlet state gives rise to an extremely large Stokes red shift.<sup>13-15</sup> For 4-nitro-4'-aminostilbene (1) and 2, Schulte-Frohlinde first proposed that the triplet state is involved in the trans  $\rightarrow$  cis photoisomerization.<sup>6</sup> Fischer and co-workers have added to the knowledge about 2 by investigating the effect of temperature on  $\Phi_{t \to c}$  and  $\Phi_{c \to t}$ .<sup>7</sup> A mixed singlet-triplet mechanism for the trans  $\rightarrow$  cis photoisomerization has been advanced for 2 and 4-nitro-4'-(diethylamino)stilbene (3) in nonpolar solvents<sup>10</sup> and a "double activated mechanism" for  $\mathbf{2}$  in toluene solution<sup>11</sup> (see also Discussion). In order to account for the small  $\Phi_{t\rightarrow c}$  values of 2 in polar solvents, it has been proposed that internal conversion not involving twisting about the central double bond should be significant.<sup>9</sup> The question arises as to the origin of this internal conversion step. One conceivable possibility would be a rotation of the dimethylamino group into a highly twisted conformation (perpendicular relative to the phenyl ring).

This work aims at illuminating the effect of solvent polarity on the deactivation channels of the excited trans singlet state  $({}^{1}t^{*})$ of push-pull compounds like 4-nitro-4'-(dialkylamino)stilbenes. Since nothing is known about  $\Phi_f$  of 1 and 3, and only little about





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the effect of environment on  $\Phi_f$  of 2,<sup>15</sup> a systematic study appeared to us to be desirable. For comparison and in order to probe for

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<sup>&</sup>lt;sup>‡</sup>Current address: Goethestrasse 4, D-4030 Ratingen, Federal Republic of Germany

Part 16: Cis-Trans Isomerization of Nitrostilbenes. Part 15: Reference 10.

possible involvement of a TICT state, <sup>19,20</sup> analogues of trans-2, in which the alkylamino component is part of a "stiff" dihydroindole ring (trans-4 and trans-5), were synthesized and investigated.

The Stokes shift and values for  $\Phi_f$  and  $\Phi_{t\rightarrow c}$  are presented for trans-1-trans-5 in various solvents and as a function of temperature. The character of the absorption and emission spectra, the magnitude of  $\Phi_{f}$ , and its temperature dependence give no evidence for the involvement of an additional fluorescing state (e.g., a TICT state) for the three stilbenes and the two "stiffened" compounds. The effect of solvent polarity on the deactivation pathways of excited trans-4-nitro-4'-(dialkylamino)stilbenes will be discussed.

#### **Experimental Section**

Apparatus and Procedure. The corrected emission spectra were recorded on a Spex Fluorolog that was equipped with a photoncounting detection system using a photomultiplier (RCA C31034) and a unit that corrects for the spectral sensitivity of the photomultiplier and the lamp.<sup>21</sup>  $\Phi_f$  values were determined with either 9,10-diphenylanthracene ( $\Phi_f = 0.9$ ) or rhodamine 101 ( $\Phi_f = 1.0$ ) both in argon-saturated ethanol at 24 °C as standards<sup>22</sup> and the same absorbance at  $\lambda_{exc}$ , typically 0.2–0.4. Corrections were made for the temperature dependence of the extinction coefficient. A correction of  $\Phi_f$  for the refractive index of the solvents did not seem necessary in view of the magnitude of this effect relative to that of the change in solvent polarity. In nonpolar solvents where trans  $\rightarrow$  cis photoisomerization could contribute, the samples were irradiated for the shortest periods possible (the conversion was less than 10%). The experimental error of small  $\Phi_f$  values is typically  $\pm 30\%$  and  $\pm 10\%$  for  $\Phi_f \ge 0.2$ . The effect of oxygen on  $\Phi_f$  was measured by monitoring the intensity  $(I_f)$  on a Perkin-Elmer Model LS-5 spectrofluorometer and repeated purging with argon and oxygen; it was found that  $I_f(O_2)/I_f(Ar)$  equals  $\Phi_{\rm f}({\rm O}_2)/\Phi_{\rm f}({\rm Ar}).$ 

The absorption spectra were recorded on a spectrophotometer (Perkin-Elmer, Model 554). For  $\Phi_{t \rightarrow c}$  measurements, a 1000-W high-pressure xenon-mercury lamp and a monochromator (Schoeffel; bandwidth 12 nm) were used. The incident light intensity was measured either by the Aberchrome 540 actinometer<sup>23</sup> or by comparison of  $\Phi_{t\rightarrow c}$  for 4-nitrostilbene in benzene.<sup>24</sup> All solutions (typical concentration, 40  $\mu$ M) were purged with argon, and the procedure for determination of  $\Phi_{t\rightarrow c}$  values was the same as described elsewhere:<sup>1,2,10</sup> error ±20% for  $\Phi_{t\rightarrow c} \ge 0.1$ and  $\pm 40\%$  for the smaller values. In general, the samples were freshly dissolved and handled under red light.

Materials. Trans isomers of 1 and 2 were prepared and purified as previously reported,<sup>2</sup> and trans-3 was prepared by an analogous method. (If not indicated otherwise, 1-5 denote the trans isomers.) The precursors of 4 and 5, 5-formylindoline and 1-methyl-5formylindoline, respectively, were synthesized as follows. The latter compound was prepared by a Vilsmaier-formylation reaction; a known procedure<sup>25</sup> was followed, but a lower ratio of phosphorus

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Figure 1. Absorption, fluorescence excitation, and corresponding emission spectra (dotted, dashed, and full lines, respectively) of trans-1 (a) in toluene and (b) in n-pentane and emission of trans-1 (c) in MTHF. Conditions: 24 °C,  $\lambda_{exc} = 366$  nm,  $\lambda_f$  as in Table I.

oxychloride (0.15 M) to 1-methylindoline (0.135 M) was employed. The reaction product, containing the mono- and diformylindolines as well as other unknown compounds, was purified by column chromatography on basic alumina with a mixture of cyclohexane-ethyl acetate (7:3) as eluent. The first fractions were recrystallized from a mixture of cyclohexane-isooctane (20:1) to yield almost colorless fine needles (mp 37-39 °C; purity by GC analysis 99.5%). TLC on silica gel with the former solvent mixture showed a single yellow band. Absence of diformylindoline was indicated by comparison with a fraction isolated in the chromatography and shown to be a dialdehyde.<sup>26</sup> 5-Formylindoline was obtained by a Fries rearrangement of 1-formylindoline in the presence of phosphorus oxychloride as described for homologous compounds.<sup>25</sup> The MS and NMR data, as well as IR and UV absorption spectra, are consistent with the assigned structures.

Compounds 4 and 5 were prepared by the method of Pfeiffer<sup>26</sup> but in chlorobenzene as solvent. 1-Methyl-5-formylindoline (3 g), 4-nitrophenylacetic acid (3.5 g), piperidine (1 mL, dried over CaCl<sub>2</sub>), and chlorobenzene (15 mL) were heated to 136-140 °C, maintained at this temperature for 1-2 h, and then allowed to crystallize. The precipitate was filtered off, washed with chlorobenzene followed by cyclohexane, and subsequently dried. A second fraction could be isolated on prolonged standing (yield of the combined fractions, 40%). The reaction product was recrystallized several times from ethanol. The clusters of rectangular crystals rearranged to needles at 172-176 °C and melted at 180-181 °C (uncorrected) (purity by GC analysis 98%). TLC on silica gel with cyclohexane-ethyl acetate (7:3) showed only one spot. Compound 4 was synthesized in an analogous fashion (35% yield). The recrystallized product also showed a solid-state structural change between 174 and 176 °C and melted at 182-184 °C

The structures assigned to compounds 4 and 5 were confirmed by MS, NMR, IR, and UV-vis spectra. The integrity of the indoline ring in 4 and 5 is supported by the reaction with 2,3dichloro-5,6-dicyanobenzoquinone as oxidant. Facile hydrogen transfer occurs in dioxane with formation of the corresponding

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TABLE I: Maxima of Absorption and Fluorescence Spec
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			λ <sub>a</sub> , nm					$\lambda_{f}^{b}$ nm		
solvent	1	2	3	4	5	1	2	3	4	5
n-pentane <sup>c</sup>	370	411	418	400	410	440	465	470	470	485
-						460	490	502	493	515
						490 sh	520 sh	532	515	545 sh
		(412)	(420)	(403)	$(413)^{d}$					
cyclohexane <sup>c</sup>	380	417	427	408	420	445	470	478	475	495
-						468	502	509	504	525
						500 sh	535 sh	545	540	560
		(418)		(408)	$(419)^{d}$					
carbon tetrachloride	390	423	429	412	426	514	548	556	559	578
<i>m</i> -xylene	398	428	434	419	430	544	570	580	590	605
di-n-butyl ether	398	428			432	556	562		585	590
toluene	399	428	438	426	433	554	583	589	600	619
	(402)	(429)		(424)	(435) <sup>d</sup>					
benzene	398	429	439	424	437	558	596	595	607	627
diethyl ether	402	422	430	418	428	590	602	602	635	640
dioxane	404	424	434	422	432	598	620	621	630	660
MTHF	410	425	438	430	436	633	655	658	677	695
						[582]	[586]	[602]	[609]	[620] <b>"</b>
THF	411	426	442		435	647	670	670	696	725
acetic acid ethyl ester	406	424	434		428	648	674	680	702	720
chloroform	399	434	447		438	682	735	785		770
dichloromethane	400	435	447	423	439	694	770	820	770	850
acetone	410	433	441		433	740	800	830		>850
DMF	412	440	440		445	830	850	>830		>850
acetonitrile	406	435			432	>850	>850	>850		>850
ethanol	404	428	432		426	>850	>850	>850		>850
						[590]	[590]	[605]		[620] <sup>e</sup>

<sup>a</sup> In argon-saturated solutions at 24 °C. No deviations were found in the presence of air. <sup>b</sup> Corrected fluorescence emission maximum:  $\lambda_{exc} = 366$  nm. No difference was found in nonpolar and slightly polar solvents when excited within ±10 nm of  $\lambda_a$  [for observation of a second emission for 4 and 5 ( $E_T(30) > 36$  kcal/mol), see text]. <sup>c</sup> Data for 1-3 are taken from ref 10. <sup>d</sup> Values in parentheses refer to the corrected fluorescence excitation maximum. <sup>c</sup> Values in brackets refer to -196 °C.

2,3-dichloro-5,6-dicyanohydroquinone and indoles, e.g., 1-(4-nitrophenyl)-2-(5-N-methylindolyl)ethylene (6). Additional evidence for the presence of an NH group in 4 is provided by ready formation of an acetyl derivative with a strongly reduced fluorescence.

9,10-Diphenylanthracene (EGA) and rhodamine 101 (Lambda Physik) were used as received. Solvents (Merck or Aldrich) were spectrograde, e.g., glycerol triacetate (GT), Uvasol (acetone, acetonitrile), and Gold Label [benzene, dimethylformamide (DMF)], purified by distillation [methylcyclohexane (MCH), toluene, 2-methyltetrahydrofuran (MTHF; free of peroxides), *m*-xylene], or purified by chromatography [tetrahydrofuran (THF), chloroform] and checked for absorbing or fluorescing impurities.

#### Results

Absorption and Fluorescence Spectra. Absorption, fluorescence excitation, and emission spectra for trans-1 and trans-5 in *n*-pentane and toluene solutions at room temperature are shown in Figures 1 and 2. The corrected fluorescence excitation spectrum and the absorption spectrum of 5 coincide in *n*-pentane and nearly so for 1 and 5 in toluene. Similar results were found for 2-4 in these solvents. The fluorescence spectra show some structure only in nonpolarizable solvents, e.g., cyclohexane and *n*-pentane, and they are red-shifted on going to toluene and 2-methyltetra-hydrofuran (MTHF).

The maxima of the absorption and fluorescence spectra ( $\lambda_a$  and  $\lambda_f$ , respectively) are listed in Table I. The pattern of a red shift of  $\lambda_a$  for *trans*-2 and an even larger Stokes shift on going to more polar (or polarizable) solvents is in good agreement with previous data from Lippert et al.<sup>13-15</sup> Generally, the spectra in a given solvent are similar for the five trans isomers (Table I). Values for  $\lambda_a$  increase slightly and those for  $\lambda_f$  moderately in the sequence 1, 2, and 3. A small red shift of  $\lambda_a$  on going from 1 to 4 and from 2 to 5 is in accord with enhanced  $\pi$ -electron delocalization in the ground and excited singlet states of the compound with nonrotatable dialkylamino groups (4 and 5).

The dependence of the Stokes shift  $(\tilde{\nu}_a - \tilde{\nu}_f)$  on the solvent polarity is illustrated in Figure 3 for 1, 2, and 5. When the



Figure 2. Absorption, fluorescence excitation, and corresponding emission spectra (dotted, dashed, and full lines, respectively) of *trans-5* (a) in toluene and (b) in *n*-pentane and emission of *trans-1* (c) in MTHF. Conditions: 24 °C,  $\lambda_{exc} = 366$  nm,  $\lambda_{f}$  as in Table I.

empirical Dimroth parameter  $[E_T(30)]$ , used as a measure for the solvent polarity,<sup>27</sup> was increased,  $\tilde{\nu}_a - \tilde{\nu}_f$  increases almost linearly for the five compounds in the range between 30 and approximately 44 kcal/mol. The plot may extend even above  $E_T(30) = 44$ kcal/mol ( $\tilde{\nu}_f$  values smaller than 11 800 cm<sup>-1</sup> could not be mea-

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Figure 3. Stokes shift plotted vs the  $E_T(30)$  polarity parameter for *trans*-1 (squares), *trans*-2 (circles), and *trans*-5 (triangles) in solution at 24 °C. For *trans*-CDMAS (dashed line) see ref 2.

sured under our conditions). Despite some scatter, the slopes of these dependences are similar. Data in Figure 3 show a trend to a larger Stokes shift for 5 as compared to that of 2. Interestingly, the larger  $\tilde{\nu}_{f}$  values for 1 are essentially compensated by larger  $\tilde{\nu}_{a}$  values. For comparison, the Stokes shift is also shown for the cyano analogue *trans*-CDMAS;<sup>2</sup> this slope is markedly smaller than for the five nitrostilbenes.

The fluorescence spectra of 1-3 in toluene and MTHF solutions are independent of the wavelength of excitation (e.g.,  $\lambda_{exc}$  between 366 and 490 nm for 2). For 4 and 5 in MTHF, only one fluorescence band was found on excitation at the long-wavelength part ( $\lambda_{exc}$  = 490 nm). However, on excitation at shorter wavelengths ( $\lambda_{exc}$  between 313 and 436 nm), a second 10-fold weaker emission band was observed (e.g., around 560 nm for 5). This fluorescence is to be attributed to compound trans-6 as an impurity in 5. The "impurity" fluorescence could only be observed for 5 (and to a smaller degree for 4) in solvents of medium polarity  $(E_{\tau}(30) \approx 36-42 \text{ kcal/mol})$ . The emission spectra of 1-3 do not provide evidence for a "growing in" of a second fluorescence component (especially at longer wavelengths) on increasing the solvent polarity. For example, in toluene and benzene at ambient temperature there is no discernible indication of a second emission band in the 640-850-nm region. In more polar solvents (e.g., DMF or acetonitrile), the fluorescence intensity at  $\lambda > 850$  nm was too weak to be analyzed. For 2 and 5, it was checked whether or not the width of the fluorescence band exhibits an unusual effect at room temperature. Generally, the bandwidth is slightly larger for 2 than for 5, but no marked difference was found in solvents of small and large polarity.

In MTHF and ethanol at -196 °C,  $\lambda_f$  is blue-shifted compared to fluid media (Figure 4 and Table I); this effect was also found for 2 in glassy glycerol triacetate (GT) at -75 °C ( $\lambda_f = 590$  nm). A blue shift of  $\lambda_f$  on increasing the solvent viscosity has often been observed, especially for molecules with a large Stokes shift.<sup>2,15,28</sup> The temperature dependence of  $\tilde{\nu}_f$  is illustrated in Figure 4 for 1, 2, and 5 in MTHF. On cooling,  $\tilde{\nu}_f$  first decreases but then increases significantly below -150 °C, where the viscosity increases by about 10 orders of magnitude.<sup>29</sup> A similar behaviour has been



Figure 4. Temperature dependence of the fluorescence maximum of *trans*-1 (squares), *trans*-2 (circles), and *trans*-5 (triangles) in MTHF:  $\lambda_{exc} = 366$  nm.

TABLE II: Quantum Yield of Fluorescence<sup>a</sup>

	$E_{\pi}(30)$			$\Phi_{\rm f}$		
solvent	kcal/mol	1	2	3	4	5
n-pentane		0.004	0.14	0.28	0.12	0.38
cyclohexane <sup>b</sup>	31.2	0.002	0.33	0.34	0.20	0.40
ŃСН		0.002	0.30	0.36	0.3	0.2
carbon	32.5	0.2	0.4	0.5	0.4	0.5
tetrachloride						
<i>m</i> -xylene	33.3	0.37	0.55	0.53	0.50	0.55
di-n-butyl ether	33.4	0.36	0.54	0.52	0.52	0.54
toluene	33.9	0.42	0.53	0.50	0.45	0.40
benzene <sup>c</sup>	34.5	0.48	0.53	0.54	0.46	0.40
diethyl ether	34.6	0.47	0.55	0.60	0.33	0.45
dioxane	36.0	0.38	0.32	0.55	0.25	0.35
MTHF <sup>d</sup>	36.5	0.22	0.15	0.22	0.08	0.12
THF	37.4	0.17	0.11	0.15	0.04	0.05
acetic acid ethyl ester	38.1	0.15	0.06	0.11	0.03	0.03
chloroform	39.1	0.05	0.018	0.023		0.015
dichloromethane	41.1	0.038	0.008	0.014	<0.01	0.010
acetone	42.2	0.006	0.005	< 0.005		0.005
DMF	43.8	0.002	0.002	< 0.002		< 0.002
acetonitrile	46.0	<0.002	<0.002			<0.002

<sup>a</sup>At 24 ± 2 °C. Measured in argon-saturated solutions [or in air-saturated solutions and corrected for the presence of oxygen using the  $\Phi_{\Gamma}$  (Ar)/ $\Phi_{f}(air)$  ratio].  $\lambda_{exc} = 366$  nm unless indicated otherwise. <sup>b</sup> Data for 1-3 are taken from ref 10. <sup>c</sup> Within ±10%, the same values were obtained with  $\lambda_{exc} = 436$  nm for 2, 4, and 5. <sup>d</sup> Within experimental error (±20%), the same values were obtained with  $\lambda_{exc} = 405$  nm for 1 and 436 nm for 2-5.

found for the cyano analogue CDMAS.<sup>2</sup>

Quantum Yield of Fluorescence.  $\Phi_f$  values for the five trans isomers in various solvents at room temperature are listed in Table II. The data reveal a significant dependence on solvent properties, specifically on  $E_T(30)$ . For 1,  $\Phi_f$  increases strongly from 0.002 in cyclohexane to 0.42 in toluene while for 2-5 it increases only slightly, starting from 0.12 (and 0.14) for 4 (and 2) in *n*-pentane. For all five compounds,  $\Phi_f$  reaches maximum values of 0.4-0.60 in slightly polar (or polarizable) solvents ( $E_T(30)$  between 33 and 36 kcal/mol). On  $E_T(30)$  being increased further,  $\Phi_f$  decreases roughly exponentially over a range of 3 orders of magnitude (Figures 5 and 6).  $\Phi_f$  values smaller than 0.05, showing only little dependence on the structure, were found in solvents with  $E_T(30)$ = 39-46 kcal/mol (Table II).

Basically,  $\Phi_f$  values for 4 and 5 at room temperature show a solvent dependence similar to that for 1-3 (Table II). In other words, a common trend for  $\Phi_f$ , except for minor deviations, was observed both for the stilbenes with a "free" dialkylamino group and those in which rotation is prevented. To mention one devi-



Figure 5. Semilogarithmic plot of  $\Phi_f$  vs  $E_T(30)$  for *trans*-1 (squares) and *trans*-5 (triangles) in argon-saturated solutions at 24 °C:  $\lambda_{exc} = 366$  nm  $[E_T(30) = 30.5 \text{ kcal/mol was assumed for$ *n*-pentane].



**Figure 6.** Semilogarithmic plot of  $\Phi_f$  (open circles) and  $\Phi_{t \to c}$  (filled circles) vs  $E_T(30)$  for 2 in argon-saturated solutions at 24 °C;  $\lambda_{exc} = 366$  nm.

ation,  $\Phi_f$  is smaller for 5 than for 2 in more polar solvents ( $E_T(30)$  > 38 kcal/mol), whereas the opposite was found in nonpolar solvents.

In the presence of oxygen, the fluorescence spectrum is not changed but  $\Phi_f$  decreases to varying degrees. The oxygen effect was measured by comparing deoxygenated with oxygen-saturated solutions ( $\Phi_f(Ar)$  and  $\Phi_f(O_2)$ , respectively). In solvents in which  $\Phi_f$  is large ( $\geq 0.4$ ), the ratio  $\Phi_f(Ar)/\Phi_f(O_2)$  was found to be ap-

TABLE III:	Temper	femperature Dependence of $\Phi_f$ in Several Solvents <sup>a</sup>									
solvent	temp, °C	1	2	3	4	5					
MCH	95	< 0.002	0.09	0.10	0.08	0.06					
	24	< 0.002	0.30	0.36	0.3	0.7					
	-60	< 0.01	0.62	0.76		0.7					
n-pentane	24	0.004	0.14	0.28	0.12	0.38					
-	-50		0.6	0.65		0.6					
<i>m</i> -xylene	95	0.1	0.08	0.1		0.12					
	24	0.37	0.55	0.53	0.50	0.55					
toluene	95	0.13	0.26	0.2	0.2	0.16					
	24	0.42	0.53	0.50	0.45	0.40					
	-50	0.64	0.69			0.59					
dioxane	95		0.05			0.03					
	24	0.38	0.32	0.55	0.925	0.12					
MTHF	24	0.22	0.15	0.22	0.08	0.12					
	-196	0.3	0.3	0.2	0.3	0.4					
GT	24	0.02	0.035		0.01	0.01					
	-75		0.25		0.3	0.2					
ethanol	24	< 0.002	< 0.002	< 0.002	< 0.002	<0.002)					
	-196	0.1	0.3			0.2					

<sup>a</sup> In argon-saturated solution:  $\lambda_{exc} = 366$  nm.



Figure 7. Semilogarithmic plot of  $\Phi_f$  (open symbols) and  $\Phi_{t\rightarrow c}$  (filled symbols) vs  $T^{-1}$  for 1 (squares) and 5 (triangles) in argon-saturated toluene:  $\lambda_{exc} = 366$  nm.

proximately 1.3-1.4 and in other cases correspondingly smaller.

The temperature dependence of  $\Phi_f$  also shows the same trend for the five trans isomers (Table III). In all solvents used,  $\Phi_f$ increases on going to lower temperatures. The decrease of  $\Phi_f$  on going above room temperature was measured in several solvents of small polarity (Table III). A plot of log  $\Phi_f$  vs  $T^{-1}$  is shown for 1 and 5 in toluene (Figure 7). Such semilogarithmic plots of  $\Phi_f$  vs  $T^{-1}$  are smooth curves without a minimum. The activation energy  $(E_p)$  was calculated from eq 1. Here,  $k_f$  is the rate constant

$$\ln \left[\Phi_{\rm f}^{-1} - (\Phi_{\rm f}^{\rm max})^{-1}\right] = \ln \left(A_{\nu}/k_{\rm f}\right) - E_{\nu}/RT \qquad (1)$$

for fluorescence and  $A_{\nu}$  is the preexponential factor. (Alternatively,  $E_{\nu}$  can be obtained from the linear part of log  $\Phi_{\rm f}$  vs  $T^{-1}$  at higher temperatures.)  $E_{\nu}$  is given in Table IV for several cases. In polar solvents,  $E_{\nu}$  is generally small or zero. The changes of  $\Phi_{\rm f}$  in GT and ethanol (Table III) are essentially attributed to a viscosity effect. Even in glassy MTHF and ethanol,  $\Phi_{\rm f}$  is far from unity, indicating a radiationless deactivation step not involving rotation around the C=C double bond.

Quantum Yield of Trans  $\rightarrow$  Cis Photoisomerization. Values for  $\Phi_{t\rightarrow c}$  at room temperature and the percentage of cis in the photostationary state [(% cis)<sub>s</sub>] are listed in Table V. For the five trans isomers,  $\Phi_{t\rightarrow c}$  is substantial in *n*-pentane and cyclohexane; it decreases strongly for 1-5 on going to *m*-xylene, toluene,

TABLE IV: Activation Energies from  $\Phi_f$  and  $\Phi_{rest}$  Measurements<sup>a</sup>

		ter	mp		ter	np	
		rang	e, °C	Е	range	e, °C	E
compd	solvent	high	low	kcal/mol	high	low	kcal/mol
2 <sup>b</sup>	n-pentane				+24	-70	4
2 <sup>b</sup>	MCH	+90	0	4	+24	-60	4
36		+90	0	4	+24	-40	4
4		+90	0	4	+24	-40	4.5
5		+90	0	4	+24	-40	5
1	<i>m</i> -xylene				+95	+24	7
2		+95	+24	4	+95	+24	9.5
3					+95	+24	9
4					+95	+24	9
5		+95	+24	4	+85	+24	12
1	toluene	+95	-50	4.4	+95	-30	6.4°
2		+95	-50	<4	+95	0	10.5
3		+95	-50	<4	+95	0	9
4		+95	-50	<4	+95	+24	10
5		+95	-50	3.7	+95	+24	13°
2	benzene	+75	+24	<3	+70	+24	10
1	dioxane				+90	+24	10
2		+90	+24	4	+90	+24	13
3					+95	+24	12
4					+90	+24	>12
5					+90	+24	14
2	MTHF	+24	-100	<1			
5	MTHF	+24	-100	<1			

<sup>a</sup>Obtained from experimental data partially presented in Tables III, V, and VI. The experimental error for the activation energies is typically  $\pm 15\%$ . <sup>b</sup>Taken from ref 10. <sup>c</sup>E<sub>3</sub> from eq 6 is  $\simeq$  4 and 11 for 1 and 5 in toluene, respectively.

benzene, and dioxane; and it becomes practically zero in solvents of moderate or strong polarity (e.g., dichloromethane, DMF, acetonitrile) and in alcohols. This dependence on  $E_T(30)$ , a change

in  $\Phi_{t\rightarrow c}$  by 2 orders of magnitude, is illustrated in Figure 6 for 2. For this nitrostilbene, it has already been shown that  $\Phi_{c\rightarrow t}$ , in contrast to  $\Phi_{t\rightarrow c}$ , is almost independent of the solvent polarity.<sup>6,7,10</sup> The similarity of  $\Phi_{t\rightarrow c}$  and (% cis)<sub>s</sub> for the five isomers in a given solvent indicates that, for 4 and 5 too,  $\Phi_{c\rightarrow t}$  is only slightly affected by the nature of the solvent (Table V). As a result of the changes in  $\Phi_{t\rightarrow c}$  rather than  $\Phi_{c\rightarrow t}$ , the position of the photostationary state is shifted from approximately 65–75% cis to <1% cis on increasing the solvent polarity. All attempts to find polar environments (e.g., at high temperatures) with  $\Phi_{t\rightarrow c}$  values larger than 0.01 failed; for example,  $\Phi_{t\rightarrow c}$  is smaller than this limit for 1 and 2 in DMF even at 100 °C.

The temperature dependence of  $\Phi_{t\to c}$  was studied in two nonpolar solvents and three solvents of moderate polarity ( $E_T(30)$ = 33-36 kcal/mol). Data presented in Tables IV and VI show the following: (i)  $\Phi_{t\to c}$  increases with increasing temperature. (ii) The position of the photostationary state at high temperatures is correspondingly shifted to the cis side, indicating that  $\Phi_{c\to t}$  is only weakly temperature dependent. (iii) At lower temperatures, log  $\Phi_{t\to c}$  depends almost linearly on  $T^{-1}$  and levels off at high temperatures (Figure 7). (iv) The activation energy ( $E_{t\to c}$ ), obtained from the Arrhenius plot of  $\Phi_{t\to c}$  at low temperatures, increases in the order saturated hydrocarbons, *m*-xylene, toluene, and dioxane (experimental error ±15%). (v) The  $E_{t\to c}$  values in a given solvent show an increasing trend in the order 1, 2 (~3, ~4), and 5 (Table IV).

#### Discussion

The structures of the nitrostilbenes under examination differ by virtue of the fact that for 1-3 the dialkylamino group can rotate almost freely about the single bond to the phenyl ring whereas this is impossible in 4 and 5 since the dialkylamino group is part of the indoline ring. A marked increase in  $\Phi_f$  would be expected on going from 1 to 4 or from 2 to 5 if this rotation mode would

TABLE V: Quantum Yield of Trans  $\rightarrow$  Cis Photoisomerization and Position of the Photostationary State<sup>a</sup>

			Φ <sub>t→c</sub>		$(\% \text{ cis})_{s}$					
solvent	1	2	3	4	5	1	2	3	4	5
n-pentane	0.4	0.25	0.16	0.25	0.28	75	72	65	70	72
cyclohexane	0.45	0.28	0.18	0.25	0.25	76	70	60	70	68
carbon tetrachloride <sup>b</sup>	0.4	0.2	0.2	0.3	0.25	>60	>50	>50	>60	>60
<i>m</i> -xylene	0.15	0.038	0.03	0.04	0.013	55	19	10	20	8
toluene	0.11	0.035	0.02	0.02	0.011	48	17	10	18	6
benzene	0.1	0.02	<0.01	<0.005	<0.01	45	10	<5	<5	<5
dioxane	0.02	0.008	0.006	<0.004	<0.003	18	2	<2	<2	<2
MTHF		0.004					<0.5			
GT		<0.002					<0.5			
ethanol		< 0.001			<0.001		<0.1			<0.1

<sup>a</sup> In argon-saturated solutions at 24 °C:  $\lambda_{irr}$  = 436 nm unless otherwise indicated. 1 in nonpolar solvents:  $\lambda_{irr}$  = 366 nm. <sup>b</sup>A decomposition was observed on prolonged irradiation.

TABLE VI: Temperature Dependence of  $\Phi_{t \rightarrow c}$  and Position of the Photostationary State in Several Solvents<sup>a</sup>

			Φ <sub>t→c</sub>						
solvent	temp, °C	1	2	3	4	5	2	5	
МСН	95	0.5	>0.35	0.3	0.36	0.38	75	78	
	24	0.45	0.28	0.20	0.2	0.15	70	60	
	-50	0.4	0.05	0.03	0.008	<0.01	20	<5	
<i>m</i> -xylene	95	0.45	0.4	0.33	0.35	0.35	75	70	
•	70	0.4	0.2	0.13	0.25	0.25	60	60	
	24	0.1	0.038	0.2	0.3	0.25	19	8	
toluene	95	0.40	0.35	0.36	0.38	0.35	70	70	
	50	0.25	0.18	0.13	0.15	0.06	55	20	
	0	0.05	0.008	0.005		< 0.005	2	<2	
	-20	0.015	0.004				<1		
benzene	75		0.33				60		
	24		0.02				10		
dioxane	95	0.25	0.22	0.23	0.065	0.13	55	60	
	70	0.17	0.062	0.08	0.022	0.06	15	16	
	24	0.02	0.008	0.006	<0.004	< 0.003	2	<2	
DMF	100	<0.01	<0.01				<2		
	24	< 0.002	< 0.002						

<sup>a</sup> In argon-satured solutions:  $\lambda_{exc}$  = 436 nm unless indicated otherwise. 1 in MCH:  $\lambda_{exc}$  = 366 nm.

play a role. However, such a trend was not found. Except for nonpolar solvents,  $\Phi_f$  is even smaller for the rigid isomer 5 than for the flexible one (2) (Table II). This excludes rotation of the dialkylamino group as a significant mode for dissipation of energy after population of the <sup>1</sup>t\* state.

Fluorescence Properties. The first step after excitation into the Frank-Condon state of the trans configuration  $({}^{1}t^{*'})$  is a solvent-solute relaxation. This leads to rapid population of the <sup>1</sup>t\* state from which the fluorescence occurs. The Stokes shift, as a measure of the energy difference between 1t\*' and 1t\*, ranges from  $(4-5) \times 10^3$  cm<sup>-1</sup> in nonpolar solvents at room temperature to more than  $1.1 \times 10^4$  cm<sup>-1</sup> in polar solvents. A picosecond study could improve the understanding of the rearrangement dynamics of excited trans-(dialkylamino)stilbenes. At present, time-resolved rearrangement studies have mainly been reported for the parent stilbene.30

Plots of the Stokes shift against the polarity parameter for compounds 1, 2, and 5 (Figure 3) show an almost linear dependence and only slight scatter, supporting the hypothesis of a common emitting state for all five isomers with very similar dipole moments. The Stokes shift is markedly reduced in rigid media (see Figure 4 and Table I). This is a result of the well-known effect of viscosity on the solute-solvent rearrangement,2,15,28 leading to a smaller lowering of the level of <sup>1</sup>t\* and virtually no polarity effect.

The characteristic solvent dependence of  $\Phi_f$  at room temperature (Figures 5 and 6 and Table II) is due to the relaxation steps competing with fluorescence (see below). The temperature dependence of  $\Phi_f$  can be expressed by eq 2, which implies that there

$$\Phi_{\rm f} = \frac{k_{\rm f}}{k_{\rm f} + k_0 + A_{\nu} \exp(-E_{\nu}/RT)}$$
(2)

is one activated and at least one nonactivated decay step in competition to fluorescence. Here,  $k_0$  is a rate constant summarizing all radiationless nonactivated steps, and  $k_f/(k_f + k_0)$ =  $\Phi_{f}^{\text{max}}$  in eq 1.  $E_{\nu}$  values of about 4 kcal/mol have been found for 2 in toluene and for 1-3 in saturated hydrocarbons.<sup>10,11</sup> Data in Table IV show that 4 and 5 behave similarly.

For 2 in toluene, the temperature dependence of  $\Phi_{\rm f}$  has been assigned to the transition  ${}^{1}t^{*} \rightarrow A^{*}$ , where  $A^{*}$  is probably an excited singlet state with trans configuration.<sup>11</sup> Although the properties of A<sup>\*</sup> (in toluene and other media with similar  $E_{T}(30)$ ) values] are unknown, it appears to be nonemitting. On the basis of our current knowledge, A\* cannot be assigned to a conformation in which the plane of the dimethylamino group is perpendicular to the phenyl ring.

There is no apparent evidence for the presence of a second low-energy emission band attributable to a transition from a TICT state of trans-1-trans-3 in the spectral range examined (up to 850 nm). Moreover, the plot of log  $\Phi_f$  vs  $T^{-1}$  for 2 in toluene (Figure 7) and other solvents (Table IV) yields a smooth ascending curve that tends to  $\Phi_{f}^{max}$ , the maximum value at low temperatures. This differs from the properties of a TICT state in systems such as p-(N,N-dimethylamino)benzonitrile.<sup>19,20</sup> A comparison of the nitrostilbenes with two characteristic aminocoumarins, one of which has a "free" dialkylamino group while the analogue has a group constrained into planarity,<sup>31</sup> may be instructive. For these coumarins,  $\Phi_f$  also decreases on increasing the solvent polarity but is substantially larger for the rigid coumarin. While no dual emission has been observed, a general broadening of the fluorescence band has been found for the coumarin with the rotatable dialkylamino group. Therefore, the occurrence of a TICT state involving a rotation of the amino group was inferred.<sup>31</sup> However, a slightly larger bandwidth was also found for compound

2 (as compared to 5) where no such TICT state is involved. Trans  $\rightarrow$  Cis Photoisomerization. In a preceding paper, it has been suggested that trans  $\rightarrow$  cis photoisomerization of 1 in saturated hydrocarbons occurs mainly via the triplet route.<sup>10</sup>

$${}^{1}t^{*} \rightarrow {}^{3}t^{*} \rightleftharpoons {}^{3}p^{*} \rightarrow {}^{1}p \rightarrow (1-\alpha){}^{1}c$$
 (3)

Here, <sup>3</sup>t\* and <sup>3</sup>p\*, respectively, are the trans and twisted configurations (perpendicular with respect to the C=C double bond) of the lowest triplet, <sup>1</sup>p is the twisted ground state, and  $1 - \alpha$  is the fraction of triplet decaying into the cis form. For 2 and 3, in addition to the major route (reaction 3), a second minor pathway ( $\leq$ 30%) via excited singlet states contributes (1 –  $\beta$  is the fraction of perpendicular singlet configuration decaying into the cis form):<sup>10</sup>

$$t^* \to {}^1p^* \to {}^1p \to (1-\beta){}^1c \tag{4}$$

The similarity of the results in saturated hydrocarbons (see Tables IV-VI) is in support of the assumption of a major contribution of the triplet mechanism also for 4 and 5.

In toluene, by contrast, a consecutive, double-activated pathway has been proposed previously for 2:11

$$^{1}t^{*} \xrightarrow{\Delta} A^{*} \xrightarrow{\Delta} ^{1}p^{*} \xrightarrow{} ^{1}p \xrightarrow{} (1-\beta)^{1}c$$
 (5)

Sequence 5 differs from the singlet pathway (reaction 4)<sup>32</sup> in that (i) the excited perpendicular configuration is not necessarily the lowest excited singlet (which we assume here for simplicity) and that (ii) a second excited trans state (A\*) is involved. Since intersystem crossing is substantial only in nonpolar solvents,<sup>8,10</sup> the principal barrier on the pathway to the cis isomer in the singlet manifold lies between A\* and <sup>1</sup>p\*.

The temperature dependence of  $\Phi_{t \rightarrow c}$  can be analyzed by using eq 6.<sup>10</sup> Here,  $E_1$  and  $E_3$  are the activation energies of the steps  ${}^{1}t^{*} \rightarrow A^{*}$  and  $A^{*} \rightarrow {}^{1}p^{*}$ , respectively,  $A_{1}$  and  $A_{3}$  are their respective preexponential factors, and  $k_2$  is the rate constant for the transition  $A^* \rightarrow {}^1t$ . For the step  $A^* \rightarrow {}^1p^*$ , the molecule has

$$\Phi_{t \to c}^{-1} = \left(1 + \frac{k_{\rm f} + k_0}{A_1} e^{E_1/RT}\right) \left(1 + \frac{k_2}{A_3} e^{E_3/RT}\right) \frac{1}{1 - \beta}$$
(6)

to overcome an activation barrier that is markedly higher than that of the initial step  $({}^{1}t^{*} \rightarrow A^{*})$ , competing with fluorescence. The temperature dependence of  $\Phi_{t\rightarrow c}$  reflects essentially the larger activation energy in the transition from <sup>1</sup>t\* to <sup>1</sup>p\*. Application of eq 6 gives  $E_3 \approx 4$  kcal/mol for 1 in toluene, compared to  $E_{t\rightarrow c}$ = 6.4 kcal/mol. In most cases,  $E_{t\rightarrow c}$  is larger than 9 kcal/mol whereas  $E_{\nu} \leq 4$  kcal/mol. Therefore, the approach  $E_{t \rightarrow c} \approx E_3$ could be used. For example,  $E_3 = 11 \text{ kcal/mol and } E_{t \rightarrow c} = 13$ kcal/mol for 5 in toluene.

The values of  $E_{t\to c}$ , in combination with the  $E_{\nu}$  values, for 1-5 in toluene (Table IV) are in agreement with the conclusion already derived for  $2^{10}$  Fluorescence and trans  $\rightarrow$  cis photoisomerization are not coupled directly since the activation energies  $E_{\nu}$  and  $E_{t\rightarrow c}$ are different. For 2 route 5 seems to be followed also in *m*-xylene, benzene, and dioxane. The results for 4 and 5 in these solvents of moderate polarity (Tables IV-VI) are in agreement with this pathway. The postulated state A\* should therefore be involved in all five 4-nitro-4'-(dialkylamino)stilbenes.

The increases in  $E_{t\to c}$  with increasing solvent polarity from 4 kcal/mol (MCH) to 13 kcal/mol (dioxane) for 2 or 14 kcal/mol for 5 are striking. The barrier is much larger in polar solvents. For example, for 2 in DMF,  $E_{t\rightarrow c}$  is probably larger than 25 kcal/mol. This indicates that charge separation in A\*, as compared with that in the transition state leading to  $^{1}p^{*}$ , is stabilized and that the energy of A\* is reduced on raising the solvent polarity. This property of A\* is in accord with that of a TICT state which, however, cannot be one involving rotation of the amino group, as mentioned. Lowering of the energy level of A\* should facilitate radiationless decay on the trans side of the reaction coordinate. The method of transient dielectric loss, as used for studying the dipole moment of nonemitting TICT states,<sup>17</sup> could provide ex-

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<sup>72. 391.</sup> 

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perimental access to the character of A\*.

Deactivation Pathways Competing with Fluorescence and Photoisomerization. The decrease in  $\Phi_{t\rightarrow c}$  on going from a nonpolar to a slightly polar solvent is partly compensated by the increase in  $\Phi_f$  (see Tables II and V). In polar solvents, however, no such correlation between  $\Phi_{t\rightarrow c}$  and  $\Phi_f$  was found since both  $\Phi_{t\rightarrow c}$ and  $\Phi_f$  become smaller than 0.01 at room temperature. A close similarity in  $\Phi_{t\rightarrow c}$  was found for 2 and the sterically fixed analogues in a given solvent. Therefore, rotation of the dialkylamino group cannot be responsible for the inhibition of trans  $\rightarrow$  cis photoisomerization in polar solvents.

On the basis of triplet yield and sensitized  $cis \Rightarrow$  trans photoisomerization measurements for 2, the existence of a radiationless step  $({}^{1}t^{*} \rightarrow {}^{1}t)$  as been postulated.<sup>9</sup> In addition,  ${}^{1}t^{*}$  is deactivated by an intersystem crossing step. However, the relative triplet yield decreases by a factor of 5-10 when cyclohexane is replaced by polarizable or more polar solvents.8 A value for the quantum yield of intersystem crossing (at the trans side) of  $\Phi_{isc} = 0.04$  may be estimated in the latter cases with use of  $\Phi_{isc} = 0.4$  in cyclohexane.<sup>10</sup> In saturated hydrocarbons,  $k_0$  in eq 1 is ascribed mainly to intersystem crossing.<sup>10</sup> In more polar solvents, however,  $k_0$  is ascribed essentially to the internal conversion step  ${}^{1}t^{*} \rightarrow {}^{1}t$  since  $\Phi_{isc}$  is small<sup>8</sup> and  $\Phi_{f}$  in glassy MTHF and ethanol is smaller than 0.5 (Table III). Internal conversion competes effectively with fluorescence in slightly polar solvents at room temperature. When the polarity is further increased,  $\Phi_f$  decreases dramatically (Figures 5 and 6) and the energy gap between the relaxed excited singlet and the ground state is reduced.

Since  $\Phi_{t\to c}$  is practically zero in solvents with  $E_T(30) > 35$ kcal/mol (Figure 6 and Table V), we conclude that twisting about the C=C double bond in the triplet state and subsequent decay into the cis form play no role in polar solvents. The reason may be (i) an activation barrier between  ${}^{3}t^{*}$  and  ${}^{3}p^{*}$  that cannot be overcome at room temperature or (ii) intersystem crossing to <sup>1</sup>t at a location on the potential energy surface smaller than 90°. Both possibilities are in line with a result obtained from sensitized trans  $\rightarrow$  cis photoisomerization, namely that the photostationary state in methanol contains less than 5% cis isomer.<sup>9</sup> It may be anticipated that 1 and 3-5 exhibit a similar behavior. It is noteworthy that for trans-4,4'-diaminostilbene the rate of trans  $\rightarrow$  cis photoisomerization increases when the solvent becomes more polar.<sup>33</sup> Apparently, the presence of  $(n,\pi^*)$  states, introduced by the nitro group and the interaction between electron donating and accepting groups give rise to internal conversion in a yield close to unity in polar solvents.

Effect of Solvent Polarity. Taking the above arguments together, we propose that the mechanism of trans  $\rightarrow$  cis photoisomerization for 1-3 and the two "rigid" compounds is the same since the values for  $\Phi_{t\rightarrow c}$  and (% cis), are very similar for 2-5 and only slightly higher for 1. The effect of solvent polarity on the energetics of the states involved in trans  $\rightarrow$  cis photoisomerization of 1-5 and the effect of temperature on the contribution of the other relaxation pathways is illustrated schematically in Figure 8.

In saturated hydrocarbons, trans  $\rightarrow$  cis photoisomerization of 1 via the well-known triplet mechanism<sup>12,24,32</sup> is the dominant deactivation route of <sup>1</sup>t<sup>\*</sup>. For 2 and 3<sup>10</sup> and most likely also for 4 and 5 in such solvents, a minor contribution of the singlet route comes into play. The markedly increased  $\Phi_f$  values for 2–5, compared to 1, should reflect a longer fluorescence lifetime. Concerning the properties of <sup>1</sup>t<sup>\*</sup>, 1 in saturated hydrocarbons resembles other nitrostilbenes, especially 4-nitro-4'-methoxystilbene.<sup>6-8,12,24</sup> A lowering of the level of <sup>1</sup>t<sup>\*</sup> for 2–5 (Table I) may open the singlet pathway, but the cause of this difference has not been explored.

In slightly polar solvents, i.e., in those with  $E_T(30)$  values between 33 and 36 kcal/mol,  $\Phi_f$  of all five trans isomers is larger than in the other solvents (Table II). The correspondingly prolonged fluorescence lifetime is suggested to be due to population



Figure 8. Scheme for deactivation of the excited trans isomer (1-5) and pathways leading to the cis isomer in solvents of different polarity: (a) nonpolar,  $E_T(30) < 32$  kcal/mol; (b) slightly polar,  $E_T(30) = 33-36$  kcal/mol; and (c) moderately and strongly polar,  $E_T(30) > 37$  kcal/mol. Note: Presence of A\* in nonpolar solvents only postulated (<sup>3</sup>p\* is also deactivated to <sup>1</sup>t).

of the A\* state with a rather small rate constant at room temperature, i.e., comparable to  $k_{\rm f}$ . Intersystem crossing and internal conversion from <sup>1</sup>t\* to <sup>1</sup>t may contribute to a certain degree, but the main radiationless pathway is suggested to follow route 5.

The trend of  $E_{\nu}$  values indicates that the energy level of A<sup>\*</sup> decreases with increasing  $E_T(30)$  more than that of <sup>1</sup>t<sup>\*</sup>. Assuming that the energy level of <sup>1</sup>p<sup>\*</sup> remains essentially unaffected by the polarity, the drastic increase in the activation energy associated with A<sup>\*</sup> means that the energy of A<sup>\*</sup> is correspondingly lowered and hence the radiationless deactivation on the trans side greatly enhanced. For (dialkylamino)coumarins, an enhanced lowering of a proposed TICT state as compared to a polar solvent relaxed excited singlet state has been advanced.<sup>34</sup>

In all solvents with  $E_T(30)$  values larger than 36 kcal/mol, trans  $\rightarrow$  cis photoisomerization is virtually impossible even at elevated temperatures. What is the reason? Obviously, the activation barrier between <sup>1</sup>t\* and <sup>1</sup>p\* is too large (>25 kcal/mol) to overcome. Solute-solvent interaction lowers the energy of the emitting state very substantially. In dichloromethane, for example, where  $\lambda_f$  of 5 approaches the detection limit of 850 nm, the Stokes shift is 26 and 31 kcal/mol for 1 and 5, respectively. It is larger than 31 kcal/mol in polar solvents like acetonitrile or ethanol. At least 1/2 of this energy difference should contribute to the solvent-induced relaxation in the excited singlet state.

In order to account for the decrease of  $\log \Phi_f vs E_T(30)$  (Figures 5 and 6 and Table II), the radiationless decay step must become considerably more effective, most probably due to the lowering of the energy of the state involved. We propose that charge separation is involved even to the extent of a biradicaloid zwitterionic (intramolecular charge-transfer) state that does not emit. A potential candidate for the structure involved could be the following:



Formally speaking, an electron has been transferred from the (dimethylamino)stilbenyl moiety into an antibonding orbital of the nitro group; the latter is probably orthogonal to the remainder of the molecule. The proposed structure for  $A^*$  is tentative and representative of a distribution of rotamers about the geometry suggested. TICT states in which the 4'-(dimethylamino)phenyl or 4'-(dimethylamino)styryl fragments are twisted relative to the remainder of the molecule are viable alternatives. In *trans*-1-

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(4-(N,N-dimethylamino)phenyl)-2-nitroethylene, a homologoussystem, it has been concluded on the basis of luminescence studies and theoretical calculations that the  $(\pi,\pi^*)$  state has predominantly CT character with the lowest  $\pi^*$  orbital located in the region of the nitro group.<sup>35</sup> This should also hold for correspondingly substituted stilbenes. A second nonfluorescent excited state, postulated for the nitrostyrenes,<sup>35</sup> may well be analogous to A\* for compounds 1-5.

### Conclusion

The relaxation phenomena of the excited singlet state of the three trans-4-nitro-4'-(dialkylamino)stilbenes and the two analogues (4 and 5) are very similar in each of a variety of solvents.

This excludes rotation of the dialkylamino group about the C-N bond as an accessible deactivation step for 1-3. The role of the state A\* in the deactivation of <sup>1</sup>t\* is outlined; the energy of A\* is lowered significantly on increasing the solvent polarity.

Acknowledgment. We thank Professor D. Schulte-Frohlinde for stimulating discussions, H. Steffen for skillful preparative work, and A. Keil, C. Hüsken, and L. J. Currell for technical assistance as well as M. W. Riemer and J. Bitter for NMR measurements.

Registry No. trans-1, 7297-52-1; trans-2, 2844-15-7; trans-3. 65644-11-3; trans-4, 122069-80-1; trans-5, 122069-81-2; MTHF, 96-47-9; THF, 109-99-9; DMF, 68-12-2; MCH, 108-87-2; GT, 102-76-1; n-pentane, 109-66-0; cyclohexane, 110-82-7; carbon tetrachloride, 56-23-5; m-xylene, 108-38-3; di-n-butyl ether, 142-96-1; toluene, 108-88-3; benzene, 71-43-2; diethyl ether, 60-29-7; dioxane, 123-91-1; acetic acid ethyl ester, 141-78-6; chloroform, 67-66-3; dichloromethane, 75-09-2; acetone, 67-64-1; acetonitrile, 75-05-8; ethanol, 64-17-5.

## **Reinvestigation of Ultrasonic Absorption Mechanisms in tert-Butylamine Aqueous** Solution

#### Sadakatsu Nishikawa\* and Yasuko Harano

Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan (Received: February 3, 1989; In Final Form: April 17, 1989)

Ultrasonic absorption coefficients were measured in the frequency range from 7.59 to 221.1 MHz and at a velocity of 2.5 MHz in a wide concentration range (49 concentrations) of aqueous solutions of tert-butylamine at 25 °C in order to elucidate the characteristic absorption mechanisms. A clear single relaxational absorption was observed in the concentration range from 0.0048 to 1.1 mol dm-3, and the cause was attributed to the perturbation of an equilibrium associated with the proton-transfer reaction. The rate and thermodynamic parameters for the reaction were determined from reactant-concentration dependences of the relaxation frequency and the maximum excess absorption per wavelength. At the concentration range above 1.3 mol dm<sup>-3</sup>, the absorption coefficients divided by the square of the frequency,  $\alpha/f^2$ , were found to be well expressed by a fourth-order polynomial function of the analytical concentration. Then, after subtraction of the absorption due to the proton-transfer reaction, we found that, at any concentrations between 1.7 and 3.4 mol dm<sup>-3</sup>, the frequency dependence of the residual absorption was reexpressed by a single relaxational equation. Such residual absorption was estimated to be due to an aggregation reaction associated with a hydrophobic interaction,  $3A = A_3$ , from the concentration dependences of the relaxation frequency and the maximum excess absorption per wavelength. It was shown that the separation of two relaxation processes was now possible if one mechanism of relaxation was precisely determined.

#### Introduction

In our previous studies in aqueous solutions of various amines by means of ultrasonic methods, we have shown two characteristic relaxational absorptions in a pulse frequency range.<sup>1,2</sup> One is associated with a relaxation due to a proton-transfer reaction (hydrolysis), the mechanism of which has been originally proposed by Eigen et al.<sup>3</sup> and the consistent interpretation between the experiments and the theory seems to have been given as a diffusion-controlled reaction. The effects of some additives on the reaction are now investigated in relation to the biological systems.4-6

The other is the absorption observed in more concentrated solutions in which the solutes consist of a relatively large hydrophobic group. The absorption is characterized by a peak sound absorption and velocity concentrations; i.e., the absorption coefficients divided by the square of the frequency and the sound velocity show their maxima at typical concentrations. These

phenomena were first considered by Barfield and Schneider,<sup>7</sup> and the cause of the absorption has been further investigated with various models.<sup>8</sup> We have also proposed<sup>1,2,9</sup> that it may be due to a relaxation associated with an aggregation reaction of nonionized molecules with a hydrophobic interaction.

In the studies of the isomeric butylamine solutions, we have also shown the existence of such a relaxation. However, it has been too difficult to distinguish between two relaxations when the two relaxation times are expected to be close to each other. This is the case when the solute hydrophobicity is not so large. Especially, in the solution of tert-butylamine, the distinction has not been performed.10

On the other hand, Atkinson et al.<sup>11</sup> have analyzed the absorption in the aqueous solution using a Romanov and Solov'ev's fluctuation model.<sup>12</sup> In their analysis, the residual absorptions except that due to a hydrolysis have been taken into account, and they have reported that the residual ones are not well expressed by a single relaxational equation. However, the tested concen-

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