

Intramolecular electron transfer in 4-(dialkylamino)pyrimidines. Study in solutions and supersonic jet

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Abstract. The dual fluorescence (**a** and **b**) of 4-(dialkylamino)pyrimidines (4-DAAP) in solutions is explained in terms of the TICT state model. 4-DAAP form complexes with protic solvents: efficient radiationless depopulation is “switched on” by hydrogen bonding (HB). The photoinduced electron transfer is modified by HB or by coordination to the metal ion. In nitriles, two emitting states of 4-(N,N-dimethylamino)pyrimidine (I) and 4-(N,N-diethylamino)pyrimidine (II) reach equilibrium. In protic solvents, the fluorescences **a** and **b** are not kinetically coupled: the different ground state complexes are responsible for each band. Jet-cooled 4-DAAP show only primary excited fluorescence **b**. Microsolvation of pretwisted *o*-methylated compounds III and IV by small polar molecules, contrary to more planar I and II, gives rise to the long-wave (probably TICT) fluorescence.

Keywords. Luminescence; TICT states; 4-(dialkylamino)pyrimidines; supersonic jet; electron transfer.

1. Introduction

In recent years, much interest has been generated in the dual fluorescence phenomenon of a number of electron donor-acceptor molecules linked by a formally single bond. Various mechanisms have been proposed to explain this behaviour (Lippert *et al* 1962; Rotkiewicz *et al* 1973; Visser and Varma 1980; Visser *et al* 1983; Cazeau-Dubroca *et al* 1989), the most plausible one being the TICT (twisted intramolecular charge transfer) state model, originally proposed by Grabowski and his coworkers (Grabowski *et al* 1979; Grabowski and Dobkowski 1983) and reviewed by Rettig and others (Rettig 1986; Lippert *et al* 1987). The TICT state is formed from the primary excited *B** state by electron transfer from the donor (D) to the acceptor (A) moiety. The process involves a rotation of D and A entities to a mutually perpendicular conformation to achieve and stabilize a high degree of charge separation (figure 1).

D–A molecules, interacting strongly with polar media, have been widely used for studying the structural and environmental requirements of the intramolecular electron transfer processes. It has been proved (Grabowski *et al* 1979, 1984; Rettig 1980, 1986;

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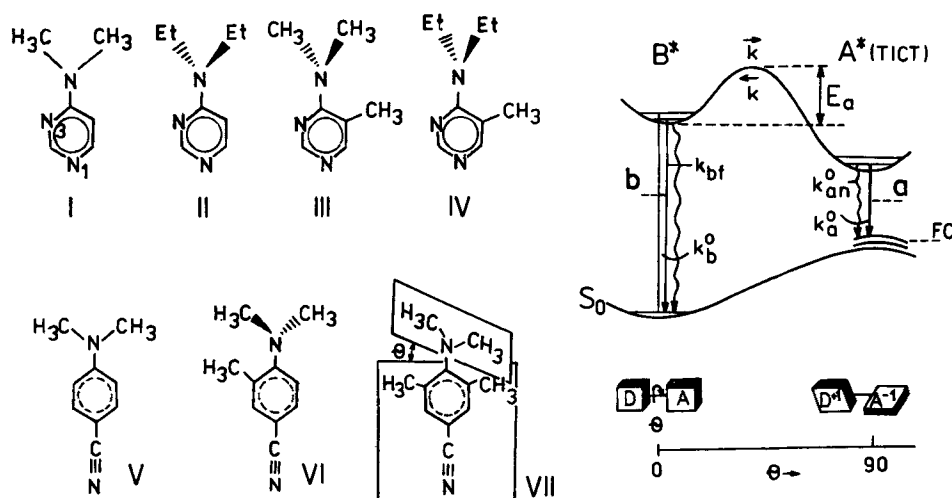


Figure 1. Formulae of the studied compounds and a model of the TICT state formation: schematic potential energy profiles along the reaction coordinate represented here by the torsional angle Θ . k_i are the rate constants of the elementary processes. FC \equiv the Franck–Condon state. Dual fluorescence **b** and **a** is due to emission from the substrate (primary excited B^* state) and product ($A^* \equiv$ TICT state) of the excited state electron transfer.

Rettig and Wermuth 1985; Lippert *et al* 1987) that the ground-state conformation of the molecule and the correlation of its lowest excited states are two of the most essential criteria for the formation of a TICT state. A steric hindrance to coplanarity between D and A entities, for example due to ortho-methylation of the benzonitrile ring in *p*-cyano-2,N,N-trimethylaniline (VI) and *p*-cyano-2,6,N,N-tetramethylaniline (VII), leads to an increase in the “twist” angle Θ of the ground-state equilibrium conformation and a reduction, or even suppression, of the torsional barrier E_a to the excited-state reaction with respect to that in planar *p*-cyano-N,N-dimethylaniline (V) (see figure 2 in Grabowski *et al* 1979). Thus, the TICT state formation is kinetically favoured in molecules VI and VII.

The role of the solvent in the excited-state reaction $B^* \rightarrow A^*$ is one of the most important and controversial questions. According to the TICT state model, the solvent predominantly acts by electrostatic stabilization of the highly polar “twisted” rotamer A^* . On the other hand, Varma and others (Visser and Varma 1980; Visser *et al* 1983–1986; Weisenborn *et al* 1986, 1988, 1989) have explained the dual luminescence of V in terms of the exciplex formation; the interactions between the lone pairs of the solvent and the “twisted” dimethylamino (DMA) group being the source of exciplex stabilization. This model involves transformation of the B^* state into a “twisted” 1:1 solute–solvent exciplex. The evidence contradicting such interpretation was provided by: (i) the finding of the highly polar long-wave fluorescence **a** of VII in a thermalized vapour (Rotkiewicz and Rubaszewska 1982; Bischof *et al* 1985), and (ii) by Suppan (1986), who found as a rule the solvation of V to be due to nonspecific electrostatic interactions. Cazeau-Dubroca *et al* (1989) attributed fluorescence **a** to the complex of V with ubiquitous traces of water which are supposed to be present in the ground state. These complexes are hydrogen-bonded at the DMA group, which is said to be already “pre-twisted”. The observation of the dual luminescence of the highly

concentrated solutions of V in especially dried acetonitrile (Pilloud *et al* 1987) seems to rule out the latter hypothesis.

The influence of the solvent on the dynamics of the charge separation in V has been attributed to static polarity effects: the energy barrier E_a (figure 1) to the TICT state formation was either correlated with the activation energy of the viscous flow of the solvent (Rettig 1980, Lippert *et al* 1987) or with the solvent polarity (Siemiarczuk *et al* 1977, 1982; Wang *et al* 1981; Wang and Eisenthal 1982; Hicks *et al* 1985, 1987). The dynamic solvent effects on intramolecular charge transfer (CT) are still very obscure. The experiments do not show any correlation between the electron transfer times $\tau_{et} = 1/\bar{k}$ (figure 1) and the longitudinal dielectric relaxation times τ_L of the solvent, not only for V (Hicks *et al* 1987; Su and Simon 1988, 1989; Leinhos *et al* 1991) and 4-(9-anthryl)-N,N-dimethylaniline (ADMA) (Barbara and Jarzeba 1990; Mataga *et al* 1990) [as is expected because the excited-state reaction in the latter compounds is thermally activated (Grabowski *et al* 1979; Siemiarczuk *et al* 1977, 1982)], but also for the molecules having very small, if any, potential barrier E_a to torsion, e.g. for VII (Weisenborn 1989), and bianthryl (BA) (Kahlow *et al* 1987; Kang *et al* 1988). τ_{et} values for BA, however, are in agreement with the experimentally determined microscopic solvation times τ_s of the corresponding solvents (Kang *et al* 1988). This fact suggests that the barrierless intramolecular excited-state electron transfer in BA is controlled by solvation dynamics.

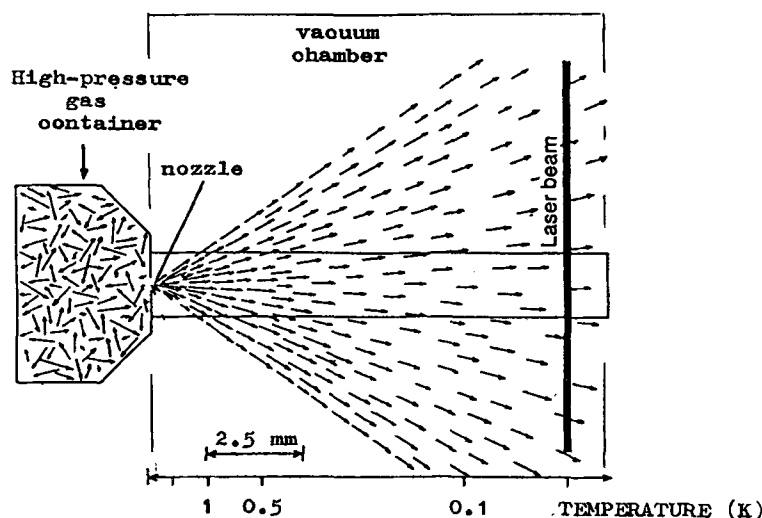


Figure 2. The simplified picture of the supersonic jet technique (Ashkenas 1966; Anderson 1974; Levy 1980) being the adiabatic expansion of an inert carrier gas (helium or argon for example) and seeded gaseous forms of the molecules. A pumping system expands the gases from the high-pressure gas container, through a nozzle of typically a few hundred μm diameter, to a vacuum chamber. The laws of thermodynamics require that an expanding gas jet must cool, which means that the distribution of velocities of an assembly of atoms will narrow. The width of this velocity distribution is associated with a local temperature. The cooling is shown schematically by directed flow of atoms (for simplicity in one direction). The excitation of the supercooled molecules by a tunable, spectrally narrow, laser beam, makes it possible to record highly resolved laser induced fluorescence and excitation spectra of individual species (for example: bare monomeric forms of compounds, their clusters as well as complexes with other "solvent" molecules).

Most experiments have been carried out in solutions. Much less is known about conditions that enable the occurrence of CT in the excited state of molecules in a supersonic molecular beam. The free jet expansion technique (figure 2) generates supercooled species; translational and rotational temperatures being as low as 0.5 K, vibrational temperatures are higher. The cooling and a consequent spectral simplification offer a chance to study the structural changes in, and the dynamics of, the excited-state processes.

A few results concerning TICT state formation in a supersonic jet have been recently reported. The monomeric form of jet-cooled V, either bare or clustered (e.g. with water, methanol, acetonitrile, acetone, dichloro- and trifluoromethane), shows only primary fluorescence **b** (Kobayashi *et al* 1986; Gibson *et al* 1987, 1988; Peng *et al* 1987). For jet-cooled VII (Kobayashi *et al* 1987), a long wave emission was found, which has also been observed in a thermalized vapour and in nonpolar solvents (Rotkiewicz and Rubaszewska 1982; Bischof *et al* 1985); this fluorescence was attributed to a TICT state. These findings seem to confirm that the electron transfer can be promoted by the degree of deviation of the DMA group from the coplanarity in the ground state. The bare BA molecule exhibits fluorescence **b**, but microsolvation by probably just one acetone molecule gives rise to a red shifted emission **a** (Kajimoto *et al* 1986). Complexes of higher stoichiometry further stabilize the CT state. August *et al* (1988) claim to have found TICT emission in 4-(dialkylamino)-benzoic acid esters, but this was refuted by Howell *et al* (1989), who assign the long-wave emission to excimers.

The vibrational structure of the laser induced fluorescence and excitation spectra as well as the rotational contour analysis of vibrational bands of supercooled molecules offer a unique chance to study the change of the potential energy profiles for individual intramolecular motions, which may follow electronic excitation. V is nearly planar in the ground state, but Grassian *et al* (1989, 1990), Warren *et al* (1988) and Gordon (1990) claim that upon excitation the DMA group undergoes a rotation of about 30° with respect to the plane of the ring. The ground-state equilibrium conformation of ADMA corresponds to a close perpendicularity between electron donor (dimethylaniline) and acceptor (anthracene) entities ($\Theta \cong 90^\circ$), whereas in the excited B^* state the "twist" angle Θ is about 60° (Kajimoto *et al* 1991). Similar effects were found for BA (Subaric-Leitis 1990).

In this paper we present the investigations (being partly published in Herbich *et al* (1989, 1991) of the photoinduced intramolecular electron transfer in four members of a series of 4-(N,N-dialkylamino)pyrimidines, 4-DAAP (I–IV). The ground-state conformation of the molecule is one of our main variables in studying the TICT state formation. The calculated values of the torsional angle Θ between D and A moieties in 4-DAAP by the molecular mechanics method (Allinger 1976) are as follows: $\Theta(\text{I}) \cong 0^\circ$, $\Theta(\text{II}) \cong 6.5^\circ$, $\Theta(\text{III}) \cong \Theta(\text{IV}) \cong 18^\circ$. One can compare the values with those obtained for V–VII: $\Theta(\text{VII}) \cong 55^\circ > \Theta(\text{VI}) \cong 25^\circ > \Theta(\text{V}) \cong 0^\circ$. The *o*-methylated molecules one can call "pre-twisted" as "prepared" for the TICT state formation.

It should be pointed out that the excited-state charge separation in 4-DAAP is thermodynamically possible: the exothermicity of the reaction in acetonitrile, ΔG_0 (being very similar to that of V), was evaluated from Weller's equation (Weller 1982) (see (1) in Herbich *et al* 1989):

$$\Delta G_0(\text{I}) \cong \Delta G_0(\text{V}) \cong -0.6 \text{ eV}; \quad \Delta G_0(\text{II}) \cong -0.5 \text{ eV}$$

Thus, the thermodynamics of the excited-state intramolecular electron transfer is very similar in I–IV and in V and its ortho-methylated derivatives VI and VII (usually the methyl substitution at the ring shifts the $E_{1/2}^{\text{red}}(A)$ value by not more than -0.1 eV).

2. Experimental

4-(Dimethylamino)pyrimidine (I), 4-(diethylamino)pyrimidine (II), 4-(dimethylamino)-5-methylpyrimidine (III) and 5-methyl-4-(diethylamino)pyrimidine (IV) were synthesized and purified as described previously (Herbich *et al* 1989).

Spectroscopic grade alcohols were used. Nitriles were carefully dried and purified as in Herbich *et al* (1989). Content of the protic impurities in nitriles has been checked by means of spectrophotometric measurements of the amount of cation after dissolving the lactone of rhodamine B in the respective solvent (J Karpiuk and Z R Grabowski, to be published). All solvents do not show any traces of luminescence. The solutions were deaerated by freeze-pump-thaw cycles or by a nitrogen or argon gas stream.

Absorption, fluorescence and excitation spectra were recorded as in Herbich *et al* (1989). Quinine sulphate in $0.1 \text{ N H}_2\text{SO}_4$ ($\eta_f = 0.51$) served as the quantum yield standard. Fluorescence decays were measured by the sampling technique, as in Karpiuk and Grabowski (1989). Second harmonic of a rhodamine 6G dye laser pumped by the IGT 50 nitrogen laser has been used as an excitation source with pulse duration of 0.6 ns (FWHM).

The supersonic jet apparatus has been described elsewhere (Herbich *et al* 1991).

3. Results and discussion

3.1 Study in solution

The room temperature absorption and fluorescence spectra of I, II and III in acetonitrile (CH_3CN) are compared with those in methanol (CH_3OH) in figure 3.

I exhibits in aprotic polar solvents the short-wave fluorescence band, its long tail hiding a weak second band. Distinct dual fluorescence of I appears in alcohols. Contrary to I, the diethyl derivative II reveals both emission bands already in sufficiently polar (aprotic) solvents. In alcoholic solutions the relative intensity of the short-wave fluorescence is drastically reduced. Nonplanar *o*-methylated compounds III and IV show only low energy luminescence in polar environments, the spectral position of its maximum ($\tilde{\nu}_{\text{max}}$) in alcohols being red-shifted to about 2000 cm^{-1} with respect to that in aprotic solvents of similar polarity. The protonated and N-methylated cations do not show any traces of luminescence between $13,000 \text{ cm}^{-1}$ and $30,000 \text{ cm}^{-1}$ at room temperature.

The comparison of the luminescence behaviour of planar molecule I with that of its pretwisted derivative III in polar (aprotic) solvents allowed us (Herbich *et al* 1989) to attribute: (i) the dominant emission band **b** to the primary excited state B^* , and (ii) the luminescence of III (and IV) as well as the red-shifted band **a** of II to the TICT state. The large Stokes shift (about $15,000 \text{ cm}^{-1}$ in CH_3CN) and the polar character of the fluorescence **a** (the dipole moment value $\mu_e \cong 11 \text{ D}$ of A^* state of III in polar

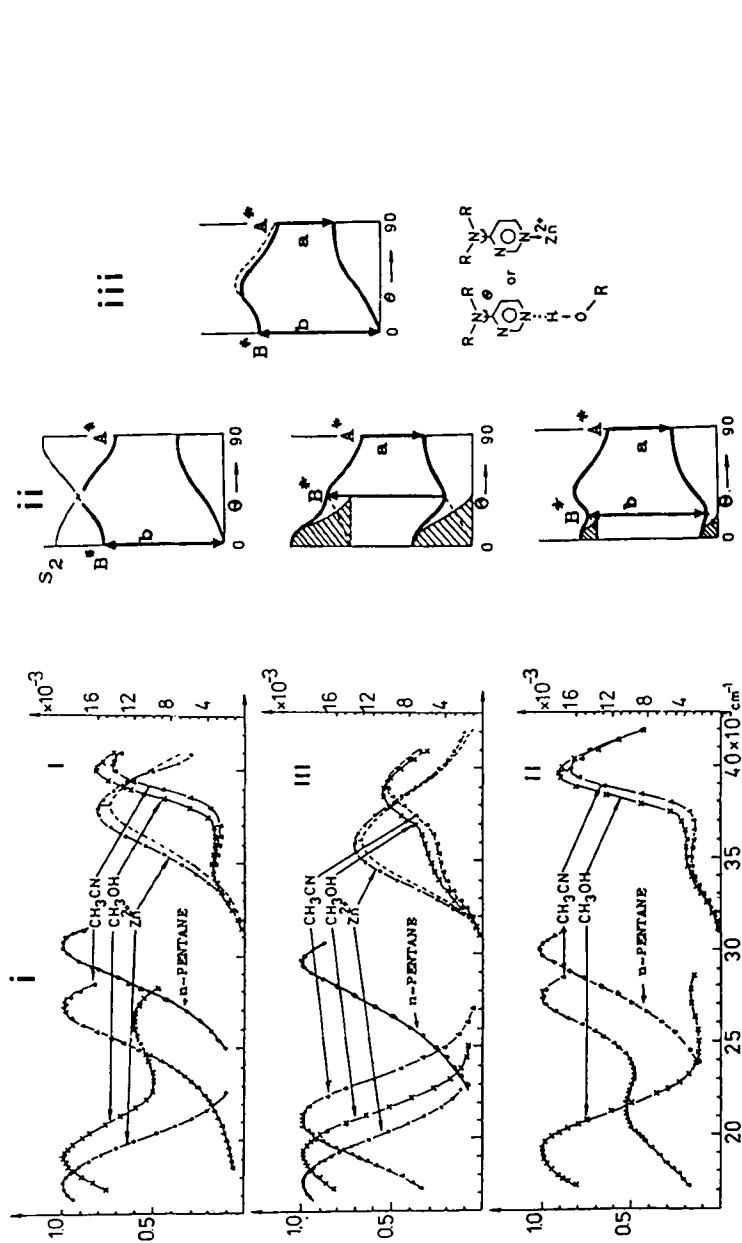


Figure 3. (i) Room temperature absorption and (corrected and normalized) fluorescence spectra of I, III and II in selected solvents (acetonitrile —▲—▲—, methanol —x—x—x— and n-pentane —●—●—●—) and of the corresponding protonated cations (---) and 1:1 complexes with Zn^{2+} ions in acetonitrile (—○—○—). The spectra of IV in polar solvents are very similar to those of III, in n-pentane, however, the spectral position of the fluorescence maximum of IV is centred at about $27,400 \text{ cm}^{-1}$. The varying of the concentration of I–IV in polar solvents from $5 \times 10^{-5} \text{ M}$ to $5 \times 10^{-3} \text{ M}$ does not change the spectra; in nonpolar solvents, however, the formation of aggregates is observed.

The right part of the figure shows a schematic potential energy profile along the reaction coordinate of the internal rotation (torsion): (ii) polar aprotic solvents: high barrier E_a in I prevents the efficient TICT state formation within the lifetime; the barrier is lowered in III or probably disappears in III and IV due to the steric interaction energy (shaded); (iii) complexing increases the electron affinity of the ring and the barrier is lowered.

(aprotic) solvents by fluorescence solvatochromic shift method, Bilot and Kowski 1962, was determined), contrary to **b**, confirm this interpretation.

I and **II** in nonpolar solvents emit short-wave fluorescence **b**: the spectral position of the maxima, $\tilde{\nu}_{\max}^b$, in *n*-pentane being: 30,500 cm⁻¹ (**I**) and 30,200 cm⁻¹ (**II**). The assignment of the luminescence of **III** and **IV**, however, is ambiguous: $\tilde{\nu}_{\max}(\text{III})$ is 29,400 cm⁻¹ and $\tilde{\nu}_{\max}(\text{IV})$ is 27,400 cm⁻¹ in *n*-pentane. The origin of this red shift in the case of **IV** (and **III**) is probably analogous to that in **VI** and **VII** (Grabowski *et al* 1979; Rotkiewicz and Rubaszewska 1982; Rotkiewicz 1986), being related to the deviations from coplanarity and to the topology of the ground and excited state potential hypersurfaces.

What is the mechanism of such large structural and environmental effects on the luminescence properties of 4-DAAP? The lowest absorption band of **I** in *n*-pentane is centred at $\tilde{\nu}_a \cong 35,250$ cm⁻¹; the maximum of this band in pretwisted molecules **III** and **IV** being probably shifted to the higher $\tilde{\nu}_a$ values (figure 3). On the other hand the second absorption maximum of **III** (39,700 cm⁻¹) and **IV** (39,500 cm⁻¹) is markedly red-shifted with respect to that of **I**, being about 41,100 cm⁻¹. From these findings and from INDO/S calculated energies of electronic transitions of **I** as a function of the angle of "twist" Θ , it was concluded (Herbich *et al* 1989) that the second excited ¹(π, π^*) state in planar conformation is a precursor of the TICT state. The correlation of states, similarly to **V** (Grabowski *et al* 1979; Lipiński *et al* 1980), leads to an energy barrier E_a to the excited-state reaction (figure 3ii). The peculiarity of the pyrimidine derivatives is that the torsional barrier E_a in **I**, even in highly polar (but aprotic) solvents, seems to be high enough to prevent any efficient formation of the TICT state within the lifetime of the primary excited state. Thus, the dominant band of fluorescence **b** is observed. Contrary to that, the steric interactions in **III** and **IV**, similarly to **VI** and **VII** (Grabowski *et al* 1979; Rotkiewicz and Rubaszewska 1982; Rotkiewicz 1986), lead to a reduction, or even suppression, of E_a in a polar surrounding: only the TICT emission is observed. In **II**, probably the small steric interactions lower E_a and cause the fluorescence **a** to appear distinctly in a polar environment. The absence of the electrostatic stabilization energy of the highly polar TICT state in nonpolar solvents leads to an increase of the barrier height E_a : both thermodynamic (the driving force of the intramolecular electron transfer, ΔG_0 , is less negative or even close to zero) and kinetic factors do not favour the excited-state reaction.

Undoubtedly, the important result is provided by the different photophysics of 4-DAAP in nitriles and in alcohols (figure 3). This points to a specific solute-solvent interaction and suggests that **I-IV** form the emitting hydrogen-bonded complexes with alcohols. This was confirmed by fluorescence quenching experiments (Herbich *et al* 1989). The primary excited fluorescence **b** of **I** in CH₃CN is very efficiently quenched by proton donating solvents (as water or CH₃OH) as well as by Zn²⁺ ions, with a simultaneous appearance of the long-wave emission **a**. The spectral positions of the maximum of the fluorescence of the 1:1 complexes between **I** and **III** and Zn²⁺ ions are nearly identical ($\tilde{\nu}_{\max}^a \cong 17,600$ cm⁻¹) and both fluorescences lie about 1500 cm⁻¹ lower than $\tilde{\nu}_{\max}^a$ observed in CH₃OH (being about 19,000 cm⁻¹ and 19,100 cm⁻¹, respectively). The energies and huge Stokes shift of the transitions agree well with the TICT state model. The hydrogen bonding (and coordination of the Zn²⁺ ions) seems to occur at the pyrimidine nitrogen atom (or atoms). In the protonated form of 4-aminopyrimidines (4-AP), the proton is bonded to the N1 nitrogen atom (see figure 1), which is also the centre of basicity in 4-DAAP (Brown

et al 1955; Proba and Wierzchowski 1975). The absorption spectra of **I** and **II** in mixed *n*-pentane-butanol solutions also confirm this supposition. The maximum of the second absorption band ($\tilde{\nu}_a \cong 41100 \text{ cm}^{-1}$ and $40,600 \text{ cm}^{-1}$ of **I** and **II** in *n*-pentane, respectively) shifts to the red by about 400 cm^{-1} upon gradual addition of *n*-butanol up to $2 \times 10^{-1} \text{ M}$ (this amount of alcohol was enough to bind nearly all solute molecules. This was seen in emission: the long-wave fluorescence band **a** of the intensity higher than fluorescence **b** observed in *n*-pentane was recorded). No isobestic point, however, was found in absorption and moreover, no significant change of the first absorption band was observed. With regard to the fact that the excitation spectra of both fluorescence, **a** and **b**, of **I** and **II** in *n*-propanol are not distinguishable, one can conclude that the hydrogen bonding mostly occurs at the N1 and N3 atoms. The hydrogen bond at the amino nitrogen should result in a blue shift of the lowest absorption bands due to the pyramidalisation of the amino group, its relatively weak coupling to the π -electronic system of the ring, and thus an increasing similarity to the spectrum of pyrimidine.

The simple explanation of the luminescence behaviour of the complexes, proposed in Herbich *et al* (1989), is shown in figure 3iii. The hydrogen bonding (or coordination of Zn^{2+}) at the pyrimidine ring nitrogen atom enhances its electron affinity. This corresponds to the lowering in energy of the TICT state [see (4) in Grabowski and Dobkowski 1983] and to a probable reduction of the potential barrier E_a . Thus, the TICT emission appears, being strongly red-shifted.

In order to check the validity of the TICT state model, the measurements of the luminescence quantum yield and excited-state depopulation kinetics of 4-DAAP in nitriles and alcohols were recently performed. The values of quantum yields, η_a and η_b , of fluorescences **a** and **b** of **II** in nitriles and in protic solvents as well as the nanosecond kinetic data at room temperature are collected in table 1. Short wave fluorescence **b** is very efficiently quenched by protic solvents: in alcoholic solutions,

Table 1. Quantum yields (η) and lifetimes (τ) of the short-wave (**b**) and TICT (**a**) fluorescences of **II** in nitriles and protic solvents at room temperature. α - index of solvent hydrogen bond donor ability (Kamlet *et al* 1981).

Solvent	α	Quantum yields*		Lifetime [ns]**	
		η_a	η_b	τ_a	τ_b
Acetonitrile	—	0.01	0.022	3.0 (± 0.2)	3.1 (± 0.2)
Butyronitrile	—	0.011	0.046	3.2 (± 0.2)	3.2 (± 0.2)
Methanol	0.98	0.0013	0.00025	0.5	
Ethanol	0.86	0.0025	0.0005	0.9 (± 0.2)	
<i>n</i> -Propanol	0.80	0.0047	0.001	1.2 (± 0.2)	***
<i>n</i> -Butanol	0.79	0.0044	0.0013	1.2 (± 0.2)	
Formamide	0.77	~0.0050	—	—	

*The error being about 10–20%, $\tilde{\nu}_{exc} \cong 33,000 \text{ cm}^{-1}$;

** τ_b was determined at $\tilde{\nu}_{obs} \cong 28,000 \text{ cm}^{-1}$ and τ_a at $\tilde{\nu}_{obs} \cong 19,000 \text{ cm}^{-1}$;

***the decay of **b** of **II** in alcohols is not monoexponential. Two exponential analysis improves the fit, but with the lifetimes quite different from that of the decay of the TICT emission. The long-lived components of **b** are: $\tau(\text{ethanol}) = 2.4 (\pm .3) \text{ ns}$, $\tau(\text{propanol}) = 2.3 (\pm .3) \text{ ns}$, $\tau(\text{butanol}) = 3.2 (\pm .3) \text{ ns}$.

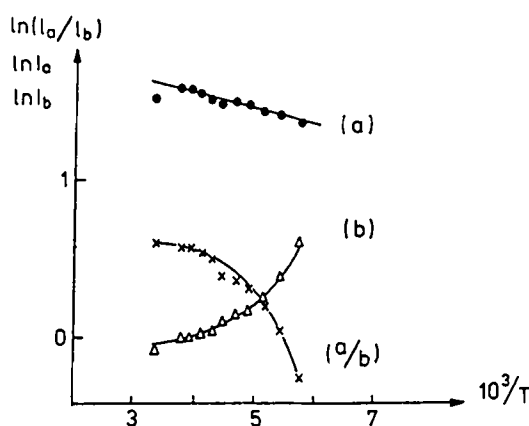


Figure 4. Temperature dependence of the intensity of the long-wave (a), the short-wave (b) fluorescences and their ratio (a/b) of II in butyronitrile. The curves are shifted arbitrarily along the ($\ln I$) scale.

η_b values decrease about two orders of magnitude with respect to those in aprotic solvents of similar polarity. The η_a values in CH_3CN or butyronitrile are also larger than those in CH_3OH or *n*-propanol, respectively. In protic solvents the quantum yields markedly decrease with increasing parameter α , describing the acidity of hydrogen bonding solvents (Kamlet *et al* 1981). The results indicate the existence of a nonradiative channel of increasing importance with growing proton-donating ability, ultimately resulting in the lack of the fluorescence in water ($\alpha = 1.1$) and of the N1-protonated or N1-methylated cations.

The nanosecond kinetic data for II in nitriles at room temperature unambiguously show the common decay of both fluorescences a and b. Temperature effects on the intensities of a and b of II in butyronitrile and on their ratio (a/b) (figure 4) are consistent with a two state kinetic model including three thermally activated elementary processes $\bar{k}(T)$, $\bar{k}(T)$ and $k_{af}(T)$ (figure 1, see figure 4 in Grabowski *et al* 1978), and suggest that at room temperature the equilibrium $B^* \rightleftharpoons A^*$ is attained during the lifetime. In order to check the anticipated bimodal kinetics of the reversible excited-state reaction (Birks 1977), the picosecond experiments are in progress (Herbich *et al*, to be published).

Contrary to that, the dual luminescence of II in alcohols could not be explained in terms of the excited-state reaction starting upon the excitation of a single ground-state species. Both fluorescences, a and b, are not kinetically coupled: the multiexponential decay of the short-wave band b of II is observed, whereas the monoexponential decay time of the long-wave emission a does not correspond to any of the components recovered for b. These facts lead us to suspect the different ground state complexes may be responsible for two emission bands, only one of them undergoing the excited-state process of transformation into the fluorescent TICT state.

3.2 Study in a supersonic jet

The structural and microsolvation effects on the intramolecular electron transfer (IET) in I–VII under supersonic beam conditions are discussed in Herbich *et al* (1991). Thus, in this paper we present additional evidence on the spectroscopic properties

Table 2. Presence (+) or absence (–) of the distinct long-wave (TICT) luminescence in jet-cooled molecules or complexes with methanol.

Compound		Bare		Remarks
		molecule	Complexes	
Planar:	I	–	–	a
	II	–	–	a, b
	V	–	–	c
"Pretwisted"	III	–	+	a
	IV	–	+	a, b
	VI	–	+	a
Highly "pretwisted"	VII	+		d

(a) Present work and Herbich (1991);

(b) also complexes with water and acetonitrile;

(c) References: Kobayashi *et al* (1986), Gibson *et al* (1987, 1988) Peng *et al* (1987);

(d) Reference: Kobayashi *et al* (1987).

of supercooled complexes of **II** and **IV** with water, and we concentrate on the qualitative summary of the results (table 2) providing insight into the following problems concerning the TICT state formation:

(1) what are the conditions that enable the occurrence of the IET in the excited states of isolated monomeric forms of molecules?

Laser induced fluorescence excitation (LIF-excitation) and dispersed fluorescence spectra of jet-cooled planar molecules (i.e. **I**, **II**, **V**) as well as their "pretwisted" derivatives (**III–IV** and **VI–VII**) can provide the information on the influence of the steric hindrance on IET.

(2) what is the relation between the "solute"–"solvent" interactions and the TICT process?

4-DAAP (**I–IV**), which form ground-state hydrogen-bonded complexes with protic solvents, seem to be an attractive family of compounds to study this relation. The idea of the beam work is to generate 1:*n* "solute" to "solvent" complexes, and to investigate the various issues of the excited state reaction, for example: the critical number of "solvent" molecules and the type of interactions (hydrogen bonding, dipolar etc.).

3.2a Bare molecules: LIF-excitation spectra of **I–IV** were recorded in the wavelength range 270–325 nm; typical spectra of monomers, recorded for each molecule except **III**, are shown in figure 5. In the O_0^0 -region many vibronic transitions can be observed, which most probably are associated with inversion and torsion of the dialkylamino group.

The rotational contours of several vibronic bands in the first 200 cm^{-1} were measured and analysed by means of a homewritten program (Kunst 1991). For **I**, the O_0^0 transition exhibits a rotational contour characteristic of a *c*-type transition (perpendicular to the molecular plane), whereas for **II** and **IV** the O_0^0 transition is *a*-type (in-plane, long axis polarized).

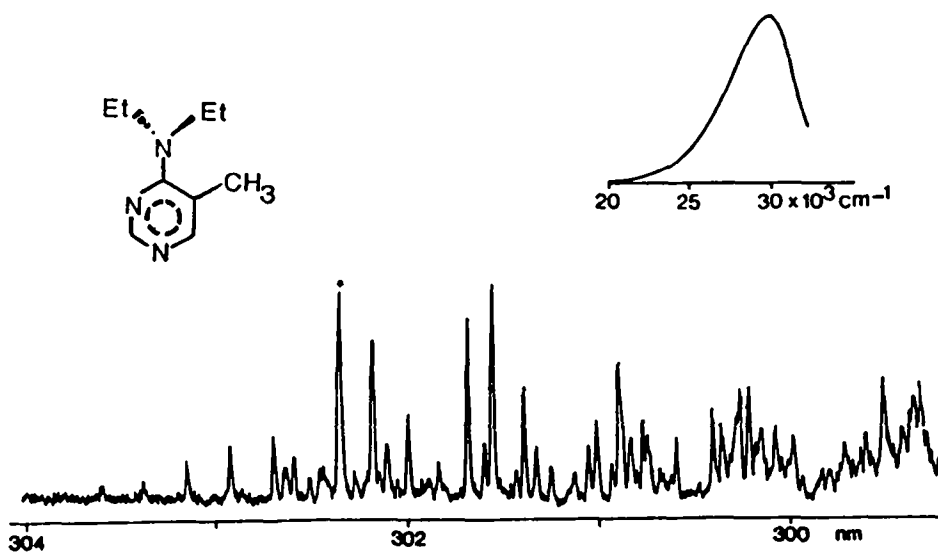


Figure 5. LIF-excitation (left side) and dispersed fluorescence spectra of the monomer of IV. The excitation position is indicated by an asterisk; the detection wavelength for the excitation spectrum was 340 nm. The spectral resolution of the detection monochromator (Zeiss M20) was about 10 nm.

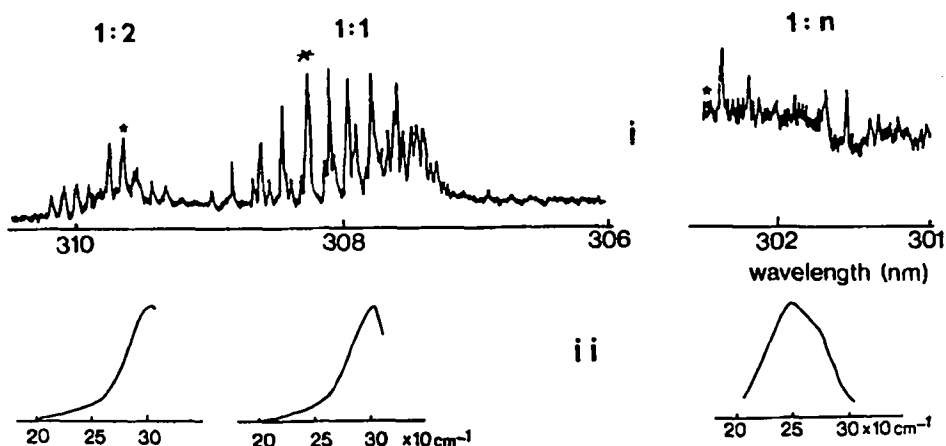


Figure 6. LIF-excitation spectra (i) and dispersed fluorescence spectra (ii) of IV-(CH₃CN)_n complexes. The excitation position is indicated by an asterisk. Partial pressure of acetonitrile is 0.5% of the stagnation pressure. 1:1, 1:2 and 1:n ($n > 2$) indicates various parts of the spectrum corresponding to complexes of different stoichiometry.

The maximum of the dispersed fluorescence spectra of monomeric forms of I, II and IV is centred at 340–345 nm. Thus, the LIF-excitation was attributed to the primary excited B^* state.

3.2b *Microsolvation by polar molecules:* The complexation of 4-DAAP with water, CH₃OH and CH₃CN has been examined. An interesting result is provided by the LIF-spectroscopy of the complexes between IV and CH₃CN (figure 6). The excitation spectra of the 1:1 and 1:2 complexes reveal a vibronic structure shifted to the red

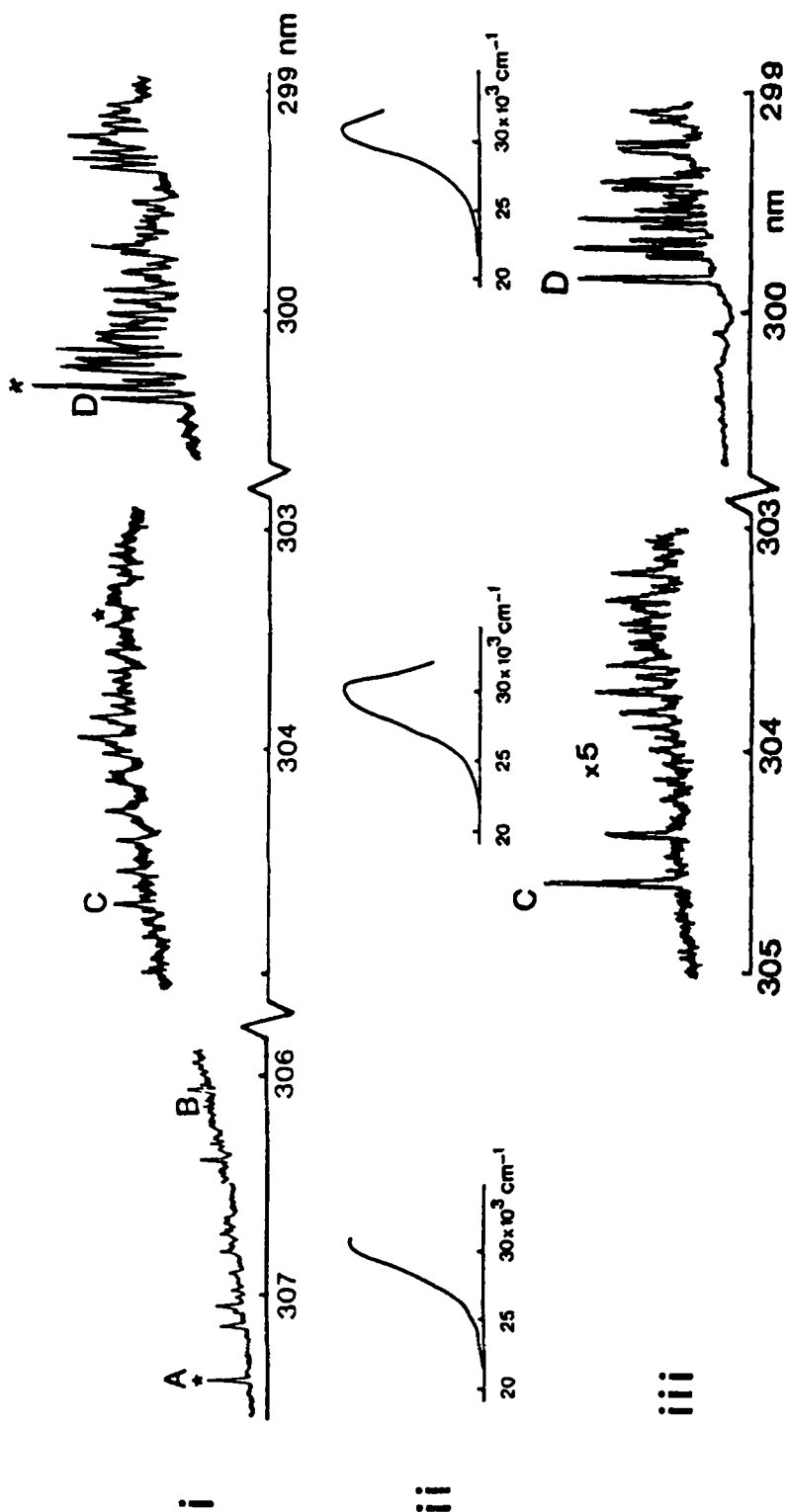


Figure 7. LIF-excitation spectra of various complexes of II with methanol (i) and water (iii). The partial pressure of CH_3OH is 1%, and that of water 0.3% of the stagnation pressure. The spectra are not corrected for the dye laser intensity. Intensity scales are identical for the displayed regions, unless indicated otherwise. The electronic origins of the various complexes are labelled A-D (the spectra of the complexes with water do not reveal the low energy part (A, B) corresponding to $\text{II}-(\text{CH}_3\text{OH})_n$, ($n \geq 2$) complexes (Herbich *et al.* 1991). In the wavelength range of 303–305 nm the underlying continuum is observed, which is assigned to higher complexes. In (ii), the dispersed fluorescence spectra of the complexes of II with CH_3OH , following excitation in the bands indicated by an asterisk, are shown. The emission spectra of the complexes of II with water are very similar to these presented here.

with respect to the monomer by 595 and 720 cm^{-1} , respectively. These complexes emit short-wave fluorescence **b**. If the background underlying the LIF-excitation spectra (being assigned to the complexes of higher stoichiometry) is excited, a broad and strongly red-shifted emission band is observed, with its maximum at about $25,000\text{ cm}^{-1}$.

The next important result is provided by the different photophysics of the complexes of the planar (**I**, **II**) and nonplanar (**III**, **IV**) molecules with protic solvents. Microsolvation of **I** and **II** by water or CH_3OH results in the formation of several complexes showing nicely structured excitation spectra; the origins being either blue- or red-shifted with respect to that of the bare molecule. All complexes emit primary fluorescence **b** (figure 7).

On the other hand, complexes of *o*-methylated molecules **III** and **IV** with protic solvents show a structureless excitation spectra between 298 nm and 315 nm . Excitation of these complexes gives rise to a red-shifted emission attributed to a stabilized charge transfer state. As an example, figure 8 displays the dispersed fluorescence spectra of **IV**, seeded in helium containing various amounts of CH_3OH .

The lack of any vibrational structure in the excitation spectra of the complexes

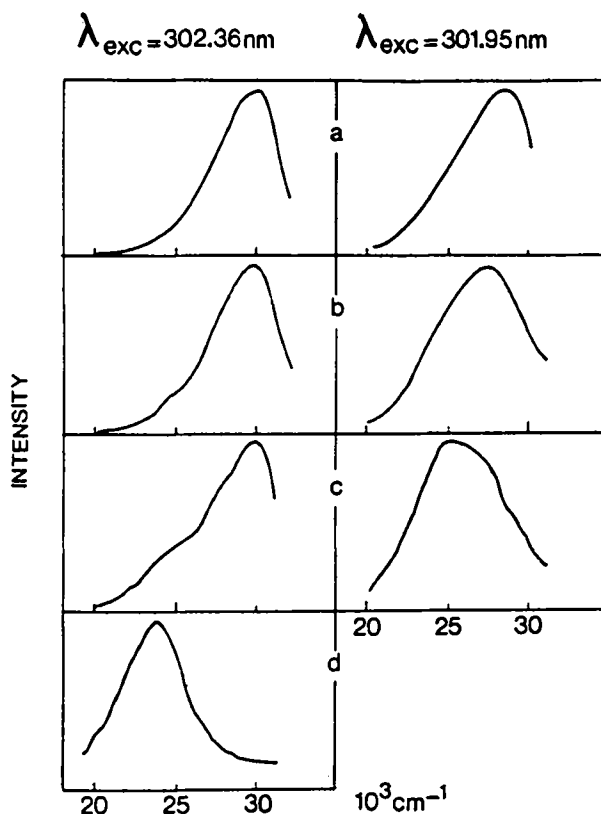


Figure 8. Dispersed fluorescence spectra of **IV** and complexes between **IV** and methanol upon excitation in both; a vibrational band of the bare molecule ($\lambda_{\text{exc}} = 302.36\text{ nm}$, see figure 5) and a position in the underlying continuum ($\lambda_{\text{exc}} = 301.95\text{ nm}$). (a) no methanol added to the helium flow, (b) partial pressure of methanol $p(\text{CH}_3\text{OH}) = 0.1\%$ of the stagnation pressure, (c) $p(\text{CH}_3\text{OH}) = 0.6\%$, (d) $p(\text{CH}_3\text{OH}) = 3\%$.

emitting the long-wave fluorescence indicates the absence of a Franck–Condon minimum at the hypersurface of the excited state or the extremely rapid intramolecular vibrational redistribution (IVR) reducing the lifetime of the optically excited state. It is not probable that this effect could be due to the occurrence of many ground-state complexes with different geometries (the LIF-excitation spectra of the complexes of **I** and **II** with protic solvents as well as **IV**-(CH₃CN)_n (*n* = 1, 2) complexes show a nicely resolved vibrational structure). A disappearance of the barrier or a rapid IVR seems to produce the TICT state. The hydrogen bonding at the pyrimidine ring nitrogen atom is expected to favour the excited-state reaction. We must conclude that the addition of just one water or methanol molecule to a “pretwisted” compound is sufficient to accelerate the TICT state formation. On the contrary, a critical number (*n* > 2?) of acetonitrile molecules seems to be necessary to allow the process to occur within the lifetime of the excited state.

A qualitative summary of the results is given in table 2.

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