

## TICT states in *p*-cyano-*N,N*-dimethylaniline derivatives. The structural and environmental effects

KRYSTYNA ROTKIEWICZ\*<sup>1</sup>, JERZY HERBICH<sup>1</sup>,  
FRANCISCA PÉREZ SALGADO<sup>2</sup> and WOLFGANG RETTIG<sup>3</sup>

<sup>1</sup>Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

<sup>2</sup>Laboratory of Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127, 1018 WS Amsterdam, The Netherlands

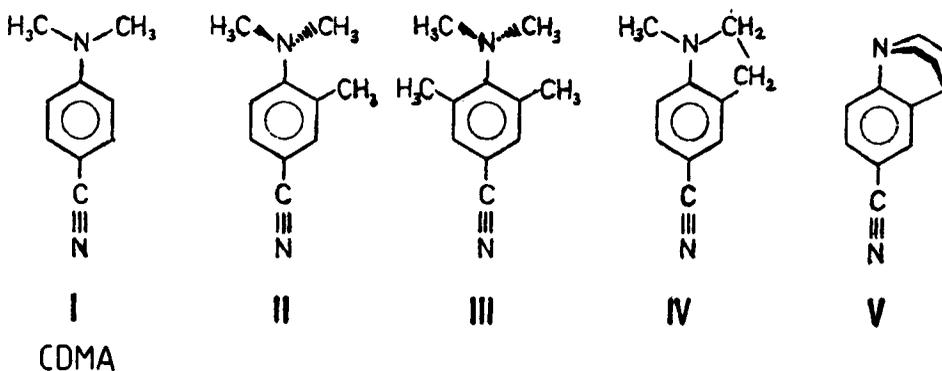
<sup>3</sup>Iwan N. Stranski-Institute of Physical and Theoretical Chemistry, Straße des 17. Juni 112, W-1000 Berlin, Germany

**Abstract.** The photophysical properties of *p*-cyano-*N,N*-dimethylaniline (CDMA) and its derivatives in various surroundings are reviewed. New results on the luminescence in the solid phase near liquid helium temperature and in a supersonic beam are presented.

**Keywords.** TICT states; luminescence; electron transfer; supersonic jet; *p*-cyano-*N,N*-dimethylanilines.

### 1. Introduction

The peculiar phenomenon of the dual fluorescence **a** and **b** of *p*-cyano-*N,N*-dimethylaniline (CDMA **I**), discovered by Lippert *et al* (1962), was initially explained as the emission from two different excited states (<sup>1</sup>*L*<sub>b</sub> and <sup>1</sup>*L*<sub>a</sub> in Platt's notation), one of them being strongly polar (<sup>1</sup>*L*<sub>a</sub>). This mechanism was reinterpreted by Rotkiewicz



Formulae

\* For correspondence



The main experimental confirmations of the TICT state model are the following.

- (1) The convincing evidence of the geometrical structure of the highly polar  $A^*$  state was supplied by the fluorescence of the model compounds with a structurally fixed either planar (IV) or "twisted" (V) ground state conformation (Rotkiewicz *et al* 1973; Grabowski *et al* 1979; Rettig 1986).
- (2) The large value of the dipole moment of the fluorescent TICT state (Grabowski *et al* 1979; Rotkiewicz and Rubaszewska 1980, 1982; Visser *et al* 1984; Bischof *et al* 1985; Rotkiewicz 1986; Weisenborn *et al* 1986) corresponds well to full electron transfer between D and A moieties.
- (3) The spectral position of the maximum of the fluorescence  $\lambda$  in polar solvents agrees with that estimated for a noninteracting (except Coulombic energy) radical ion-pair (Grabowski and Dobkowski 1983).
- (4) The transient absorption spectra  $S_n \leftarrow A^*$  of CDMA and some of its pretwisted derivatives (Okada *et al* 1987) as well as of some carbonyl compounds (Rullière *et al* 1987) are very similar to those of the corresponding radical anions  $A^-$ .

The TICT-state model is also supported by quantum chemical calculations (Rettig and Bonačić-Koutecký 1979; Lipiński *et al* 1980; Bonačić-Koutecký and Michl 1985).

The following alternative models have also been proposed in the last few years:

- (1) Varma and coworkers (Visser and Varma 1980; Visser *et al* 1983, 1984, 1985, 1986; Weisenborn *et al* 1986) explained the dual fluorescence of CDMA in terms of exciplex formation. This model involves transformation of the  $B^*$  state into a 1:1 planar or "twisted" solute-polar solvent exciplex. Arguments favouring this proposition might be found in the stoichiometry of the fluorescence quenching (Visser and Varma 1980) and in the results of the excited state dipole moment measurements (Visser *et al* 1984; Weisenborn *et al* 1986). The evidence contradicting such an interpretation was provided: (i) by the finding of a long wave fluorescence  $\lambda$  for III in a thermalized vapour (Rotkiewicz and Rubaszewska 1982) and (ii) by Suppan (1986), who suggested, as a rule, the solvation of CDMA to be due to nonspecific interactions as definitely shown in the case of fluorinated solvents.
- (2) Cazeau-Dubroca *et al* (1986, 1989) attributed the fluorescence  $\lambda$  of CDMA to hydrogen-bonded complexes of CDMA with ubiquitous traces of water. Evidence against this assignment was presented in Pilloud *et al* (1987).
- (3) Very recently, Zachariasse and coworkers (Leinhos *et al* 1991) found that the dual fluorescence of CDMA can also be observed (well-separated bands at low temperature) in the nonpolar solvents benzene and toluene. They proved the parent-daughter relationship between both emitting species and the reversible kinetics between them on the basis of picosecond studies. Although the planar model compound IV did not exhibit a long wavelength fluorescence band, as expected from the TICT model, it showed rise and decay behaviour within the short wavelength band. This may indicate an additional process independent of TICT formation, the nature of which is still unclear.

The kinetics of the excited state process  $B^* \rightarrow A^*$  is very fast at room temperature (Rotkiewicz *et al* 1975; Kirkor-Kamińska *et al* 1978). The first picosecond spectroscopic investigations of CDMA in polar solvents have confirmed that: (i) the  $B^*$  state is the precursor of the  $A^*$  state and (ii) the equilibrium between these two states is

established during their lifetime (Huppert *et al* 1981; Wang *et al* 1981; Wang and Eisenthal 1982; Hicks *et al* 1985, 1987).

Because of the highly polar character of the  $A^*$  state, the stabilisation of this state, the pathway of the relaxation process and the resulting kinetics should be dramatically affected by the environment.

Most investigations of the relaxation process to the TICT state have been carried out in liquid solutions. In recent years the formation of the TICT state in CDMA, **II** and **III** has also been investigated in a thermalized vapour (Rotkiewicz and Rubaszewska 1982; Peng *et al* 1987) or in a supersonic beam (Peng *et al* 1987; Kobayashi *et al* 1986, 1987; Gibson *et al* 1987, 1988; Warren *et al* 1988; Grassian *et al* 1989, 1990; Gordon 1990; Herbich *et al* 1991; R Rexwinkel and R P H Rettschnick, unpublished results).

In this paper we compare the results of spectroscopic investigations of CDMA and its pretwisted derivatives **II** and **III** in various surroundings: in the condensed phase (polar and nonpolar, fluid and frozen solvents), as well as in supercooled isolated molecules and their complexes with small polar molecules in a supersonic jet. The studies were partially described in previous papers. Additional evidence is presented here on the luminescence of **II** and **III** in the solid phase near helium temperature and on the spectroscopic properties of supercooled **II**.

## 2. Experimental details

CDMA (Aldrich, 98%) was purified by crystallization from ethanol and sublimation. Its ortho-methylated derivatives **II** and **III** were synthesized and purified as described previously (Rotkiewicz *et al* 1976). Solvents used were of spectroscopic grade.

Fluorescence spectra at room temperature were recorded with the fluorescence unit, as described previously (Köhler *et al* 1982); and the luminescence spectra at temperatures down to 77 K by means of a Jasny spectrofluorimeter (Jasny 1978). Another series of the low temperature experiments (down to 3.5 K) was performed at the Freie Universität Berlin with a helium cryostat (Oxford Instruments) and recorded with a Spectrofluorimeter Shimadzu RF-540.

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

The fluorescence decay time measurements were carried out using an Edinburgh Instruments single photon counting apparatus at the Technische Universität Berlin filled with the cryostat from the Freie Universität Berlin.

The molecular mechanics calculations were carried out using program MMX Force-Field, Serena Software, Bloomington, Indiana.

## 3. Results and discussion

### 3.1 Condensed phase

Typical room temperature fluorescence spectra of CDMA, **II** and **III** in *n*-hexane and ethanol (in the case of CDMA in *n*-butyl chloride also) are shown in figure 2.

CDMA in nonpolar solvents reveals only the short wavelength fluorescence band **b**, whereas in polar solvents the dual fluorescence is observed.

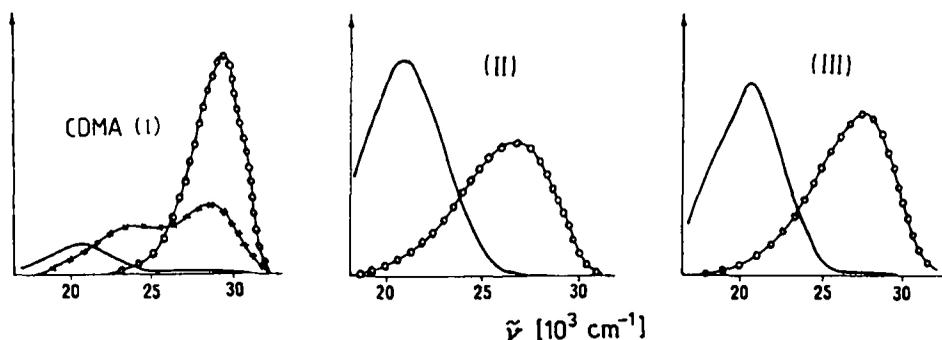


Figure 2. Corrected room temperature fluorescence spectra of CDMA(I), II and III in *n*-hexane (○-○-○-○-), *n*-butyl chloride (-×-×-×-×-) and ethanol (—),  $c = 10^{-5}$  M.

The correlation of states (figure 1) leads to an intrinsic energy barrier  $E_a$  for the TICT state formation in CDMA (Rettig and Bonačić-Koutecký 1979; Lipiński *et al* 1980). This energy barrier  $E_a$  has been correlated with the activation energy of viscous flow of the solvent (Rettig 1980; Lippert *et al* 1987) and/or with solvent polarity (Hicks *et al* 1985, 1987). The latter hypothesis gives a simple explanation for the appearance of fluorescence of CDMA in polar solvents and its lack in alkanes: a certain polarity is required before the barrier  $E_a$  is low enough to allow the efficient TICT population within the lifetime of the initially excited  $B^*$  state.

According to Hicks *et al* (1985, 1987)  $E_a$  depends linearly on the polarity described by an empirical parameter  $E_T$ :

$$E_a = E_a^0 - \text{const} \times E_T. \quad (1)$$

On the basis of simple considerations on the relation between the energies of CDMA states, either bare or solvated, in the planar or twisted conformation, it can be shown that the term  $\text{const.} \times E_T$  in (1) reflects the stabilisation energy of the strongly polar  ${}^1L_a$  state, because of: (i) similar polarity of  ${}^1L_a$  and TICT states, and (ii) practically much smaller dipolar character of the  ${}^1L_b$  state.

Thus, the dominant solvent effects on the dynamics of electron transfer in this case can be attributed to static polarity effects (Rettig 1980; Wang and Eisenthal 1982; Hicks *et al* 1985, 1987; Lippert *et al* 1987). The proposal seems to be in agreement with recent femto/picosecond investigations of the excited state depopulation kinetics of CDMA: a lack of correlation between the time of the forward reaction ( $\tau = 1/\bar{k}$ ) (figure 1) and the longitudinal dielectric relaxation time ( $\tau_L$ ) was determined (Simon and Su 1990; Leinhos *et al* 1991).

The *o*-methylated molecules II and III, with a steric hindrance to coplanarity between the D and A entities, show only a single fluorescence band characterized by a large Stokes shift present already in nonpolar solvents (figure 2).

This emission was assigned to the TICT state because of: (i) the high polarity of the emitting state (the dipole moment value being 12–15 D) (Bischof *et al* 1985; Rotkiewicz 1986) and (ii) a low probability of the radiative depopulation ( $k_{ar} < 10^7 \text{ s}^{-1}$ ) (van der Auweraer *et al* 1991). The TICT emission is expected to be strongly forbidden because of a minimum overlap of the orbitals involved in the transition, and often by the symmetry selection rules (e.g.  $A_2 \rightarrow A_1$  in the  $C_{2v}$  point group, Grabowski *et al* 1979; Lipiński *et al* 1980).

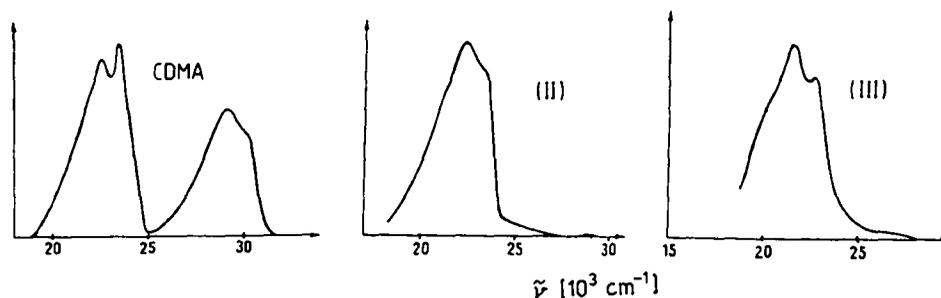
The relative increase of the TICT state formation rate in **II** and **III**, with respect to **I**, is linked to a decrease of the energy barrier  $E_a$  due to the steric repulsion (figures 1b, c). The ground state minimum of **II** and **III** corresponds to the following values of a twist angle  $\Theta$ : (i)  $40^\circ$  and  $60^\circ$ , respectively, from the absorption data (Rotkiewicz and Rubaszewska 1982; Rotkiewicz 1986), (ii)  $25 \pm 3^\circ$  and  $55 \pm 5^\circ$ , correspondingly, from the calculation by the molecular mechanics method (Allinger 1976) ( $\Theta$  for CDMA being  $0 \pm 3^\circ$ ). According to X-ray analysis  $\Theta$  for **III** is  $58^\circ$  (R Luboradzki, unpublished results).

Therefore, the potential barrier  $E_a$  should be the highest in CDMA and lowest, if present at all, in **III**. It should be pointed out, however, that **III** in cooled solvents also shows short-wavelength fluorescence but only upon high energy excitation (Rotkiewicz and Rubaszewska 1982) (a similar effect was observed in a supersonic jet (Kobayashi *et al* 1987)). This fluorescence was identified with the emission from the higher excited state  $S_2$ . No such effect has been found for **II**.

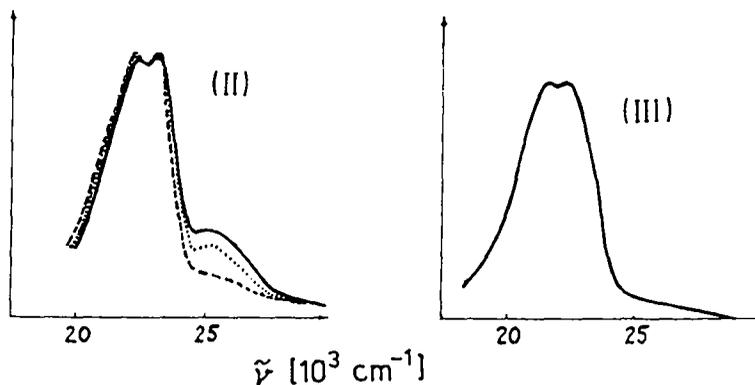
All three compounds, CDMA, **II** and **III**, show relatively intense phosphorescence in glassy polar solvents (figure 3) – the lowest triplet state being the locally excited  $^3L_a$  state (Grabner *et al* 1989).

The unexpected results were obtained for **II** and **III** in alcoholic solvent (97% ethanol + 3% methanol, v/v) below 60 K (figure 4).

Both compounds show phosphorescence and fluorescence bands. The shape of the luminescence of **III** and the ratio of the phosphorescence to fluorescence intensities



**Figure 3.** Corrected luminescence spectra of CDMA, **II** and **III** in ethanolic glass at 77 K. Low energy band – phosphorescence (long lifetime, can be measured with chopper), and high energy one – fluorescence.



**Figure 4.** Corrected luminescence spectra of **II** in alcoholic glass: at 60 (---), 30 (.....) and 3.5 K (—). The spectrum for **III** was recorded at 15 K.

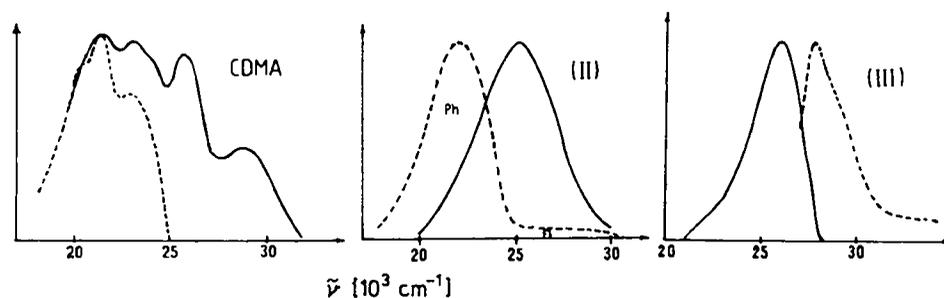
remain practically unchanged between 15 and 77 K. Contrary to that, the fluorescence intensity of **II** markedly increases upon cooling, whereas the phosphorescence does not vary. The enhancement of the fluorescence for **II** is followed by an increase of its decay time from 3 ns at room temperature to 11 ns at 15 K. The fluorescence is assigned to the TICT state because of its large Stokes shift (figure 4). Probably, this temperature effect is connected with the retardation of an internal conversion process (quenching) from the TICT state. This agrees with the finding that the fluorescence **a** of CDMA and **II** is quenched by protic solvents; its intensity increases in deuterated alcohols (Grellmann and Rotkiewicz 1972). A solvent isotope effect does not appear in the case of the fluorescence from **III**.

Interesting results are provided by the formation of selfcomplexes of CDMA and **II** in cooled nonpolar solvents. This was deduced from the temperature and concentration dependence of the absorption and fluorescence spectra (Rotkiewicz and Rubaszewska 1984), as well as from the fluorescence decay time analysis (Rotkiewicz *et al* 1989). The formation of dimers of **III** and larger clusters of CDMA has been postulated. Fluorescence of microcrystallites of **II** has also been observed for sufficiently concentrated solutions.

The luminescence spectra of CDMA, **II** and **III** in supercooled alkanes are presented in figure 5. The low energy bands are assigned to dimers or higher clusters on the basis of concentration effects. The large Stokes shift and the long radiative lifetime of the fluorescence of the dimeric species suggest the CT character of the emitting state. Theoretical calculations performed on CDMA as a model compound predict that the first excited singlet state of the dimer could be the charge separated  $\pi\sigma^*$  state of a planar molecule complexed by a second one with a "twisted" dialkylamino group (Rotkiewicz *et al* 1989).  $\sigma^*$  orbital is the in-plane orbital of the  $-C \equiv N$  group.

### 3.2 Supercooled molecules

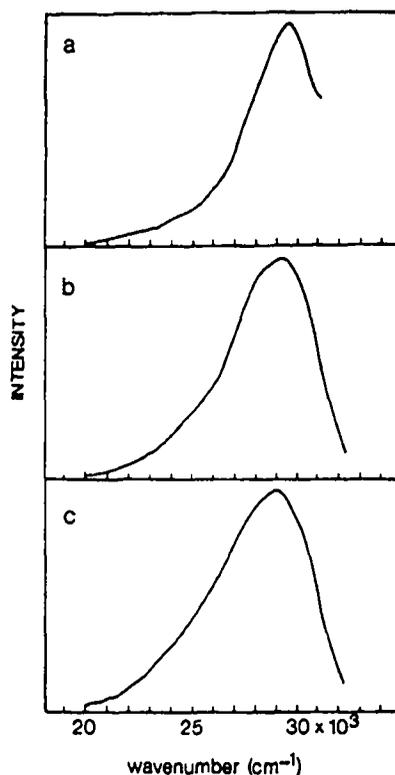
CDMA (Kobayashi *et al* 1986; Gibson *et al* 1987, 1988; Peng *et al* 1987; Warren *et al* 1988; Grassian *et al* 1989, 1990; Gordon 1990) and its *o,o'*-dimethyl derivative (**III**) (Kobayashi *et al* 1987) were used for studying structural and microsolvation effects on the TICT state formation under supersonic jet conditions. Jet-cooled CDMA



**Figure 5.** The corrected total luminescence spectra (—) of CDMA in 2,2-dimethylbutane + *n*-pentane (3:8 v/v) at 77 K (---- phosphorescence, recorded with chopper),  $c \cong 2 \times 10^{-4}$  M; **II**,  $c \cong 10^{-4}$  M in isopentane (— in supercooled glass, ---- in crystalline matrix, after cracking of the glass, Ph - phosphorescence); **III** — in methylcyclohexane + isopentane (1:4 v/v) at 77 K,  $c \cong 10^{-3}$  M, fluorescence, ---- excitation spectrum.

exhibits only primary excited fluorescence. The complexation with various small molecules (e.g. water, methanol, acetonitrile, acetone, dichloro- and trifluoromethane) does not yield any evidence of TICT emission. On the contrary, **III** shows a red-shifted emission. This fluorescence was previously observed in a thermalized vapour – the Stokes shift being about  $8000\text{ cm}^{-1}$  (Rotkiewicz and Rubaszewska 1982). The large dipole moment of the fluorescent state in the gas phase indicates its charge transfer character (Bischof *et al* 1985). Therefore, the luminescence from **III** was assigned as TICT emission.

Recently, the laser induced fluorescence excitation (LIF excitation) and dispersed fluorescence (LIF emission) spectra of jet-cooled **II** were also examined (Herbich *et al* 1991). The LIF emission spectrum, recorded upon excitation in the  $O_0^0$ -region was attributed to the primary excited state. We have examined the shape and position of the fluorescence spectrum of **II** as a function of the excitation energy. With increasing energy (up to  $4500\text{ cm}^{-1}$ ) the maximum shifts to the red and the halfwidth of the spectrum markedly increases, but no distinct shoulder to the red is found (figure 6). For **I** similar results were observed: Peng *et al* (1987) did not observe any TICT emission upon excitation up to  $3400\text{ cm}^{-1}$  above the  $O_0^0$  transition. Comparison of **II** with **III** leads us to the conclusion that the TICT emission is not markedly populated in **II**. The excess energy might be insufficient, or the IVR processes are too slow with



**Figure 6.** Effect of increasing the excess excitation energy on the emission bands of compound **II**. (a)  $\lambda_{exc} = 301.35\text{ nm}$ ; (b)  $\lambda_{exc} = 290\text{ nm}$ ; (c)  $\lambda_{exc} = 270\text{ nm}$ . A broadening of the band and a slight red shift in the position of the maximum is observed when the excitation is at higher energies.

respect to the lifetime of the excited state to cross to the TICT state. An explanation for the relatively strong red shift and broadening of the emission from **II** upon increasing excess energy could be the existence of vibrational modes with strongly reduced frequencies in the excited state in comparison with the frequencies in the ground state. The torsional mode of the dimethylamino group could be such a mode.

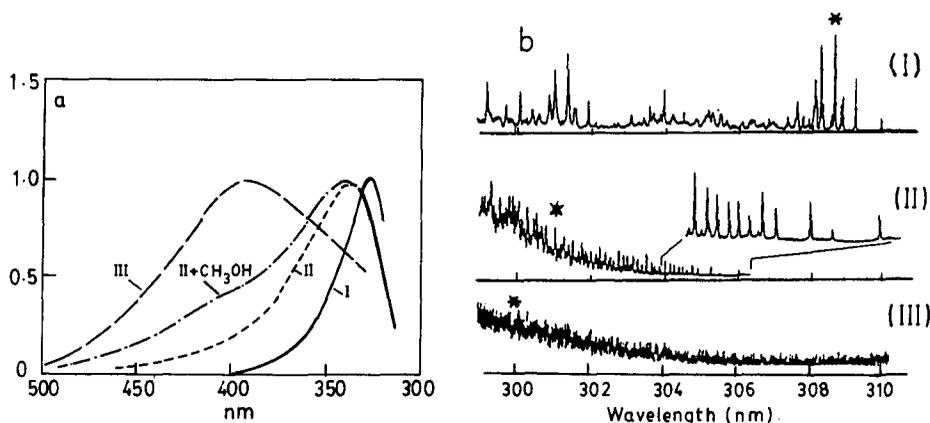
Figure 7 displays the emission and excitation spectra of investigated compounds.

The results presented provide insight in the TICT state model. The lack of any TICT emission in CDMA, and the absence of a distinct CT band in **II**, contrary to **III**, could be linked (similarly as in solutions) to the different ground state geometries of the molecules (figure 1b, c). In the model proposed by Rotkiewicz and Rubaszewska (1982), the TICT emission in **III** results from direct population of the CT state. A reduced value of the equilibrium twist angle  $\Theta$  in **II** prevents the latter process and a primary excited emission  $S_1 \rightarrow S_0$  appears upon excitation.

The barrier height to internal rotation in the excited state seems to be one of the essential criteria for the formation of the TICT state. However, a suitable coupling of the optically active modes with the vibrations along the reaction path to the TICT state seems also important. The reaction in **II**, when excited high above the origin and most probably above the barrier, seems to be prevented by the intramolecular vibrational redistribution (IVR) dynamics.

The LIF excitation spectra of CDMA (Kobayashi *et al* 1986; Gibson *et al* 1987, 1988; Warren *et al* 1988; Grassian *et al* 1989, 1990; Gordon 1990; R Rexwinkel and R P H Rettschnick, unpublished results), and especially **II** (figure 7) are very rich and show a pattern of low-frequency vibrations. On the contrary, the excitation spectrum of the CT emission in jet-cooled **III** (Kobayashi *et al* 1987) is structureless. A possible explanation for the diffuseness is the broadening of the individual lines as a result of a short lifetime of the optically excited state caused by rapid intramolecular vibrational redistribution (IVR) preceding the TICT state formation.

The vibrational structure of the fluorescence and excitation spectra offers a unique chance to study the change of the potential energy profiles for individual intramolecular motions and structural changes of the molecules. The low frequency



**Figure 7.** LIF emission (a) and LIF excitation (b) spectra of jet-cooled **I**, **II** and **III**. The excitation position is indicated by an asterisk. The detection wavelength for the excitation spectra was 340 nm (**I** and **II**) or 400 nm (**III**). Dispersed fluorescence spectrum of the complexes of **II** with methanol is also presented.

structure of the LIF excitation spectra of CDMA has been analysed (Grassian *et al* 1989, 1990; Gordon 1990) in terms of the internal rotation (torsion) and inversion of the dimethylamino group. The ring methyl group in **II** causes extra vibrational motions; in addition, the barrier to torsion in the excited state is lowered. The resulting reduction of the frequency of the torsional mode is expected to contribute to the more complex vibrational structure of **II**.

From rotational contour analysis of the  $O_0^0$ -transitions of **I** and **II** we have found the contour to be of the *b*-type (in-plane, short axis polarized). This *b*-type contour indicates that the transitions have  $\pi\pi^*$ -character; it is also found for related molecules as benzonitrile (Brandt *et al* 1966) and aniline (Thakur *et al* 1970). For **I**, contrary to Grassian *et al* (1989, 1990) and Gordon (1990), the small change ( $0$ – $20^\circ$ ) in twist-angle  $\Delta\theta$  upon excitation is determined.

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