DYNAMICS OF THE DUAL FLUORESCENCES OF
p-DIMETHYLAMINOBENZONITRILE[†]

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Summary

The time-resolved dual-fluorescence picosecond kinetics of *p*-dimethyl-aminobenzonitrile in dodecanol, decanol, hexanol and methanol were studied. Pulse-limited rise times were found in the emission of the b* state which feeds directly the rise time of a* state emission. We found that the b* state fluorescence decay times follow the solvent viscosity. The a* state fluorescence kinetics vary with solvent and temperature, which suggests either thermally assisted intersystem crossing to a solvated triplet or thermally activated internal conversion to the ground state.

1. Introduction

The dual fluorescences of *p*-dimethylaminobenzonitrile (DAB) in polar solvents have been attributed by Lippert to separate fluorescence bands originating from the ^1L_a and ^1L_b states of the benzene substrate [1, 2]. The maximum of the b band at approximately 350 nm shows red shifts of 6000 cm^{-1} from the first absorption band at about 295 nm; however, the a band in polar solvents at about 470 nm is assigned to a highly polar excited state.

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Fluorescence [3] and kinetic [4] studies show that the DAB emitting states a* and b* do not correspond to low-lying $^1(\pi,\pi^*)$ states nor to the first absorption band in DAB [4]. Steric evidence [4] now suggests that a* is a strongly dipolar twisted internal charge transfer ^{1}(TICT) state [5] which relaxes to a perpendicular conformation between phenyl and dimethylamino groups. ^{1}(TICT) states should display diluted radiative lifetimes because of the small overlap between the donor and acceptor orbitals [5].

The kinetics of a* formation and b* decay in DAB have been studied by high pressure O_2 fluorescence quenching [6, 7] and picosecond spectroscopy [8]. These results suggest reaction half-times as short as about 2 ps for DAB in methylene chloride and about 1 ps for another TICT-state-forming molecule, p-dimethylaminoacetophenone, in acetonitrile.

These rate constants derived from the quenching kinetics data are indirect, and for better reliability they should be compared with the direct kinetic measurements. Rise times of about 40 ps have been found for DAB a* fluorescence monitored at approximately 470 nm in methanol, ethanol and n-butanol [9].

In this work we elucidate the formation kinetics of the a* state by monitoring the b* fluorescence decay and the fluorescence rise times of a* in various solvents and at various temperatures.

2. Experimental details

Commercial DAB was purified by recrystallization from methanol. For room temperature studies the samples were placed in 1 mm quartz cells, while low temperature studies were conducted in a 200 μm copper cell with quartz windows in thermal contact with a liquid helium cryostat. Solvents were either spectro quality or reagent grade. Negligible emission intensities were recorded by the solvents above compared with those from samples of about 10^{-4} M DAB. 1-Dodecanol showed a long-lived fluorescing impurity from 310 to 380 nm; however, it did not contribute significantly to the measurement of b* state emission at 350 nm.

Samples were excited with a 266 nm, 20 ps pulse frequency quadrupled from the 1064 nm pulse extracted from the output of a passively mode-locked Nd^{3+}:YAG laser. The fluorescence was observed directly with an Imacon 675 Photochron II streak camera with a resolution of approximately 5 ps. Wavelength selectivity was achieved by combinations of interference and colored glass filters. Streak images were registered and digitized in a PARC 1205A optical multichannel analyzer and were stored for processing by a Nova 1230 minicomputer.

Digital time-resolved emission traces were fitted by computer curves derived by convolution of the experimental 266 nm excitation pulse profile with a calculated fluorescing state population [10]. The fluorescing state population was simulated by first-order formation and decay kinetics with respective inverse rate constants τ_r and τ_f. Rise times as small as 5 ps and fitted fluorescence decay times accurate to ±15% were achieved.

3. Results

The time dependence of the DAB b* state fluorescence, at about 20 °C and 350 ± 15 nm, is shown for a series of alkanols with decreasing viscosity [11] in Fig. 1. The peak intensity varied linearly with excitation pulse
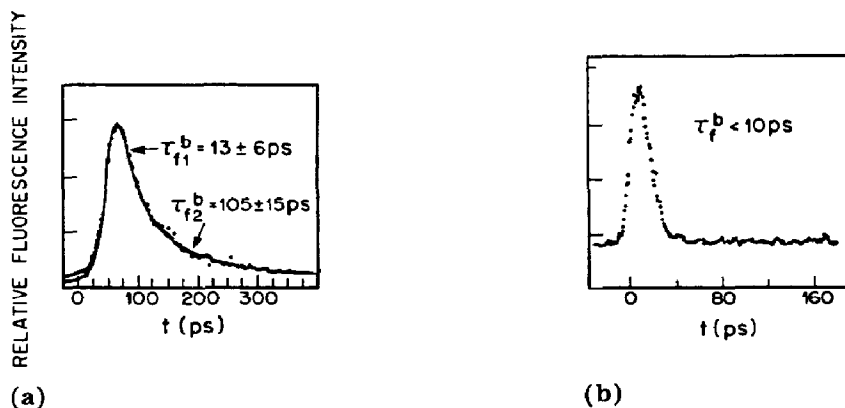

(a)   (b)

Fig. 1. Time-resolved b* fluorescence of about 10^{-4} M solutions of DAB excited by 266 nm excitation pulses in (a) 1-hexanol and (b) methanol at 20 °C. The experimental biexponential decays were calculated by computer simulation using the method of Ware [12]. The errors of the fast and slow decay components $\tau_{f1}{}^b$ and $\tau_{f2}{}^b$ are estimated to be 50% and 15% respectively.

intensity for the pulse energies used. The b* fluorescence rise times were found to be pulse limited in all solvents throughout this work. The b* fluorescence decay times $\tau_f{}^b$ (Fig. 1) were biphasic in all the linear alcohols studied with the possible exception of methanol, where $\tau_f{}^b$ was within the experimental resolution. Within experimental error, the time constants of the long component of the b* biphasic decay observed for 1-hexanol were linearly related to the viscosity.

The time-resolved a* fluorescence was studied at wavelengths of 520 nm or more. We found that the room temperature a* fluorescence rise times $\tau_r{}^a$ were the same as the decay times $\tau_f{}^b$. This was based on the data shown in Fig. 2 for DAB dissolved in 1-dodecanol, 1-decanol and 1-hexanol. Since this relationship between $\tau_r{}^a$ and $\tau_f{}^b$ occurred irrespective of the values of $\tau_r{}^a$ and $\tau_f{}^b$, we propose that in most cases the b* state is the kinetic precursor of the a* state. This supports earlier conclusions based on fluorescence quantum yields [6] that the b* and a* states are formed sequentially.

As in the b* state, the a* state decay times exhibited a substantial solvent dependence (Table 1 and Fig. 3). The effect of temperature on $\tau_f{}^a$ was also apparent: the first-order a* fluorescence decay time increased from 1.4 to 5.8 ns between 20 and −140 °C in methanol. This temperature
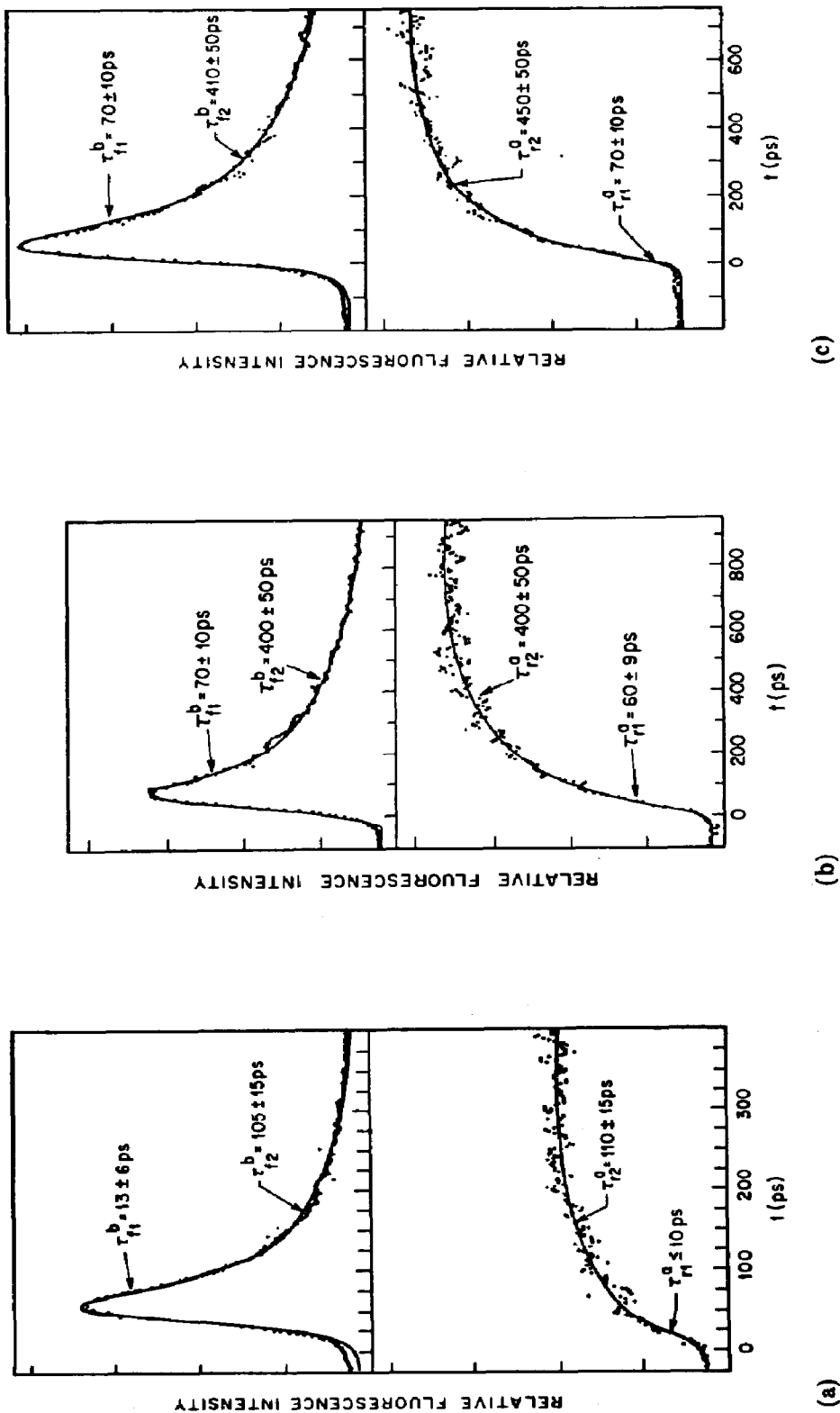
Fig. 2. Complementarity of b* fluorescence decay times τ_f^a for DAB in (a) 1-hexanol, (b) 1-decanol and (c) 1-dodecanol (solid) at 20 °C. Five to eight laser shots are averaged in each trace.

TABLE 1

Room temperature (about 20 °C) kinetic parameters for p-dimethylaminobenzonitrile dual fluorescences

Solvent	η (cP)	τ_1^c (ps)	τ_2^c (ps)	τ_f^b		τ_r^a		τ_f^a (ns)
				τ_{f1}^b (ps)	τ_{f2}^b (ps)	τ_{r1}^a (ps)	τ_{r2}^a (ps)	
Methanol	0.59				< 10		< 10	1.4
1-hexanol	5.3	1210	31	≈ 15[d]	105	≈ 10[d]	110	3.4
1-decanol		2019	48	≈ 70	400	≈ 60[d]	400	3.7
1-dodecanol		2230[e]		≈ 70	410	≈ 60[d]	450	3.6

[c]Dielectric relaxation times [13].
[d]The error is estimated to be 50%.
[e]For 22 °C.

dependence of τ_f^a we attribute to a thermally activated non-radiative process.

4. Discussion

The data presented show that the b* fluorescing state is always formed promptly, within about 5 ps, even in methanol at 4 K. The primary photophysical event after excitation to a singlet is expected to be rapid internal conversion to the b* state. The viscosity-limited conversion of the DAB b* state to the a* state was measured by its emission in the range 520 - 600 nm. The time constant for the b* to a* decay is not directly related to any of the three dielectric relaxation time constants τ_1, τ_2 and τ_3 as defined by Garg and Smyth [13]. τ_1 and τ_2 depend strongly on the temperature and size of the alcohol, while τ_3 is only slightly affected by these parameters. Table 1 shows that the time constants τ_{f1}^b for the short component of the b* state decay have the same trend as τ_2, but the experimental values are not the same. The long components of the b* state decay and a* state rise time are found to be larger than τ_2 but to have a similar dependence to τ_2 on molecular size. τ_1 is found to be smaller by a factor of 5 - 10 than the experimental values of the long component.

We found that the solvent reorientation and the internal rotations in solute molecules are viscosity dependent. Recently, Rettig [14] has found that the activation energies of the b* → a* process vary for several derivatives of DAB with different substituents at the amino group. Our data suggest that the b* state is the kinetic precursor of the a* state under these conditions, as suggested by Rotkiewicz et al. [6].

The a* decay was found to be single exponential and was temperature dependent.
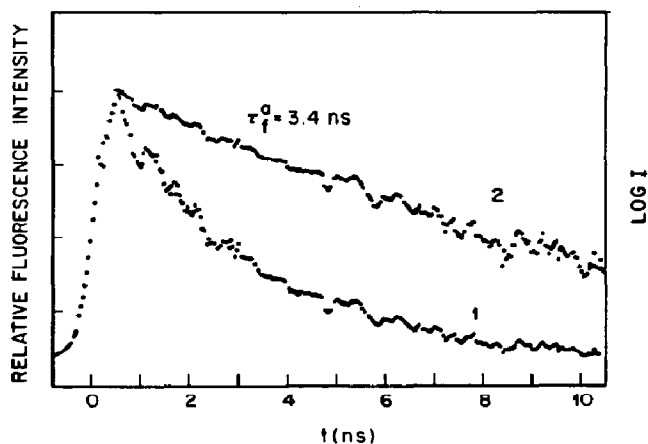
(a)
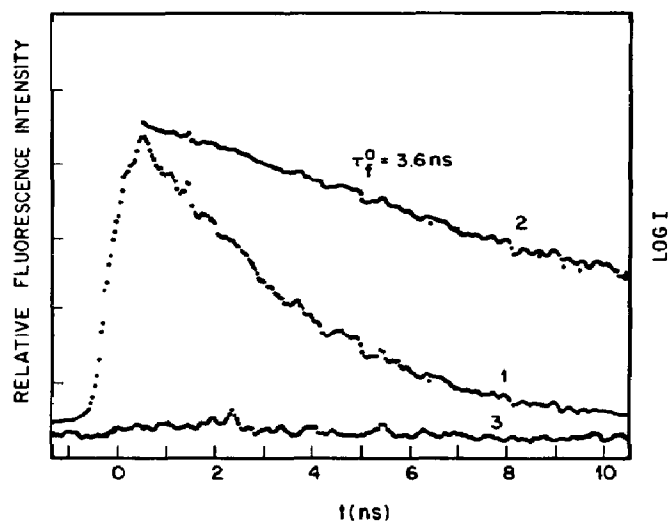
(b)

Fig. 3. Decay kinetics of DAB at 20 °C in (a) hexanol and (b) dodecanol between 520 and 600 nm: curves 1, the decay in the form I vs. t, i.e. linear; curves 2, the decay in the form log I vs. t, i.e. logarithmic; curves 3, the intensity of the dodecanol background fluorescence in the same spectral region, under identical experimental conditions as curves 1 and 2.

Biexponential decay of the b* state and the corresponding time constants for the formation of the a* band were observed in the alcohols shown in Figs. 1 - 3 and Table 1 for 1-hexanol, 1-decanol and 1-dodecanol. The short b* lifetimes of 13 ps and 70 ps for hexanol and dodecanol solutions, and the corresponding short rise times of the a* band in these long-chain alcohols, probably reflect the reorganization of these polar solvents. The nature of the charge transfer process presented here may be quite general in polar media.

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