

Steady-state and Time-resolved Spectroscopic Studies of Benzanilides

Józef Heldt^{a,b}, Janina R. Heldt^b, and Jerzy Kamiński^b

^a Institute of Physics, Pedagogical University at Słupsk, 76-200 Słupsk, Poland

^b Institute of Experimental Physics, University of Gdańsk, 80-952 Gdańsk, Poland

Reprint requests to Dr. J. R. Heldt; Fax: +48-58 341-31-75

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Steady-state and time-resolved spectroscopic studies of benzanilide (I) and *N*-methylbenzanilide (II) were performed at 298 and 77 K in various solvents. The results indicate that benzanilide fluorescence in non-polar solvents at room temperature involves three independent modes of emission: F_1 (LE) normal fluorescence from the initially excited state S_1 (LE) with $\lambda_{\max} = 320$ nm, F_2 (PT) fluorescence from the proton transfer tautomer with $\lambda_{\max} = 468$ nm, F_2' (CT) fluorescence from the species where intramolecular charge transfer appears, with $\lambda_{\max} = 510$ nm. At 77 K in MCH a new fluorescence band, F_{ag} , appears at $\lambda_{\max} = 415$ nm instead of the F_2 (PT) and F_2' (CT) fluorescence. This new emission originates from benzanilide dipolar aggregates or *cis*-imidol dimers. The decay times of these emission modes are different.

N-methylbenzanilide, dissolved in nonpolar and weakly polar solvents at room temperature and at 77 K, shows only two fluorescence modes, i.e., the normal and the charge-transfer emissions at 320 nm and 520 nm, respectively. The fluorescence is deactivated with two decay times, 30 ps and 2.05 ns, in MCH solution.

Key words: Benzanilides; Absorption; Emission and Picosecond Transient Absorption Spectra; Fluorescence Decay Times.

1. Introduction

In [1–3] it has been shown that the fluorescence of benzanilide at room temperature involves three independent electronic bands. These are associated with the transition from the initially excited state S_1 (LE) of the molecular moiety, from the proton-transfer imidol-tautomer excited state S_1' (PT), and from the intramolecular charge-transfer excited state S_1'' (CT) of the molecule.

The fluorescence decay-time measurements, steady-state absorption and emission spectra and picosecond transient absorption spectra of benzanilide (I) and *N*-methylbenzanilide (II) reported here provide additional confirmation that excitation of the benzanilides results in the appearance of three or two co-existing singlet excit-

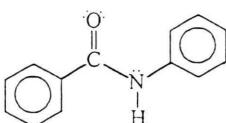
ed of the parent molecule. The chemical structures of the molecules under study are shown in Chart 1. The kind of emission observed depends mainly on the polarity of the solvent molecules and the temperature. Taking advantage of this dependence, the decay times of the different fluorescence modes of benzanilide and *N*-methylbenzanilide have been determined.

2. Experimental

The absorption spectra at room temperature of I and its *N*-methyl derivative II, were obtained using a Cary 15 recording spectrophotometer. The fluorescence (at 298 and 77 K) and phosphorescence spectra (at 77 K) were taken on a Baird-Atomic Model SRF 100 spectrofluorimeter. The spectra presented are corrected for the sensitivity of the photomultiplier used.

Picosecond transient absorption and time-resolved emission experiments were conducted using the system described in [4]. The sample was excited with the fourth harmonic (266 nm) of the Nd:YAG laser operating at 10 Hz. The laser beam which provides the excitation for the fluorescence decay-time measurements was synchronously chopped with a shutter, yield-

I - Benzanilide



II - *N*-methylbenzanilide

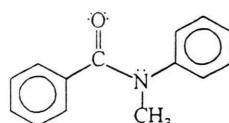


Chart 1. Molecular structure of benzanilide and *N*-methylbenzanilide.



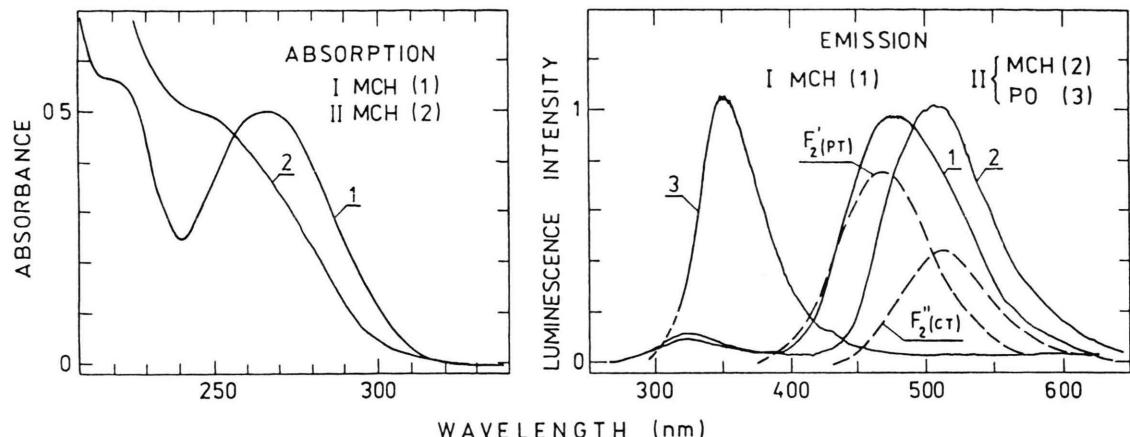


Fig. 1. Absorption and emission spectra of benzanilide 1 and *N*-methylbenzanilide 2 and 3. The weak band at about 320 nm belongs to the normal fluorescence F_1 (LE). The dashed lines show the decomposition of the F_2 band of benzanilide into the F_2' (PT) ($\lambda_{\max} = 468$ nm) and F_2'' (CT) ($\lambda_{\max} = 510$ nm) bands with participation factors of 64 and 36 percent.

ing a 2 Hz laser beam, to prevent a non-linear response of the Silicon Intensified Target (SIT) tube. The temporal width of a typical UV pulse is 30 ps with energies of 1–2 μ J. The experimental decay curves obtained were fitted by a convolution integral of the form

$$I_E(t) = \int_0^t F(\tau') \cdot I_F(t - \tau') d\tau', \quad (1)$$

where $F(\tau')$ is a gaussian function approximating the shape of the excitation pulse and $I_F(t - \tau')$ is the fluorescence response function measured in the experiment.

The picosecond transient absorption measurements were performed using the setup described in [4]. This includes the same Nd:YAG laser, with a pulse-width of ca. 30 ps, operating at 10 Hz and delivering the fourth-harmonic as a pump pulse ($\lambda = 266$ nm) and a broadband continuum probe pulse, both focused into the sample cell. Only the continuum is passed through the reference cell. The probe pulse, which was generated by 1064 nm irradiation of the H_2O/D_2O mixture, was delayed in time from 0 to 18 ns with respect to the pump pulse. The absorbance change in the sample was obtained using the relation:

$$A = -\log \frac{I_s - I'_s}{I_{os}} - \log \frac{I_r}{I_{or}}, \quad (2)$$

where I_s is the intensity of the probe continuum with excitation at the delay time t transmitted by the sample, I'_s is the intensity of the excitation without the continuum, I_{os} is the intensity of the continuum without excitation, measured 100 ms after the time t , and I_r , I_{or} are the inten-

sities of the continuum at delay time t and 100 ms after t , respectively, for the reference cell. The data collection and the evaluation procedure was accomplished using an IBM-PC software package written by Schmidt and Hilinski [4]. The average energy per laser pulse was ca. 0.2 mJ. The solution concentrations were about $5 \cdot 10^{-4}$ M, so that the optical density at the excitation wavelength 266 nm was about 1–1.5 in the cell with 0.5 cm path-length. The solution in the cell circulated in an atmosphere of N_2 .

Benzanilide (purchased from Aldrich Chemical Co.) was twice recrystallized from methanol before use. *N*-methylbenzanilide was synthesized using benzanilide according to a standard methylation procedure and after recrystallized twice from cyclohexane. The solvents propylene oxide (OP), isopentane (IP) and ethyl ether (EE) were of spectroscopic quality and were used without further purification. Cyclohexane (CH) and methylcyclohexane (MCH) of spectroscopic grade treated with a sodium-potassium alloy were distilled before used. Samples (in 2 mm diameter quartz tube) at 77 K were immersed in liquid nitrogen.

3. Results and Discussion

a. Steady-State Spectra

Figure 1 shows the absorption and fluorescence spectra of I and II in MCH and OP. The absorption spectrum for both compounds has an onset at c. 320 nm. The spectrum of I shows a broad band with λ_{\max} at 265 nm and

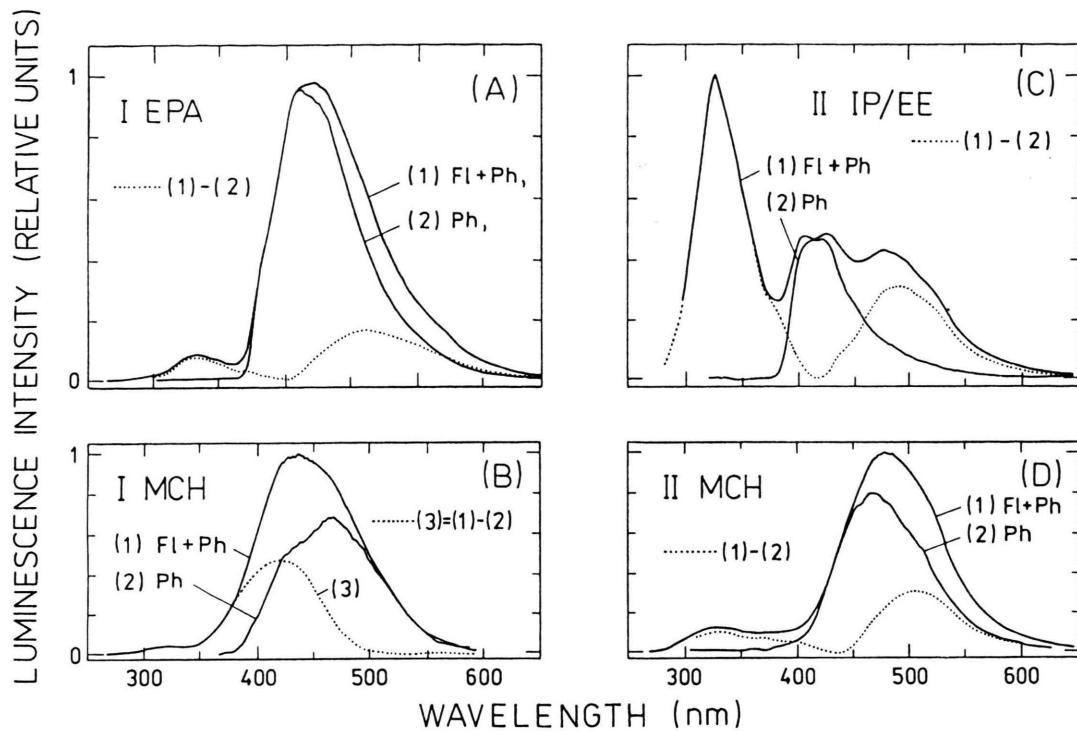


Fig. 2. The emission spectra, total luminescence 1 and phosphorescence 2 of benzanilide in EPA mixture (panel A) and MCH solution (panel B) and *N*-methylbenzanilide in IP/EE mixture (C) and MCH solution (D) at 77 K. The dotted curves represent the F_1 (LE) band. The solid lines represent the charge transfer fluorescence spectrum F_2' (CT) (panels A, C, D) of compounds I and II and the dipolar aggregate fluorescence spectrum (panel B) of benzanilide in MCH solutions.

220 nm. The position of these maxima do not differ significantly when changing the solvent from a hydrocarbon to a polar protic or non-protic type.

The absorption spectrum of II does not show resolved bands. Nevertheless, on the basis of the second derivative of the absorbance, two transitions, at λ 255 and 275 nm, can be indicated (see Figure 1).

The fluorescence spectra of I and II depend strongly on the polarity of the solvent. In hydrocarbon and weakly-polar solvents, the fluorescence spectra contain two bands, a weak normal fluorescence emission at 320 nm (F_1 (LE)) and a stronger band F_2 at λ_{\max} 477 and 510 nm for I and II, respectively. In polar nonprotic solvents ($8 < \epsilon < 12$), only the short-wave length emission appears, although somewhat more strongly. In dipolar solvents, e.g. ethyl and methyl alcohol, EPA and acetonitrile, formed specific dipole-dipole complexes quench the fluorescence completely at room temperature. As was shown in [1-3], the long-wave fluorescence band F_2 of I at $\lambda_{\max} = 477$ nm in CH and MCH solutions has dual nature. It results from emissions of the imidol-tautomer,

S_1' (PT) $\rightarrow S_0'$ (PT) ($\lambda_{\max} \approx 468$ nm), and from an intramolecular charge-transfer isomer, S_1'' (CT) $\rightarrow S_0''$ (CT) ($\lambda_{\max} \approx 510$ nm). These bands can be obtained decomposing the wide F_2 band into two bands possessing equal half-width to that of II in MCH (see Fig. 1 the two dashed bands). Its contributions amount to 64 and 36 percent, respectively. For II, the corresponding emission at 510 nm results only from a twisted intramolecular charge-transfer complex, S_1'' (CT) $\rightarrow S_0''$ (CT), since the tautomerizing proton has been replaced by a methyl group.

In rigid media, (see Fig. 2) both compounds under study show fluorescence and phosphorescence. It must be pointed out that long-wavelength bands in the total emission spectra of both compounds (curve 1) differ from those of pure phosphorescence spectrum (curve 2). Moreover, the F_2 fluorescence bands of these two compounds at 298 K (see Fig. 1 and Fig. 1 in [1]) show a pronounced anomaly, i.e. the fluorescence band has its maximum at a longer wavelength than the phosphorescence band, and for 77 K λ_{\max} (FL + Ph) $> \lambda_{\max}$ (Ph) (see Fig. 2, panel A,

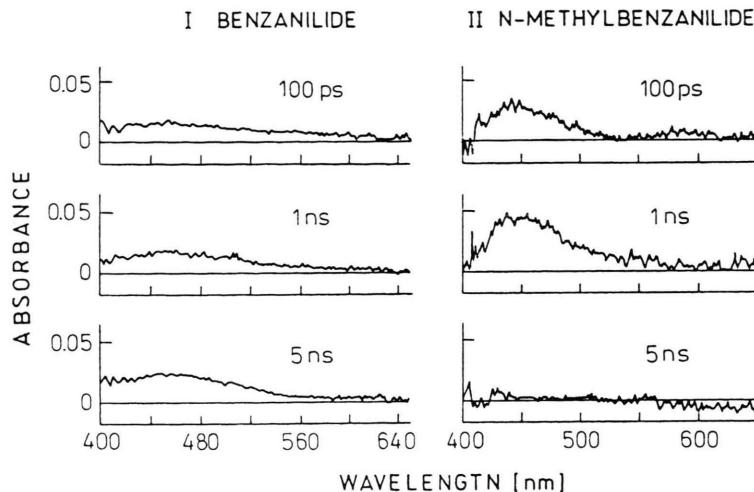


Fig. 3. Room temperature picosecond transient absorption spectra of benzanilide and *N*-methylbenzanilide in cyclohexane solution at 298 K.

C, and D). An opposite inequality is true for I in MCH where λ_{\max} (FL + Ph) > λ_{\max} (Ph) (Fig. 2 panel B). In EPA and isopentane-ethyl ether mixture (IP/EE, 1 : 1 *v/v*), I and II show dual fluorescence attributed to the emission from the S_1 (LE) and S_1'' (CT) states (bands marked by a dotted curve in Fig. 2 panel A and C). The fluorescence bands are obtained by subtracting the normalized intensity of the phosphorescence (Ph) spectrum from the total luminescence (Fl + Ph). The fluorescence spectra of both compounds in MCH, analyzed in the same way, give bands whose maxima are at λ 415 nm and 473 nm, respectively. As it has been shown in [1, 2], the broad maximum at 473 nm (see Fig. 2 panel D) can be attributed to the S_1'' (CT) \rightarrow S_0'' (CT) transition. We suppose that the new band at 415 nm (see Fig. 2 panel B) originates from benzanilide dipolar aggregates or from the *cis*-imidol dimer emission, as has been suggested in [5] and [6]. The maxima of the F_2'' (CT) bands of I and II in MCH at 77 K are shifted to shorter wavelengths by about 4 nm in comparison with their positions at room temperature [1, 5]. Such a temperature shift of the fluorescence spectrum has been observed by many authors [7].

The low temperature spectroscopic studies of both molecules can be summarised as:

1. In non polar solvents (MCH) at 77 K the total luminescence spectrum of I consists of a very weak F_1 (LE) band (onset 290 nm λ_{\max} = 314 nm), a fluorescence band of dipolar aggregates (onset of 350 nm, λ_{\max} \approx 420 nm), and a phosphorescence band at λ_{\max} = 460 nm. The F_2' (PT) and F_2'' (CT) emissions are not observed. The total

luminescence spectrum of II consists of the normal fluorescence band F_1 (LE) (onset 290 nm, λ_{\max} = 326 nm), the charge transfer fluorescence band F_2'' (CT) (onset 440 nm, λ_{\max} = 510 nm) and the phosphorescence band F_{Ph} (onset 400 nm, λ_{\max} = 460 nm).

2. In polar solvents (EPA and IP/EE mixtures) at 77 K the total luminescence spectrum of both molecules consists of the normal fluorescence band F_1 (LE) (onset 300 nm, λ_{\max} = 330 nm), the charge transfer fluorescence band F_2'' (CT) (onset 420 nm, λ_{\max} = 460 nm for I and \sim 500 nm for II) and the phosphorescence band F_{Ph} (onset \sim 370 nm, λ_{\max} = 415 nm for I and II).

The noted blue shift of the phosphorescence spectrum ($\Delta\lambda \approx 45$ nm) by increase of the solvent polarity indicates that the T_1 state of both molecules possesses (*n*, π^*) character [8].

b. Picosecond Transient Absorption Spectroscopy

Figure 3 shows the picosecond transient absorption spectra of I and II in cyclohexane at room temperature for various delay times of the probe beam with respect to the excitation beam. The transient absorption spectra show a very broad absorption band, extending across the visible region from 400 to ca. 560 nm in the case of I and a more pronounced, somewhat narrower band with λ_{\max} at 450 nm for II. For II, the transient absorption band has disappeared almost completely in 5 ns, whereas in the case of I, some absorption still persists even after 18 ns. A plot of the transient absorbance changes monitored at 450 nm for both molecules (shown in Fig. 4) yields a

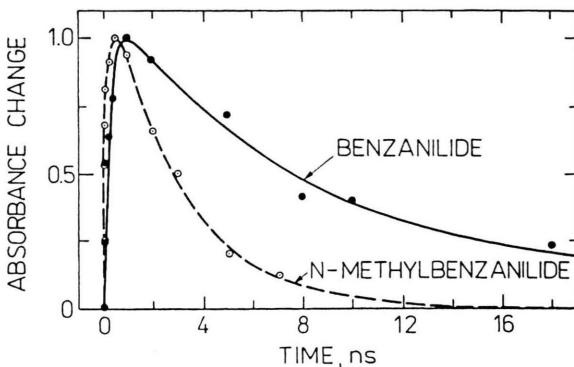


Fig. 4. Room temperature transient absorbance changes monitored at 450 nm of benzanilide and *N*-methylbenzanilide in cyclohexane solution at 298 K.

decay time of (11.2 ± 2) ns and a rise time of (200 ± 20) ps for benzanilide and of (2.90 ± 0.8) ns and (150 ± 20) ps, respectively, for *N*-methylbenzanilide. The different time development of the transient absorbance of the two molecules as well as the different excited state transient absorbance profiles indicate that the transient absorbance spectra have somewhat different origins. The broad absorption band for I is inferred to consist of absorption transitions originating from the S_1' (PT) and S_1' (CT) as well as from the ground-state tautomer of benzanilide, S_0' (PT) (see Figure 6). For that reason, the transient absorption decay time of I, (11.2 ± 2) ns, cannot be identified with the fluorescence decay time as usual. The time evolution of the transient absorption spectrum of II in CH suggests that mainly the S_n'' (CT) \leftarrow S_1' (CT) transition gives rise to the transient absorption ($\lambda_{\max} = 450$ nm). Nevertheless, the transient absorption decay time differs significantly from the F_2'' (CT) fluorescence decay time of II $((2.90 \pm 0.8)$ ns versus (1.76 ± 0.05) ns; see Table 1) which can be caused by a weak absorption from the S_0'' (CT) state.

Fig. 6 shows the energy scheme indicating the origins of the three competitive fluorescence transitions, F_1 (LE), F_2'' (PT) and F_2'' (CT), the supposed transient absorption transitions (dashed arrows) and the observed phosphorescence transition. The dot-dashed levels (S_1'' (CT), S_n'' (CT)) and dashed levels (S_0' (PT), T_1 (PT), S_1' (PT) and S_n'' (PT)) represent energy values of the tautomeric forms of both molecules. It must be noticed that the phosphorescence emission of both compounds originates from the initially excited molecule i.e. from the T_1 (LE) state. This is in agreement with the predictions made by Kasha et al. [9].

The results of the fluorescence decay time measurements at different temperatures and in various solvents will give arguments concerning the correctness of the proposed transition scheme.

c. Fluorescence Decay Measurements

Figure 5 shows the F_1 and F_2 fluorescence curves of benzanilide emission attributed to the S_1 (LE) \rightarrow S_0 (LE) and S_1' (PT) \rightarrow S_0' (PT) and S_1'' (CT) \rightarrow S_0'' (CT) transitions. The observations were performed at room and liquid nitrogen temperatures. The risetime of the F_1 - and F_2 , F_2'' -fluorescences at room temperature and at 77 K are in the limit of the half-width of the exciting pulse. Therefore it can not be determined with the apparatus used, where the half width of the exciting pulse is about 15 ps. The F_1 (LE) fluorescence emission at 320 nm of I and II in MCH and CH at 298 K is very weak (the quantum yield $Q_F \approx 10^{-4}$ [10], which does not allow fluorescence decay measurements. In polar non-protic solvents and at low temperatures the F_1 (LE) intensity is sufficient to perform decay time measurements. Figure 5D shows the F_1 (LE) decay curve of I in PO solution at 298 K obtained using the 500 ps window of the streak camera. The reason for the short decay time of the F_1 (LE) fluorescence, about 20 ps, is the large value of the rate constant of the excited-state proton transfer k_{PT} and twisted intramolecular charge transfer k_{CT} process. They are bigger than the sum of the, k_F , internal conversion, k_{IC} , and intersystem crossing, k_{ISC} , fluorescence rate constants, i.e. $k_{PT}, k_{CT} \gg k_F + k_{IC} + k_{ISC}$. It can be seen from Figs. 5A and B that the fluorescence decay curves of F_2 emission of I at room and liquid nitrogen temperatures fit well to a curve with a single rise time and one exponential decay.

The decay times of the different fluorescence modes of I and II obtained for two temperatures and different solvents are summarized in Table 1. Here the participation factors are given in brackets beside the associated decay time. The τ values connected by a clamp were obtained fitting the experimental points to a two-component decay curve (see Fig. 5 panel B and D). An exception are the τ values of benzanilide in MCH and CH (see Fig. 5 panel A), which satisfy in the same degree a mono- and bi-exponential fit.

Analyzing the decay time data in connection with the results of spectroscopic studies it follows that:

1. The decay time of the initially excited state, S_1 (LE), is very short for both molecules. The reason for it are the large values of the rate constants of excited-state proton transfer k_{PT} and twisted intramolecular charge transfer

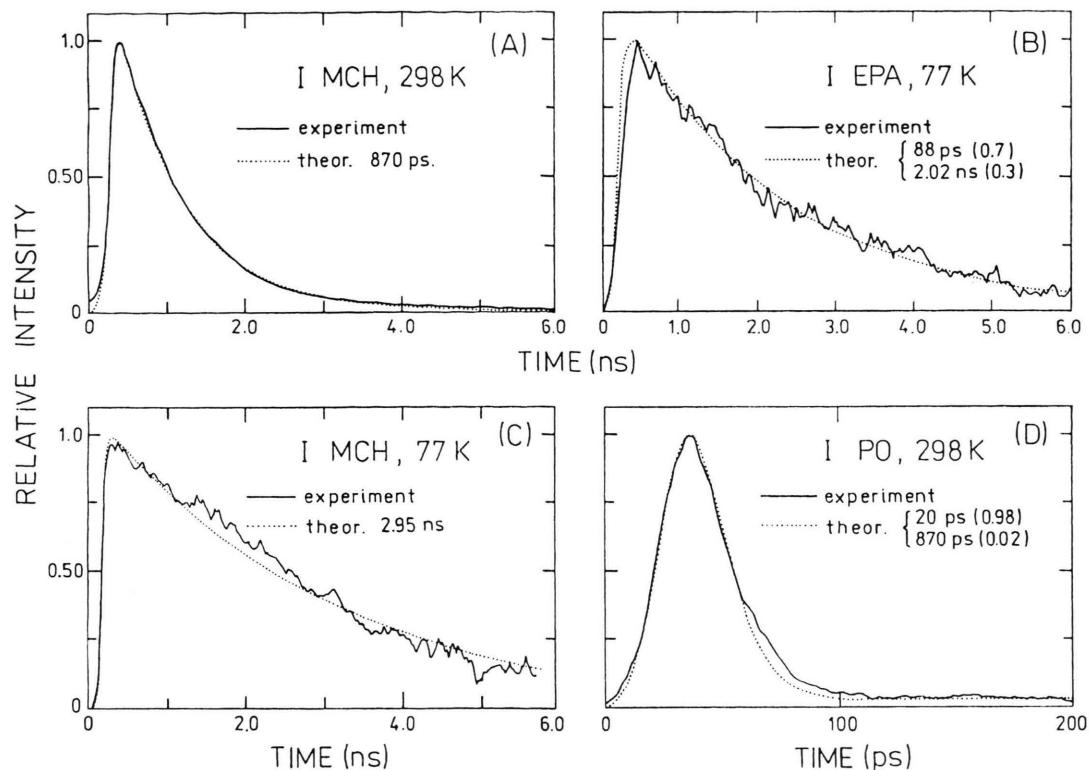


Fig. 5. Decay curves of the F_2 (panels A and B) and F_1 (panel D) fluorescences of benzanilide in EPA mixture and propylene oxide. Panel C shows the fluorescence decay curve of benzanilide in MCH at 77 K.

Table 1. Fluorescence decay time (ns) of benzanilide and *N*-methylbenzanilide for different solvents and temperatures.

Solvent	Benzanilide		<i>N</i> -methylbenzanilide		
	τ_F (298 K)	τ_F (77 K)	τ_F (298 K)	τ_F (77 K)	
MCH	0.880	{ 0.750 (0.80) ^a 1.50 (0.20) ^b	2.95 (1.0)	1.76 (1.0)	{ 0.105 (0.40) ^c 2.05 (0.60) ^b
CH	0.870	{ 0.770 (0.68) ^a 1.45 (0.32) ^b		1.45 (1.0)	
EPA		{ 0.088 (0.7) ^c 2.02 (0.3) ^a		{ 0.120 (0.35) ^c 1.65 (0.65) ^b	
IP/EE	0.830	{ 0.720 (0.85) ^a 1.48 (0.15) ^b	{ 0.042 (0.92) ^c 2.10 (0.08) ^a	1.70 (1.0)	{ 0.135 (0.40) ^c 2.10 (0.60) ^b
PO		{ 0.020 (0.98) ^c 0.870 (0.02) ^a		{ 0.150 (0.97) ^c 1.45 (0.03) ^b	

Note: Decay time of the ^a F'_2 (PT), ^b F''_2 (CT) and ^c F_1 (LE) fluorescence modes are obtained by fitting the experimental points to the bi-exponential function. The other τ values result from a mono-exponential fit (see text).

k_{CT} . A small contribution of a slow component in the F_1 (LE) fluorescence decay, e.g. in PO, is attributed to the proton-transfer emission or the emission of Fries photo-reaction products [11].

2. The F_2 fluorescence decay curve of I in MCH, CH and IP/EE solutions at 298 K are well described by a mono-exponential fit (see Fig. 4A) with the decay times of 0.88, 0.87 and 0.83 ns, respectively. An equal rank result can be obtained using a biexponential fit. In this case, the fluorescence decay profiles consist of a short-time component with $\tau \approx 0.70$ ns and a long-time component with $\tau = 1.45$ ns. The participation factors of the two components are: 0.75 and 0.25; 0.78 and 0.28, and 0.85 and 0.15, respectively, for MCH, CH, and IP/EE benzanilide solutions. In accordance with our earlier work [12] and these studies, the above two components identify the S'_1 (PT) \rightarrow S'_0 (PT) and S''_1 (CT) \rightarrow S''_0 (CT) fluorescence decay modes. The above participation factors show a good coincidence with the ratio of the F'_2 (PT) to F''_2 (CT) band intensities.

3. The F_2 fluorescence decay curve of I in rigid (77 K) MCH solutions is well described by a monoexponential

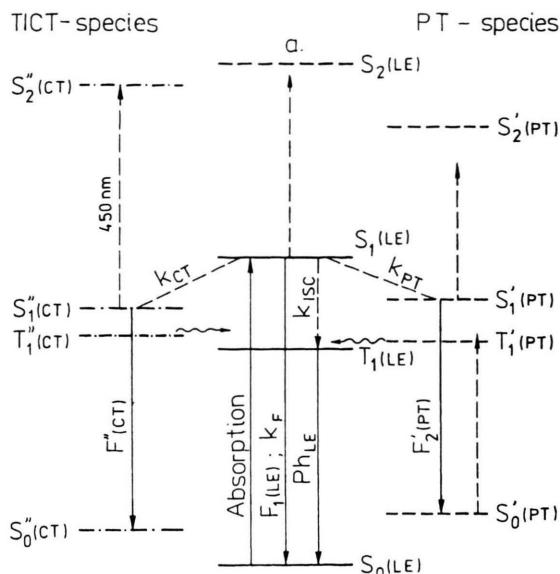


Fig. 6. Energy level diagram indicating the origins of the three competitive fluorescence transitions and supposed transient absorption transitions noted for benzanilide and *N*-methylbenzanilide. The electronic states of the proton-transfer and TICT species are given by dashed and dot-dashed lines.

fit with a lifetime of 2.95 ns. For the EPA and IP/EE matrix, only a bi-exponential fit gives satisfactory results. The decay times of the two fluorescence emission modes in the EPA and IP/EE glasses correspond to the fluorescence decay of the $S_1(\text{LE})$ and $S_1''(\text{CT})$ states. The coexistence of these emission modes is supported by the results of the total luminescence spectrum (Fl + Ph) analysis (see Fig. 2).

4. The fluorescence decay curve of the longwave fluorescence of II at 77 and 298 K in all solvents used is well described by one exponential fit, which indicates the presence of the $S_1''(\text{CT}) \rightarrow S_0''(\text{CT})$ emission only. We believe that the discrepancy between the decay time of transient absorption and the $F_2''(\text{CT})$ fluorescence decay time is due to transient absorption of photoreaction products and absorption from other than the $S_1''(\text{CT})$ state.

3. Conclusions

To summarize the experimental data, the energy scheme of the ground state and excited species with trans-

sitions studied are given in Figure 6. As it follows from the energy scheme after excitation, the excited molecule undergoes an excited-state proton-transfer reaction, a dielectric relaxation process (including a twist of the moieties to a more planar conformation) or an emission from the excited moiety.

The fluorescence decay time from the $S_1(\text{LE})$ state is very short (see Fig. 5C and Table 1) due to the strong competition of the excited state proton transfer reaction and the intramolecular charge transfer process. The fluorescence emission from the $S_1'(\text{PT})$ and $S_1''(\text{CT})$ states persists in the region of nonoseconds. These decay times depend on the viscosity (temperature) of the solvent. This finding implies that the intramolecular charge-transfer fluorescence as well as the intermolecular double proton-transfer fluorescence [13] depend on the twisting possibility of the molecular moieties. This dependence was proved by other authors [14, 15]. The τ value obtained for I in MCH at room temperature and at 77 K is in good agreement with the results of [16] and [17].

The picosecond transient absorption measurements indicate that this absorption has partly different origins for both compounds. The supplementary reasons are: the pronounced single band (onset at $\lambda \approx 400 \text{ nm}$, $\lambda_{\text{max}} \approx 450 \text{ nm}$ and cut-off at $\lambda \approx 520 \text{ nm}$) observed for II is not seen in the same way in the I spectra. For I, a very broad band (onset at $\lambda \approx 400 \text{ nm}$, $\lambda_{\text{max}} \approx 460 \text{ nm}$ and cut-off $\lambda \approx 560 \text{ nm}$) suggests that this spectrum consists of more than one transition. The time dependence studies of the transient absorption is inferred to assign this absorption to three independent transitions, e.g. to $S_1''(\text{CT}) \rightarrow S_0''(\text{CT})$ and $S_0'(\text{PT}) \rightarrow S_1'(\text{PT}) \rightarrow S_0'(\text{PT})$, respectively (Figure 6). It must be noticed that the fluorescence decay time data in connection with the results of spectroscopy studies give persuasive arguments that the F_2 fluorescence band of benzanilide consist of two transitions.

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