

## Excited state relaxation processes in the case of some acetophenone derivatives

J DOBKOWSKI\*<sup>1</sup>, Z R GRABOWSKI<sup>1</sup>, J WALUK<sup>1</sup>,  
W KÜHNLE<sup>2</sup>, W RETTIG<sup>3</sup>, C RULLIÈRE<sup>4</sup>, W YANG<sup>4</sup>,  
J ADAMUS<sup>5</sup> and J GEBICKI<sup>5</sup>

<sup>1</sup>Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

<sup>2</sup>Max-Planck-Institute for Biophysical Chemistry, Göttingen, Germany

<sup>3</sup>Iwan N. Stranski-Institute for Physical and Theoretical Chemistry, Technical University of Berlin, 1000 Berlin-12, Germany

<sup>4</sup>Centre de Physique Moléculaire Optique et Hertzienne, Université de Bordeaux I, 33405 Talence, France

<sup>5</sup>Institute of Applied Radiation Chemistry, Technical University, Łódź, Poland

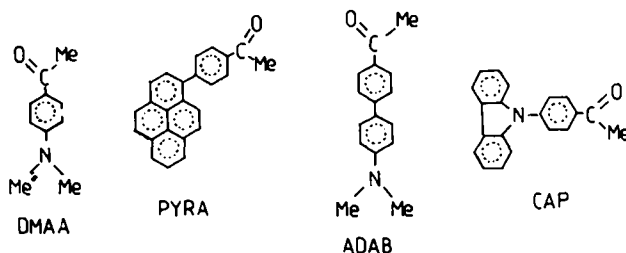
**Abstract.** Stationary fluorescence spectra of four acetophenone derivatives were measured in a number of solvents at several temperatures. For 4'-(1-pyrenyl) acetophenone (PYRA) nanosecond fluorescence decay curves and picosecond time-resolved spectra were recorded. Quantum chemical (INDO/S) calculations of the energies, electronic transitions, oscillator strengths and dipole moments were performed for four different conformers of PYRA. Two models are discussed: (i) TICT state formation; (ii) inversion of two low-lying singlet states.

**Keywords.** Charge transfer state; acetophenone derivatives.

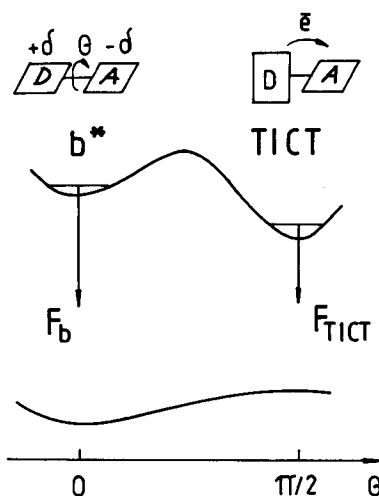
### 1. Introduction

During the last two decades it has been discovered that numerous para-substituted aromatic molecules of the type D–Ar–A (where Ar represents an aromatic ring system) in polar solvents undergo relaxation to a highly polar state, and that emission occurs from two different states (figure 1). The experimental facts are well explained in terms of a twisted intramolecular charge transfer (TICT) state formation model (Grabowski *et al* 1979) (figure 1).

We have studied molecules having acetophenone as the acceptor and different donor groups substituted in its para position.



\* For correspondence



**Figure 1.** TICT model. Schematic cross-section of the ground state and lowest excited singlet state potential hypersurfaces along the reaction coordinate represented here by the twist angle  $\Theta$ .

The aim of our studies is to investigate whether in the case of molecules characterized by donor groups with extended  $\pi$ -electron systems (PYRA, ADAB, CAP) relaxation to the TICT state occurs in a way similar to that in DMAA (Dobkowski *et al* 1982; Grabowski *et al* 1984). In this paper, mainly the results obtained for PYRA will be presented.

## 2. Experimental and calculations

*p*-Dimethylaminoacetophenone (DMAA) (Chemipan, Warsaw) was purified by recrystallizations and checked by TLC. 4'-(1-Pyrenyl)acetophenone (PYRA) was obtained by the Gomberg reaction from pyrene and *p*-amino-acetophenone. The product was purified by column chromatography (NMR, IR). 4-Acetyl-4'-*N,N*-dimethylamino-biphenyl (ADAB) was prepared by the following procedure: commercial 4-acetyl-biphenyl was nitrated by cooled 82.5%  $\text{HNO}_3$ ; the product, 4-acetyl-4'-nitro-biphenyl, precipitating upon dilution with water, was crystallized from methanol. This was catalytically reduced ( $\text{H}_2/\text{PtO}_2$ ) in ethanol. The filtrate, 4-acetyl-4'-amino-biphenyl was evaporated, dried and subsequently methylated under reflux in boiling methanol + anhydrous  $\text{Na}_2\text{CO}_3$ . After evaporation, the residue was shaken with  $\text{H}_2\text{O}$  and extracted twice with  $\text{CHCl}_3$ . Joined organic phases were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and the filtrate evaporated. Pure ADAB (MS, NMR, IR, EA, mp. 119.1°C) was obtained after chromatographic purification and crystallisation from toluene.

*N*-(*p*-acetylphenyl)-carbazole (CAP) was obtained by Ullmann reaction. Carbazole was melted in  $\text{KOH}$  (200°–250°). The product was mixed with *p*-bromoacetophenone and heated at 200°. The final product (CAP) was extracted by  $\text{CHCl}_3$  and purified by column chromatography and TLC (NMR).

Butyronitrile was repeatedly distilled over  $\text{CaCl}_2$  and over  $\text{P}_2\text{O}_5$ . Other solvents (Merck for spectroscopy) were used without further purification.

The stationary luminescence spectra were measured on a Jasný spectrofluorimeter (Jasný 1978).

Time-resolved fluorescence (TRF) spectra were recorded on a picosecond fluorimeter using the optical Kerr cell shutter (Gilabert *et al* 1987).

Fluorescence decay curves were measured using the single-photon counting technique and synchrotron radiation (BESSY, Berlin) as excitation source (single bunch mode, time resolution down to about 100 ps), as described previously (Vogel and Rettig 1987).

The standard INDO/S method (Ridley and Zerner 1973) was used for calculations of transition energies ( $E$ ), dipole moments ( $\mu$ ), and oscillator strengths ( $f$ ). The following values were used in the input geometries:  $r_{CC}$ (phenyl ring) = 1.40 Å,  $\angle CCC = 120^\circ$ ,  $r_{CN}$ (phenyl carbon–amino nitrogen) = 1.37 Å,  $r_{NC}$ (amino nitrogen–methyl carbon) = 1.50 Å,  $r_{CC}$ (phenyl carbon–acetyl carbon) = 1.47 Å,  $r_{CO} = 1.20$  Å,  $r_{CC}$ (acetyl group) = 1.47 Å,  $r_{CH}$ (phenyl ring) = 1.08 Å,  $r_{CH}$ (methyl group) = 1.09 Å.

### 3. The results for PYRA

#### 3.1 Steady-state experiments

Room temperature absorption and fluorescence spectra of PYRA were recorded in a number of protic and aprotic solvents characterized by different polarity indices. The shape and the spectral position of the absorption spectra are only slightly dependent on the solvent, whereas the spectral position of the fluorescence band is strongly dependent on it (figure 2). The largest Stokes shift is observed in the case of alcohol solutions. Because the polarities of butyronitrile and *n*-propanol are almost identical, this indicates that a specific interaction PYRA-alcohol plays an important role in the behaviour of the excited states.

The plot of the solvatochromic shift of the fluorescence maxima ( $\tilde{\nu}_{\max}^F$ ) versus the solvent polarity function  $F(\epsilon, n^2)$  reveals a different slope in low-polarity aprotic solvents as compared to that in highly polar aprotic solvents (figure 3). This shows that the nature of the emitting state changes in highly polar aprotic solvents. The dipole moment value  $\mu_e$  of PYRA for the emitting singlet state is determined from the relation (Bilot and Kawski 1962; Liptay 1965)

$$\tilde{\nu}_{\max}^F = \tilde{\nu}_{\max}^F(0) - \frac{2\bar{\mu}_e(\bar{\mu}_e - \bar{\mu}_g^{FC})}{hca_0^3} F(\epsilon, n^2), \quad (1)$$

where,

$$F(\epsilon, n^2) = \frac{2n^2 + 1}{n^2 + 1} \left( \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right), \quad (2)$$

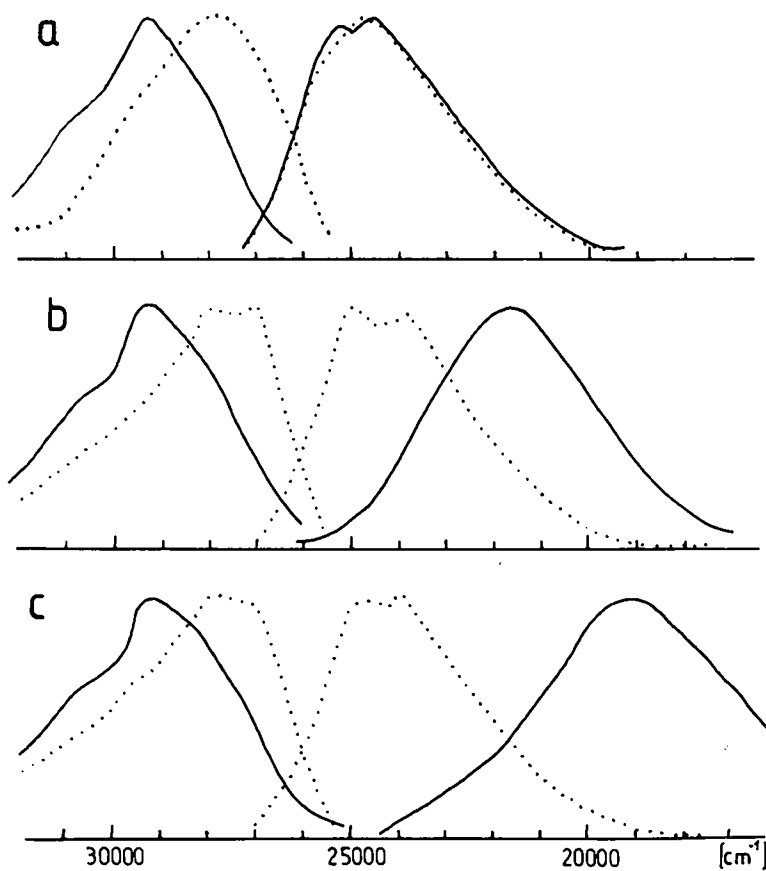
and where it has been assumed that

$$5.3 \text{ \AA} \leq a_0 \leq 6.1 \text{ \AA} \text{ and } \mu_g^{FC} = 2.9D \text{ (same as for acetophenone).}$$

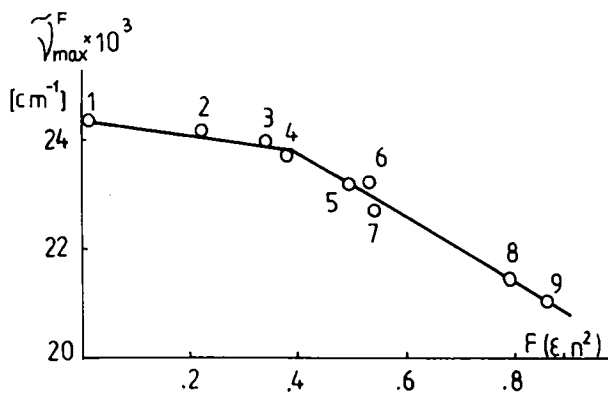
The evaluated dipole moments are:

$$6 \text{ to } 7D, \text{ for } 0 < F(\epsilon, n^2) \leq 0.4,$$

$$10 \text{ to } 13D, \text{ for } 0.4 \leq F(\epsilon, n^2) < 0.9.$$



**Figure 2.** Normalized room and low temperature spectra of PYRA in: (a) 2,2-dimethylbutane + *n*-pentane (8:3 v/v), (b) butyronitrile, (c) *n*-propanol. Solid curves – absorption and fluorescence (293 K), dotted curves – fluorescence and fluorescence excitation (77 K).



**Figure 3.** Solvatochromic shift plot of the fluorescence maxima of PYRA in aprotic solvents: 1. hexane, 2. dibutylether, 3. diisopropylether, 4. diethylether, 5. ethyl acetate, 6. 1-chlorobutane, 7. tetrahydrofuran, 8. butyronitrile, 9. acetonitrile.

**Table 1.** The fluorescence maxima ( $\tilde{\nu}_{\max}$ ,  $\text{cm}^{-1}$ ), fluorescence quantum yields ( $\eta_F$ ), lifetimes ( $\tau$ , ns), and  $\eta_F/\tau$  ( $\text{ns}^{-1}$ ) ratios measured for PYRA in a number of solvents characterized by different dielectric constants  $\epsilon$ .

Solvent	$\epsilon$	$\tilde{\nu}_{\max}$	$\eta_F$	$\tau$	$\eta_F/\tau$
Hexane	1.89	24400	0.011	< 0.1	
Diethylether	4.08	23700	0.098	0.4	0.25
Butyronitrile	20.3	21900	0.46	1.8	0.25
Acetonitrile	36.5	21000	0.58	2.6	0.22
Octanol	10.3	20250	0.48	3.6	0.13
Propanol	20.1	19150	0.35	2.6	0.13
Ethanol	24.3	18650	0.13	1.3	0.1

Moreover, concerning quantum yield ( $\eta_F$ ) and lifetime ( $\tau$ ), we have observed a difference between protic and aprotic solvents (table 1). For PYRA in a series of aprotic solvents  $\eta_F$  and  $\tau$  increase with solvent polarity,  $\eta_F/\tau$  being constant. In protic solvents  $\eta_F$  and  $\tau$  decrease with increased polarity.

*Low temperature emission:* There is no significant change in the shape or spectral position of the fluorescence band of PYRA in liquid and rigid nonpolar solvents (figure 2a). The fluorescence spectra of PYRA in polar solvents drastically change upon cooling, as shown in figures 2b, c. In rigid glasses the emission is observed in the same spectral region as fluorescence in nonpolar solvents ( $\tilde{\nu}_{\max} = 24,500 \text{ cm}^{-1}$ ). Increasing the temperature shifts the emission to the red.

### 3.2 Quantum chemical calculations

Molecular mechanics calculations indicate that in the ground state the acetophenone subunit is twisted with respect to pyrene by  $62^\circ$ . It is consistent with the results obtained in the case of 1-phenylnaphthalene for which it is well established that in the  $S_0$  and  $S_1$  states the phenyl ring is rotated by  $50^\circ$  and  $32^\circ$ , respectively (Gustav *et al* 1980). In order to investigate the behaviour of the electronic states of PYRA upon twisting of the whole acetophenone moiety ( $\Theta$ ) or of the  $-\text{COCH}_3$  group alone ( $\alpha$ ) we have performed INDO/S calculations for different values of the twisting angle of these groups. The terms calculated for  $\alpha = 0$ ,  $\Theta \neq 0$  are presented in figure 4.

For the conformer with  $-\text{COCH}_3$  group twisted by  $90^\circ$  with respect to the aromatic ring ( $\Theta = 30^\circ$ ,  $\alpha = 90^\circ$ ), calculated transitions correspond to the locally excited states of subgroups of PYRA.

*The semi-planar molecule ( $\Theta = 30^\circ$ ,  $\alpha = 0^\circ$ ) model for the delocalized excited (DE) state:* Two lowest  $\pi \rightarrow \pi^*$  transitions have been computed in the low-energy region below  $30,000 \text{ cm}^{-1}$ ; the third transition corresponds to an  $n \rightarrow \pi^*$  excitation and is mainly localized within the  $-\text{COCH}_3$  group.

*The twisted conformer ( $\Theta = 90^\circ$ ,  $\alpha = 0^\circ$ ) geometry as expected for the TICT state:* The lowest excited state is calculated to be of  $n \rightarrow \pi^*$  type. The second and third transitions ( $\pi \rightarrow \pi^*$ ) correspond to the  ${}^1L_b$  and  ${}^1L_a$  states of pyrene (Thulstrup *et al* 1970). The

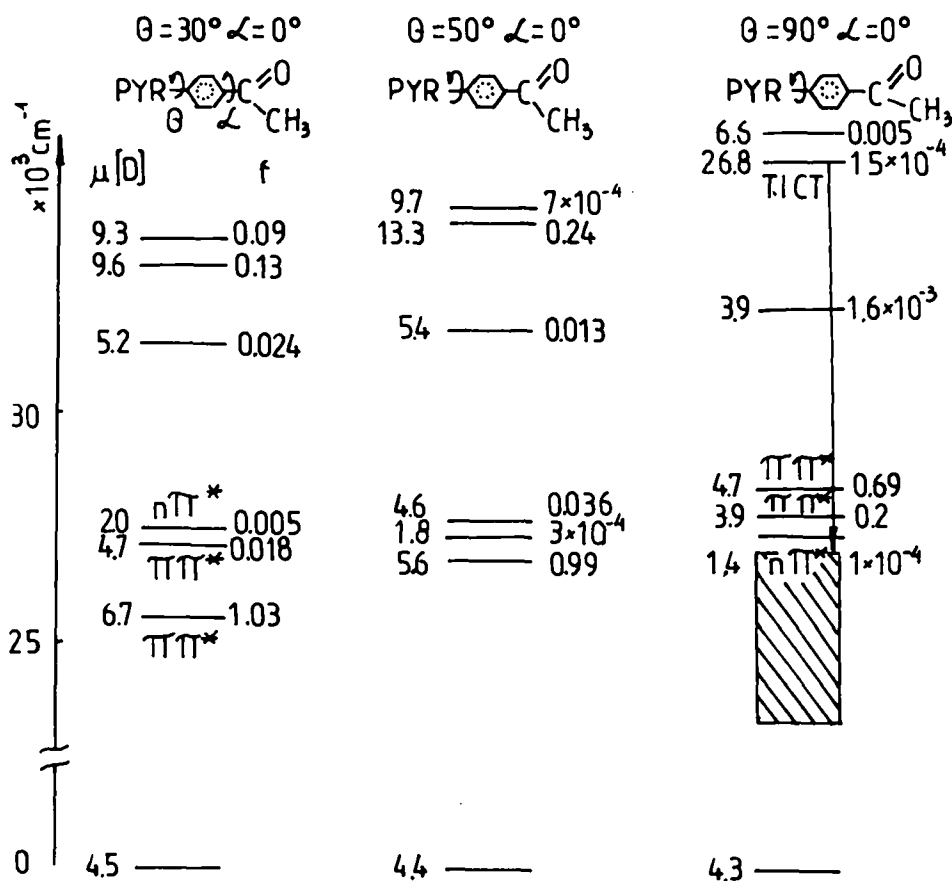


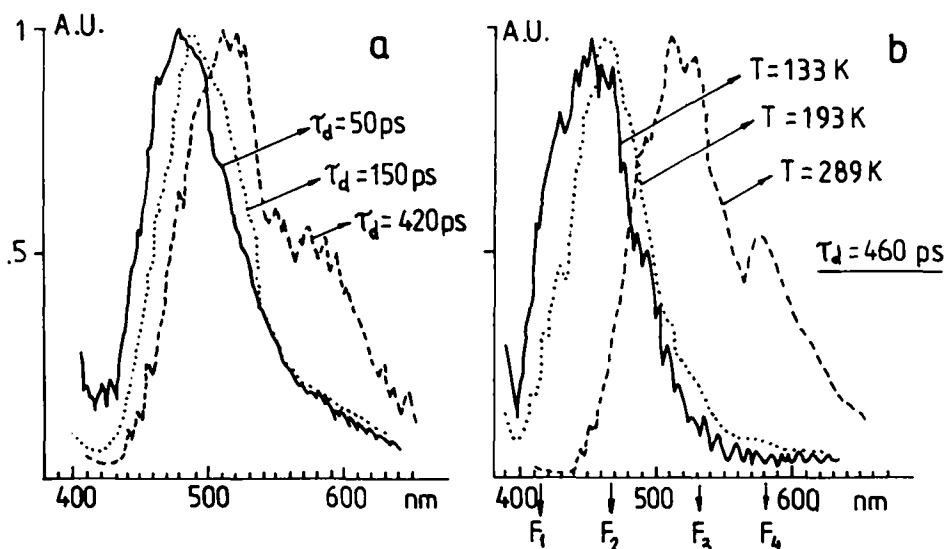
Figure 4. Scheme of energy levels of PYRA molecule calculated by INDO/S method. Numbers on the left-hand side indicate dipole moments while oscillator strengths are shown on the right. Dashed area indicates the values of the TICT state energies after allowing for the solvation (in acetonitrile).

fifth state with a very small oscillator strength and a large dipole moment ( $\mu = 26.8D$ ) can be assigned as a TICT state on the basis of the orbitals involved.

Summing up, INDO/S calculations indicate that in the case of PYRA molecule a TICT state can be generated by the rotation of the whole acetophenone group. The TICT emission has been observed mostly in polar solvents; the solvation energy must be taken into account (Dobkowski *et al.* 1982). Solvation of the TICT state by strongly polar solvents may turn it into the lowest excited state (figure 4).

### 3.3 Picosecond time-resolved fluorescence

The time-resolved fluorescence (TRF) spectra were recorded in *n*-propanol as a function of the excitation-emission delay time and of the temperature (figures 5a, b). The TRF band of PYRA observed in butyronitrile ( $\lambda_{\max} = 470$  nm) does not change very much as a function of the delay time or temperature (273–193 K). Contrary to this, in *n*-propanol a temporal evolution of the TRF is clearly seen, which may be summarized as follows. On the blue side of the TRF at early time, due to drastic



**Figure 5.** TRF spectra of PYRA in *n*-propanol as a function of (a) delay time ( $\tau_d$ ) at  $T = 293$  K, and (b) temperature. The spectra are normalized but not corrected for the spectral response of the instrument.

drop of the apparatus' spectral sensitivity, we observed only the long wave tail of the blue emission band ( $F_1$ ) – corresponding to the stationary emission observed at 77 K with  $\lambda_{\text{max}} = 400$  nm (see figure 2c).

As the time progresses or the temperature increases, the TRF spectra gradually shift to the red with slight change of their shape. At longer times ( $\tau_d > 300$  ps) a new longest-wave emission band appears ( $F_4$ ). The question now is the evolution of the TRF spectra between 50 ps and 300 ps. Is it a single emission band which shifts, or is the spectrum composed of two emission bands? In fact the time-dependent shift of the fluorescence maximum is not a mono- or biexponential, but a step-like function. This indicates that two bands exist in the spectral range 450–530 nm, the intensity of the first one ( $F_2$ ) decreasing with the rise of the second one ( $F_3$ ) (figure 5). The same behaviour is observed at fixed delay time  $\tau_d$  on changing the temperature. The picosecond experiments demonstrate the complexity of the evolution of the fluorescence bands of PYRA in polar protic solvents. It was quite difficult to obtain accurate picosecond decay curves of the fluorescence monitored at different wavelengths. That was the reason why these measurements were performed using nanosecond time resolved single photon counting technique.

### 3.4 Nanosecond time-resolved experiments

For the short-wave region of the observation (400–490 nm) biexponential decays were recorded, for longer wavelengths a rise followed by the decay of the fluorescence was observed (table 2). The short decay times (400–490 nm) and the rise times depend strongly on  $\lambda_{\text{obs}}$ . For both regions the decay time of the long-lived component is almost constant, its amplitude increasing with  $\lambda_{\text{obs}}$ . Even in rigid propanol ( $T = 77$  K) a biexponential decay was observed:  $\tau_1 = 0.7$  ns,  $\tau_2 = 2$  ns ( $\lambda_{\text{obs}} = 400$  nm).

**Table 2.** The fluorescence lifetimes,  $\tau$ (ns) and amplitudes,  $A$ , of PYRA in *n*-propanol at 191 K measured as a function of the observation wavelength  $\lambda_{\text{obs}}$ (nm).  $\tau_D$  – decay time,  $\tau_R$  – rise time (indicated by the negative amplitude  $A$ ). Biexponential fit.

$\lambda_{\text{obs}}$	$\tau_1(A_1)$	$\tau_2(A_2)$
400	$\tau_D = 1.0(-13)$ ,	$\tau_D = 8.3(-0005)^*$
435	$\tau_D = 1.4(-24)$ ,	$\tau_D = 4.5(-0041)$
450	$\tau_D = 1.7(-22)$ ,	$\tau_D = 4.6(-0081)$
490	$\tau_D = 2.6(-18)$ ,	$\tau_D = 5.3(-024)$
530	$\tau_R = 0.9(-.14)$ ,	$\tau_D = 4.3(-22)$
570	$\tau_R = 1.9(-.35)$ ,	$\tau_D = 4.4(-45)$
610	$\tau_R = 2.4(-.66)$ ,	$\tau_D = 4.1(-7)$

\*Impurity?

**Table 3.** Donor–acceptor ground state twist angles ( $\Theta$ ) calculated by the molecular mechanics method; maxima ( $\tilde{\nu}_{\text{max}}^F$  in  $\text{cm}^{-1}$ ) and quantum yields ( $\eta$ ) of fluorescence ( $T = 293$  K).

Molecule	$\Theta$	Butyronitrile		
		PrOH $\tilde{\nu}_{\text{max}}^F$	$\tilde{\nu}_{\text{max}}^F$	$\eta$
PYRA	62	19200	21900	0.46
CAP	39 <sup>a</sup>	18400	21000	0.2 <sup>b</sup>
ADAB	45	18200	19700	—

<sup>a</sup>Calculated for phenyl carbazole (Rettig *et al* 1982);

<sup>b</sup>in acetonitrile

### 3.5 Possibility of excited state enolization

It is well known that for phenyl ketones formation of transient photoenols may occur (Gebicki *et al* 1990). Hydrogen–tritium exchange may be used for probing their formation. To check the role of this mechanism in relaxation of the excited states of acetophenone derivatives, the photochemically induced hydrogen–tritium exchange with methanol has been studied. Deoxygenated solutions of the investigated ketones (DMAA, PYRA or DMABA) in tritiated methanol (MeOT) (0.3GBq/mol) were irradiated in a reactor at 350 nm ( $1.53 \times 10^{17}$  quanta/ml s). After irradiation, the ketones were separated by thin-layer chromatography (TLC) and their radioactivities were measured by liquid scintillation counting. The value of the quantum yield of the hydrogen–tritium exchange in the case of PYRA molecule was  $\Phi_{\text{ex}}^T = 8 \times 10^{-5}$ . For DMABA and DMAA the value of  $\Phi_{\text{ex}}^T$  was not measurable ( $< 10^{-7}$ ). We can conclude that excited state enolization does not play an important role in this class of compounds.

## 4. Discussion of results for ADAB and CAP

In these compounds the same general behaviour as in PYRA is observed. Table 3 lists the fluorescence maxima for the compounds studied, measured in *n*-propanol and butyronitrile.



In alcohols, the fluorescence spectra are significantly red-shifted in comparison to those recorded in nitriles as solvents. TRF spectra of ADAB and CAP in protic solvents show a temporal evolution similar to that observed in the case of PYRA (figure 5).

## 5. Conclusions

To explain the results we propose two alternative schemes with two emitting states for the studied *p*-substituted derivatives of acetophenone in polar aprotic solvents: (i) Mechanism A, involving an inversion of two delocalized excited states; (ii) Mechanism B, involving the formation of the TICT state (figure 6).

Large values of the radiative rate constant ( $k_f \sim 10^9 \text{ s}^{-1}$ ) suggest that in the case of scheme B the strong interaction between TICT and higher locally excited singlet state must be assumed (since TICT fluorescence should be strongly forbidden). Also the dipole moment (figure 3) is much lower than expected for a full separation of charges.

Two other experimental facts do not seem to support the B-scheme of the energy degradation:

(i) The picosecond transient absorption band of PYRA in polar aprotic solvent is not a superposition of the absorption of the pyrene radical cation and the acetophenone radical anion. Unfortunately, in the case of ADAB, stimulated fluorescence strongly overlapped with transient absorption so that comparison of this band with the corresponding absorption of the radical ions was impossible. It should be stressed that for the DMAA molecule the transient absorption band perfectly matches that of the acetophenone radical anion (Rullière *et al* 1987).

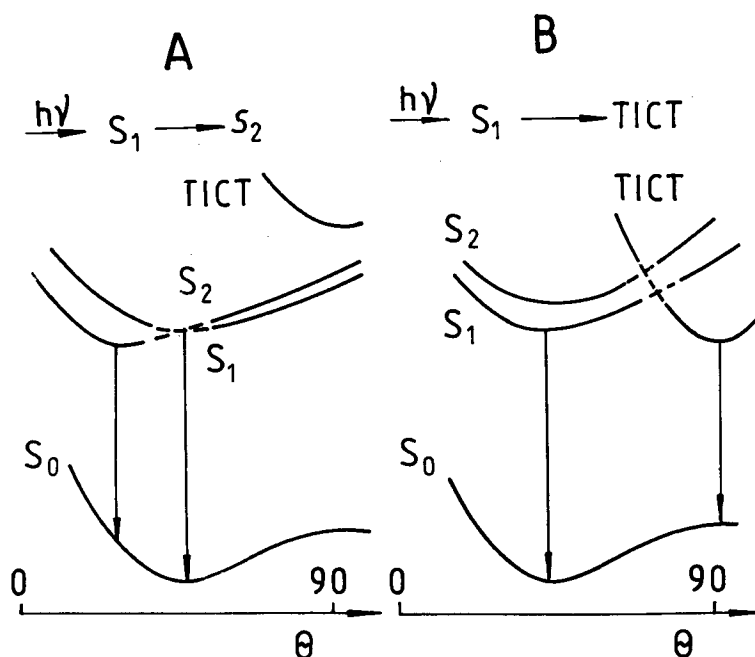


Figure 6. Proposed two alternative schematic cross-sections along the internal rotation coordinate  $\Theta$  on the energy hypersurface of ground and excited singlet states. See the text.

(ii) For the model compound, 4-acetyl-4'-p-N,N-dimethylamino-2,2'-dimethylbiphenyl with N,N-dimethylaniline and acetophenone groups twisted mutually around the central bond no low energy fluorescence was observed; it suggests that the ADAB molecule does not relax to the TICT state.

For polar protic solvents the experimental evidence indicates a multistep relaxation process. Its nature requires further investigation.

### Acknowledgement

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