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Excited state properties of pre-twisted 7-diethylamino coumarinyl benzopyrano pyridine: an experimental and AM1 study

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Abstract

A detailed investigation of the photophysical properties of a new coumarin heterodimer: 2-(7-diethylamino-3-coumarinyl)-5-oxo-4-methyl[1]benzopyrano(3,4-c)pyridine (CBP) has been performed in a range of nonpolar and polar solvents at room temperature. In addition, the influence of temperature on the excited state properties of CBP in dichloromethane, methanol and dimethylsulfoxide has also been investigated. These studies indicate that the fluorescence of the dye is from the *pre-twisted* intramolecular charge transfer (ICT) state. AM1 semiempirical calculations performed for CBP in the ground, excited singlet and triplet states are in conformity with the experimental results. The presence of *second* coumarin is found to introduce a larger charge transfer character to the *parent* coumarin molecule when compared to other diethylamino coumarins. From this study it is also evident that such coumarin hetero dimers behave more like any other single absorbing and emitting chromophoric-systems. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Recently, there is a renewed interest to achieve lasing from organic materials (dyes and polymers) by electrical and optical excitation [1,2]. Changing the functional groups—sometimes leading to significant changes in photochemistry and photophysics—within the classes of strongly fluorescent dyes is a very useful way to create new organic materials for such applications. Bichromophoric molecules with variable chromophore–chromophore (donor–acceptor) separation and orientation and, hence, displaying excited-state intramolecular charge transfer characteristics are also capable of being efficiently used as molecular assemblies yielding interesting optical and electrical bulk properties [3,4]. Aminocoumarins are one of the well-known examples of such donor–acceptor systems.

The application of substituted aminocoumarins as laser dyes [5], as probes to study solvent relaxation dynamics [6] and polarity and viscosity of the surrounding media [7] and, more recently, in nonlinear optical applications [8] stems from the presence of a highly polar ground state that becomes

even more polar on electronic excitation to higher singlet states. Absorption and fluorescence characteristics of coumarins are significantly altered by appropriate substitutions at the 3- and 7-positions. This is because the π-electron delocalization increases by more extensive conjugation at the 3-position in the pyron ring. To compliment this effect a strong electron donating substitutions at the 7-position is very useful [9,10]. A redistribution of charges is known to occur upon excitation of the aminocoumarin molecules, leading to a substantially different distribution of the electronic charge in the excited-state. The lowest π,π^* transition of aminocoumarins is polarized along the long molecular axis and is localized in the pyron ring [9]. Recent semiempirical calculations [11] also lead to a similar conclusion.

Synthesis of coupled/bridged coumarins has earlier been attempted in an effort to find application as efficient laser dyes [12], organic scintillators [13] and triplet sensitizers [14,15]. Biscoumarins, with substitution of a second coumarin at the 3-position of the primary coumarin, were synthesized with a view to increase the fluorescence spectral range and tunability when used in dye laser applications. The photophysical investigations carried out in several solvents, however, showed only a marginal bathochromic shift of the absorption and fluorescence maxima compared to that observed in corresponding primary coumarins implying that

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the predicted increase in the conjugation length was not fully achieved due to the noncoplanarity of the two coumarins [12]. Bifluoroforic molecules consisting of two coumarins linked by a short saturated chain were found to show an intramolecular energy transfer efficiency close to unity and hence well suited for various applications as organic scintillators and fluorescent solar converters [13]. In an another effort [14], it has been shown that by selective substitution, primarily by an aroyl group in the 3-position, coumarin and several ketocoumarins—in which the two coumarin moieties are coplanar—can have high inter-system crossing yields (some nearly unity) and can be used as efficient triplet sensitizers. Urano et al. [15] observed fluorescence quenching of flexible diethylamino ketocoumarins in acetonitrile which they attributed to the formation of nonfluorescent Twisted Intramolecular Charge Transfer (TICT) state.

Aminocoumarinyl benzopyrano pyridine dyes constitute another interesting class of coupled coumarins in that they consist of two coumarin derivatives bridged by a single covalent bond. The specialty of aminocoumarinyl benzopyrano pyridine (and other coupled aminocoumarin) dyes is that they contain a single electron donating group and at least two electron acceptors (carbonyl groups) both distinctly separated by a large distance from one another (Scheme 1). Substitution of additional electron withdrawing groups, such as, –CN on the parent coumarin has been found to produce interesting photophysical properties and these have been explained in terms of the ICT–TICT hypothesis [16]. Thus, the extent of the π-electron delocalization determines the differences in the photophysical properties of these compounds when compared to the corresponding primary coumarins. In order to obtain a better understanding of the processes involved in the excited state of such dimer systems, a more detailed investigation of the excited state properties of 2-(7-diethylamino-3-coumarinyl)-5-oxo-4-methyl[1]-benzopyrano(3,4-c)pyridine (CBP) has been carried out in solvents of different polarity and hydrogen-bonding ability.

In addition, semi empirical AM1 calculations, as a function of the twisting of the dihedral angles θ and δ (Scheme 1), are performed on the dye in the ground, excited singlet and triplet states. Theoretical calculations, such as semiempirical AM1 parametrization, of unsubstituted and substituted coumarins and other molecules have so far been restricted to simple systems mostly containing a single donor and acceptor group [11,17–19]. McCarthy and Blanchard [11] and Awad et al. [20] have found from their studies on coumarins and a carbocyanine (DODCI) that AM1 parametrization overestimates the barrier heights. In the present study, the calculated barriers are obtained in order to explain the trend rather than to give quantitative correlation.

2. Experimental and theoretical methods

Synthesis of CBP has been described elsewhere [21]. For simplicity of explanation, we denote the coumarin nucleus
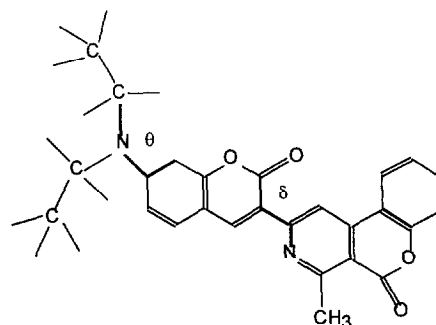
Scheme 1.

having a diethylamino substitution as the *parent* coumarin and the pyridine-conjugated coumarin as *second* coumarin. Solvents used were all of spectroscopy or analar grade (Merck or Aldrich) and used as received. Absorption spectra of the dye have been recorded on a Beckman DU 70 single-beam UV–visible absorption spectrophotometer. Steady state fluorescence spectra were recorded in highly diluted solutions (optical density at excitation wavelengths $\leq 0.2\,cm^{-1}$) using right angle geometry on a Spex Fluorolog 112 spectrofluorimeter, equipped with Glan–Thompson polarizers and cooled Hammamatsu R938 photomultiplier tube. Excitation was vertically polarized while the emission was measured at magic angle. Bandwidth of the excitation and emission slits (2 on each side) was 3.7 and 1.6 nm, respectively. Fluorescence spectra were corrected for the nonlinearities in the response of the monochromator and photomultiplier tube. Coumarin 515 (Exciton) in acetonitrile was used as fluorescent reference dye [17] relative to which fluorescence quantum efficiency of the dye was calculated using the relation [22]:

$$\Phi_{f_s} = \Phi_{f_r} \frac{F_s(\tilde{\nu})A_r n_s^2}{F_r(\tilde{\nu})A_s n_r^2} \tag{1}$$

where, $F(\tilde{\nu})$ represents the corrected fluorescence peak area, A is the absorbance at the excitation wavelength, n is the refractive index of the solvent used, Φ_f is the fluorescence quantum efficiency and the subscripts s and r refer to sample and reference dye, respectively. The percentage of error in estimation of these values is $\pm 5\%$. Fluorescence lifetimes were measured with PRA 3000 series transient configuration nanosecond fluorescence spectrometer using time correlated single photon counting method [23] using thyratron-gated deuterium-filled flash lamp as an excitation source. More details are given in Ref. [24]. For the temperature dependent steady state and time resolved fluorescence measurements, water-cooled peltier element was used to regulate the temperature. The sample compartment was constantly purged with nitrogen to prevent condensation on the cuvette.

In aminocoumarinyl benzopyrano pyridines, variation of two dihedral angles can be of importance for the electronic properties: (i) twist of the bond between the diethylamino group and the coumarin ring, i.e., dihedral angle θ (Scheme 1), (ii) twist of the bond connecting the two coumarin moieties, i.e., dihedral angle δ. In the present study, theoretical

calculations were concentrated on the influence of the rotation of the dihedral angle θ as well as δ on the ground (S_0), excited singlet (S_1) and triplet (T_1) state energies of CBP molecule.

Ground state geometries were optimized with the AM1 Hamiltonian in MOPAC 93 in the CS MOPAC software [25]. RHF calculations of excited singlet and triplet states were performed using 100 microstates (configuration interaction, C.I. = 5). The excited state calculations were done with the geometries from the ground state optimizations. Two AM1-calculated stable ground-state conformations were further examined both by HF/3-21G ab initio and by density functional (DFT) [26] computations with Spartan 4.1.1 software [27]. For the DFT method, the local-spin-density-approximation functional in Spartan by Vosko, Wilk and Nusair (LSDA/VWN) [28], and the DN** double numerical basis set with polarization functions were chosen. This basis is comparable in size with the 6-31G** basis. The dihedral angle θ was varied, in steps of 10° from 9 to 99°, while δ was varied, also in steps of 10°, from −180 to 0°. In addition to the calculation of the state energies, charge distribution in the S_0 and S_1 states was also determined in order to obtain a theoretical estimate of the dipole moment in these states for different twist angles θ and δ. Only gas phase calculations were attempted.

3. Results and discussions

3.1. Absorption and fluorescence spectra

Normalized absorption and fluorescence spectra of the dye in various solvents are shown in Figs. 1 and 2, respectively.
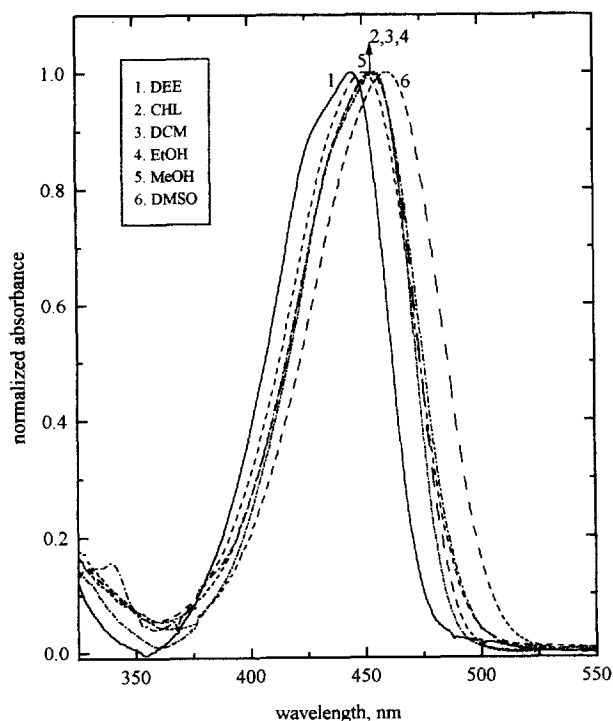

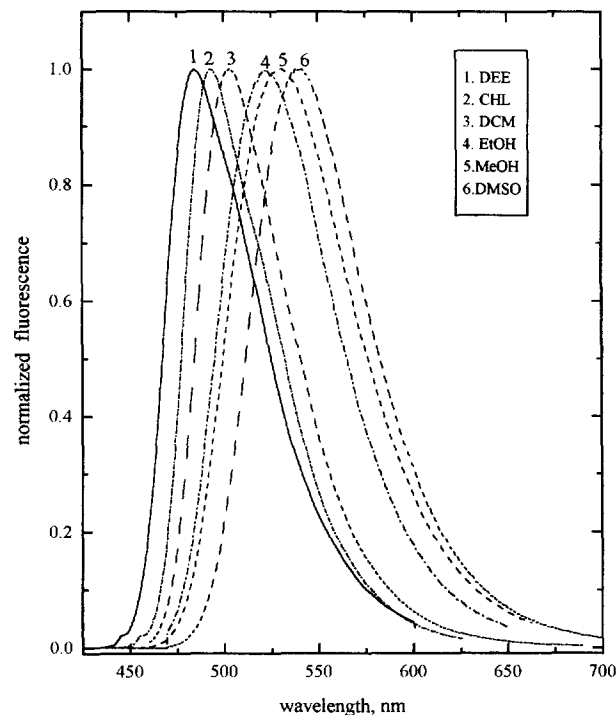Fig. 1. Normalized absorption spectra of CBP in several nonpolar and polar solvents.

Fig. 2. Normalized fluorescence spectra of CBP in several nonpolar and polar solvents.

The corresponding spectral characteristics in all the solvents studied are given in Table 1. The absorption spectrum is characterized by a single, strong absorption band in the visible region. No spectral broadening to indicate overlap of several absorption bands is observed. A recent study on several coumarin derivatives has shown [19] that the S_1 state is n,π^* for coumarin in any solvent and due to additional substitution and/or increase in solvent polarity the energy gap between the $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$ states decreases promoting the mixing of the states finally inducing an inversion to $S_1(\pi,\pi^*)$ state. The long-wavelength absorption band of the primary coumarin is centered on 309 nm in DMSO and that of 7-diethylamino-4-methylcoumarin is at 375 nm in the same solvent [32]. The longest wavelength absorption band of CBP can also be attributed to the π,π^* transition. This is also confirmed from the positive solvatochromic shift of this band in acidic environments. Fluorescence maxima (λ_f) of the dye is found to show a greater sensitivity to the changes in the solvent polarity. This is in contrast to the very minimal dependence of the absorption maxima (λ_a) of the dye on the polarity of the solvent. A greater solvent sensitive bathochromic shift of the fluorescence maxima also implies an increase in the dipole moment of the dye in the excited state compared to that in the ground state.

Determination of the extent of increase in the dipole moment of the dye on electronic excitation can be made from Lippert–Mataga plots using the equation [33–35]:

$$\Delta\tilde{\nu} = \frac{2\Delta\mu^2}{hca_o^3}\left[\frac{(\varepsilon-1)}{(2\varepsilon+1)} - \frac{(n^2-1)}{(2n^2+1)}\right] + \text{Constant} \qquad (2)$$

Table 1
Maximum wavelength of absorption and fluorescence and Stokes shift for the dye CBP in the solvents studied

Solvent	Δf^a	$E_T(30)^b$ (kcal mol^{-1})	λ_a (nm)	$\tilde{\nu}_a$ (cm^{-1})	λ_f (nm)	$\tilde{\nu}_e$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})
(1) Diethylether (DEE)	0.161	34.5	445	22471	484	20661	1811
(2) Chloroform (CHCl$_3$)	0.148	39.1	455	21978	493	20283	1694
(3) Dioxane (DXN)	0.02/0.198^c	36	450	22222	494	20242	1979
(4) Dichloromethane (DCM)	0.218	40.7	453	22075	506	19762	2312
(5) Acetonitrile (ACN)	0.305	45.6	450	22222	528	18939	3283
(6) Dimethylformamide (DMF)	0.275	43.8	458	21834	532	18796	3037
(7) Dimethylsulfoxide (DMSO)	0.267	45.1	460	21739	541	18484	3255
(8) Isopropanol (IPA)	0.273	48.4	450	22222	517	19342	2880
(9) Ethanol (EtOH)	0.288	51.9	453	22075	523	19120	2955
(10) Methanol (MeOH)	0.310	55.4	450	22222	531	18832	3390

See text for details of column titles.
[a] Polarity function for each solvent is based on the value of dielectric constant and refractive index of the solvents given in Ref. [29].
[b] Values taken from Ref. [30].
[c] Bulk dielectric constant of dioxane is 2.02 (at room temperature) and this corresponds to a Δf of 0.02. However, it is known to have a dynamic dielectric constant varying between 5 and 7 in the presence of strongly polar solute dipoles [31]. A dielectric constant value of 7 has been considered in the present study. This corresponds to a Δf of 0.198.
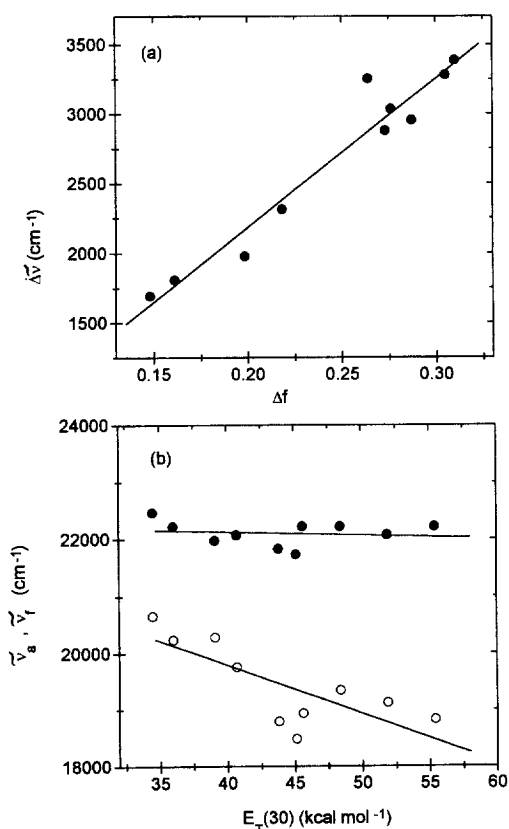

Fig. 3. (a) Lippert–Mataga plots relating the Stokes shift ($\Delta\tilde{\nu}$) to the solvent polarity–polarizability parameter (Δf). (b) Dependence of absorption ($\tilde{\nu}_a$, closed circles) and fluorescence maxima ($\tilde{\nu}_e$, open circles) on solvent $E_T(30)$. The solid lines are the best linear least-square fits to the data.

where $\Delta\tilde{\nu}$ is the Stokes shift (in cm^{-1}) and given by: $\Delta\tilde{\nu} = (\tilde{\nu}_a - \tilde{\nu}_e)$, where, $\tilde{\nu}_a$ and $\tilde{\nu}_e$ are the spectral positions (frequencies) of the absorption maxima and solvent-equilibrated fluorescence maxima, respectively. The value in the square parentheses is referred to as Δf, the polarity–polariz-

ability parameter of the solvent where n is the refractive index and ε is the dielectric constant of the solvent (both at room temperature). These values are taken from Ref. [29]. The other terms in Eq. (2) are Planck's constant (h), speed of light (c), Onsager cavity radius of the solute molecule (a_o) and $\Delta\mu$ ($= \mu_e - \mu_g$) which is the magnitude of the change in the dipole moment on excitation from the ground state to the excited state, where, μ_g and μ_e are the dipole moments of the molecule in the ground and excited state, respectively. $\Delta\mu$ is obtained from the slope of the plot of Stokes shift vs. the polarity function. The underlying assumptions in this treatment are that the solute is a point dipole and that $\vec{\mu}_g$ and $\vec{\mu}_e$ are parallel to each other. A plot of $\Delta\tilde{\nu}$ vs. Δf is shown in Fig. 3a. Least square linear regression analysis gives a good correlation according to:

$$\Delta\tilde{\nu} = 10703.2\Delta f + 47.95 \quad (r = 0.97, n = 10)$$

Deviations from linearity in the Lippert–Mataga treatment, typically observed in case of alcohols, are characteristics of specific solvent effects arising from specific solute–solvent interactions such as hydrogen bonding, etc. In the present study, Stokes shift observed in acetonitrile and methanol, and similarly in dimethylformamide and isopropanol, i.e., pair of aprotic and protic solvents having almost identical Δf value, is the same (Table 2). This eliminates the possible influence of the above mentioned specific-solvent effects on the photophysical properties of the dye. This is also evident from the plots of the absorption and emission maxima vs. $E_T(30)$ value—the parameter indicative of solvent polarity and hydrogen bonding (Fig. 3b). A large Stokes shift and its concomitant increase with the polarity function of the solvent suggests that the potential energy surface of the emitting state is considerably different from that of the ground state and has a considerable charge transfer character, i.e., a large increase in the excited state dipole moment.

Table 2
Photophysical properties of CBP in selected solvents

Solvent	Φ_f	τ_f (ns)	$k_r \times 10^{-8}$ (S^{-1})	$k_{nr} \times 10^{-8}$ (S^{-1})
(1) Diethylether	—	—	—	—
(2) Chloroform	0.73	2.06	3.54	1.31
(3) Dioxane	0.62	2.06	3.01	1.84
(4) Dichloromethane	0.85	2.29	3.86	0.68
(5) Acetonitrile	0.64	2.46	2.63	1.48
(6) Dimethylformamide	0.64	2.32	2.76	1.55
(7) Dimethylsulfoxide	0.62	2.40	2.58	1.58
(8) Isopropanol	0.70	—	—	—
(9) Ethanol	0.71	2.33	3.05	1.24
(10) Methanol	0.70	2.64	2.65	1.14

See text for details of column titles.

In view of the nonspherical shape of the molecule, accurate estimation of the radius of the molecule and hence its excited state dipole moment is not trivial. Onsager cavity radius has been approximated, following the suggestion by Lippert [33] for elongated nonspherical molecules, as 40% of the long axis of CBP. This was estimated to be 5.4 Å (obtained from the optimized ground state geometry and including the van der Waals radii). The ground-state dipole moment of the pre-twisted form of the dye molecule is found to be 7.8 D (see below). The excited-state dipole moment is then found to be 20.7 D.

Fluorescence quantum efficiency (Φ_f) of CBP is found to be generally very high and almost constant in all solvents studied. The lifetime of the lowest excited singlet state (τ_f) is also found to be rather insensitive to the nature of the solvent (see Table 2). A high Φ_f and a low τ_f imply a larger probability for radiative dissipation at the expense of nonradiative relaxation of the molecule from the excited state. This is characteristic of highly fluorescent aminocoumarins. The rate constant for radiative transition (k_r), which describes the electric dipolar coupling of the excited states with the ground states, and that for radiationless transition (k_{nr}), which describes the role of vibronic and spin-orbit interactions, can be determined using the standard equations: $k_r = \Phi_f / \tau_f$ and $k_{nr} = (1 - \Phi_f) / \tau_f$. These values are given in Table 2.

The more than two fold increase in the excited-state dipole moment is much higher than that reported for several 3- and 4-substituted aminocoumarins [11,17–19] and also to the theoretically calculated value for the pre-twisted form of CBP (see below). The unusually high value of μ_e for CBP is comparable to that determined for DMABN—the best-known example of a dye displaying dual fluorescence and TICT characteristics [31]. However, the allowedness of the radiative emission reflected by a high Φ_f and short τ_f and the absence of dual fluorescence do not point towards an excited state with a TICT character. The fluorescence of the dye is hence from an ICT state.

The steady state fluorescence spectrum of CBP shows asymmetric broadening at longer wavelengths in all the solvents studied (Fig. 2). This is characteristic of a possible
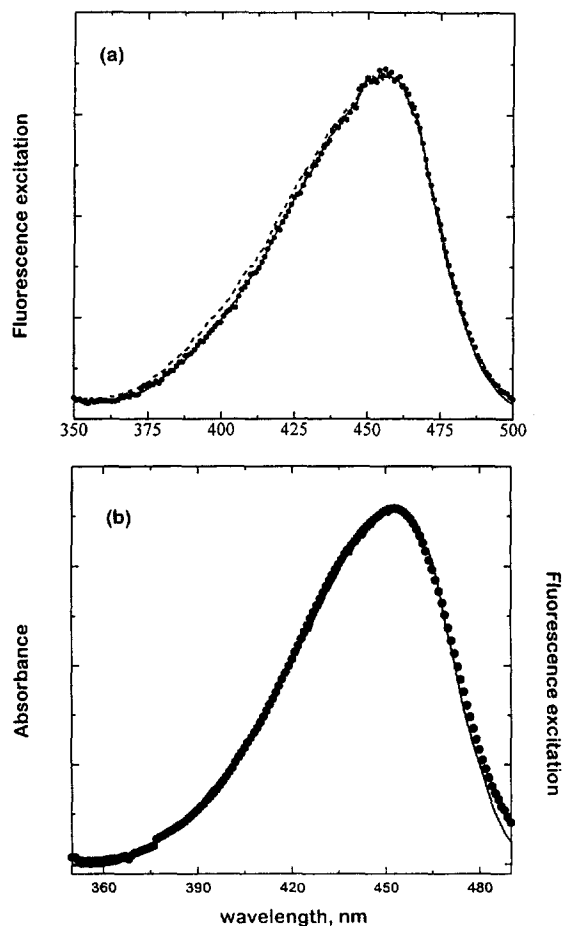

Fig. 4. (a) Normalized fluorescence excitation spectra of highly diluted solutions of CBP ($\lambda_f = 490$ (smooth line), 535 (dashed line) and 600 (dash-dot line) nm). The solvent is ethanol. (b) Normalized absorption (smooth line) and fluorescence excitation spectrum ($\lambda_f = 531$ nm, dash-dot line) of CBP in ethanol.

overlap of more than one fluorescence transition associated with more than one (conformation of) fluorescent chromophore. Further investigations were carried out to verify this feature.

Steady state fluorescence spectrum of CBP measured in different solvents at room temperature did not show any dependence on excitation wavelength. Similarly, fluorescence excitation spectra of highly diluted samples measured for different emission wavelengths ($\lambda_f = 490$, 535 and 600 nm) were found to be identical (Fig. 4a) and overlapping with the absorption spectrum (Fig. 4b). Thus there is only a single absorbing and emitting species. These results also indicate the absence of possible rotamers (excimers or exciplexes) or a fast equilibrium between them.

3.2. Temperature dependence of the emission properties

Steady state and time resolved fluorescence measurements of CBP were made in selected solvents to obtain a deeper insight into the thermodynamic behavior of the emission characteristics of the dye. Three solvents of varying polarity, viscosity and refractive index, DCM, methanol and DMSO,
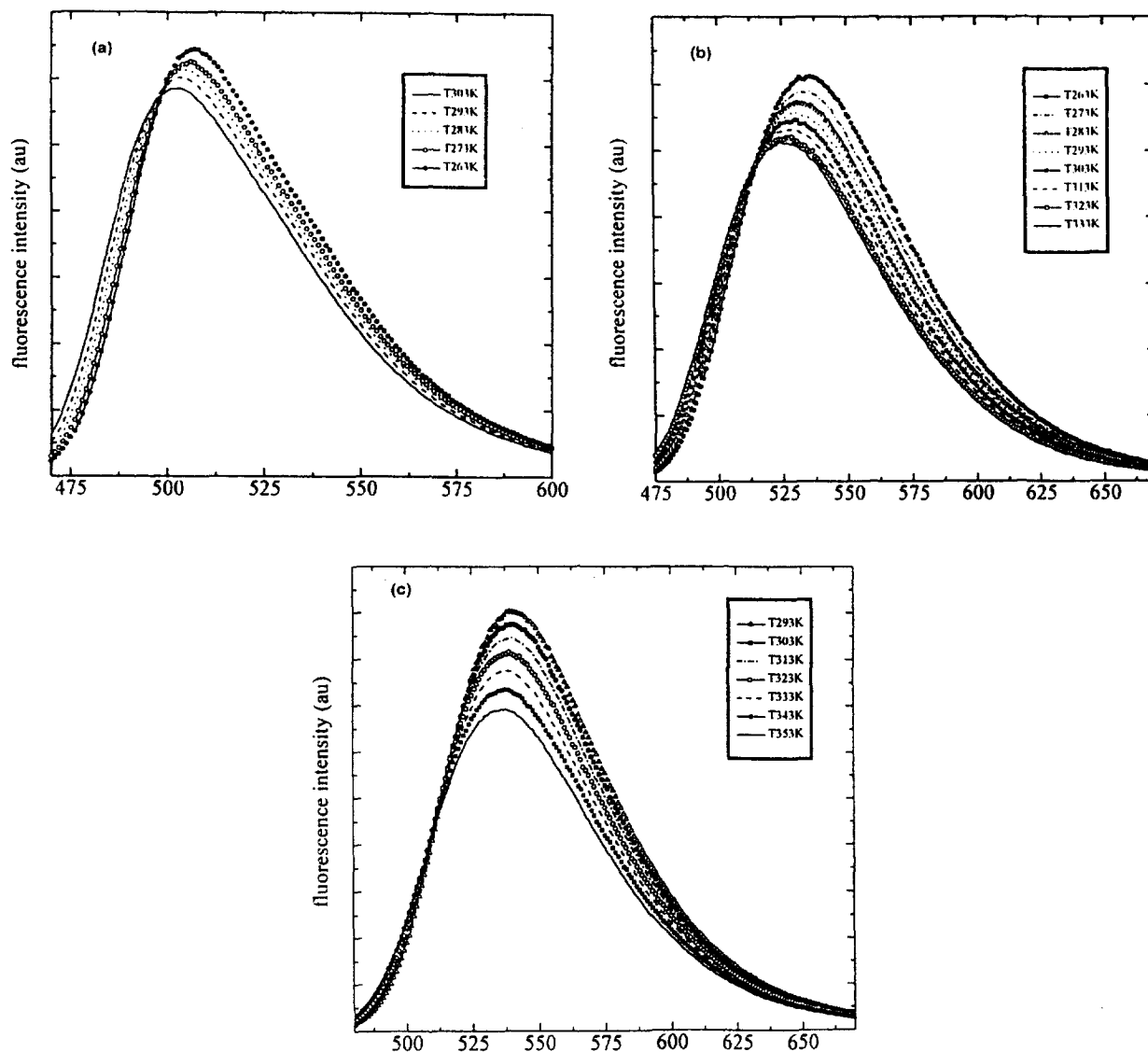
Fig. 5. Temperature dependence of the emission spectra of CBP in (a) DCM (b) MeOH and (c) DMSO.

were considered. Fluorescence maxima showed a blue shift of 3 to 6 nm with increase in temperature (Fig. 5). A greater temperature dependence of Φ_f and τ_f is observed in DMSO, followed by in methanol. The most important result of the temperature-dependent fluorescence decay measurements is the mono-exponential decay obtained for CBP in all three solvents and at all temperatures measured. The effect of temperature on the radiative rate constant, although present, is thus not significant and k_r can be generally accepted to be temperature-invariant. The temperature-dependent photophysical properties of CBP are given in Table 3.

The rate of nonradiative decay, k_{nr}, in contrast to the above, increases with increase in temperature and solvent polarity and is observed to follow, as shown in Fig. 6, the Arrhenius relation:

$$\ln k_{nr} = \ln A - E_a / RT \tag{6}$$

where the factor A is the pre-exponential factor and E_a is the activation energy in kJ mol^{-1}, T is the temperature in degree Kelvin and R is the universal gas constant.

The activation energy is found to be 2.31, 4.10 and 6.02 kJ mol^{-1} in DCM, methanol and DMSO, respectively. As the temperature is increased both viscosity and polarity of the solvent decrease [29] and either of this can result in quenching of the fluorescence emission. The values obtained for the activation barrier in the present study are much smaller than the activation energy of viscous flow in the respective solvents. The small blue shift of the fluorescence spectrum and the increase in k_{nr} with increase in temperature can hence be understood in terms of quenching due to internal conversion, inter-system crossing or collisions between the solute and solvent molecules, of which the latter becomes very important at higher temperatures [36]. An increase in thermal motion of the system and decrease of the macroviscosity of the solution would introduce a red shift of the fluorescence spectrum.

Table 3

Temperature dependence of some of the photophysical properties: Φ_f, τ_f, k_r and k_{nr} of CBP in DCM, MeOH and DMSO

Temperature (K)	Φ_f	τ_f (ns)	$k_r \times 10^{-8}$ (S^{-1})	$k_{nr} \times 10^{-7}$ (S^{-1})	λ_f (nm)
Dichloromethane					
273	0.86	2.26	3.79	6.36	506
283	0.86	2.27	3.92	6.66	505
293	0.85	2.29	3.86	6.81	503
Methanol					
263	0.76	2.60	2.93	9.18	536
273	0.74	2.63	2.80	10.05	535
283	0.72	2.63	2.72	10.08	531
293	0.70	2.64	2.65	11.36	531
303	0.69	2.62	2.68	11.93	530
313	0.67	2.61	2.58	12.48	528
323	0.66	2.59	2.55	13.18	529
Dimethylsulfoxide					
293	0.62	2.40	2.58	15.80	541
303	0.61	2.37	2.56	16.60	541
313	0.59	2.30	2.57	17.70	540
323	0.57	2.20	2.60	19.40	539
333	0.55	2.16	2.55	20.80	537
343	0.53	2.11	2.50	22.50	537

The last column is the fluorescence maxima (λ_f) at the corresponding temperature.

The absence of an isosbestic point in the steady-state fluorescence spectra and a mono-exponential decay of the emission with change in temperature in the solvents studied indicates the absence of more than one emitting chromophore/conformation. The broad and structureless fluorescence spectra observed in all the solvents can then be explained as due to the strong interaction between a highly polar solute and solvent molecules [37,38].

3.3. Theoretical calculations

The AM1 optimized structure of CBP in the ground state has the orbital with the lone pair electrons on the diethylamino nitrogen oriented out of the plane of coumarinyl system, i.e., the dihedral angle θ is 9° (Scheme 1). The two coumarin moieties make a dihedral angle δ of 151°, showing that the molecule is already twisted out of plane even in the ground state. This conformation is referred to as *pre-twisted* form. The dipole moment for this preferred conformation was found to be 7.8 D in the ground state. A second stable conformation of CBP according to the AM1 calculations has the opposite orientation of the coumarin components; i.e., the dihedral angle δ is 52°, while the dihedral angle θ is the same as for the most stable conformer. The energy for the second conformer is 2.8 kcal mol^{-1} higher than that of the conformer with $\delta = 151°$ at the AM1 level. Further energy minimization of these two conformers using a density functional theory (DFT) method as described above, gave a similar difference between the two structures (3.3 kcal mol^{-1}), while energy minimization at the HF/3-21G ab initio level showed a larger
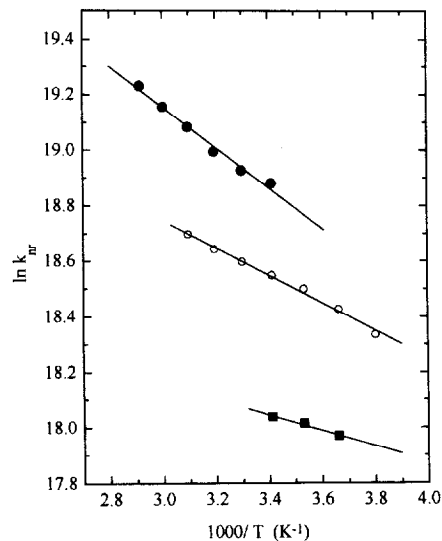

Fig. 6. Arrhenius plots showing the dependence of the nonradiative rate constant on the temperature in DCM (solid squares), MeOH (open circles) and DMSO (solid circles).

difference (11.6 kcal mol^{-1}). This validated that the first mentioned conformation ($\delta = 151°$) indeed corresponds to the structure of lowest energy, and that the population of the second conformer should be negligible.

AM1 calculations show that the ground state energy of the dye molecule increases with increase in the twist of the dihedral angle θ (Fig. 7a). In addition, μ_g was found to decrease from 7.8 to 5.8 D on increasing the twist angle. Similarly a decrease in μ_e from 13.2 to 4.7 D was also observed on going from the *pre-twisted form* ($\theta = 9°$) to the *twisted form*
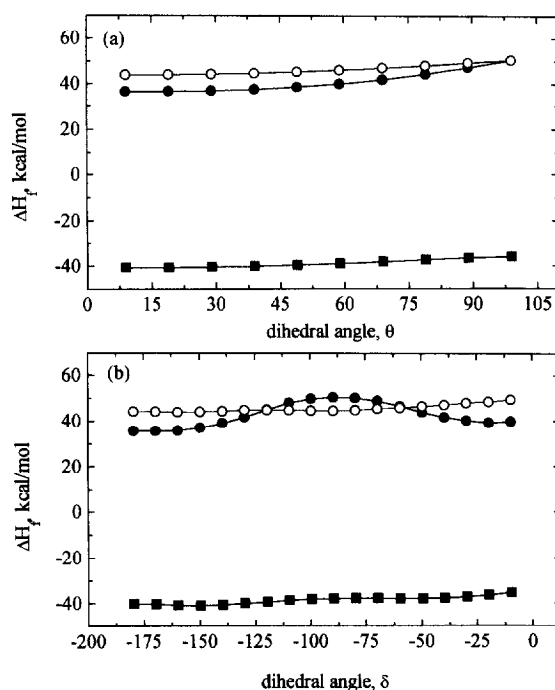

Fig. 7. AM1 calculated dependence of the energy (ΔH_f) of S_0 (solid squares), S_1 (solid circles) and T_1 (open circles) states of CBP on the rotation of the dihedral angle (a) θ and (b) δ.

($\theta = 99°$). This validates the assumption made above while using the Lippert–Mataga equation (Eq. (2)). Evidently, the *pre-twisted form* is more stable than the *twisted form*. The ground and excited state dipoles for the *pre-twisted* form are found to be collinear. Singlet and triplet state calculations also gave a lower heat of formation for the *pre-twisted form* than for the *twisted form* with a significant barrier (13.8 and 6.58 kcal mol^{-1}, in the S_1 and T_1 states, respectively) for twisting. This shows that the *pre-twisted form* is more stabilized than the *twisted form* even in the excited singlet and triplet states. Inter-system crossing to T_1 state on optical excitation is however known to be less probable for coumarins under normal excitations [11,17,18]. In view of this, triplet state energy levels could only be determined by sensitization [14], pulse radiolysis technique [39] and by multi-photon excitation [40].

Calculation of the potential energy of the surfaces as a function of the twist angle δ showed some variation for ΔH_f of the S_0, S_1 and T_1 states (Fig. 7b). Thus the possibility of co-existence of different isomers with different twist angles δ cannot be ruled out. However, the mono-exponential fit of the fluorescence decay collected at different temperatures in several solvents and other experimental results presented above indicate that the isomers, even if co-existing, have identical spectroscopic behavior.

4. Conclusions

Experimental investigations of the photophysical characteristics of *pre-twisted* CBP in several solvents show that the fluorescence emission of the dye is from the highly polar intramolecular charge transfer state. Further, excited state properties of the dye are not susceptible to further twisting of either the diethylamino group or the *second* coumarin moiety. AM1 semiempirical quantum mechanical calculations also lead to the same conclusions. Aminocoumarinyl benzopyrano pyridines are thus single absorbing and emitting chromophore systems. The present study also shows that preventing the twisting of the amino group is not a pre-requisite to obtain highly fluorescent substituted aminocoumarins.

Acknowledgements

References

[1] M. Breggren, A. Dodabalapur, R.E. Slusher, Z. Bao, Nature 389 (1997) 466.
[2] V.G. Kozlov, V. Bulovic, P.E. Burrows, S.R. Forrest, Nature 389 (1997) 362 and references therein.
[3] W. Rettig, Appl. Phys. B 45 (1988) 145.
[4] L.S. Stolarczyk, L. Piela, Chem. Phys. 85 (1984) 451.
[5] K.H. Drexhage, in: F.P. Schäfer (Ed.), Topics in Applied Physics, Vol. 1, Dye Lasers, 2nd edn., Springer Verlag, New York, 1977.
[6] M.L. Horng, J.A. Gardecki, A. Papazyan, M. Maroncelli, J. Phys. Chem. 99 (1995) 17311.
[7] G. Jones II, W.R. Jackson, S. Kanoktanporn, W.R. Bergmark, Photochem. Photobiol. 42 (1985) 477.
[8] C.R. Moylan, J. Phys. Chem. 98 (1994) 13513.
[9] E.J. Schimitschek, J.A. Trias, P.R. Hammond, R.A. Henry, R.L. Atkins, Opt. Commun. 16 (1976) 313.
[10] M.R. Padhye, T.S. Varadarajan, A.V. Deshpande, Spectrosc. Lett. 15 (1982) 597.
[11] P.K. McCarthy, G.J. Blanchard, J. Phys. Chem. 97 (1993) 12205.
[12] M.R. Padhye, T.S. Varadarajan, A.V. Deshpande, Spectrosc. Lett. 18 (1985) 705.
[13] J. Bourson, J. Mugnier, B. Valeur, Chem. Phys. Lett. 92 (1982) 430.
[14] P. Sprecht, P.A. Martic, S. Farid, Tetrahedron 38 (1982) 1203.
[15] T. Urano, H. Nagasaka, M. Tsuchiyama, S. Shimizu, K. Kawazoe, M. Shimizu, T. Yamaoka, Bull. Chem. Soc. Jpn. 68 (1995) 1661.
[16] B. Bangar Raju, J. Phys. Chem. A 101 (1997) 981.
[17] K. Rechthaler, G. Köhler, Chem. Phys. 189 (1994) 99.
[18] G. Jones II, C.Y. Choi, W.R. Jackson, W.R. Bergmark, J. Phys. Chem. 89 (1974) 294.
[19] J.S.S. de Melo, R.S. Becker, A.L. Macanita, J. Phys. Chem. 98 (1994) 6054.
[20] M.M. Awad, P.K. McCarthy, G.J. Blanchard, J. Phys. Chem. 98 (1994) 1454.
[21] S. Pal, Doctoral Dissertation, Bombay University, India, 1991.
[22] J.N. Demas, G.A. Crosby, J. Phys. Chem. 64 (1960) 762.
[23] D.V. O'Connor, D. Phillips in Time Correlated Single Photon Counting, Academic Press, London, 1984.
[24] J. Karolin, L.B.-Å. Johansson, L. Strandberg, T. Ny, J. Am. Chem. Soc. 116 (1994) 7801.
[25] CS MOPAC v. 3.50, Cambridge Soft, 875 Massachusetts Ave., Cambridge, MA 02139, USA.
[26] R.O. Jones, O. Gunnarsson, The density functional formalism, its applications and prospects, Rev. Mod. Phys. 61 (1989) 689.
[27] Spartan v. 4.1.1, Wavefunction, 18401 Von Karman Ave., #370, Irvine, CA 92715, USA.
[28] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200.
[29] R.C. West (Ed.), CRC Handbook of Chemistry and Physics, 5th edn. CRC Press, OH, 1974.
[30] C. Reichardt, Chem. Rev. 94 (1994) 2319.
[31] W. Schuddeboom, S.A. Jonker, J.M. Warman, U. Leinhos, W. Kühnle, K.A. Zachariasse, J. Phys. Chem. 96 (1992) 10809.
[32] J.-J. Aaron, M. Buna, C. Parkanyi, M.S. Antonious, A. Tine, L. Camine, J. Fluorescence 5 (1995) 337.
[33] E. Lippert, Z. Naturforsch. Teil A 10 (1955) 541.
[34] N. Mataga, Y. Kaifu, M. Azumi, Bull. Chem. Soc. Jpn. 29 (1956) 465.
[35] G. McRae, J. Phys. Chem. 61 (1957) 562.
[36] J.R. Lackowicz, in: Principles of Fluorescence Spectroscopy, Plenum, New York, 1983.
[37] M. Maroncelli, G.R. Fleming, J. Chem. Phys. 86 (1987) 6221.
[38] A. Baczyński, P. Targowski, B. Zietek, D. Radomska, Z. Naturforsch. 45a (1990) 1349.
[39] P.K.I. Priyadarshini, D.B. Naik, P.N. Moorthy, Chem. Phys. Lett. 148 (1988) 572.
[40] R.V. Sahyun, D.K. Sharma, Chem. Phys. Lett. 189 (1992) 571.