THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 105, NUMBER 7, FEBRUARY 22, 2001

ARTICLES

Unusual Photophysical Properties of Coumarin-151

Sanjukta Nad and Haridas Pal*

Radiation Chemistry and Chemical Dynamics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Received: August 31, 2000

The photophysical properties of 7-amino-4-trifluoromethyl-1,2-benzopyrone (coumarin-151; C151) in nonpolar (NP) solvents are drastically different than those in other solvents of moderate to higher polarities. Thus, the absorption and fluorescence maxima are largely blue-shifted and the Stokes' shifts unusually low in NP solvents compared to those in the other solvents. The fluorescence quantum yields (Φ_f) in NP solvents are also exceptionally lower. While in all other solvents the fluorescence decays of C151 are single-exponential, in NP solvents the decays show non-single-exponential behavior. The average fluorescence lifetimes (τ_f) in NP solvents are also substantially shorter. Low Φ_f and τ_f values in NP solvents indicate very fast nonradiative deactivation for the S_1 state of C151. Investigating the triplet characteristics of C151 by using picosecond laser flash photolysis and pulse radiolysis techniques, it has been established that the fast nonradiative deactivation in NP solvents is not due to an enhancement in the intersystem crossing rate. It is inferred from the present results that in NP solvents the 7-NH_2 group of C151 exists as a free substituent without participating in resonance with the benzopyrone moiety and the flip-flop motion of the NH_2 group introduces the fast deactivation channel for the S_1 state of the dye. In other solvents of moderate to higher polarities, there is an intramolecular charge transfer (ICT) from the 7-NH_2 group to the benzopyrone moiety, resulting in a planar structure for the S_1 state in which the flip-flop motion of the 7-NH_2 group is restricted. Involvement of the ICT structure in moderate to higher polarity solvents causes very high Φ_f and τ_f values and large Stokes' shifts for the dye compared to those in NP solvents.

1. Introduction

1,2-Benzopyrone and its derivatives (coumarin dyes) are the well-known laser dyes for the blue-green region.[1−7] The 1,2-benzopyrone derivatives with amino or substituted amino groups at the 7-position (the 7-aminocoumarins) are of special importance in this regard. Fluorescence quantum yields (Φ_f) of the coumarin dyes are usually very high, often close to unity.[1−9] Though in some of the coumarins the internal conversion (IC) contributes to some extent in deactivating the S_1 state, the contribution of the intersystem crossing (ISC) process in coumarin dyes is usually very low or negligible.[8,9] For the majority of the coumarin dyes, there is a substantial difference between the ground-state and excited-state dipole moments.[1−9] This state-dependent variation in the dipole moments makes the coumarin dyes very useful probes in investigating many physiochemical processes in condensed phase.[8−16] In 7-aminocoumarins, very large Stokes' shifts are observed between the absorption and the fluorescence maxima.[8−16] These Stokes' shifts are again very sensitive to the solvent polarities and environments.[8−16] Due to these interesting properties, a number of 7-aminocoumarins have found their applications in studying the solvatochromic behaviors and polarities of different environ-

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* Corresponding Author. E-mail: hpal@apsara.barc.ernet.in.

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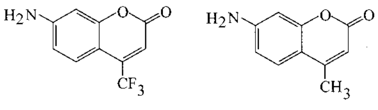
CHART 1



(C151 ; I) **(C120 ; II)**

ments and also in measuring the solvent relaxation times (τ_s) using dynamic Stokes' shift method.[10−16]

Recently, Rechthaler and Köhler[17] have reported the photophysical properties of a number of 7-aminocoumarins in several organic solvents. It has been observed that the coumarin dyes with 7-NH_2 group behave differently than the other coumarins having substituted amino groups at the 7-position.[17] Thus, coumarin-151 (C151; 7-amino-4-trifluoromethyl-1,2-benzopyrone; structure I, Chart 1) and coumarin-120 (C120; 7-amino-4-methyl-1,2-benzopyrone; structure II, Chart 1) show very low fluorescence quantum yields (Φ_f) in nonpolar solvents such as hexane (HX) and heptane (HP) in comparison to other polar and moderately polar solvents.[17] Such a strong reduction in the Φ_f values for C151 and C120 in HX and HP is an unusual phenomena and urges a detailed investigation to understand the mechanism behind such strong quenching. In the present work, the photophysical properties of C151 have been investigated in detail in a large number of organic solvents and solvent mixtures using ground-state absorption and steady-state (SS) and time-resolved (TR) fluorescence measurements. Temperature-dependent fluorescence measurements have also been carried out to substantiate the observed results in different solvents. Picosecond laser flash photolysis and pulse radiolysis experiments have also been carried out to obtain the triplet-state characteristics of C151 and thus to understand if the ISC process plays any role in deactivating the S_1 state of the dye. The chemical structures of C151 and C120 are shown in Chart 1.

2. Materials and Methods

Experiments were carried out with laser-grade C151 samples obtained from Lambda Physik and Exciton. Similar results were obtained with both the samples. All the solvents used were of spectroscopic grade from Spectrochem India. Dielectric constants (ϵ) and refractive indices (n) of the pure solvents were taken from literature,[18] and those of the mixed solvents (ϵ_{MS} and n_{MS}) were estimated from the volume fractions (f) of the cosolvents using eqs 1 and 2, respectively[19−21]

$$\epsilon_{MS} = f_A\epsilon_A + f_B\epsilon_B \tag{1}$$

$$n_{MS}^{\ 2} = f_A n_A^{\ 2} + f_B n_B^{\ 2} \tag{2}$$

where the subscripts A and B represent the respective cosolvents. The solvent polarities obtained from the ϵ_{MS} and n_{MS} values thus estimated using eqs 1 and 2 are reported to correlate nicely to a number of physicochemical properties of many probe molecules in different solvents and solvent mixtures.[19−23]

Absorption spectra were recorded using a Shimadzu model UV-160A spectrophotometer. Fluorescence spectra were recorded with corrections for the wavelength-dependent instrument responses using a Hitachi model F-4010 spectrofluorimeter. The Φ_f values were measured in a comparative method,[24,25] using Φ_f of C151 in HX as the reference ($\Phi_f^R = 0.19$)[17] and applying corrections for the refractive indices of the solvents.[24,25] For all the fluorescence measurements, the optical density (OD) of the solutions were kept quite low (∼0.2) at the excitation wavelength.

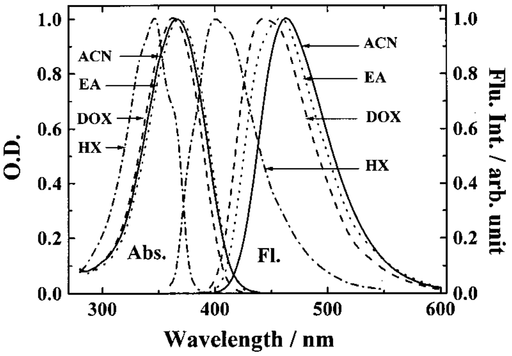


Figure 1. Normalized absorption (Abs.) and fluorescence (Fl.) spectra of C151 in some of the representative solvents of varying polarities. The solvents are HX (hexane), DOX (1,4-dioxane), EA (ethyl acetate), and ACN (acetonitrile).

Fluorescence lifetime measurements were taken using a time-correlated-single-photon-counting spectrometer[26,27] (model 199, Edinburgh Instrument, U.K.), the details of which are described elsewhere.[28,29] The fluorescence decays were analyzed by a reconvolution procedure,[26,27] using a proper instrument response function obtained by replacing the sample with a light scatterer. The single-exponential or biexponential nature of the fluorescence decays were judged from the reduced χ^2 values and the distribution of the weighted residuals among the data channels.[26,27]

Picosecond laser flash photolysis experiments were carried out using a pump−probe transient spectrometer, the details of which are described elsewhere.[30,31] The third harmonic output (355 nm, 7 mJ, 35 ps) of an actively−passively mode-locked Nd:YAG laser (Continuum, USA, model 501-C-10) was used for sample excitation. A white light continuum (∼440−900 nm), produced by focusing a part of the 1064 nm Nd:YAG laser light onto a 10 cm path-length quartz cell containing a 50:50 (v/v) H_2O-D_2O mixture, was used as the monitoring light source.

Pulse radiolysis experiments were carried out using 50 ns electron pulses from a 7 MeV linear electron accelerator (LINAC, from Ray Technology, England) for sample irradiation and detecting the transients by kinetic spectrometric method. The radiation doses used in these experiments were about 14−17 Gy, as estimated using air-saturated KSCN dosimetery.[32]

3. Results

3.1. Absorption and Fluorescence Spectral Characteristics. Absorption and fluorescence spectra of C151 were recorded in different solvents and solvent mixtures. It is observed that both absorption and fluorescence spectra are strongly dependent on the solvent polarities. Figure 1 shows the absorption and fluorescence spectra of C151 in some of the representative solvents having very low (e.g., HX, $\epsilon = 1.89$)[18] to very high polarities (e.g., acetonitrile; ACN, $\epsilon = 37.5$).[18] Table 1 lists the wavelengths of the absorption and fluorescence maxima (λ_{abs}^{max} and λ_{fl}^{max}, respectively) of C151 in different solvents and solvent mixtures. Table 1 also lists the solvent polarity function Δf, defined as[33−36]

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 - 1} \tag{3}$$

Figure 2 plots the wavenumbers for the absorption and fluorescence maxima ($\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$, respectively) of C151 against the Δf values of the solvents. It is seen from this figure that in all the solvents excluding the nonpolar (NP) ones such as HX,

TABLE 1: Photophysical Characteristics of C151 in Different Solvents and Solvent Mixtures

solvents[a]	Δf	λ_{abs}^{max}/nm	λ_{em}^{max}/ nm	$\Delta\bar{\nu}$/cm^{-1}
HX	0	347	401	3855
2MP	0	347	399	3756
3MP	0	347	400	3860
CHX	0	348	401	3798
MCHX	0	348	401	3798
DL	0.002	349	404	3934
$M_{70}D_{30}$	0.008	360	438	4947
DOX	0.021	364	442	4886
$M_{95}E_5$	0.025	359	439	5076
$M_{90}E_{10}$	0.046	361	440	4974
$M_{80}E_{20}$	0.081	362	441	4949
$M_{60}E_{40}$	0.128	364	447	5101
$M_{40}E_{60}$	0.160	366	451	5149
EA	0.201	368	456	5244
OcOH	0.226	383	480	5276
HxOH	0.243	384	481	5252
BuOH	0.263	383	484	5449
DMSO	0.264	386	487	5386
DMF	0.276	378	480	5482
ISP	0.277	384	481	5252
ACT	0.284	371	466	5495
EtOH	0.290	383	485	5525
ACN	0.305	367	461	5556
MeOH	0.309	378	487	5921

[a] Abbreviations for the solvents are HX (hexane), 2MP (2-methyl pentane), 3MP (3-methyl pentane), CHX (cyclohexane), MCHX (methyl cyclohexane), DL (decalin), DOX (1,4-dioxane), EA (ethyl acetate), OcOH (octanol), HxOH (hexanol), BuOH (butanol), DMSO (dimethyl sulfoxide), DMF (dimethyl formamide), ISP (2-propanol), ACT (acetone), EtOH (ethanol), ACN (acetonitrile), MeOH (methanol), $M_{70}D_{30}$ (70% 3MP and 30% DOX, v/v), $M_{95}E_5$ (95% 3MP and 5% EA, v/v), $M_{90}E_{10}$ (90% 3MP and 10% EA, v/v), $M_{80}E_{20}$ (80% 3MP and 20% EA, v/v), $M_{60}E_{40}$ (60% 3MP and 40% EA, v/v), and $M_{40}E_{60}$(40% 3MP and 60% EA, v/v).

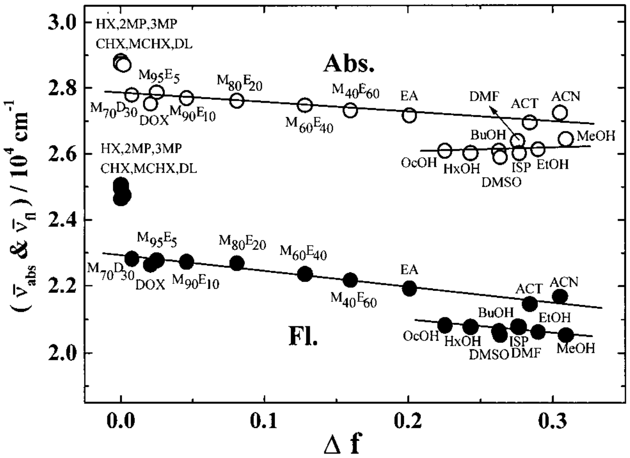


Figure 2. Plot of absorption (Abs.) and fluorescence (Fl.) maxima of C151 ($\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$, respectively) against solvent polarity function, Δf. The abbreviations for the solvents are as given in the footnote of Table 1.

cyclohexane (CHX), methyl cyclohexane (MCHX), 2-methyl pentane (2MP), 3-methyl pentane (3MP) and Decalin (DL), both $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ follow linear relationships with Δf. In NP solvents, however, both $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values are substantially deviated toward higher energies from the above linearities, indicating that the dye behave differently in the NP solvents than in other solvents.

It is seen from Figure 2 that for protic solvents, e.g., alcohols, and for solvents such as dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF), the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values are somewhat lower compared to those in other aprotic solvents of similar polarities. It is seen, however, that the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values in these solvents follow linear correlations with Δf, which are more or less parallel to the correlations observed for the other aprotic solvents. We attribute this lowering in $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values in alcohols, DMSO, and DMF to the intermolecular hydrogen bonding interaction between C151 and the solvent molecules, which causes an extra stabilization for both S_0 and S_1 states of the dye.

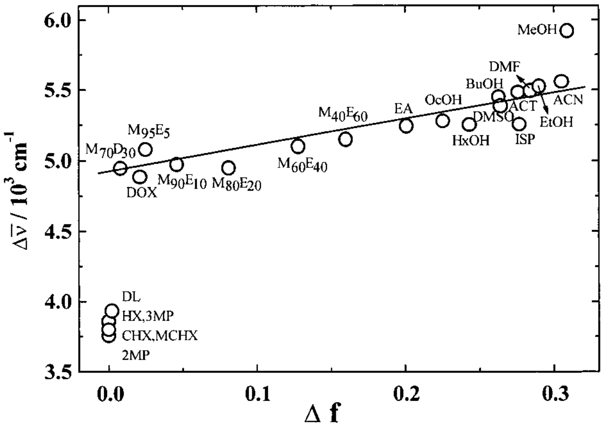


Figure 3. Plot of Stokes' shifts ($\Delta\bar{\nu}$) for C151 against the solvent polarity function, Δf. The abbreviations for the solvents are as given in the footnote of Table 1.

Since no specific solute−solvent interaction is expected in NP solvents, the appearance of the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ at much higher energies in these solvents is a very interesting observation. To substantiate these results, we also tried to correlate the Stokes' shifts (i.e., $\Delta\bar{\nu} = \bar{\nu}_{abs} - \bar{\nu}_{fl}$) with the Δf values of the solvents. It is generally assumed that the longer-wavelength absorption and the fluorescence bands of a molecule are due to the transitions between the same two ground and excited electronic states.[24,25,33,34] Thus, the Stokes' shifts for a molecule in different solvents are expected to correlated with the solvent polarities.[24,25,33,34] Lippert and Mataga derived the following linear relationship (eq 4) correlating $\Delta\bar{\nu}$ with the Δf values of the solvents:[35,36]

$$\Delta\bar{\nu} = \Delta\bar{\nu}_0 + \frac{2\Delta\mu^2}{hcr^3}\Delta f \qquad (4)$$

where $\Delta\mu = \mu_e - \mu_g$ is the difference between the excited-state and ground-state dipole moments, μ_e and μ_g respectively, h is Planck's constant, c is the velocity of light, and r is the Onsager radius for the interaction sphere of the dipole in a solvent. Table 1 lists the $\Delta\bar{\nu}$ values for C151 in different solvents and solvent mixtures. Figure 3 shows the plot of $\Delta\bar{\nu}$ against the Δf values of the solvents. It is seen from this figure that though for almost all the solvents and solvent mixtures the $\Delta\bar{\nu}$ versus Δf plot is linear within experimental error, the $\Delta\bar{\nu}$ values for the NP solvents are unusually small and largely deviated from the above linear correlation.

One more interesting point to be noted from Figure 3 is in relation to the alcoholic solvents, DMSO, and DMF. We have seen earlier (cf. Figure 2) that the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values in these solvents are somewhat lower than those in other aprotic solvents of similar polarities. In Figure 3 however, it is seen that the $\Delta\bar{\nu}$ values in alcohols, DMSO, and DMF fall under the same linear correlation, along with the values observed in other aprotic solvents of moderate to higher polarities. These results thus indicate that the S_0 and S_1 states of C151 are of the same nature

TABLE 2: Photophysical Characteristics of C151 in Different Solvents and Solvent Mixtures

solvents[a]	Δf	Φ_f	τ_f/ns[b]	$k_f/10^7 s^{-1}$	$k_{nr}/10^7 s^{-1}$
HX	0	0.19	0.68 (74), 1.35 (26)	22.24	94.82
2MP	0	0.17	0.64(75), 1.43 (25)	20.18	98.52
3MP	0	0.18	0.65 (74), 1.39 (26)	21.36	89.86
CHX	0	0.28	0.93 (60), 1.60 (40)	23.37	61.72
MCHX	0	0.29	0.8 (40), 1.50 (60)	23.77	58.20
DL	0.002	0.32	1.34 (35), 2.2 (65)	16.85	35.81
$M_{70}D_{30}$	0.008	0.65	1.30 (7), 4.50 (93)	15.20	8.19
DOX	0.021	0.71	4.65	15.27	6.23
$M_{95}E_5$	0.025	0.66	4.03	15.88	8.93
$M_{90}E_{10}$	0.046	0.66	4.04	16.34	8.42
$M_{80}E_{20}$	0.081	0.66	4.31	15.31	7.89
$M_{60}E_{40}$	0.128	0.62	4.50	13.78	8.44
$M_{40}E_{60}$	0.160	0.63	4.61	13.67	8.03
EA	0.201	0.62	4.67	13.27	8.14
OcOH	0.226	0.63	5.40	10.66	7.85
HxOH	0.243	0.54	5.29	10.20	8.70
BuOH	0.263	0.48	5.24	9.16	9.92
DMSO	0.264	0.48	5.00	9.60	10.4
DMF	0.276	0.49	5.22	9.40	9.76
ISP	0.277	0.52	5.28	9.84	9.10
ACT	0.284	0.59	4.97	11.87	8.25
EtOH	0.290	0.49	5.38	9.10	9.48
ACN	0.305	0.57	5.13	11.11	8.38
MeOH	0.309	0.37	5.31	6.97	11.86

[a] Abbreviations for the solvents are as given in the footnote of Table 1. [b] For NP solvents and $M_{70}D_{30}$, the short-lifetime (τ_1) and the long-lifetime (τ_2) components (cf. section 3.3) are presented with their respective percentage contributions (a_1 and a_2) in parentheses.

in all these solvents, including alcohols, DMSO, and DMF. Present results also indicate that the extent of stabilization due to intermolecular hydrogen bonding is more or less similar for both S_0 and S_1 states of the dye.

From the slope of the $\Delta\bar{\nu}$ versus Δf plot for the moderate to higher polarity solvents, the μ_e value of C151 was estimated to be about 7.3 D. In this estimation, the μ_g and r values were assumed to 4.49 D and 3.46 Å, respectively.[37] A μ_e value of 7.3 D indicates that the S_1 state of the dye is quite polar in moderate to higher polarity solvents. We attribute this to the intramolecular charge transfer (ICT) state, produced by a good extent of charge transfer (CT) from the 7-NH_2 substituent to the C=O group of the benzopyrone moiety. Considering the μ_g value of 4.49 D, the S_0 state of the dye is also expected to have the ICT character.

As Figure 3 indicates, in NP solvents the Stokes' shifts are unusually small. It is thus expected that unlike in other solvents, the dye might not have the same ICT character in NP solvents. We propose that in NP solvents the 7-NH_2 group of C151 remains as a free substituent without participating in any resonance with the benzopyrone moiety. Thus, both S_0 and S_1 states of the dye in NP solvents will have nonpolar character, and hence, the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ are expected to appear at much higher energies, and the Stokes' shifts are expected to be very small.

3.2. Fluorescence Quantum Yields. Fluorescence quantum yields (Φ_f) of C151 in different solvents and solvent mixtures were estimated at room temperature and are listed in Table 2. Figure 4 shows the plot of Φ_f versus the Δf values of the solvents. It is seen that the Φ_f values in NP solvents are drastically lower in comparison to those in other solvents. Excluding the NP solvents, the Φ_f values in all other solvents are quite high and are not much dependent on Δf. In alcohols, DMSO, and DMF, however, the Φ_f values are seen to be slightly lower in comparison to those in other solvents of similar polarities. We attribute this reduction in the Φ_f values to the intermolecular hydrogen bonding effect (cf. section 3.1).

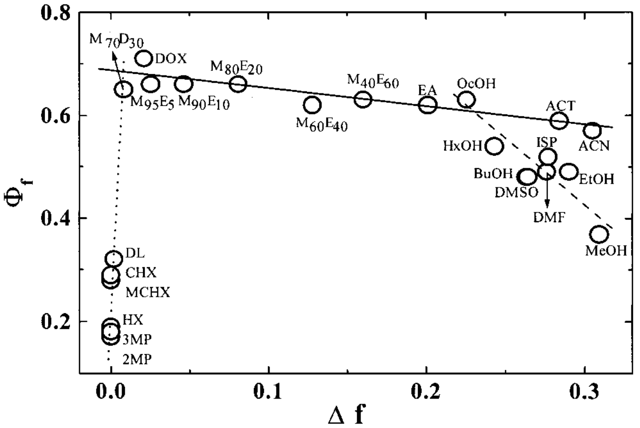


Figure 4. Variations in the fluorescence quantum yields (Φ_f) of C151 with the solvent polarity function, Δf. The abbreviations for the solvents are as given in the foot note of Table 1.

In NP solvents, since no specific solute−solvent interaction is expected, the large reduction in the Φ_f values seems to be an unusual observation. In section 3.1, it was inferred from the solvent polarity effect on spectral shifts that the S_0 and S_1 states of the dye in NP solvents are of different characteristics than in other solvents. If this is so, it is possible to have Φ_f values in NP solvents quite different than those in other solvents.

3.3. Fluorescence Decays. Fluorescence decays of C151 in different solvents were measured at room-temperature, keeping the wavelength of measurement at λ_{fl}^{max} of the dye in respective solvents. It is seen that, excluding the NP solvents, the fluorescence decays of C151 in all other solvents are single-exponential. The fluorescence lifetimes (τ_f) thus estimated in different solvents are listed in Table 2. It is seen that in all these solvents, the τ_f values are more or less in the similar range, about 4.5−5.2 ns, and show only a minor increase with Δf. Following Einstein's treatment for the electronic transitions,[33,34] the decay rate constant for spontaneous fluoresence (k_f) is proportional to the cube of $\bar{\nu}_{fl}$. Since $\bar{\nu}_{fl}$ shifts to the lower energies with Δf (cf. section 3.1 and Table 1), it is expected that τ_f should increase to some extent with solvent polarities.

The fluorescence decays of C151 in NP solvents are seen to be very fast and unusually non-single-exponential. We analyzed these decays assuming a biexponential function. The two lifetimes (τ_1 and τ_2) and the respective percentage contributions (a_1 and a_2) thus estimated in different NP solvents are listed in Table 2. It is seen from this table that the percentage contributions of the two lifetime components are different for different NP solvents. In solvents such as HX, 2MP, and 3MP, the percentage contributions (a_1) of the short component (τ_1) are as high as about 75%. Also in these solvents, τ_1 is as short as ~0.65 ns. In solvents such as CHX, MCHX, and DL, not only does a_1 decrease, but there is also an increase in both τ_1 and τ_2 values. In a very low polarity solvent mixture, namely, 70% 3MP and 30% dioxane by volume ($M_{70}D_{30}$), it is interestingly seen that the fluorescence decay fits better to a biexponential function than to a single-exponential function. In this case, however, a_1 is very small, only about 5%. Further, τ_2 in $M_{70}D_{30}$ is very long and close to the τ_f values observed in other solvents of moderate to higher polarities. Thus, it appears that the solvent $M_{70}D_{30}$ behaves as a bridge between the NP solvents and the other solvents and solvent mixtures of moderate to higher polarities.

The radiative (k_f) and nonradiative (k_{nr}) decay rate constants for the S_1 state of C151 in different solvents were estimated

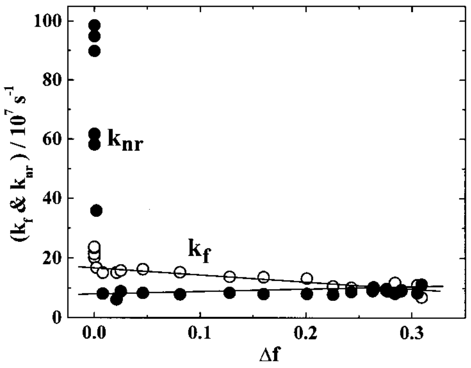


Figure 5. Plot of radiative (k_f) and nonradiative (k_{nr}) decay rate constants for C151 against the solvent polarity function, Δf. The k_{nr} values in NP solvents are dramatically higher in comparison to those in other solvents of moderate to higher polarities.

using the measured Φ_f and τ_f values and are listed in Table 2. For the NP solvents and $M_{70}D_{30}$, the average fluorescence lifetimes $\langle\tau_f\rangle$ as defined by eq 5, were used to estimate the k_f and k_{nr} values

$$\langle\tau_f\rangle = (a_1\tau_1 + a_2\tau_2) \times \frac{1}{100} \tag{5}$$

Figure 5 shows the plot of k_f and k_{nr} values against the solvent polarity function Δf. It is seen from Table 2 and Figure 5 that the k_f and k_{nr} values in moderate to higher polarity solvents are not much dependent on the solvent polarities, except a nominal reduction in the k_f values as the Δf is increased. For NP solvents, however, it is seen that both k_f and k_{nr} values are always higher than those in other solvents. The k_{nr} values in NP solvents are in fact exceptionally higher compared to those in other solvents. Thus, in solvents such as HX, 2MP, and 3MP, the k_{nr} values are about 10 times higher than the average k_{nr} values observed in moderate to higher polarity solvents. It is thus evident that there is a fast nonradiative deactivation channel operative for the S_1 state of C151 in NP solvents.

For solvents such as alcohols, DMSO, and DMF, it is seen from Table 2 that the k_f values are slightly lower and the k_{nr} values are slightly higher compared to those in other aprotic solvents of similar polarities. It is inferred from these results that the intermolecular hydrogen bonding between C151 and the solvent molecules of alcohols, DMSO, and DMF not only enhances the nonradiative deexcitation rate but also reduces the absolute fluorescence rate to some extent.

3.4. Temperature Effect on the Fluorescence Quantum Yields. The temperature effect on the SS fluorescence properties of C151 was investigated in all the NP solvents and in some of the selective solvents of moderate to higher polarities. In the NP solvents, it is seen that the SS fluorescence intensity is strongly temperature-dependent. The typical temperature effect on the SS fluorescence spectra of C151 in HX is shown in Figure 6A. Similar results were also obtained in other NP solvents. Figure 6B shows the plot of Φ_f in HX versus the absolute temperature (T) of the solution. Following the definition of Φ_f and assuming that the k_f is mostly temperature-independent,[24,25,33,34] we find that the temperature effect on the Φ_f values in NP solvents should arise through k_{nr}. For excited molecules, the observed k_{nr} may have contributions from both activation-controlled and activationless nonradiative processes. In NP solvents, since the Φ_f values are strongly temperature-dependent and the k_{nr} values are much higher than those in other solvents

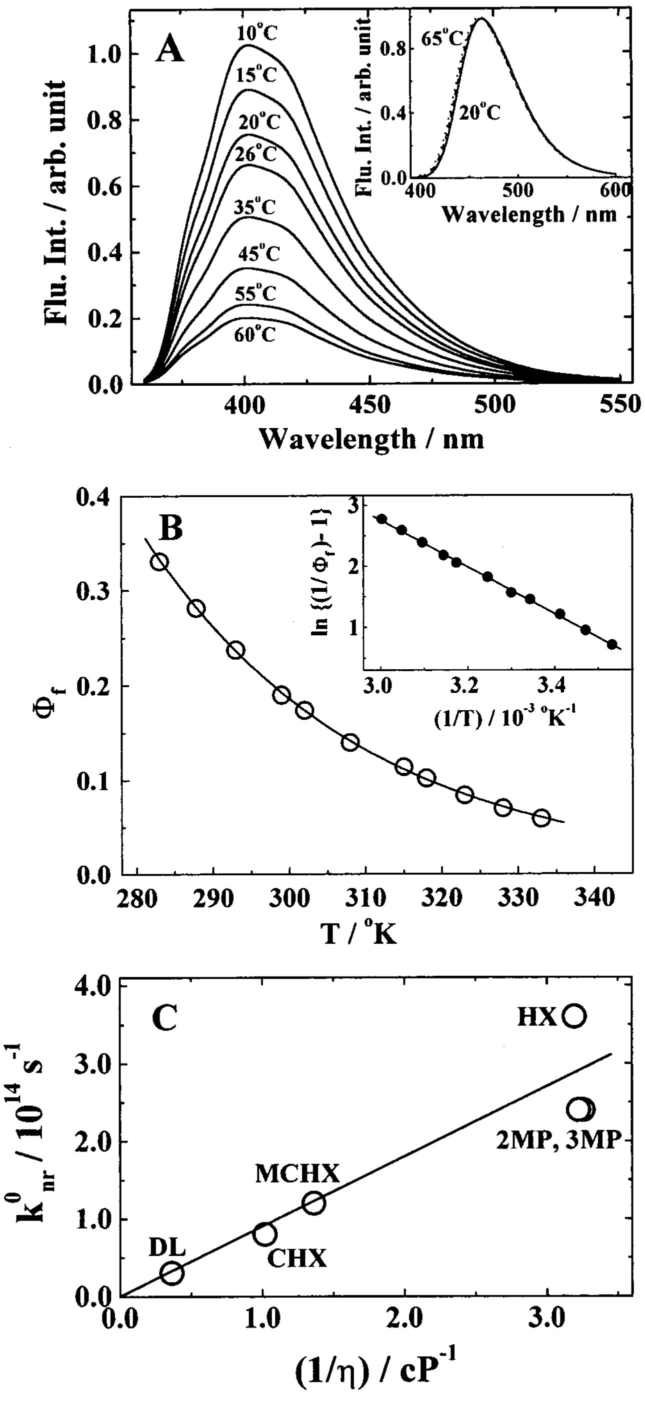


Figure 6. (A) Temperature effect on the steady-state fluorescence spectra of C151 in hexane. Fluorescence intensity reduces drastically on increasing the temperature of the solution. Inset: Temperature effect on the steady-state fluorescence spectra of C151 in acetonitrile. There is hardly any change in the fluorescence intensity with temperature. (B) Variations in the fluorescence quantum yields (Φ_f) of C151 in hexane solution with the absolute temperature (T). Inset: Plot of ln $\{(1/\Phi_f) - 1\}$ vs $1/T$ in the same solvent. As expected from eq 6, the plot is linear within experimental error. (C) Plot of k^0_{nr} (cf. eq 6) vs the inverse of the solvent viscosities (η) for C151 in NP solvents. The solvent abbreviations are as given in the foot note of Table 1.

of moderate to higher polarities (cf. Table 2), we assume that in these solvents the k_{nr} is mostly activation-controlled. Thus, the temperature dependence of Φ_f in NP solvents can be expressed in the following form (eq 6) of Arrhenius-type[38] expression:

$$\frac{1}{\Phi_f} = 1 + \frac{k_{nr}}{k_f} = 1 + \left(\frac{1}{k_f}\right) k_{nr}^0 \exp\left(\frac{-\Delta E}{RT}\right) \qquad (6)$$

where k_{nr}^0 is the preexponential factor and ΔE is the activation energy. According to eq 6, a plot of $\ln\{(1/\Phi_f) - 1\}$ versus $1/T$ should yield a straight line. A typical plot for C151 in HX is shown in the inset of Figure 6B. It is seen that the plot is linear within the experimental error. Similar linear plots were also obtained for the other NP solvents. The ΔE values for different NP solvents were estimated from the slopes of these plots and are listed in Table 3. It is seen that for all the NP solvents, the ΔE values are more or less in the similar range. The k_{nr}^0 values for different NP solvents were estimated from the intercept of the $\ln\{(1/\Phi_f) - 1\}$ versus $1/T$ plots and using the average k_f values for the respective solvents (cf. Table 2). The k_{nr}^0 values thus estimated for different NP solvents are listed in Table 3. It is seen that the k_{nr}^0 values are quite solvent-dependent, having a maximum value for HX and a minimum value for DL. Table 3 also lists the viscosities (η) of the NP solvents at 20 °C.[18] A comparison of the k_{nr}^0 values with the η values of the solvents indicates that the two are inversely related to each other. Figure 6C shows the plot of k_{nr}^0 versus $1/\eta$ for the NP solvents investigated. It is seen that even with large fluctuations, especially for HX, 2MP, and 3MP, the plot seems to be linear. Such an observation indicates that the collision between the solute and solvent molecules causes the former to cross over the activation barrier during the nonradiative deactivation of the S_1 state.

Contrary to the NP solvents, in other solvents of moderate to higher polarities, the SS fluorescence intensities are seen to be more or less temperature-independent. Typical SS fluorescence results thus obtained for C151 in ACN solution are shown in the inset of Figure 6A. Similar results were also obtained for the other moderate to higher polarity solvents investigated. These results thus indicate that there is no activation-controlled deexcitation channel for the S_1 state of C151 in these solvents.

3.5. Temperature Effect on the Fluorescence Decays. The fluorescence decays of C151 in NP solvents are seen to be strongly temperature-dependent. Thus, as the temperature is increased, the fluorescence decay gradually becomes faster. Following biexponential analysis, it is seen that as the temperature is increased, both short-lifetime (τ_1) and long-lifetime (τ_2) components gradually become shorter. The temperature effect on τ_1, however, is seen to be much more dominant than that on τ_2. Further, it is seen that as the temperature is increased, the percentage contribution a_1 for the short-lifetime component gradually increases. For solvents such as HX, 2MP, and 3MP, it is in fact seen that at very high temperature (≥60 °C), a_1 approaches almost 100%, making the fluorescence decays close to single-exponential. Similarly, at very low temperature (≤−50 °C), the percentage contribution a_2 for the long-lifetime component is almost 100%, and thus, the fluorescence decays are again effectively single-exponential. For other NP solvents, the highest and lowest temperatures attained were not sufficient enough to get either a_1 or a_2 close to 100%. However, the observed trend indicates that at sufficiently high and low temperatures, the fluorescence decays of C151 would have been effectively single-exponential even in CHX, MCHX, and DL. Figure 7A shows the effect of temperature on τ_1 and τ_2 in HX. The inset of Figure 7A shows the variations of a_1 and a_2 with temperature in the same solvent.

TABLE 3: Arhenious Parameters Obtained for C151 in Different NP Solvents

solvents[a]	η (20 °C)/cP	ΔE/kcal mol^{-1}	$k_{nr}^0/10^{14}$ s^{-1}
3MP	0.307	7.4	2.4
2MP	0.310	7.3	2.3
HX	0.313	7.7	3.6
MCHX	0.734	7.2	1.2
CHX	0.98	6.8	0.8
DL	2.75	6.8	0.3

[a] Abbreviations for the solvents are as given in the footnote of Table 1.

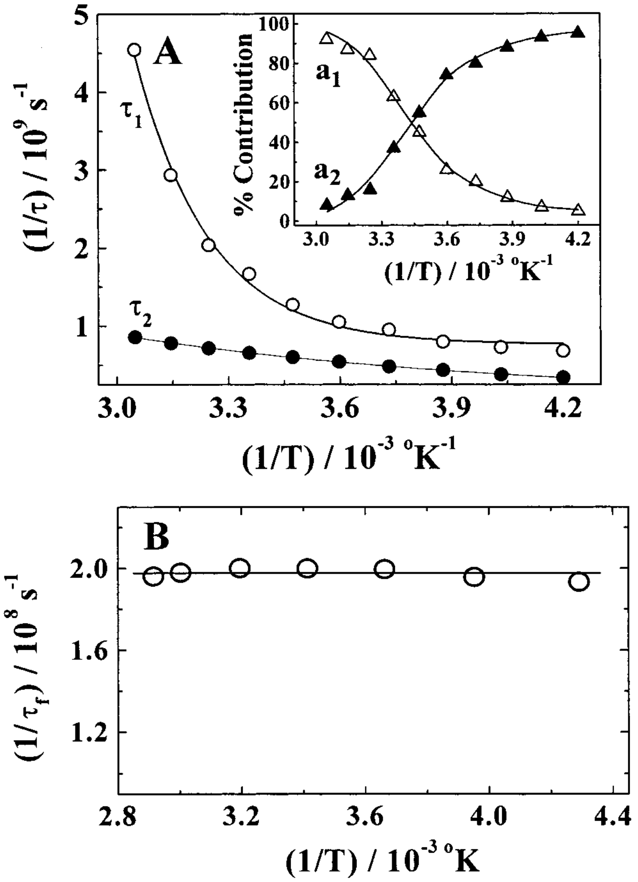


Figure 7. (A) Plot of the inverse of short (τ_1) and long (τ_2) fluorescence lifetime components of C151 in hexane against the inverse of absolute temperature (T). Inset: Variations in the percentage contributions for τ_1 and τ_2 (a_1 and a_2, respectively) against $1/T$ in the same solvent. (B) Plot of the inverse of the fluorescence lifetime (τ_f) of C151 in acetonitrile against $1/T$. τ_f is seen to be temperature-independent in this solvent.

Excluding the NP solvents, in all other solvents the fluorescence decays are seen to be always single-exponential and temperature-independent. Typical results obtained in ACN solution at different temperatures are shown in Figure 7B. In section 3.4, we have seen that the Φ_f values in moderate to higher polarity solvents are also temperature-independent. It is thus clearly indicate that in moderate to higher polarity solvents, there is no activation-controlled deexcitation channel for the S_1 state of C151. The fact that in NP solvents the nonradiative process is strongly activation-controlled where as in other solvents there is no activation-controlled deexcitation channel indicates that the S_1 state of the dye in the two sets of solvents must be structurally different.

3.6. Triplet-State Characteristics of C151. With the unusual observations made in the S_1-state characteristics of C151 in NP solvents, it is of utmost importance to investigate the triplet-state characteristics of the dye to understand if the nonradiative deactivation process is related to the triplet-state formation. This is especially important in relation to the report of Rechthaler and Köhler,[17] where they suggest from their AM1/CI calculations that in coumarins such as C151 and C120, the S_1 state is very close in energy to a triplet state (T_n) and thus a fast ISC process is likely to cause a drastic reduction in the Φ_f values of these dyes. To verify this, we investigated the triplet-state characteristics of C151 using both picosecond laser flash photolysis (LFP) and pulse radiolysis (PR) techniques. To the best of our knowledge, the triplet-state characteristics of C151 are not reported in the literature.

3.6.1. Picosecond Laser Flash Photolysis Studies. Picosecond LFP of C151 was carried out in solvents of different polarities. In none of the solvents could we observe any detectable transient absorptions in the available spectral range (~440−900 nm) and time delays (0−6000 ps) of our spectrometer. At short time delays, however, some negative absorptions are seen in the 450−550 nm region, which are quite strong and relatively long-lived in solvents other than the NP ones. We attribute these negative absorptions to the stimulated emissions, as the SS fluorescence spectra of C151 appear in this spectral region.

From the LFP results, it is evident that the S_1 state of C151 does not have any detectable absorption band in the 440−900 nm region. With the experimental conditions used in the present studies, the transients having molar extinction coefficients greater than about 500 $dm^3\ mol^{-1}\ cm^{-1}$ should have been detected. Regarding the T_1 state, however, the absence of transient absorptions in the LFP experiments indicates two possibilities. The first possibility could be that the T_1 state of C151 does not have any detectable absorption band in the 440−900 nm region. The second possibility could be that the ISC rate for the S_1 state of C151 is so low that there is hardly any triplet formation. It is usually seen that the ISC process of an excited molecule is temperature-dependent.[24,25,33,34] The fact that the Φ_f and τ_f values of C151 in moderate to higher polarity solvents are temperature-independent indicates that there could be hardly any ISC process in these solvents and the observed k_{nr} could be mainly due to the IC. For a large number of coumarin dyes, it is in fact reported that the nonradiative deactivation channel for their S_1 states are solely due to the IC process.[8,9,39−41]

In NP solvents, since Φ_f and τ_f values are strongly temperature-dependent, it is difficult to conclude whether IC or ISC is responsible for large k_{nr}. Following Rechthaler and Köhler,[17] if large k_{nr} values in NP solvents were due to the ISC process, the quantum yield for the triplet-state formation (Φ_T) would be expected to be quite high. Thus, from LFP results one should infer from Rechthaler and Köhler[17] that the T_1 state of C151 does not have any detectable absorption band in the 440−900 nm region. To verify this, we carried out the pulse radiolysis experiments of C151 in a suitable solvent to obtain the authentic absorption spectrum for the T_1 state of C151.

3.6.2. Pulse Radiolysis Studies. PR experiments were carried out in benzene (BZ) solutions using 50 ns, 7 MeV electron pulses for sample irradiation. On the PR of liquid BZ, the triplet state of BZ is formed in a good yield (G value, ~4.2),[42] via the following sequence of reactions:[42]

$$\mathrm{BZ} \overset{\text{Irradiation}}{\rightsquigarrow} \mathrm{BZ}^{**}, (\mathrm{BZ}^{+} + \mathrm{e}^{-}) \qquad (7)$$

$$(\mathrm{BZ}^{+} + \mathrm{e}^{-}) \xrightarrow{\text{Ion Recombination}} \mathrm{BZ}^{**} \qquad (8)$$

$$\mathrm{BZ}^{**} \xrightarrow{\text{IC}} {}^{1}\mathrm{BZ}^{*} \qquad (9)$$

$$^{1}\mathrm{BZ}^{*} \xrightarrow{\text{ICS}} {}^{3}\mathrm{BZ}^{*} \qquad (10)$$

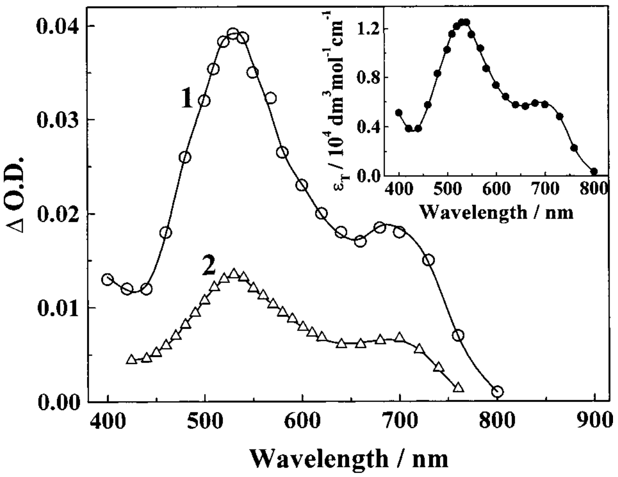


Figure 8. Observed transient absorption spectra for the triplet state of C151 in benzene solutions, as obtained in the pulse radiolysis experiments. The spectra correspond to the solutions in benzene containing (1) 0.05 mol dm^{-3} of benzophenone and 2×10^{-3} mol dm^{-3} of C151 and (2) 0.005 mol dm^{-3} of C151 only. Inset: True absorption spectrum of the triplet state of C151 in BZ, as obtained by correcting the spectrum 1 in Figure 8 using eq 12.

where BZ**, ^{1}BZ*, and ^{3}BZ* represent the higher excited, S_1, and T_1 states of BZ, respectively. The ^{3}BZ* thus formed can sensitize the T_1 state of the solute (S) present in the solution via the triplet−triplet energy transfer (TTET) mechanism[43]

$$^{3}\mathrm{BZ}^{*} + \mathrm{S} \xrightarrow{\text{TTET}} \mathrm{BZ} + {}^{3}\mathrm{S}^{*} \qquad (11)$$

However, since the lifetime of ^{3}BZ* is very short ($\tau_T \approx 3.4$ ns)[44] and the maximum solubility of C151 in BZ is also quite low (~0.005 mol dm^{-3}), even with the saturated solution of the dye, the production of its T_1 state (^{3}C151*) was not that appreciable. In the present work, we thus used a high concentration of benzophenone (BP) to convert ^{3}BZ* efficiently to ^{3}BP* in the first step. The ^{3}BP* thus formed was then used in situ to convert C151 to ^{3}C151*. Since the τ_T of ^{3}BP* is quite long (~3.5 μs),[45] it was possible to convert ^{3}BP* to ^{3}C151* almost quantitatively, even on using a dye concentration as low as about 2×10^{-3} mol dm^{-3}.

The triplet−triplet absorption spectra for ^{3}C151* were obtained following the PR of 0.05 mol dm^{-3} of BP and 2×10^{-3} mol dm^{-3} of C151 in BZ solution. The typical transient absorption spectrum thus obtained at about 90 μs after the electron pulse, a time delay in which the formation of ^{3}C151* is completed, is shown as spectrum 1 in Figure 8. It is seen from this figure that ^{3}C151* has a very strong absorption band in the 450−750 nm region, with an absorption peak at about 530 nm. To confirm this further, we also recorded the transient absorption spectra in a saturated solution of C151 in BZ in absence of BP. Though the ODs were smaller, the spectra thus obtained (cf. spectrum 2 in Figure 8) seem to be very similar to those obtained in the presence of BP. The absorption spectra of ^{3}C151* were also verified using other triplet sensitizers such as naphthalene and pyrene. The ^{3}C151* was seen to decay following first-order kinetics with the decay rate constant of $k_T \approx 8 \times 10^4\ s^{-1}$.

The molar extinction coefficients (ϵ_T) for ^{3}C151* absorptions were estimated in the following way. PR experiment was first carried out with only 0.1 mol dm^{-3} of BP in BZ. The maximum OD for ^{3}BP* thus formed was noted at 525 nm (λ_{abs}^{max}; ϵ_T = 6000 $dm^3\ mol^{-1}\ cm^{-1}$).[45] The second set of experiments were carried out with 0.1 mol dm^{-3} of BP and varying concentrations of C151. It was seen that the maximum OD at 530 nm for ^{3}C151* gets saturated with a C151 concentration of about 2 × 10^{-3} mol dm^{-3}. Above this concentration of C151, it was assumed that all the ^{3}BP* is quantitatively converted to ^{3}C151*. Thus, the ϵ_T for ^{3}C151* at 530 nm was estimated to be $\epsilon_T(530) = 1.25 \times 10^4$ dm^3 mol^{-1} cm^{-1}.

The true absorption spectrum of ^{3}C151* was obtained by correcting transient absorption spectrum 1 in Figure 8 following eq 12

$$\epsilon_T(\lambda) = \epsilon_g(\lambda) + \frac{\Delta OD(\lambda)}{\Delta OD(530)} \times \epsilon_T(530) \qquad (12)$$

where $\epsilon_T(\lambda)$ and $\epsilon_g(\lambda)$ are the respective molar extinction coefficients for ^{3}C151* and the C151 ground state at wavelength λ and ΔOD(λ) and ΔOD(530) are the transient ODs at λ and 530 nm, respectively. The true absorption spectrum for ^{3}C151* thus obtained is shown in the inset of Figure 8. It is indicated from this figure that ^{3}C151* has a strong absorption band in the 450−750 nm region.

The triplet-state energy (E_T) of C151 was also estimated using TTET method.[43−46] It was seen that where the triplet states of BP (E_T = 69 kcal mol^{-1}),[46] biphenyl (E_T = 65 kcal mol^{-1}),[46] naphthalene (E_T = 61 kcal mol^{-1}),[46] and pyrene (E_T = 49 kcal mol^{-1})[46] can efficiently sensitize the triplet state of C151, the latter cannot be sensitized by using the triplet states of anthracene (E_T = 42 kcal mol^{-1})[46] and C$_{60}$ (E_T = 36 kcal mol^{-1}).[46] It was seen, however, that ^{3}C151* can efficiently sensitize the triplet states of anthracene and C$_{60}$. From these results, it is inferred that the E_T value of C151 is in the range of 42−49 kcal mol^{-1}.

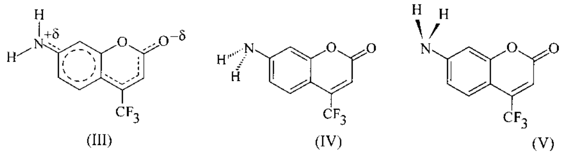
4. Discussion

From the Φ_f and τ_f measurements, it is indicated that the S$_1$ state of C151 undergoes very fast nonradiative deactivation in NP solvents. Though Rechthaler and Köhler[17] suggested the involvement of the ISC process for the fast nonradiative deactivation of the S$_1$ state of C151 in NP solvents, the present picosecond laser flash photolysis and pulse radiolysis results completely disagree with such a mechanism.

Excluding the ISC process, the other possible mechanisms for the fast nonradiative deactivation channel for the S$_1$ state of C151 could be visualized with respect to the flexibility of the 7-NH$_2$ group. In this regard, the commonly discussed mechanism is the involvement of the highly polar twisted intramolecular charge transfer (TICT) state.[47−52] Such a mechanism, however, is very unlikely in NP solvents, where the TICT structure will hardly have any solvent stabilization. Further, if a TICT mechanism were operative, it would be expected that the Φ_f and τ_f values in polar solvents would have been much more reduced than those in NP solvents. The experimental results are just opposite to these expectations and thus exclude the possibility of the TICT mechanism.

The TICT mechanism in the present systems is also excluded from the following considerations. For 7-aminocoumarins, the possibility of the TICT state formation is largely determined by the electron-donating power of the 7-amino group. Since the NH$_2$ group is a much weaker electron donor than the N-alkyl amino and *N,N*-dialkyl amino groups, it is expected that the coumarin dyes with 7-substituted amino groups should have a better possibility for the TICT state formation than in the case of C151. Thus, considering the TICT mechanism, the nonradiative deactivation process for the S$_1$ state was expected to be much faster for the coumarin dyes having 7-substituted amino groups than observed for C151. It is seen, however, that on substituting just one of the 7-NH$_2$ group hydrogens of C151 by an alkyl group, e.g., coumarin-500 (C500; 7-*N*-ethylamino-4-trifluoromethyl-1,2-benzopyrone), the unusual behavior in NP solvents completely disappears.[53] These results thus indicate that the TICT mechanism is not responsible for the unusual photophysical behavior of C151 in NP solvents.

CHART 2



From the solvent polarity effect on the Stokes' shifts in moderate to higher polarity solvents, it is clearly indicated that the S$_1$ state of C151 is of ICT character ($\mu_e \approx$ 7.3 D). From the structural point of view, the ICT state is expected to have a planar configuration with the N−Φ bond acquiring a substantial double-bond character, as shown by structure III in Chart 2. In this configuration, since the amino group is quite rigidly bound to the benzopyrone moiety, there is hardly any flexibility for this group. Thus, in the ICT structure, it is expected that the nonradiative deactivation process will be quite slow, resulting in high Φ_f and τ_f values for the dye.

In NP solvents, since no specific solute−solvent interaction is expected, the unusual blue shift in the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ values (cf. Figure 2) and the exceptionally lower $\Delta\bar{\nu}$ values (cf. Figure 3) indicate that the S$_1$ state of C151 must exist in a nonpolar structure in these solvents. It is thus logical to think that in NP solvents the 7-NH$_2$ group of C151 might remain as a free substituent without participating in resonance with the benzopyrone moiety. Thus, two equivalent nonplanar structures, IV and V in Chart 2, can be assigned to the S$_1$ state of C151 in NP solvents. In these structures, since the NH$_2$ nitrogen is bonded to the benzopyrone moiety by a single bond, the group is very flexible. It is thus expected that the excited dye molecules can dissipate their excess energy very fast to the solvent bath in a nonradiative way through the flip-flop motion of the NH$_2$ group.[54−57] The fact that the fluorescence decays of C151 in NP solvents are non-single-exponential indicates that structures IV and V must interconvert to each other via a large number of intermediate configurations. At very high temperature, the flip-flop motion of the NH$_2$ group is so fast that all the configurations exist in equilibrium, making the effective fluorescence decay single-exponential. At very low temperature, the nonradiative deactivation rate becomes so slow that the fluorescence decays are mostly dominated by k_f, making the decay effectively single-exponential.

Involvement of the planar structure III or the nonplanar structures IV and V are also expected in the ground state of the dye, depending on the solvent polarities. It is expected that in NP solvents, structures IV and V will have energies lower than those of the planar structure III even in the ground state. Thus, in NP solvents, since both ground and excited states of C151 are nonpolar with no resonance between the NH$_2$ group and the benzopyrone moiety, the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ appear at much higher energies compared to those in other solvents of moderate to higher polarities. For the same reason, the $\Delta\bar{\nu}$ values in NP solvents are expected to be much smaller compared to those in other solvents. Since both the ground and excited states of C151 are of ICT character in moderate to higher polarity solvents, the $\bar{\nu}_{abs}$ and $\bar{\nu}_{fl}$ undergo substantial red shift with solvent polarity.

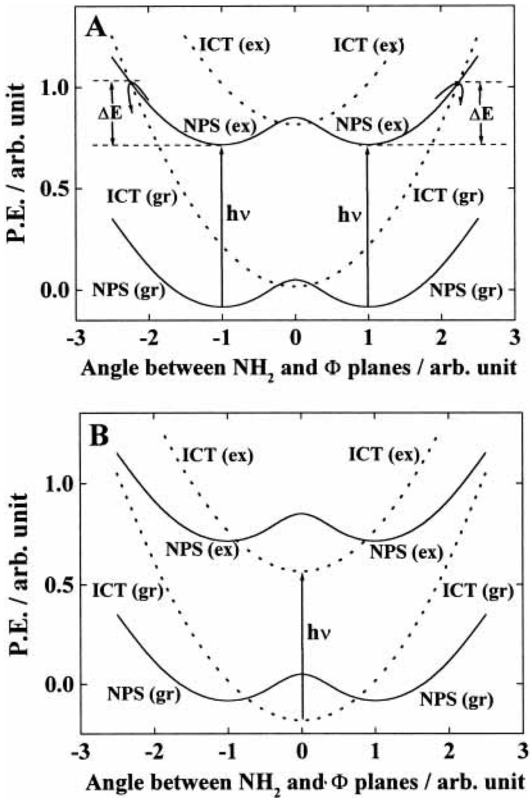


Figure 9. Conceptual potential energy (PE) diagrams for the ground (S_0) and excited (S_1) states of C151 in (A) nonpolar and (B) polar solvents. NPS(gr) and NPS(ex) represent the nonplanar structures, and ICT(gr) and ICT(ex) represent the planar intramolecular charge-transfer structures in the ground and excited states, respectively. Arrows with hν indicate the electronic transitions involved in the two cases of nonpolar and polar solvents. In case of the nonpolar solvent, there is a crossing between the PE surfaces for the NPS(ex) and the ICT(gr) states. Thus, the NPS(ex) state can undergo an activation-controlled fast-deexcitation process through this crossing point, as indicated by curved arrows.

Further, since μ_e is of much higher magnitude than μ_g in the ICT structure, the $\Delta\bar{\nu}$ gradually increases with increasing solvent polarity. Present results clearly indicate that the photophysical behavior of the dye C151 in NP solvents is drastically different than those in moderate to higher polarity solvents.

The behavior of C151 in NP and other solvents can qualitatively be understood considering the potential energy (PE) diagrams shown in Figure 9. In NP solvents, the nonplanar structures (NPS) are the lowest-energy states, whereas in other solvents of moderate to higher polarities, the ICT structure becomes the lowest-energy configuration for both ground and excited states. Following Figure 9, it is expected that in NP solvents there is a crossing in the PE surfaces of the ground-state planar ICT structure and the excited-state NPS. Thus, the excited state of C151 can undergo an activation-controlled deexcitation to the ground state through these crossing points, resulting in a large reduction in the Φ_f and τ_f values in NP solvents. In moderate to higher polarity solvents, there is no such crossing among the PE surfaces, and thus, there is no activation-controlled deexcitation channel. Figure 9 also indicates that the ΔE for the nonradiative deexcitation channel in NP solvents would be more or less similar for all the solvents, as experimentally observed. Since k_{nr}^{0} is a measure of frequency of the collisions between the solute and the solvent molecules, it must be inversely related to the solvent viscosity. This has been found to be so from the temperature-dependent fluorescence studies.

5. Conclusions

The photophysical properties of coumarin-151 (C151) is seen to be very unusual in nonpolar (NP) solvents compared to those in other solvents of moderate to higher polarities. The unusually low fluorescence quantum yields (Φ_f) and fluorescence lifetimes (τ_f) in NP solvents indicate the presence of a fast nonradiative deactivation channel for the S_1 state of the dye in these solvents. Involvement of the ISC process for these fast nonradiative deactivations in NP solvents, as suggested by Rechthaler and Köhler,[17] have been disproved in the present study from the picosecond laser flash photolysis and pulse radiolysis results. Comparing the absorption and fluorescence maxima and Stokes' shifts in different solvents, it has been inferred that in moderate to higher polarity solvents, the dye exists in a planar ICT configuration, whereas in NP solvents the dye exists in nonplanar configurations with its 7-NH_2 group not participating in resonance with the benzopyrone moiety. Since in the nonplanar configurations the NH_2 group is very flexible, it can undergo flip-flop motions and thereby couple to the solvent modes to efficiently deactivate the excited state in NP solvents. In other solvents, due to the ICT structure, the flexibility of the 7-NH_2 group is strongly restricted, and thus, the Φ_f and τ_f values are very high and also independent of temperature. Since the nature of the states involved in the electronic transitions are different in NP and other solvents, the $\bar{\nu}_{\mathrm{abs}}$, $\bar{\nu}_{\mathrm{fl}}$, and $\Delta\bar{\nu}$ values in the former solvents do not correlate with those in the other solvents. It has been understood that the unusual behavior of C151 in NP solvents arises simply due to the presence of the 7-NH_2 group, which is only weakly electron donating in nature. If just one of the 7-NH_2 hydrogens of C151 is substituted by an alkyl group, e.g., C500 (7-*N*-ethylamino-4-trifluoromethyl-1,2-benzopyrone), the electron-donating power of the amino group increases quite reasonably, causing the ICT structure to become the lowest-energy configuration even in the NP solvents.[53] Thus, no unusual behavior is seen for C500 in its photophysical properties.[53] A drastic changeover from the nonpolar to polar ICT configuration for the dye C151 on just marginal increase in the solvent polarities from the so-called NP ones is a very novel observation. To the best of our knowledge, such a drastic and unusual behavior has not been observed for any other class of organic molecules.

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