

GROUND- AND EXCITED-STATE PROPERTIES OF SOME 3,4-DIHYDRO-1-(2-*p*-SUBSTITUTED BENZYLIDENE)NAPHTHALENONES: SUBSTITUENT AND ENVIRONMENTAL EFFECTS

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Electronic absorption and steady-state fluorescence emission of seven 3,4-dihydro-1-(2-*p*-substituted benzylidene)naphthalenones (1–7) show sizable solvent dependence. The charge-transfer (CT) absorption maxima of these compounds in various solvents show a red shift for the electron-donating substituted compounds (1–5), whereas a blue shift is observed for compounds possessing electron-withdrawing substituents (6, 7). Excitation into the lowest energy absorption gives emission from the locally excited state, which relaxes to the emitting intramolecular charge-transfer state for compounds with strong electron-donating substituents (1–3) in hydroxylic solvents. However, in moderately polar solvents, dual emissions are observed for these compounds. No CT emission is observed for the compounds with moderate electron-donating substituents (3 and 4) or those with electron-withdrawing substituents (6 and 7). Compound 1 with an $-\text{N}(\text{CH}_3)_2$ substituent shows an excited-state dipole moment of 17 D. © 1997 John Wiley & Sons, Ltd.

J. Phys. Org. Chem. **10**, 687–696 (1997) No. of Figures: 9 No. of Tables: 3 No. of References: 38

Keywords: absorption; fluorescence; solvatochromism; hydrogen bonding; dipole moment; naphthalenones

Received 20 January 1997; revised 24 February 1997; accepted 15 March 1997

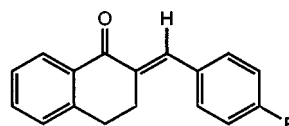
INTRODUCTION

In the past 30 years, there has been increasing interest in donor- and acceptor-containing compounds that are capable of initiating intramolecular charge-transfer (ICT) processes. Earlier studies focused on systems where conformational folding brings the donor and acceptor moieties into a parallel plane within the through-space interaction distance.^{1–3} Investigations were also focused on systems in which donor and acceptor groups are directly connected through a single bond.^{4–6} The dual fluorescence of dimethylaminobenzonitrile (DMABN) in polar solvents, discovered by Lippert *et al.*,⁷ which was attributed to a twisted intramolecular charge transfer (TICT) state,⁸ led to extensive research to explore this phenomenon in other molecules.^{9–16} Systems possessing electron donor–acceptor fragments of the type D–B–A are widely used as candidates for studying photoinduced electron transfer, where B is a rigid or a flexible bridge.^{17–21}

Much of the work on charge transfer (CT) in organic systems has been chiefly motivated by the search for organic materials with potential applications as fluorescent and laser dyes,^{22–24} optical recording media,²⁵ molecular switching devices^{26, 27} and non-linear optical materials,²⁸ or by the desire to elucidate the mechanism of electron transfer

in molecular or bimolecular systems.²⁹

In this work, a series of seven structurally related 3,4-dihydro-1-(2-*p*-substituted benzylidene)naphthalenones (Scheme 1, 1–7) were synthesized and characterized by IR and ¹H NMR spectroscopic methods. The photophysical behaviour of these compounds in various non-polar and polar solvents at room temperature, was investigated. The influence of the dielectric properties and hydrogen bonding of both the substituents and solvents on the photophysics of these compounds was closely examined.



R = $\text{N}(\text{CH}_3)_2$ (1), R = OH (2), R = OCH_3 (3)

R = CH_3 (4), R = H (5), R = Br (6)

R = NO_2 (7)

Scheme 1

* Correspondence to: I. A. Z. Al-Ansari.

EXPERIMENTAL

Materials and methods of characterization of compounds 1–7. Compounds 1–7 were prepared by regular condensation, α -tetralone being treated with NaOH solution and then reacted with the corresponding *para*-substituted aldehydes under reflux in ethanol for 2 h. The products were collected in each case and purified by recrystallization twice from a minimum volume of methanol–water (1:1). The yields were 80–90%.

3,4-Dihydro-1-(2-*p*-*N,N*-dimethylaminobenzylidene)naphthalenone (**1**): orange crystalline solid, m.p. 145–147 °C; ^1H NMR (DMSO- d_6), δ (ppm) 2.507–2.789 (m, 2H, CH₂), 2.979 [s, 6H, N(CH₃)₂], 7.315–7.965 (aromatic).

3,4-Dihydro-1-(2-*p*-hydroxybenzylidene)naphthalenone (**2**): dark-brown crystalline solid, m.p. 203–205 °C; ^1H NMR (DMSO- d_6), δ (ppm) 2.498–2.532 (m, 2H, CH₂), 2.936–3.039 (m, 2H, CH₂), 7.324–8.071 (aromatic), 9.963 (s, 1H, OH).

3,4-Dihydro-1-(2-*p*-methoxybenzylidene)naphthalenone (**3**): yellow crystalline solid, m.p. 10–109 °C; ^1H NMR (DMSO- d_6), δ (ppm) 2.503–2.934 (m, 2H, CH₂), 2.972–3.086 (m, 2H, CH₂), 3.816 (s, 3H, OCH₃), 6.986–7.997 (aromatic).

3,4-Dihydro-1-(2-*p*-methylbenzylidene)naphthalenone (**4**): yellow crystalline solid, m.p. 119–120 °C; ^1H NMR (DMSO- d_6), δ (ppm) 2.377 (s, 1H, CH₃), 2.914–2.974 (m, 2H, CH₂), 3.068–3.118 (m, 2H, CH₂), 7.174–8.169 (aromatic).

3,4-Dihydro-1-(2-benzylidene)naphthalenone (**5**): yellow crystalline solid, m.p. 103–105 °C; ^1H NMR (DMSO- d_6), δ (ppm) 2.502–2.533 (m, 2H, CH₂), 2.996–3.039 (m, 2H, CH₂), 7.326–8.020 (aromatic).

3,4-Dihydro-1-(2-*p*-bromobenzylidene)naphthalenone (**6**): yellow crystalline solid, m.p. 153–154 °C; ^1H NMR (DMSO- d_6), δ (ppm) 2.496–2.529 (m, 2H, CH₂), 2.982–3.352 (m, 2H, CH₂), 7.326–8.004 (aromatic).

3,4-Dihydro-1-(2-*p*-nitrobenzylidene)naphthalenone (**7**):

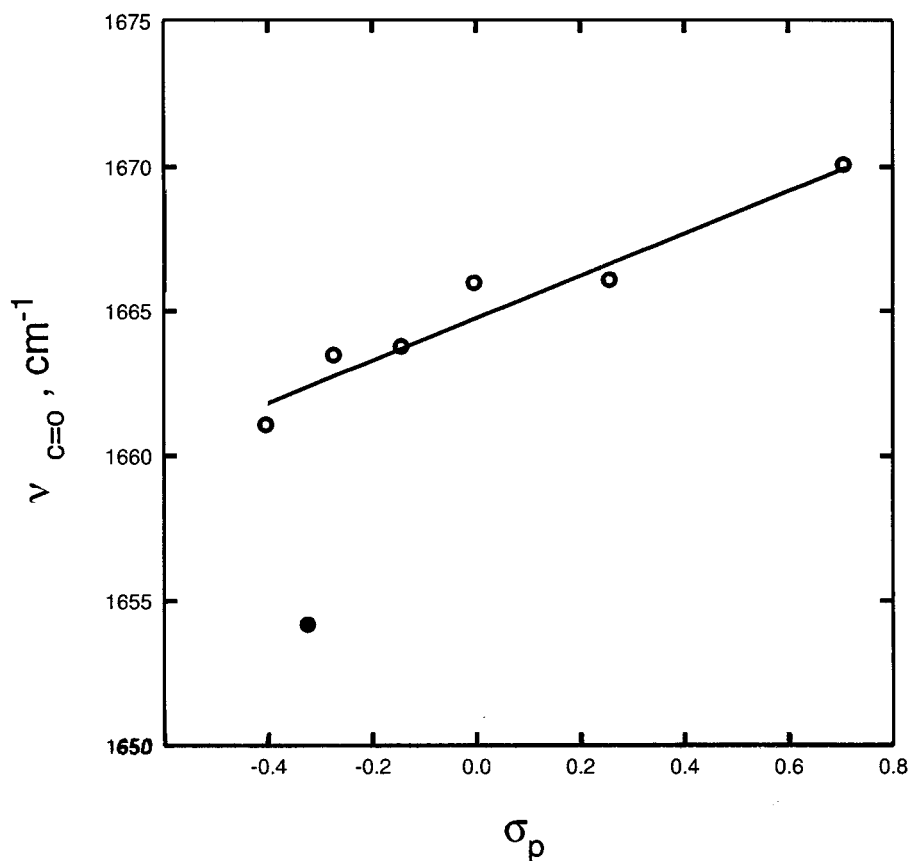


Figure 1. Plot of carbonyl vibrational frequencies ($\nu_{\text{C=O}}$) of compounds 1–7 as a function of Hammett substituent constants (σ_p). The solid line is the best fit through all frequencies except for compound **1** (filled circle)

Table 1. Ground-state properties of compounds 1–7

Compound	σ_p^a	Ionization potential (eV) ^b	$\nu_{C=O}$ (cm ⁻¹)
1	-0.32	7.12	1654
2	-0.40	8.51	1661
3	-0.27	8.21	1663
4	-0.14	8.82	1664
5	0.00	9.24	1665
6	0.26	8.98	1666
7	0.71	9.92	1670

^a Ref. 30.^b Ionization potential of substituted phenyl ring, taken from Ref. 32.

dark-pink crystalline solid, m.p. 188–190 °C; ¹H NMR (DMSO-*d*₆), δ (ppm) 2.090–2.507 (m, 2H, CH₂), 2.923–3.044 (m, 2H, CH₂), 7.358–8.337 (aromatic).

Solvents. Spectroscopy-grade *n*-hexane, diethyl ether, dichloromethane, acetonitrile dimethylformamide (DMF), ethanol, methanol, *n*-butanol, *n*-propanol and tetrahydrofuran (THF) were purchased from Fluka and used as received.

Sample preparation. Stock solutions (10⁻⁴ M) of the compounds were prepared by dissolving an accurately weighed amount of these compounds in *n*-hexane, withdrawing 1 ml and adding it to a 10 ml volumetric flask. This was then evaporated with nitrogen bubbling to leave a thin

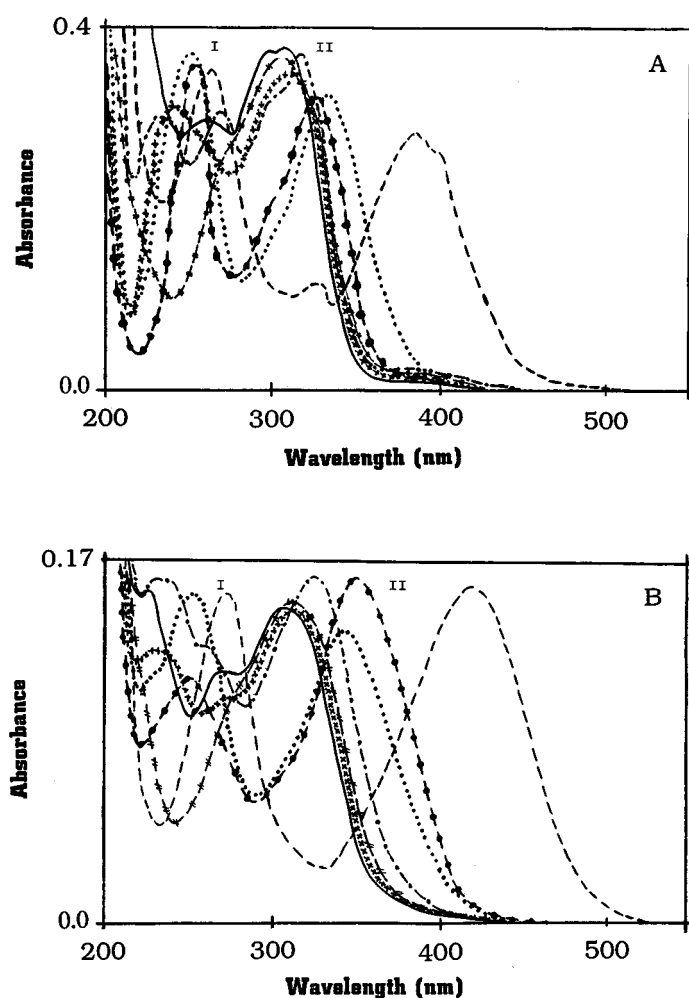
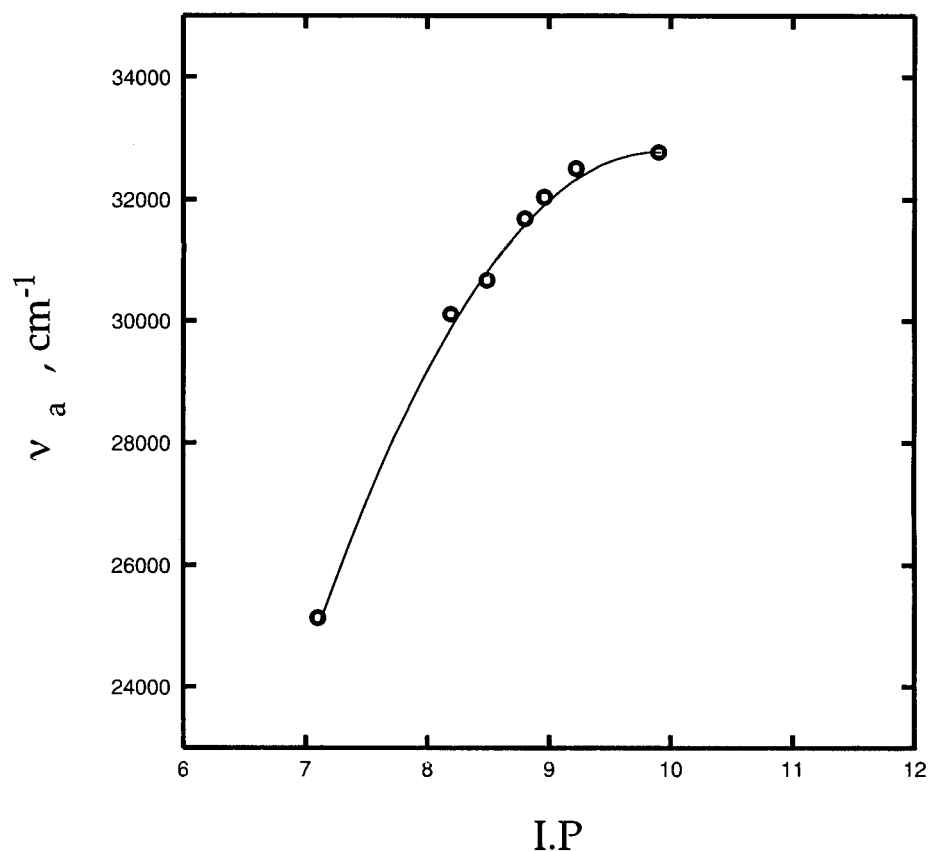


Figure 2. Absorption spectra in (A) *n*-hexane and (B) in ethanol of compounds 1 (---), 2 (●), 3 (.), 4 (-.-.-), 5 (—), 6 (×××) and 7 (###)

Table 2. Intramolecular charge-transfer absorption maxima (ν_a)^a of compounds 1–7 in various solvents

Solvent	Compound						
	1	2	3	4	5	6	7
<i>n</i> -Hexane	25·10	30·62	30·07	31·64	32·46	32·00	32·73
Diethyl ether	25·06	29·07	29·85	31·40	33·67	33·16	32·46
THF	24·70	29·10	29·58	31·00	32·15	31·74	31·84
CH ₂ Cl ₂	24·10	29·10	29·58	31·00	32·15	31·74	31·84
DMF	24·01	28·90	29·24	31·54	33·90	33·80	32·10
CH ₃ CN	24·70	29·41	29·54	30·96	33·16	31·90	31·64
Butan-1-ol	23·75	28·17	28·94	30·44	32·36	31·84	32·15
Propan-1-ol	23·78	28·73	29·07	30·72	32·00	31·74	31·84
Ethanol	23·80	28·61	29·07	30·60	32·46	32·15	32·15
Methanol	23·86	28·94	29·20	31·00	32·84	32·05	32·10
($\Delta\nu_a$) ^b	45·5	43·5	87	91	0	1000	133

^a Values in 10^{-3} cm^{-1} .^b Values in 10^{-4} cm^{-1} , $\Delta\nu_a = \nu_a(\text{ethanol}) - \nu_a(n\text{-hexane})$.Figure 3. Correlation between the charge-transfer absorption maxima (ν_a) vs ionization potential of the substituted phenyl ring (I.P)

film. The desired solvent was added and the solution was diluted to volume to give a 10^{-5} M solution.

Optical measurements. Spectra were recorded with the following spectrometers: Bruker ESP300 (260 MHz, ^1H NMR), Shimadzu UV-160 (UV-Vis) and Shimadzu RF/500 (fluorescence and excitation spectra). Chemical shifts (δ) are in parts per million relative to $(\text{CH}_3)_4\text{Si}$. Emission spectra were obtained using small angle (22.5°) front-surface excitation geometry. The excitation and emission slits were both 0.5 mm. The excitation wavelengths (λ_{exc}) were 398, 326, 332, 316, 308, 312 and 305 nm for compounds 1–7, respectively. The experiments were carried out at room temperature (24 °C) using 1 cm matched quartz cells. Fresh solutions were used for all measurements. Emissions spectra were not corrected for the spectral response of the instrument.

RESULTS AND DISCUSSION

Correlation of the carbonyl frequencies with the structure

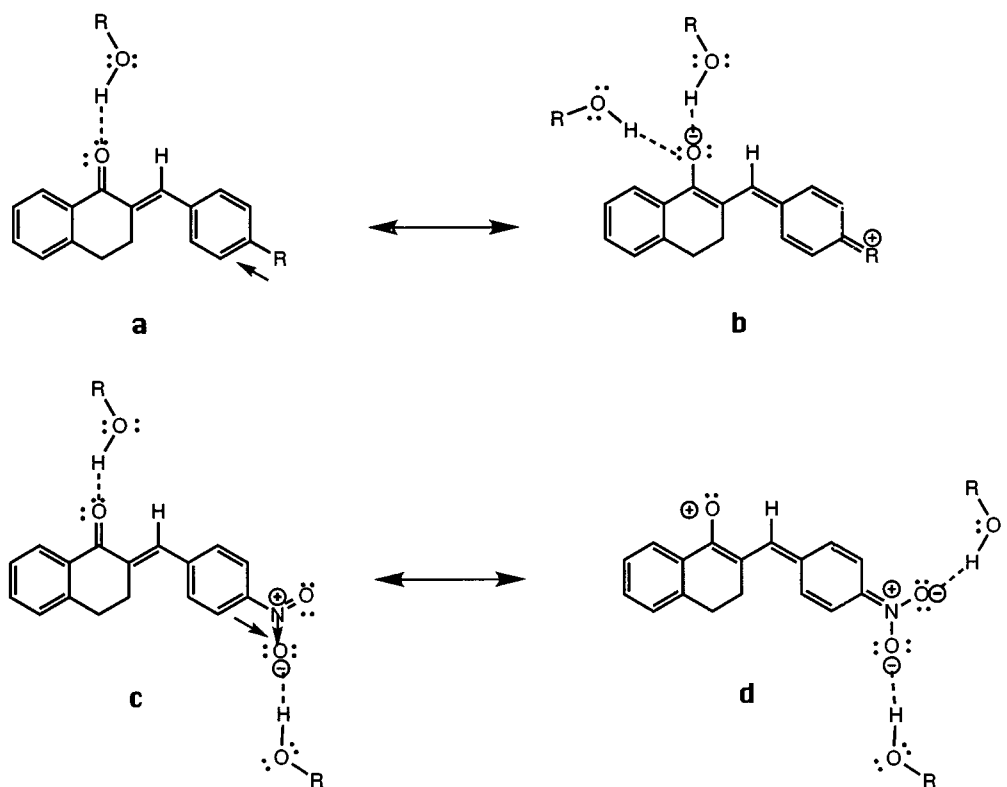
It is widely known that the Hammett equation and its modifications³⁰ [equation (1)] have been used to assess the

electronic effect of a substituent R in an aryl system on the reaction centre *para* to the reaction site:

$$\log k = \rho\sigma_R + \log k_0 \quad (1)$$

where k is the rate constant of the reaction being studied [carbonyl group vibrational frequency ($\nu_{\text{C=O}}$) in this study] with a substituent R present and k_0 is the corresponding rate constant of the unsubstituted compound (R=H).

Thus, a plot of $\nu_{\text{C=O}}$ vs Hammett substituent constant (σ_{para})³¹ gave an excellent correlation ($R^2=0.970$), excluding the value for compound 1 since it shows a very low energy for the vibrational frequency of the carbonyl group. This can be understood on the basis that this compound possesses a considerable degree of charge-transfer character originating from the *N,N*-dimethylamino lone pair and terminating at the carbonyl group, which loses its double bond character in this case. This would account for the considerable red shift in absorption in this compound with respect to the others. The experimental data and best-fit line are shown in Figure 1, and Table 1 gives the carbonyl frequencies. Our results show that from this correlation we obtain $\log k_0=1665$, which is in good agreement with the experimentally measured vibrational frequency of the carbonyl in the unsubstituted compound 5 (R=H). Further, the slope of the best-fit line gave a value of 7.35, which



Scheme 2. Molecular structure and resonance forms in hydroxylic solvents

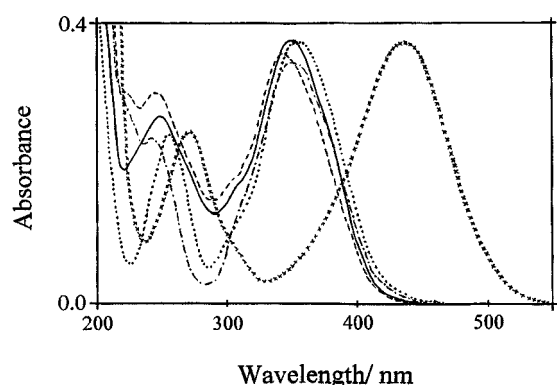


Figure 4. Absorption spectra of compound **2** in the solvents methanol (---), ethanol (—), propanol (- · - · -), butanol (·· ·) and 0.1 M NaOH (×)

corresponds to the reaction constant ρ in equation (1). This positive value indicates that the carbonyl frequencies are very sensitive to the electron-donating/withdrawing influence of the substituent attached to the phenyl moiety.

Absorption spectra

The absorption spectra of compounds **1–7** in *n*-hexane and ethanol are shown in Figure 2. Each of the spectra in these solvents and other polar protic and non-protic solvents exhibits two major broad bands.

The first band (band I) is slightly structured and located in the range 220–300 nm (Table 1), and shows moderate sensitivity both to the polarity on the solvent in each compound and to the variation of the substituent on the phenyl ring when all compounds are compared.

The second band (band II) is found in the 300–400 nm region (Table 1) and is sensitive to both solvent polarity and the substituent. This broad long-wavelength absorption band is attributed to ICT from the high-energy, occupied orbital of the substituted-phenyl donor to the low-energy, unoccupied orbital of the ketone acceptor moiety (e.g. $\pi_{\text{Ph}} \rightarrow \pi^*_{\text{C=O}}$).

Assignment of the wavelength of the absorption bands in each of these compounds to CT transition is evident from the bathochromic shift in the absorption from the non-polar to the polar solvents (see Table 2). Figure 2(A) and 2(B) show a displacement of the absorption maxima towards longer wavelength from the non-polar *n*-hexane to the protic polar ethanol. This red shift follows the order $2 > 1 > 3 > 4 > 5$. Compounds **6** and **7** show a hypsochromic shift due to the opposite direction of the charge. This order of the displacement of the CT band suggests an electronic interaction of the substituent with the electron acceptor fragment of the molecules. The order in which the wavelength of the CT absorption is affected is thus related to the ionization energy³² of the substituted phenyl ring. Figure 3 shows this relationship. The frequency shift is greater for the $-\text{N}(\text{CH}_3)_2$ substituent, in which the lone-pair participation is enhanced by the low nuclear charge on nitrogen; the shift is least for the $-\text{NO}_2$ substituent since it has a great electron-attracting capability, which is reflected in its high ionization potential.

Compounds with electron-donating substituents, **1–4**, show absorptions in polar protic solvents (alcohols) at longer wavelength (lower energy) than in polar aprotic solvents, e.g. acetonitrile (Table 2 and Figure 1). On the other hand, compounds **6** and **7**, with electron-withdrawing groups, show absorption maxima at shorter wavelength (higher energy) in hydroxylic solvents compared with aprotic solvents.

It seems that hydroxylic solvents tend to solvate the CT structure **b** (Scheme 2) which is dominant in compounds **1–3** through specific hydrogen-bonding interactions better than polar aprotic solvents. This will lower the energy of the CT state owing to additional stabilization of this state.

For compounds **6** and **7**, polar aprotic solvents stabilize structure **d** through dipole–dipole interactions, thus lowering the energy of the CT state.

Polarity effects on the CT band of compounds **1–7** depend strongly on the hydrogen bonding ability of the solvents. We noticed that the plot of the energy of the absorption maxima of compounds **1–7** against the solvent polarity parameter ($E_{\text{T}}(30)$)³³ gave good correlations only in protic solvents. We also attempted to plot the long-

Table 3. Fluorescence data (ν_{f})^a for compounds **1–7** in various solvents

Solvent	Compound						
	1	2	3	4	5	6	7
<i>n</i> -Hexane	22·22	27·70	27·17	28·41	28·10	28·10	28·10
Diethyl ether	(21·21)	26·45	27·03	26·46	26·46	26·45	26·46
THF	sh (20·16)	26·31	26·88	27·17	27·25	27·17	17·62
CH_2Cl_2	sh (19·61)	25·77 (sh)	25·91 (sh)	26·45 (21·55)	26·74 (21·83)	26·31 (21·10)	27·32 (sh)
DMF	22·12 (18·87)	25·91 (sh)	25·91 (sh)	27·17 (20·57)	27·17	27·47	27·17
CH_3CN	(18·65)	25·64 (sh)	25·91 (sh)	27·17 (20·57)	27·17	27·47	27·17
Ethanol	sh (19·38)	27·67 (22·83)	26·88 (22·73)	27·62	27·78	27·80	27·93

^a Values in 10^{-3} cm^{-1} , sh = Shoulder. The values in parentheses are from the charge-transfer state

wavelength absorption maxima against the solvatochromic parameters π^* , α and β .³⁴ We found good correlations only for compound **1**, **3** and **7** in protic and aprotic solvents with the π^* scale, which is an index of solvent dipolarity/polarizability. These findings suggest that the energy of the CT absorption bands in these compounds does not vary strongly with solvent polarity, because these compounds are polarized in the ground state.

On the other hand, the absorption maxima correlate excellently with the α -scale for compounds **1–4** in protic solvents, but moderately in aprotic solvents. The CT absorption energies, however, correlate well with the β -scale for compounds **1–3**, **5** and **7** in protic solvents, but the correlation is poor for compounds **4** and **6**. In aprotic solvents a good correlation is obtained for compound **2**, which explains the extra bathochromic shift in the absorption found for this compound in many solvents, specifically hydroxylic ones (see Table 2 and the next section).

Absorption characteristics of compound **2**

In compound **2**, both band I and band II (CT band) shift to longer wavelength with increase in the basicity³⁵ of the solvent (Figure 4). For instance, absorption maxima of band **II** are seen at 345.5, 349.5, 350 and 355 nm in methanol,

ethanol, propanol and butanol, respectively. This suggests the occurrence of a substantial increase in delocalization of charge with ionization of the hydroxyl group caused by the increase in the solvent's basicity. Thus, in hydroxylic solvents the presence of a contribution of charge from the ionized hydroxyl (conjugate base) causes extra charge transfer [compare λ_{abs} (ethanol) = 349.5 nm vs λ_{abs} (acetonitrile) = 340 nm, Table 2].

Fluorescence spectra

The fluorescence emission characteristics of compounds **1–7** were examined in various solvents of different polarity. Table 3 displays the fluorescence emission maxima (ν_f) observed upon excitation at energies corresponding to the CT absorption bands (band II), and Figure 5(A)–(G) show fluorescence spectra for compounds **1–7** in *n*-hexane and ethanol as examples.

Based on these results, compound **1** gives a broad, slightly structured band corresponding to emission from the locally excited state (LE) in non-polar solvents such as *n*-hexane, but dual bands corresponding to emission from the LE and a second lower energy, highly solvatochromic broad band in moderately polar protic and aprotic solvents [Figure

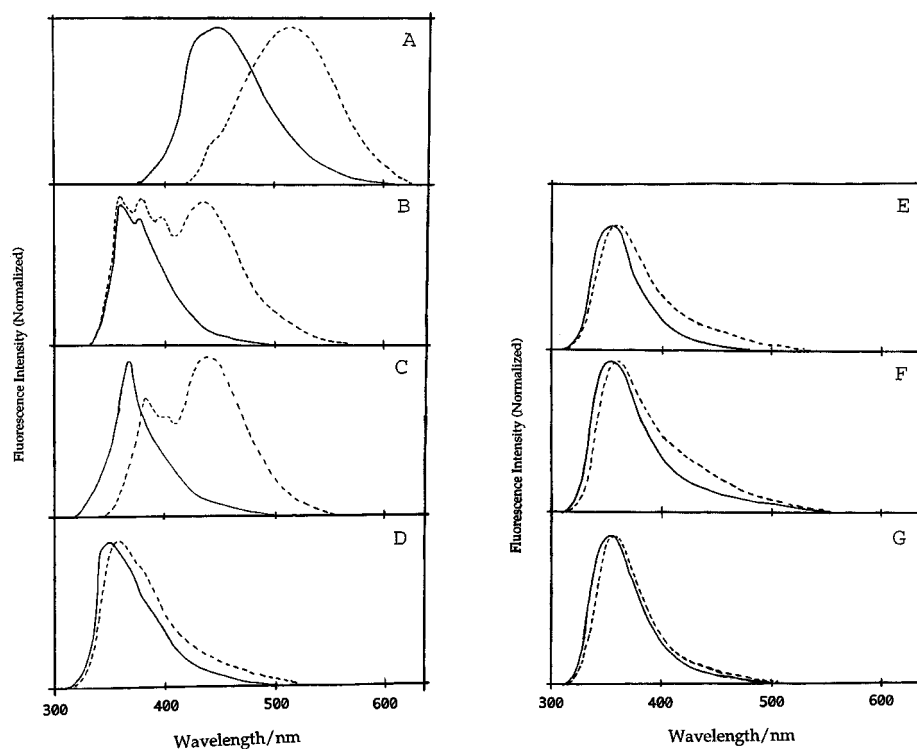


Figure 5. Fluorescence spectra in *n*-hexane (—) and ethanol (---) of compounds **1** (A), **2** (B), **3** (C), **4** (D), **5** (E), **6** (F) and **7** (G)

5(A)]. However, in highly polar solvents such as acetonitrile, only emission from the second long-wavelength band is observed. The second band is assigned as originating from the ICT.

Compounds **2** and **3**, on the other hand, show emissions from the LE state, with vibronic structure in most low and moderately polar solvents. However, in highly polar solvents, the broad CT band appears as a shoulder. The situation is different in hydroxylic solvents, where dual emission is observed for these compounds, as shown in Figure 5(B) and (C).

No CT emissions were observed for compounds **4–7** in most of the solvents studied, except in dichloromethane [Figure 5(D)–(G)]. In dichloromethane, compounds **4–6** show dual emissions but compounds **2** and **3** give emissions from the LE state and a shoulder in the region of the CT band. Compound **7**, however, gives the LE state emission along with a weak emission in the CT domain. For compound **1** only the CT band is observed in dichloromethane (Table 3).

Our measurements show that the LE state emission of compounds **4–7** in non-polar and polar solvents are structureless with a slight red shift from non-polar, e.g. *n*-hexane, to polar solvents, e.g. ethanol or acetonitrile, while a considerable red shift for compounds **1–3** and a slight red shift for compounds **4–7** are observed. The LE state bands, however, resemble those of the absorption spectra for the compounds studied.

We observed dual emission for compound **3** in acetonitrile (Table 3). The locally excited state is structured, while the CT emission is seen as broad band situated at 486 nm. However, the CT emission is only detected as a shoulder in this highly polar solvent for compounds **2** and **3**, contrary to what one would expect.

Based on these observations, it appears that compounds **1–3**, bearing strong electron-donating substituents, give CT emissions in protic solvents, due to the specific interaction through intermolecular hydrogen bonding between the hydrogen of the solvents and the charge on the carbonyl's oxygen in the excited state. This solute–solvent interaction is expected to stabilize the charge-separated state (CT).³⁶

The systematic shift in the emission maxima as a result of the substituent on these molecules can be seen from the variation of ν_t with the ionization potential of the substituted-phenyl moieties. As shown in Figure 5(A)–(C), emissions from the CT state in protic solvents are found at 516, 440 and 438 nm for compounds **1**, **3** and **2**, respectively. This trend reflects the increase in the ionization potential (see Table 1) of the substituted-phenyl moieties.

Fluorescence excitation spectra were measured for each of the compounds and were essentially identical with the absorption spectra, implying that the emitting forms are structurally close to the stable forms in the ground state.

Fluorescence excitation spectra were measured for each of the compounds and were essentially identical with the absorption spectra, implying that the emitting forms are structurally close to the stable forms in the ground state.

Dipole moment of the excited (CT) state of compound **1**

Since compound **1** bears the strongest electron-donating substituent among the series of compounds studied, emissions from the CT state are observed in both polar protic and aprotic solvents. The validity of the assumption that this state has a charge-separated nature comes from the fact that both the spectral position and the shape of the band were sensitive to changes in the polarity of the solvents. In this regard, we noticed a bathochromic shift and a gradual disappearance of the LE state band with increasing solvent polarity. This red shift is a manifestation of charge separation stabilized by the solvent, and thus an increase in the dipole moment of the compound upon excitation. Figure 6 shows the effect of the solvents on the emission spectra of compound **1**, where it can be seen that the CT state is completely stabilized in acetonitrile. In contrast, CT is not feasible in *n*-hexane since this non-polar solvent cannot stabilize the CT state.

In order to establish the magnitude of the excited-state dipole moment, we attempted to use equation (2)³⁷ to correlate the energy of the intramolecular charge transfer (CT) state with the solvent's polarity parameter Δf . The CT energy shift increases linearly with Δf in solvents of different polarities (Figure 7).

$$\bar{\nu}_t = \bar{\nu}_t(0) - \frac{2\mu_e^2 \Delta f}{hca^3} \quad (2)$$

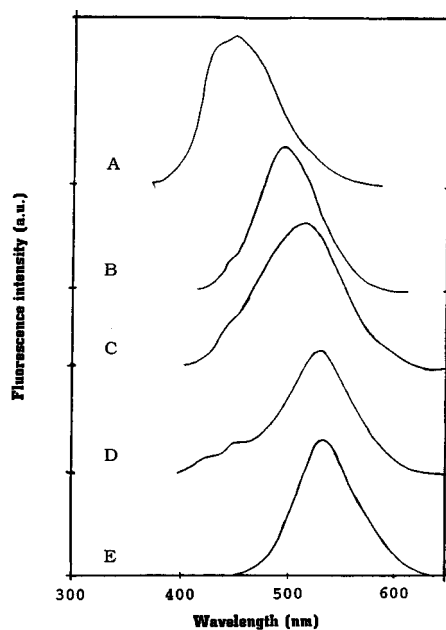


Figure 6. Fluorescence spectra of compound **1** ($\lambda_{\text{exc}}=398$ nm) in the solvents (A) *n*-hexane, (B) THF, (C) ethanol, (D) DMF and (E) acetonitrile

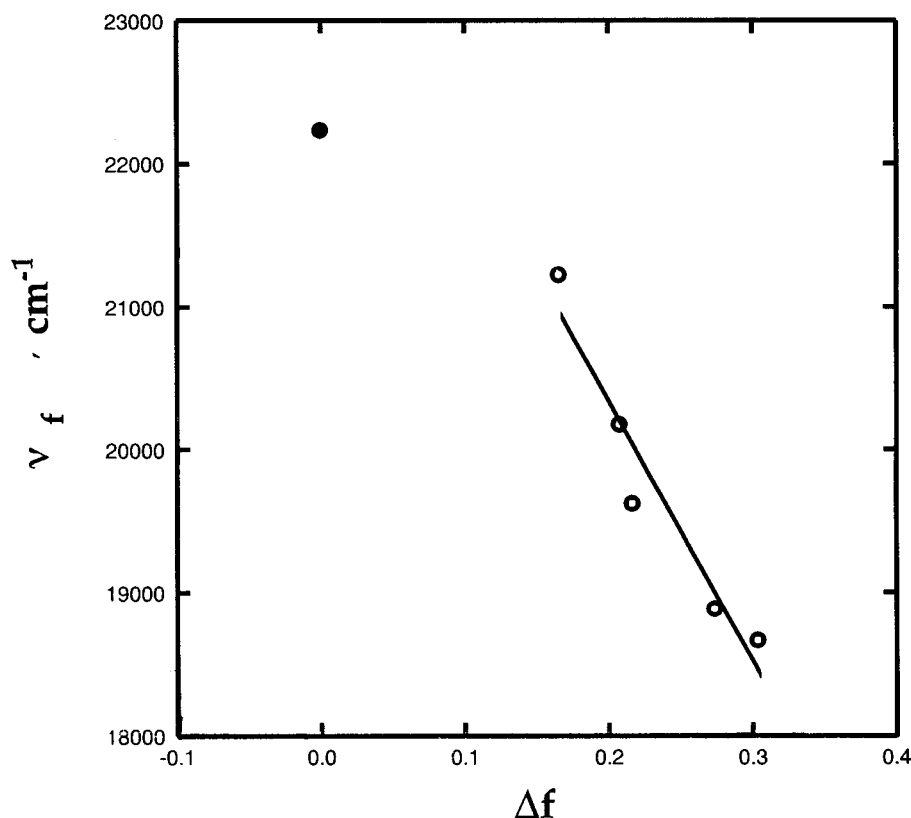


Figure 7. Plot of charge-transfer emission frequency (ν_f) of compound **1** vs the solvents parameter (Δf). The solid line is the best fit through all frequencies except for the frequency in *n*-hexane (filled circle)

$$\Delta f = \frac{\epsilon - 1}{2\epsilon - 1} - \frac{n^2 - 1}{4n^2 + 2} \quad (3)$$

In equation (2), ν_f and $\nu_f(0)$ are the fluorescence maxima (in cm^{-1}) in solution and the gas phase, respectively, μ_e is the excited state's dipole moment, a is the solvent cavity radius and h and c have their usual meanings. The plot of ν_f against Δf for compound **1** in solvents of different polarities is shown in Figure 7, where the fluorescence maximum in *n*-hexane is shown for comparison but not included in the fitting. The magnitude of μ_e is obtained from the slope ($= 18,182 \text{ cm}^{-1}$) of the best line fit through the data except for *n*-hexane, and based on estimation of the value of a , which was calculated using the three-dimensional molecular modelling program CHChe (CACHe Scientific, Beaverton, OR, USA). The program was used to calculate the interatomic distances, from which the value of a was approximated as 40% of the long axis of the ellipsoid around the molecule.³⁸ The μ_e value determined for compound **1** is 17 D. This large excited-state dipole moment suggests that considerable charge transfer occurs from the amino group donor to the carbonyl acceptor moieties, which

leads to an increase in polarity and, consequently, intensification of the donor–acceptor interaction.

CONCLUSIONS

A comparison of the electronic absorption and emission properties of seven compounds has indicated that intramolecular charge-transfer (ICT) absorption and emission are possible in the series in which the substituents are strong electron donors. CT absorption and emission are dependent on the solvent polarity, hydrogen bonding and the ionization energy of the substituted-phenyl moieties. In general, CT absorption and emission are enhanced and red shifted as the solvent polarity and hydrogen-bonding abilities increase for compounds possessing electron-donating substituents, while the reverse is true for those with electron-withdrawing substituents. The photoinduced charge separation stabilized by solvent polarity gives a large excited-state dipole moment for compound **1**.

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