

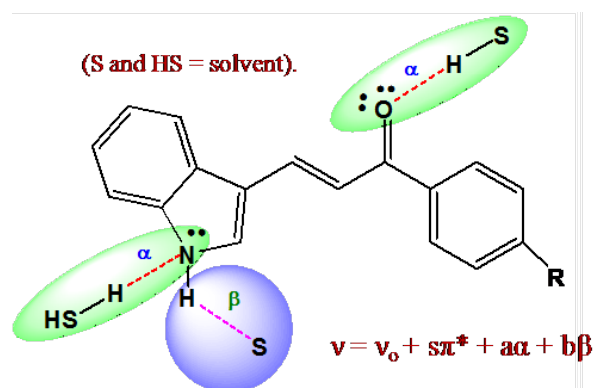
Linear solvation energy relationship of 3-(1'H-indol-3'-yl)-1-phenylprop-2-en-1-ones using Kamlet-Taft and Catalan solvent parameters

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ABSTRACT



Steady-state absorption and fluorescence techniques have been used to study the photophysical properties of the fluorescent 3-(1'H-Indol-3'-yl)-1-phenylprop-2-en-1-one (IC) derivatives *via* Kamlet-Taft and Catalán treatments. In a refined work of the non-specific interactions of these derivatives in various solvents, a complete set of Kamlet-Taft and Catalán scales has been employed, which enables to separate the polarizability, hydrogen-bond donor and hydrogen-bond acceptor abilities of these derivatives. The Kamlet-Taft and Catalán treatments of these derivatives in the ground state suggest that the IC derivatives can well behave both as hydrogen bond acceptors and donors due to the simultaneous presence of carbonyl and NH groups, whereas, in excited state only the hydrogen bond accepting ability counts.

Keywords: Excited state, Polarizability, Hydrogen bond, Photophysical property, Kamlet-Taft scale, Catalán scale.

INTRODUCTION

Life on earth depends on water, on hydrogen bonds, and on hydrophobic interactions. DNA and proteins are held together in their defined three-dimensional structures primarily by hydrogen bonds. Hydrogen bonding is one of the major forces thought to be involved in the recognition of agonists and antagonists by their receptors in biological systems. Hydrogen bonding also affects membrane transport, as well as the distribution of drugs within the

biological system. Solvation is important for understanding the solvent effects on chemical and biochemical processes. The solvent-induced changes in the electronic transition of solutes are related to the nature and extent of solute-solvent interactions developed locally in the immediate vicinity of solutes.

The solvent, in which a physicochemical process takes place is a non-inert medium that plays a major role in photophysical properties of any molecule.¹ Thus, solvents modify the rate of chemical reactions, displace chemical equilibria, and alter the spectral features of solutes. This can be explained as the effect of solvents in terms of their interactions with solutes, which can be of specific or nonspecific type. Influence of specific interactions on the absorption and fluorescence spectra is very important, depending on whether the solvent molecules can act as donors or acceptors in the formation of hydrogen bonding with the solute molecules. In comparison with an aprotic solvent, a protic one is characterized by the relatively active hydrogen that loads

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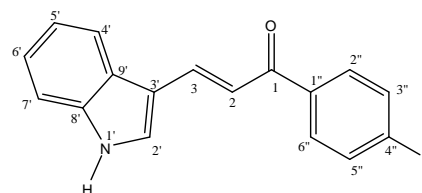
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partially-positive charge on its molecule. The polar-protic solvent may employ its H atom end as carrier to help electron transfer,² exerting influence on the fluorescence of a fluorescent molecule. There are several solvent polarity scales underlying the quantitative measurements of polarities and hydrogen bonding to study the specific interactions.¹

Kamlet, Taft and collaborators^{3,4} and Catalán^{5,6} have developed solvatochromic models that quantify the specific interactions due to H-bond donor (HBD) and H-bond acceptor (HBA) contributions of the solvents, and separate them from non-specific interactions. The polarity/polarizability, the Kamlet-Taft and Catalán scales were taken into consideration for characterization of photophysical properties. The Kamlet-Taft and Catalán empirical solvent scales are based on the polarity/polarizability (SPP/π^*), acidity (SA/α) and basicity (SB/β) to describe the respective properties of solute.

A linear regression analysis of transition energies in various solvents, for which values of α , β , π^* , SPP , SA and SB are available, allows determination of the corresponding coefficients a_α , b_β , s_{π^*} , s_{SPP} , a_{SA} and b_{SB} and that may be used as a measure of the relative importance of these factors to the solvatochromism of the investigated compound. The interpretation of these relative contributions is generally sought in specific interactions between the solvent and the solute. Acidic or hydrogen-bond-donor (HBD) solvents may affect the solvatochromic charge-transfer band of a dye by partial protonation of its donor and/or acceptor fragment. Basic or hydrogen-bond-acceptor (HBA) solvents may affect the dye CT band by interacting with acidic sites of the solute. Polarizable solvents will help stabilize dipolar forms of the solute, thus affecting its internal charge-transfer transitions. These models provide an insight into the solute-solvent interactions in the ground and first excited singlet states. The magnitudes and signs of the Kamlet-Taft and Catalán parameters are indicative of the relative stabilization or destabilization effect of the respective solvent property on the spectral feature of the solute. The magnitude of the coefficients, sometimes expressed as percentage contributions, allows us to identify the dominant solvent effect in S_0 and S_1 states.

In this paper, the effects of solvent on ground and excited states of biologically active 3-(1'H-Indol-3'-yl)-1-phenylprop-2-en-1-one (IC) derivatives have been studied (Figure 1). These molecules show anticancer,⁷ anti-inflammatory,^{8,9} neuroprotective¹⁰ and antiameobic¹¹ properties. Steady-state absorption and fluorescence spectra of the IC derivatives were recorded in sixteen solvents of different polarity and hydrogen bonding character. The purpose was to acquire a large database, covering a broad spectrum of macroscopic solvent properties and lending itself to an unambiguous analysis by using some of the well-established solvatochromic scales so that useful information could be obtained about the solute-solvent interactions in the ground and first excited singlet states. Using the spectral data, the acidity, basicity and polarizability of the IC derivatives have been determined.



Compounds	R
3-(1'H-Indol-3'-yl)-1-phenylprop-2-en-1-one (I)	H
3-(1'H-Indol-3'-yl)-1-4''-tolyl-prop-2-en-1-one (Me-I)	CH ₃
3-(1'H-Indol-3'-yl)-1-(4''-methoxyphenyl)-prop-2-en-1-one (OMe-I)	OCH ₃
1-(4''-Hydroxy-phenyl)-3-(1'H-indol-3'-yl)-prop-2-en-1-one (OH-I)	OH
3-(1'H-Indol-3'-yl)-1-(4''-aminophenyl)-prop-2-en-1-one (NH ₂ -I)	NH ₂
1-(4''-Chloro-phenyl)-3-(1'H-indol-3'-yl)-prop-2-en-1-one (Cl-I)	Cl

Figure 1. Structure of IC derivatives.

EXPERIMENTAL

MATERIALS

Starting materials and reagents for the synthesis of 3-(1'H-indol-3'-yl)-1-phenylprop-2-en-1-one derivatives purchased from Spectochem Pvt. Ltd. and used without further purification prior to use. All solvents used were of spectroscopic grade and were preliminarily checked for the absence of absorbing or fluorescent impurities within the scanned spectral ranges. The water used was triple distilled.

INSTRUMENTATION

The absorption spectra were recorded on UV-visible double-beam spectrophotometer (ANALYTIKA JENA UV WINASPECT SPECORD PC 250) using matching quartz cells of 10 mm path-length. The corrected fluorescence spectra of freshly prepared solutions were scanned in a rectangular quartz cell of 10 mm path-length using spectrofluorometer (VARIAN CARY ECLIPSE). The slit widths used were 1 nm and 5 nm for absorption and fluorescence measurements, respectively. The concentration of the compounds was kept low, depending on the intensity of fluorescence to avoid aggregation and minimize the inner filter effect. Absorption and fluorescence spectra were recorded in freshly prepared 2×10^{-5} M and 1×10^{-5} M solutions, respectively.

SYNTHESIS

The investigated 3-(1'H-indol-3'-yl)-1-phenylprop-2-en-1-one derivatives were synthesized and their purity was confirmed by TLC, IR and ¹H NMR.

3-(1'H-indol-3'-yl)-1-phenylprop-2-en-1-one (I): A solution of indole-3-carboxaldehyde (0.01 mol) and acetophenone (0.01 mol) in 8-10 ml of ethylene glycol was treated with 1 ml of piperidine and refluxed for 20-30 minutes at 170-180°C and the progress of reaction was monitored by TLC in ethyl acetate (30%) - petroleum ether (70%) solvent. After cooling the reaction mixture, 5-10 ml of water and 1 ml of glacial acetic acid were added; the crystals that deposited were recrystallized from ethanol. Other derivatives were also synthesized using the same procedure.

SPECTRAL DATA

3-(1'H-indol-3'-yl)-1-phenylprop-2-en-1-one (I)

IR (KBr, cm⁻¹): 3428, 3145, 3051, 1640, 1591, 1438, 1367; ¹H NMR (400MHz, DMSO-d₆, ppm): δ 7.19 (d, J = 12 Hz, 1H), 7.44

(d, $J = 8$ Hz, 1H), δ 7.50-7.55 (m, 2H), δ 7.57-7.61 (m, 2H), 7.98 (s, 1H), δ 7.99-8.04 (m, 5H), δ 11.89 (s, 1H); melting point: 172-174 °C.

3-(1'-H-Indol-3'-yl)-1-4''-tolylprop-2-en-1-one (Me-I)

IR (KBr, cm^{-1}): 3424, 3186, 1638, 1580, 1437, 1355; ^1H NMR (400MHz, DMSO- d_6 , ppm): δ 2.36 (s, 3H), δ 7.17-7.21 (m, 2H), δ 7.31 (d, $J = 8$ Hz, 1H), δ 7.44-7.47 (m, 2H), δ 7.58 (d, $J = 16$ Hz, 1H), δ 7.98 (s, 1H), δ 8.00-8.06 (m, 4H), δ 11.87 (s, 1H); melting point: 168-170 °C.

3-(1H-Indol-3-yl)-1-(4''-methoxyphenyl)-prop-2-en-1-one (OMe-I)

IR (KBr, cm^{-1}): 3389, 3107, 1653, 1601, 1585, 1438, 1360; ^1H NMR (400MHz, DMSO- d_6 , ppm): δ 3.80 (s, 3H), δ 7.03- (d, $J = 8$ Hz, 1H), δ 7.18-7.20 (m, 2H), δ 7.44-7.45 (m, 2H), δ 7.59 (d, $J = 16$ Hz, 1H), δ 7.96 (s, 1H), δ 8.04-8.10 (m, 4H), δ 11.83 (s, 1H); melting point: 156-158 °C.

1-(4''-Hydroxyphenyl)-3-(1H-indol-3-yl)-prop-2-en-1-one (OH-I)

IR (KBr, cm^{-1}): 3285, 3112, 2927, 1641, 1557, 1440, 1344; ^1H NMR (400MHz, DMSO- d_6 , ppm): δ 4.57 (s, 1H), δ 7.70 (d, $J = 8$ Hz, 1H), δ 8.01-8.05 (m, 2H), δ 8.29-8.31 (m, 2H), δ 8.44 (d, $J = 16$ Hz, 1H), δ 8.78 (s, 1H), δ 8.82-8.92 (m, 4H), δ 12.68 (s, 1H); melting point: 180-182 °C.

3-(1'-H-Indol-3'-yl)-1-(4''-aminophenyl)-prop-2-en-1-one (NH₂-I)

Yield: 81%; melting point: 196-198 °C; IR (KBr, cm^{-1}): 3428 $\nu(\text{NH})$, 3188, 1635 $\nu(\text{C=O})$, 1583, 1437, 1355; ^1H NMR (400 MHz, DMSO- d_6 , ppm): δ 5.98 (s, 2H, -NH₂), δ 6.57-6.59 (m, 2H, Ar-H), δ 7.16-7.18 (m, 2H, Ar-H), δ 7.42 (d, $J = 8$ Hz, 1H, -CH=CH-), δ 7.55 (d, $J = 16$ Hz, 1H, -CH=CH-), δ 7.84 (s, 1H, -NH-CH-), δ 7.86-8.01 (m, 4H, Ar-H), δ 11.72 (s, 1H, -NH).

1-(4''-Chlorophenyl)-3-(1H-indol-3-yl)-prop-2-en-1-one (Cl-I)

IR (KBr, cm^{-1}): 3427, 3186, 1629, 1572, 1435, 1356; ^1H NMR (400MHz, DMSO- d_6 , ppm): δ 7.21-7.24 (m, 2H), δ 7.47-7.49 (m, 2H), δ 7.55 (d, $J = 8$ Hz, 1H), δ 7.62 (d, $J = 12$ Hz, 1H), δ 8.02 (s, 1H), δ 8.05-8.11 (m, 4H), δ 11.91 (s, 1H); melting point: 178-180 °C.

METHODOLOGY

Determination of the Acidity, Basicity and Polarizability Behavior

The spectral behaviour of a solvatochromic probe in solution is associated with its interaction with the solvent. The solvent effect on absorption and fluorescence spectra of probe can be described on the basis of a Multiple Linear Regression Analysis (MLRA) using following expression:

$$y = y_0 + a'A + b'B + c'C \quad (2.1)$$

where y_0 stands for the physicochemical property of interest in the absence of solvent for the probe (i.e. in the gas phase) and a' , b' and c' are the coefficients that reflect the dependence of the physicochemical property (y) of probe in a given solvent having various solvent polarity parameters (A , B and C). There are two well-known multiparametric scales: Kamlet-Taft and Catalán.

Kamlet-Taft Treatment

A widely employed approach that identifies and quantifies different solute-solvent contributions to this behaviour is the Kamlet-Taft equation. Kamlet and Taft^{12,13} proposed a multiparametric approach, known as Solvatochromic Comparison

method or Linear Solvation Energy Relationship (LSER) to find the information about the individual contribution of different specific solvent effects as follows:

$$\nu = \nu_0 + s_{\pi^*}(\pi^* + d\delta) + a_{\alpha}\alpha + b_{\beta}\beta \quad (2.2)$$

where ν_0 is the vapor phase wave-number (independent of solvent effects) and the values of ν are absorption/fluorescence band maxima in a solvent. The empirical parameters π^* , α and β are a measure of the polarity/polarizability character of the solvent, its hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) capacities, respectively.¹⁴⁻¹⁶ The coefficients s_{π^*} , a_{α} and b_{β} are interpreted as solute properties. The coefficient, s_{π^*} is related to the solute's polarity/polarizability character, a_{α} describes its tendency to accept hydrogen bond from the solvent and b_{β} measures its property to donate hydrogen bond to the solvent. Coefficients s_{π^*} , a_{α} and b_{β} indicate the susceptibility of ν to a change in the corresponding parameters. The term δ used in Eq. (2.2) is a 'polarizability correction term', whose value depends on the class of solvents used; for aromatic solvents $\delta = 1$, for polyhalogenated solvents $\delta = 0.5$ and for all other solvents $\delta = 0$.¹⁷ The term 'd' is interpreted as an indicator of the change in direction of the molecular dipole moment in going from initial to transition state and is zero for all spectra that are shifted bathochromically with increasing solvent dipolarity.^{18,19} Consequently, Eq. (2.2) can be simplified as follows:

$$\nu = \nu_0 + s_{\pi^*}\pi^* + a_{\alpha}\alpha + b_{\beta}\beta \quad (2.3)$$

Therefore, Eq. (2.3) represents the simplified form of the Kamlet-Taft treatment.

Catalán Treatment

Catalán *et al.*^{20,21} proposed empirical solvent scales for polarity/polarizability (SPP), acidity (SA) and basicity (SB) to describe these properties of a solvent. The dependence of ν on the SPP, SA and SB parameters is given by

$$\nu = \nu_0 + s_{\text{SPP}}\text{SPP} + a_{\text{SA}}\text{SA} + b_{\text{SB}}\text{SB} \quad (2.4)$$

The corresponding parameters for different solvents were taken from literature²²⁻²⁵ and the same are given in Table S1 (supplementary material). All least-squares fit analyses were carried out with Microsoft EXCEL using Linest Function.²⁶

RESULT AND DISCUSSION

The absorption and fluorescence spectra of IC derivatives were recorded in different solvents and the corresponding spectral data have been summarized in Table 1 and the absorption and fluorescence spectra of Me-I derivative shown in Figure 2.

Absorption band (A4) (~ 340-400 nm) shows a large bathochromic shift (30-55 nm) with increase in polarity. The longest wavelength absorption maxima band (A4) was used as excitation wavelength to record the fluorescence spectra. A completely non-structured intense fluorescence band was observed for IC derivatives in all the solvents except highly nonpolar solvents like 1,4-dioxane and THF in the range of 430-580 nm.

On increasing solvent polarity, the emission became structureless and an appreciable bathochromic shift was detected with a band enlargement in IC derivatives. Such a behavior indicated the stabilization of the highly dipolar excited state in polar solvents. A remarkable fluorescence enhancement of IC

derivatives in protic polar solvents and a great quenching in the non-polar solvents indicates the key role of the proticity of solvents. In the protic polar solvents, the fluorescence intensity of these molecules increased along with bathochromic shift with increase in the solvent polarity (50-75 nm). Though the red shift is observed in the absorption band maxima of these derivatives, a more significant red shift is observed in fluorescence band maxima along with the increase in the bandwidth, which indicates the strong intramolecular charge transfer (ICT) character of the excited state as compared to the ground state for these derivatives.

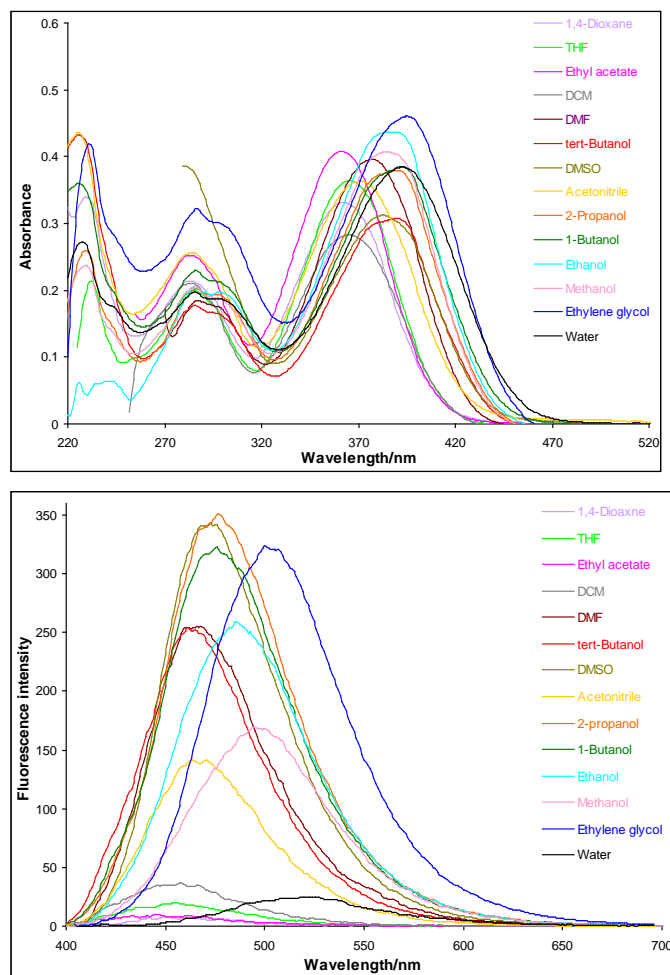


Figure 2 Absorption spectra and fluorescence spectra of Me-I in different solvents

Looking at the molecular structure of IC derivatives, one can see that it has electron donor and acceptor pairs offering two resonating structures (structures 'A' and 'B') as a result of the ICT. The resonance structure 'A' is characterized by the participation of the electron lone pair of N atom of the chromophore towards carbonyl group and the structure 'B' shows the donation of electron density from phenyl ring to the carbonyl group, which is made possible by the presence of electron donating group at *para* position of phenyl ring.

The distinct solvatochromic behaviour of all IC derivatives in protic and non-protic media must reflect different solvent effects. The absorption and fluorescence wavelength maxima obtained in

various solvents have been analyzed using the Kamlet-Taft (π^* , α and β) and Catalán (SPP, SA and SB) treatments.²⁷⁻³⁰ This approach separates the dielectric effect (π^*/SPP), hydrogen-bond donor ability (α/SA) and hydrogen-bond acceptor ability (β/SB) of the solvents on the spectral properties (Eqs. 2.3 & 2.4).

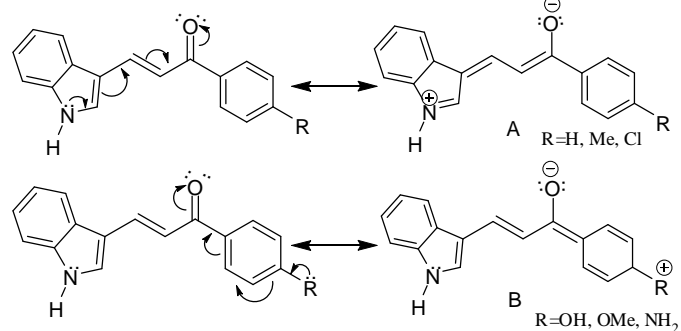


Figure 3. Intramolecular charge transfer excited states: A & B in IC derivatives.

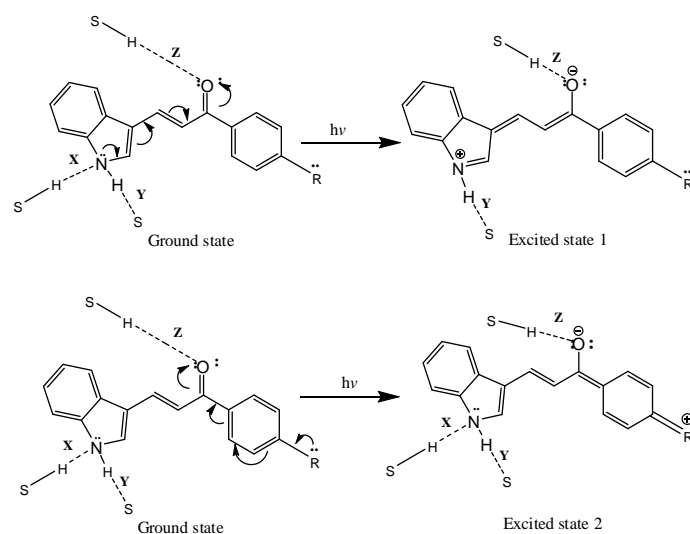


Figure 4. Simplified view of the possible hydrogen bonds involved in the ground and the excited states of IC derivatives. Hydrogen bonds may be formed on the nitrogen lone pair (type X) and the carbonyl group (type Z) by hydrogen-bond donating solvents, and hydrogen atoms on the NH group (type Y) by hydrogen-bond accepting solvents (S and HS = solvent).

Figure 4 shows the possible specific solute-solvent interactions of IC derivatives. To get information about the various solute-solvent interactions that control the solvent-induced spectral shifts, the effect of solvents on the absorption and fluorescence energies is quantified by multiple regressions, Kamlet-Taft and Catalán approaches. The results are given in Table 2-5 and the corresponding equations are given in Tables S2 & S3 (see the supplementary information). To get the dominating factors in absorbance and fluorescence in IC derivatives, coefficients of π^* , α , β , SPP, SA and SB have also been calculated in terms of relative percentage (present in parenthesis).

Table 1 Absorption (λ_{abs} / nm) and fluorescence^a band maxima of IC derivatives in different solvents

Solvent ^a	I		Me-I		OH-I		OMe-I		NH ₂ -I		Cl-I	
	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}
n-Hexane	352	-	350	-	-	-	344	-	348	-	352	-
Cyclohexane	355	-	352	-	-	-	346	-	348	-	354	-
1,4-Dioxane	367	446	366	445	362	437	366	444	366	440	376	453
THF	373	458	366	450	366	440	370	445	367	444	386	464
Ethyl acetate	367	455	370	452	362	442	366	445	364	444	378	458
DCM	368	460	367	458	365	452	367	450	366	447	377	464
DMF	385	474	383	464	376	456	382	456	382	458	393	483
<i>tert</i> -Butanol	390	467	385	464	390	455	385	458	386	457	402	477
DMSO	390	479	388	472	382	461	384	464	386	463	400	492
Acetonitrile	373	473	372	467	370	459	372	462	370	458	382	485
2-Propanol	389	480	394	476	390	465	388	469	395	465	399	490
1-Butanol	391	480	388	476	392	466	394	470	397	467	400	492
Ethanol	388	491	388	486	388	475	387	480	395	471	396	506
Methanol	386	499	385	497	385	489	385	494	395	478	392	508
Ethylene glycol	397	509	397	503	395	493	397	499	402	494	401	515
Water	391	520	392	521	393	513	393	517	399	502	407	524

The formation of specific hydrogen bonds between the solvent and the solvatochromic probe may possibly explain the UV-Vis shifts. The contribution of each of the specific interactions (solvent-carbonyl oxygen atom, solvent-indole ring nitrogen atom and solvent-indole ring hydrogen atom) can have a different effect by changing the nature and geometry of the solvent.^{31,32} This behavior explains the average correlation coefficients of the multiple square analyses, because each solvent probably interacts in a different way with the probe (>NH and >C=O).

The possible hydrogen bonds involved in the ground and the excited states of IC derivatives are shown in Figure 4. These derivatives can accept hydrogen bonds at the nitrogen lone pair (type X) and the carbonyl group (type Z) from hydrogen bond donating solvents. These derivatives can also show hydrogen bond formation between hydrogen bond accepting solvents and the H atom of the NH group (type Y).³³

The negative sign of π^* , α , β , SPP, SA and SB coefficients for all the IC derivatives is consistent with the bathochromic (lower energies) shifts of absorption and fluorescence spectra and contributes to the stabilization of the ground state as well as the excited state (Tables 2-5).^{34,35}

Absorption and fluorescence wavenumbers were calculated for IC derivatives from Kamlet-Taft and Catalán equations (Tables S2 and S3, supplementary information) and given in Table S4 for IC derivatives.

a) Excitation Process

Excitation Kamlet-Taft and Catalán equations for I derivative given as.

$$\nu_a = 28396 - 1243 \alpha - 1845 \beta - 756 \pi^* \quad \text{Kamlet-Taft eq.}$$

$$\nu_a = 30221 - 3158 \text{SA} - 1688 \text{SB} - 1570 \text{SPP} \quad \text{Catalán eq.}$$

The larger negative values of b_β point towards the higher HBD ability of the molecules, as the lone pair of electrons on N atom in indole ring participates in the formation of hydrogen bond with solvents. The large negative a_α values point towards the good HBA ability of IC derivatives).³⁶

On applying Catalán treatment to the excitation process, higher relative percentages or larger negative values of a_{SA} are obtained instead of b_{SB} as compared to those of a_α and b_β , which are obtained by the Kamlet-Taft treatment.³³ The results obtained from both the treatments for the ground state can be summarized as follows:

- Kamlet-Taft treatment shows the higher donating ability of the molecule.
- Catalán treatment shows the higher accepting ability of the molecule.

This dual capability of the molecule in the ground state suggests that the IC derivatives can well behave both as HB acceptor and HB donor due to the simultaneous presence of carbonyl (Figure 4, type Z interaction) and NH groups (type Y interaction).^{34,37} This can be substantiated by looking at the structure of the probes; the presence of carbonyl group (chalcone moiety) and >NH group leads to formation of hydrogen bonds of types X, Y and Z with the solvent (Figure 4).³³

Table 2 Multiparametric correlation of Kamlet-Taft treatment the spectral properties of IC derivatives in excitation processes

Molecule	ν_o	a_α	b_β	s_{π^*}	r^a
I	28396	-1243 (32.34%) ^b	-1845 (48.01%)	-756 (19.66%)	0.968
Me-I	28541	-1285 (32.38%)	-1798 (45.31%)	-885 (22.30%)	0.954
OH-I	28855	-1134 (25.88%)	-2033 (46.41%)	-1214 (27.70%)	0.930
OMe-I	28892	-1504 (33.68%)	-2016 (45.14%)	-945 (21.17%)	0.972
NH ₂ -I	27694	-992 (27.46%)	-1684 (46.64%)	-935 (25.90%)	0.951
Cl-I	28248	-1652 (36.56%)	-2282 (50.50%)	-585 (12.94%)	0.978

^aCorrelation coefficients of IC derivatives in their respective equations.^bThe numbers in parentheses indicate the relative percentage.**Table 3** Multiparametric correlation of Kamlet-Taft treatment towards the spectral properties of IC derivatives in emission processes

Molecule	ν_o	a_α	b_β	s_{π^*}	r^a
I	23343	-2070 (49.86%) ^b	-575 (13.85%)	-1507 (36.30%)	0.959
Me-I	23309	-1876 (48.79%)	-253 (6.57%)	-1717 (44.64%)	0.974
OH-I	23686	-1949 (51.43%)	-48 (1.28%)	-1792 (47.29%)	0.974
OMe-I	23239	-1494 (44.61%)	156 (4.65%)	-2010 (60.03%)	0.944
NH ₂ -I	23730	-1850 (49.77%)	-440 (11.85%)	-1426 (38.38%)	0.971
Cl-I	23202	-2045 (45.30%)	-1034 (22.91%)	-1435 (31.79%)	0.936

^aCorrelation coefficients of IC derivatives in their respective equations.^bThe numbers in parentheses indicate the relative percentage.**Table 4** Multiparametric correlation of Catalán treatment towards the spectral properties of IC derivatives in excitation processes

Molecule	ν_o	a_{SAA}	b_{SA}	s_{SB}	r^a
I	30221	-3158 (49.22%) ^b	-1688 (26.31%)	-1570 (24.47%)	0.968
Me-I	30410	-3210 (48.36%)	-1732 (26.09%)	-1696 (25.55%)	0.956
OH-I	31059	-3439 (44.89%)	-2114 (27.60%)	-2108 (27.51%)	0.893
OMe-I	31142	-3856 (51.02%)	-1914 (25.33%)	-1787 (23.65%)	0.975
NH ₂ -I	29144	-2490 (42.30%)	-1633 (27.75%)	-1763 (29.95%)	0.940
Cl-I	30848	-4556 (58.70%)	-1802 (23.22%)	-1403 (18.08%)	0.969
NO ₂ -I	27996	-2737 (49.35%)	-1649 (29.73%)	-1160 (20.92%)	0.971

^aCorrelation coefficients of IC derivatives in their respective equations.^bThe numbers in parentheses indicate the relative percentage.**Table 5** Multiparametric correlation of Catalán treatments towards the spectral properties of IC derivatives in emission processes

Molecule	ν_o	a_{SAA}	b_{SA}	s_{SB}	r^a
I	25648	-4351 (60.62%) ^b	-533 (7.42%)	-2294 (31.96%)	0.963
Me-I	24832	-3224 (52.62%)	-356 (5.81%)	-2548 (41.58%)	0.968
OH-I	25155	-3220 (53.81%)	-163 (2.72%)	-2601 (43.47%)	0.964
OMe-I	23572	-1402 (30.79%)	-222 (4.87%)	-2929 (64.34%)	0.941
NH ₂ -I	25319	-3285 (54.87%)	-475 (7.93%)	-2227 (37.20%)	0.974
Cl-I	25885	-4857 (61.14%)	-874 (11.00%)	-2213 (27.86%)	0.914

^aCorrelation coefficients of IC derivatives in their respective equations.^bThe numbers in parentheses indicate the relative percentage.

The Kamlet-Taft and Catalán equations point towards the spectral properties of IC derivatives in excitation processes and are given in Table S2 (supplimentary information). Plots of experimental absorption wavenumbers correlated with the calculated values of

absorption wavenumbers obtained from the multicomponent linear regressions using the π^* , α and β -scale (Kamlet-Taft) and

SPP, SA and SB (Catalán) solvent parameters for IC derivatives are shown in Figure.5.

a) Emission Process

Emission Kamlet-Taft and Catalán equations for I derivative given as.

$$\begin{aligned} \nu_I &= 23343 - 2070 \alpha - 575 \beta - 1507 \pi^* && \text{Kamlet-Taft eq.} \\ \nu_I &= 25648 - 4351 SA - 533 SB - 2294 SPP && \text{Catalán eq.} \end{aligned}$$

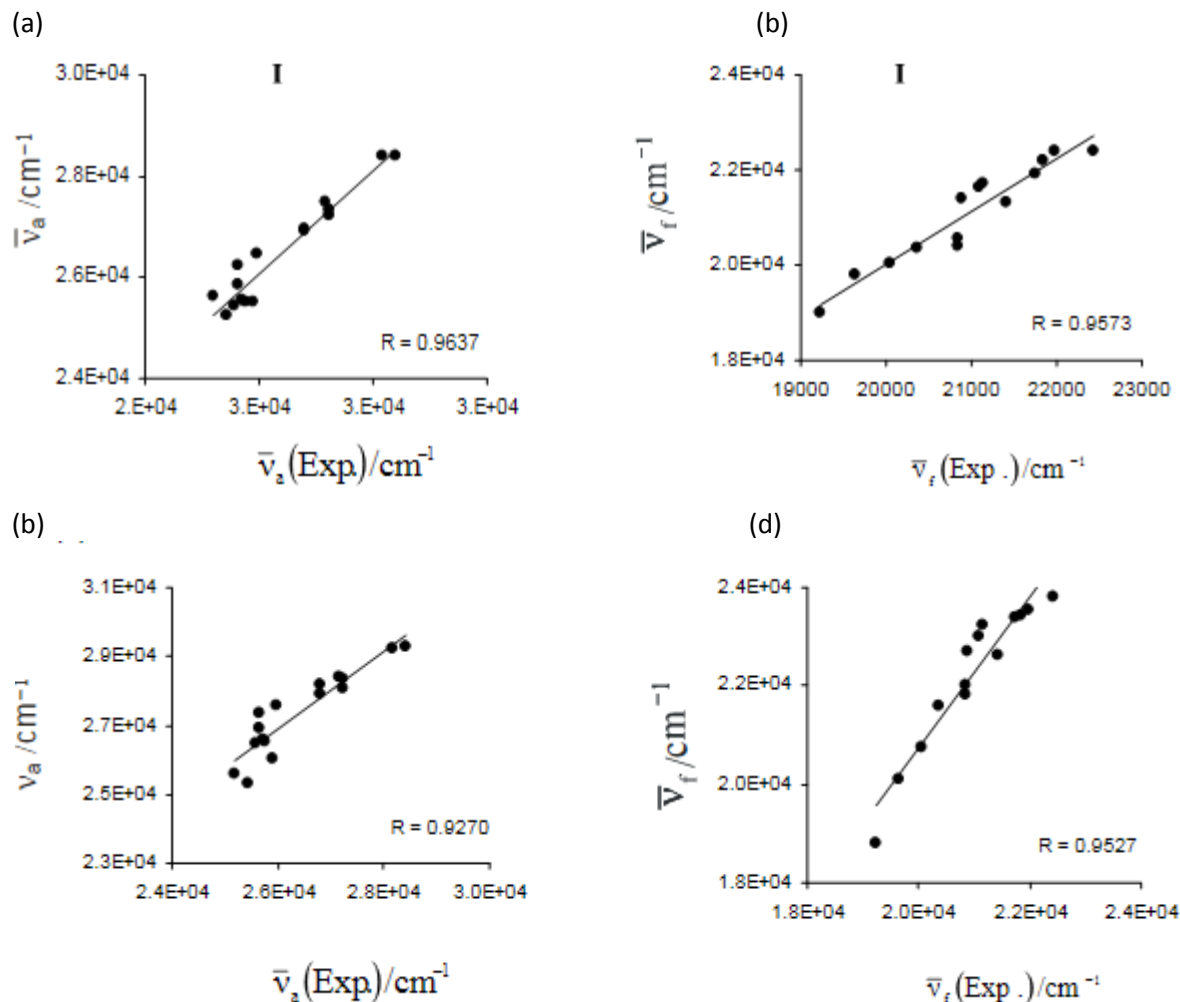


Figure 5. Plots of predicted vs. experimental absorption and Fluorescence wavenumbers of IC derivatives obtained by a multiple linear regression analysis according to (a& b) Kamlet-Taft equation (Eq. 2.3), (c&d) Catalán equation (Eq. 2.4) for 3-(1H-Indol-3'-yl)-1-phenylprop-2-en-1-one (I).

The more negative values of a_α and a_{SPP} in emission process as compared to the excitation process reveal that the HBA ability is enhanced in excited state.^{33,34} This is because of the strengthening of the hydrogen bond on the carbonyl group (type Z) (Figure 4 and Tables 2 & 4).

Hydrogen bond of type Z is thus stronger than the hydrogen bonds of types X and Y in excited state because of the formation of negative charge on carbonyl group in both the resonance forms A and B in Figure 3.³³ ICT process in the excited state results in an efficient charge populace on the carbonyl group from the donor side i.e. either the phenyl ring or the indole ring. Therefore, the contribution from α and SA properties of the solvents becomes more significant in stabilizing the excited state of IC derivatives. This result also corresponds to the presence of the bathochromic shifted (low energy) bands in protic solvents as compared to aprotic solvents.^{38,39}

The decrease in b_β and b_{SB} values in the emission process when compared with the excitation process shows that the strength of hydrogen bond donation of IC derivatives diminishes because of the higher contribution of ICT character.

In emission process, the large negative values of S_{π^*}/S_{SPP} and a_α/a_{SA} indicate that excited state has large ICT character.³⁹ Large absolute values of S_{π^*} and S_{SPP} of IC derivatives in excited state further confirm their high polarizability in the solvents. This shows that excited state is more polar and sensitive to the environment than the ground state, **OH-I** shows the lowest negative values of b_β and b_{SB} , which indicates the electron donating tendency of hydroxyl group.^{33,34} The fluorescence wavenumbers calculated from Kamlet-Taft and Catalán equations (Table S4, supplementary information) were found to show good correlation coefficients with the experimental values Figure. 5.

CONCLUSIONS

According to the Kamlet-Taft and Catalán treatments of these derivatives in the ground state, IC derivatives can well behave both as hydrogen bond acceptors and donors due to the simultaneous presence of carbonyl and NH groups, whereas, in excited state only the hydrogen bond accepting ability counts. These findings suggest that these derivatives can be used as probes to investigate the important role of solvent dynamics in electron transfer. The large difference between the ground and

excited state in the ability to form hydrogen bonds with protic solvents makes these derivatives a superb candidate to explore solvent effect.

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