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Electromeric effect of substitution at 6th position in 2-(Furan-2-yl)-3-hydroxy-4 *H*-chromen-4-one (FHC) on the absorption and emission spectra

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Abstract. Five 3-Hydroxychromones (3HCs), namely, 2-(furan-2-yl)-3-hydroxy-4*H*-chromen-4-one (FHC) and its four derivatives by substitution of -CH_3, -OH, -NO_2 and -Cl at 6th position were synthesized from their corresponding 2'-hydroxyacetophenone and furan-2-carboxaldehyde. Various spectral transitions of all these 3-hydroxychromones (3-HCs) have been assigned by interpreting their absorption spectra in cyclohexane, acetonitrile and methanol. It has been shown that the electromeric effects of substitution at 2nd and 6th positions on the 2–3 double bond in 'C' ring are similar but the effect on the double bond of 4-carbonyl group is opposite. It has been found that the substitution at 2nd position changes mainly the electron density directly at the 4-carbonyl group and substitution at 6th position changes the electron density of the 'C' ring, changing the overall dipole moment of the molecule, which in turn changes the electron density at the 4-carbonyl group. Emission spectral studies showed that the increase and decrease in dipole moment by substitution at 6th position with electron withdrawing group like NO_2 and electron donating group like -CH_3 and -OH, stabilizes and destabilizes the N* state in the polar solvents respectively.

Keywords. 3-Hydroxychromone (3HC); substitution effect; absorption and emission spectra; ESICT effect.

1. Introduction

3-Hydroxyflavones (**3HFs**) and their derivatives exhibit excited state intra-molecular proton transfer (ESIPT) reaction in such a way that emission from two excited states is exhibited simultaneously formed from the initial reactant (N*) and proton transfer reaction product (T*). Therefore, **3HFs** have attracted considerable interest in recent years due to their potential applications as molecular probes based on their spectrally separated (by about 100 nm) dual fluorescence.[1–6] The absorption and fluorescence spectra of **3HFs** have become a source of much valuable information on intermolecular interactions under different environment. Demchenko and co-workers demonstrated that the connection between solvent parameters and the absorption and emission spectra is essentially multi-parametric.[7–14] An attempt has been made to design efficient molecular sensors by proper substitution in the chromophore system. For example, substitution of 2-phenyl ring by 2-furyl or 2-benzofuryl results in a 2–3 fold increase in the fluorescence quantum yield in water and other solvents.[15] Reason for this is attributed to the higher planarity of the furyl or 2-benzofuryl-3-hydroxychromones in comparison to their 2-phenyl analogues.[14]

Recently, the detailed effect of substitution at the 2nd and 7th positions in the 3-hydroxychromones (3HCs) on the excited state proton coupled charge transfer has been reviewed.[4] Effect of various substituents at the 2nd position in the chromophore has been explained to selectively stabilize the N* state and hence increasing the population of N* state with respect to T* state.

On the other hand, the effect of substitution on the 'A' ring of 3HCs has not been studied up to the desired extent. A few studies on the substitutions at 7th position with electron donating group like (-OCH_3)[16] and (-CONHR)[15] on the absorption and emission spectra of 3HF derivatives have been made but with no clear explanation to this effect. Effect of substitution at 6th position has not been studied yet except in one report, that too by Klymchenko and Demchenko.[17]

In this paper, the effect of substitution by -CH_3, -OH, -NO_2 and -Cl at the 6th position of the title compound has been studied on the absorption and emission spectra. The change in absorption spectra is likely to give information on the change in electron density in its ground and excited states on the 4-carbonyl group of the molecule. Since ESIPT process takes place by transfer of proton from 3-hydroxy site to the 4-carbonyl

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group of 3HC's, thus showing the dual emission bands, it is obvious that any change in electron density on 4-carbonyl group will alter the rate and extent of ESIPT process and hence the position and intensity of both the emission bands of N* and T*, will be affected.

2. Experimental

2.1 *Reagents and solvents*

Acetonitrile (ACN), methanol (MeOH) and cyclohexane were of spectroscopic grade and were purchased from S.D. Fine chemicals, India and Loba Chemie. The reagents used for the preparation of 2-furyl-3-hydroxychromone derivatives were purchased from Sigma Aldrich, USA.

2.2 *Instrumentation*

Melting points of the synthesized compounds were determined in open capillary. Microanalyses were performed with a Vario Micro Cube Elementar Analyzer. IR spectra were recorded with FTIR spectrophotometer (Perkin Elmer, RZX) and ^{1}H NMR on Bruker Avance 400 NMR spectrometer with TMS as an internal standard. Double beam UV-Vis spectrophotometer (UV-1800 Shimadzu) equipped with UV-probe software, has been employed for recording the UV-Vis spectra. Fluorescence spectra were recorded on a Shimadzu spectroflurophotometer (RF-5301PC).

2.3 *Preparation, purification and characterization of 6th substituted 2-(furan-2-yl)-3-hydroxy-4H-chromen-4-one*

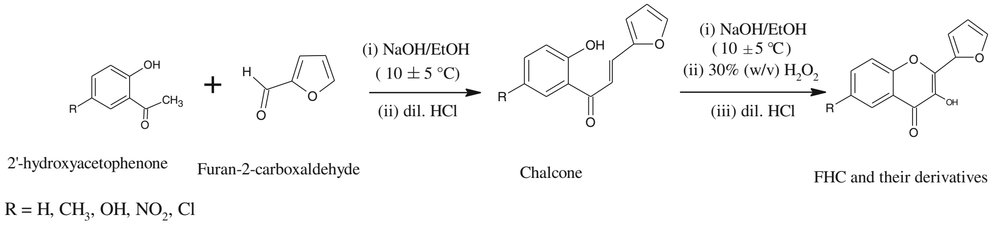
For the preparation of 2-(furan-2-yl)-3-hydroxy-4*H*-chromen-4-one and its derivatives by substitution at the 6th position with those of $-CH_3$, -OH, $-NO_2$, -Cl, (0.03 mole) of appropriately substituted 2'-hydroxyacetophenones were condensed with 2.88 g (0.03 mole) of furan-2-carboxaldehyde in the presence 3.6 g (0.09 mole) of sodium hydroxide in ethanol at 10 ± 5°C (scheme 1).

The reaction mixture which turned deep red in colour after 30 min was stirred further for 7–8 h. Thereafter, it was poured over ice, neutralised with dilute HCl and then the solid mass so obtained was crystallized from methanol to afford orange yellow needles of chalcone. The chalcone thus obtained was subjected to A.F.O. (Algar Flynn Oyamada) reaction conditions in sodium hydroxide and ethanol stirred at 10 ± 5°C with drop-wise addition of 30% (w/v) H_2O_2 over an hour. This mixture was further stirred for 5–6 h and the resulting reaction mixture on neutralization with dilute HCl, gave a yellow mass which was crystallised twice from appropriate solvents for different compounds.

Purity of the compounds was checked from the sharp M.p. single spot on TLC plate and sharp peaks in the UV-Vis spectrum. The structures have been confirmed by their IR and ^{1}H NMR spectra.

2.3a *2-(furan-2-yl)-3-hydroxy-4H-chromen-4-one*: Prepared from 2-hydroxyacetophenone and furan-2-carboxaldehyde. Crystallized from MeOH:$CHCl_3$(1:1, v/v); yellow needles; yield 85%; M.p. 178°C. **^{1}H NMR data, $CDCl_3$**: 8.24–8.26 (d, 1H, H-5, J_0 = 7.64 Hz, Ar), 7.69–7.72 (m, 2H, H-6, 7Ar), 7.61–7.63 (d, 1H, H-4′, J_0 = 8.24 Hz, Ar), 7.40–7.44 (t, 1H, H-5′, J_0 = 7.2 Hz, Ar), 7.35–7.36 (d, 1H, H-3′, J_0 = 3.2 Hz), 6.88 (s, OH exchangeable with D_2O), 6.66–6.67 (dd,1H, H-8, J_0 = 1.68 Hz, J_m = 3.4 Hz, Ar); **IR (KBr, cm^{-1})**: 3258 (OH), 2920 (CH Ar), 1616 (C=O); **Anal.calcd for** $C_{13}H_8O_4$: C, 68.42; H, 3.50. Found: C, 68.21; H, 3.76, which agrees with the reported one.[18,19]

2.3b *2-(furan-2-yl)-3-hydroxy-6-methyl-4H-chromen-4-one*: Prepared from 2-hydroxy-5-methyl-acetophenone and furan-2-carboxaldehyde. Crystallized from MeOH:$CHCl_3$ (1:1, v/v); yellow needles; yield 60%; M.p. 198°C.[20] **^{1}H NMR data, DMSO-d_6**: 9.54 (d, 1H, H-5, Ar), 7–8 (m, 5H, Ar), 6.68 (s, OH exchangeable with D_2O), 2.55 (s, 3H, CH_3-6); **IR(KBr,cm^{-1})**: 3225 (OH), 2919 (CH Ar), 1601 (C=O); **Anal.calcd for** $C_{14}H_{10}O_4$: C, 69.42; H, 4.13. Found: C, 69.31; H, 4.26.



Scheme 1. Synthetic scheme for the preparation of FHC and their derivatives.

2.3c *2-(furan-2-yl)-3,6-dihydroxy-4H-chromen-4-one*: Prepared from 2,5-dihydroxy-acetophenone and furan-2- carboxaldehyde. Crystallized from CH_3CN; Brown mass; yield 12%; M.p. 202°C. **^{1}H NMR data, DMSO-d_6**: 9.70 (s, 1H, OH-6), 9.44 (s, 1H, H-5, Ar) 7.83–7.21 (m, 5H, Ar), 6.67 (s, 1H, OH exchangeable with D_2O); **IR (KBr, cm^{-1})**: 3324 (OH), 2923 (CH Ar), 1620 (C=O); **Anal. calcd for** $C_{13}H_8O_5$: C, 63.93; H, 3.27. Found: C, 63.72; H, 3.47.

2.3d *2-(furan-2-yl)-3-hydroxy-6-nitro-4H-chromen-4-one*: Prepared from 2-hydroxy-5-nitroacetophenone and furan-2-carboxaldehyde. Crystallized from EtOH:$CHCl_3$ (1:1, v/v); yellow needles; yield 55%; M.p. 112°C. **^{1}H NMR data, $CDCl_3$**: 7.0–8.55 (m, 7H, Ar), 6.98 (s, OH exchangeable with D_2O); **IR (KBr, cm^{-1})**: 3227 (OH), 2918 (CH Ar), 1618 (C=O), 1344 (NO_2); **Anal. calcd for** $C_{13}H_7O_6$ N: C, 57.14; H, 2.56; N, 5.12. Found: C, 57.62; H, 2.88; N, 4.97.

2.3e *2-(furan-2-yl)-3-hydroxy-6-chloro-4H-chromen-4-one*: Prepared from 2-hydroxy-5-chloroacetophenone and furan-2-carboxaldehyde. Crystallized from MeOH:$CHCl_3$ (1:1, v/v); pale yellow needles; yield 71%; M.p. 167°C.[20] **^{1}H NMR data, $CDCl_3$**: 7.13–8.32 (m, 6H, Ar), 6.88 (s, OH exchangeable with D_2O); **IR (KBr, cm^{-1})**: 3452 (OH), 2943 (CH Ar), 1628 (C=O).

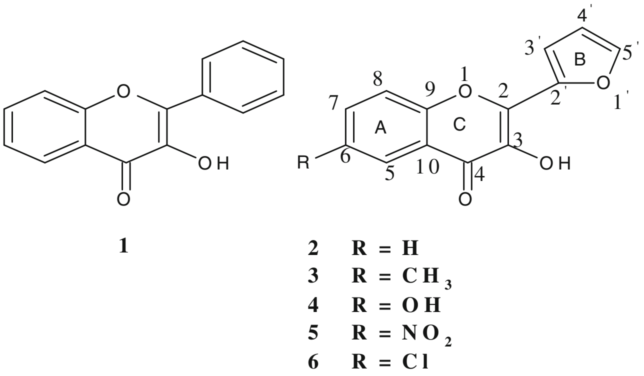


Figure 1. Structures of 2-aryl-3-hydroxychromone derivatives.

3. Results and Discussion

Absorption spectra of six variously substituted 3-HCs (figure 1) have been recorded in different solvents with varying polarity from non-polar (Cyclohexane) to polar aprotic (ACN) and polar protic (MeOH).

A representative spectrum of **FHC** has been shown in three solvents in figure 2.

By carefully examining the finer details of the spectra, it is clear that there are two sets of main bands, set I from 270 to 370 nm and set II around 250 nm. In cyclohexane, set I consists of three peaks at 365, 348 and 315 nm and two shoulders around 333 and 304 nm. Set II has main peak at 248 nm and a small peak at 254 nm. In FHC there are four oxygen atoms which have non-bonding electrons. Among these, oxygen belonging to furan ring show absorption band in the higher energy UV region (>220 nm). Therefore, here, three transitions due to the excitation of non-bonding electron (n) to π^* orbitals have been observed in cyclohexane. It is well known that n-π^* transitions become weak and their absorption band shows a blue shift in going from a non-polar to polar solvents. So here, disappearance of two weak bands in polar solvent, which appear in the form of shoulders in cyclohexane at 304 and 333 nm, shows that these are due to n-π^* transitions. By comparing the shape and position of the two bands at 365 and 348 nm, observed in cyclohexane, with those in ACN and MeOH, it is clear that the former band is blue shifted and the latter is red shifted in going from non-polar to polar solvents. It shows that 365 nm band is due to the n-π^* transition and 348 nm band is due to the π-π^* transition. The lowest energy peak at 365 nm is assigned to the excitation of most easily

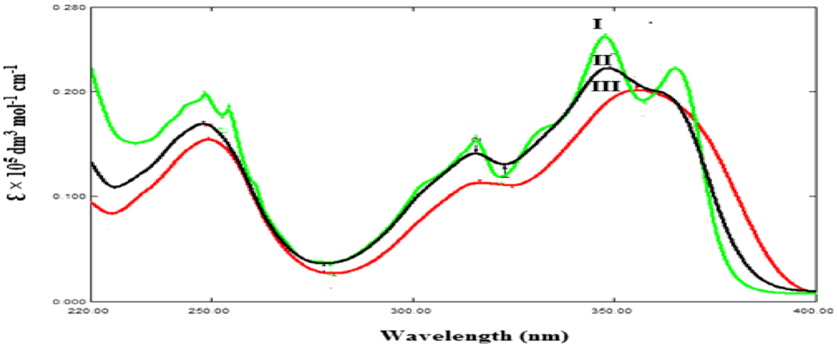


Figure 2. Absorption spectra of **FHC** (**2**) in three solvents. I, II and III are in cyclohexane, acetonitrile and methanol respectively.

available non-bonding electrons of ‘O’ at 4-carbonyl group of the molecule. One of the two shoulders (333 nm) should be due to the excitation of non-bonding electrons of ‘O’ of 3-OH group and other shoulder (304 nm) seems to be due to 1-oxygen heteroatom in the ‘C’ ring. The other low energy peak at 348 nm in cyclohexane, which is red shifted by 1 nm in ACN and by 7.5 nm in MeOH should be due to the π-π^* transition because of the excitation of the electrons belonging to the double bond of the 4-carbonyl group, which is highly conjugated. The next band at 315.5 nm in cyclohexane, which remains at the same position in all the solvents is due to the excitation of π-electrons of the 2–3 double bond in the ‘C’ ring as it remains isolated from the intermolecular solute-solvent interactions. Last band at 248.4 nm (set II) in cyclohexane, which remains at the same position in all the three solvents is because of the benzoylic moiety of the molecule. The story with all the other four derivatives (**3–6**) is nearly similar to **FHC**.

During electronic excitation of various derivatives of 3HC, there is excited state intramolecular charge transfer (ESICT), which in the case of **3HF** is induced mainly by 1-oxygen heteroatom towards 4-carbonyl group. The contribution of phenyl ring at the 2nd position to ESICT effect on 4-carbonyl, is little due to its non-planarity and non-conjugation.[15,16] In **FHC**, furyl, which replaces phenyl, is the major contributor as electron donor in the molecule because planarity due to its small size increases conjugation in the molecule and is also richer in electrons as compared to phenyl ring. This observation has been reported earlier and is also observed here in our spectral data (table 1).[4,14,15,21] There is a red shift in all the n-π^* and π-π^* bands and also intensity of all the bands is increased by going from **3HF** to **FHC**. This perspective of studying ESICT at the 4-carbonyl group,

Table 1. Spectral data for the absorption maxima (λ_{max}) of the studied 3-Hydroxychromones in three solvents.

		Band I					
		Cyclohexane		Acetonitrile		Methanol	
Sr. No.	Compound	λ_{max} for the Peaks	$\varepsilon \times 10^{-5}$ ($dm^3mol^{-1}cm^{-1}$)	λ_{max} for the Peaks	$\varepsilon \times 10^{-5}$ ($dm^3mol^{-1}cm^{-1}$)	λ_{max} for the Peaks	$\varepsilon \times 10^{-5}$ ($dm^3mol^{-1}cm^{-1}$)
1	3HF	354.60	0.112	....	....	....	....
		340.00	0.141	340.0	0.178	344.20	0.145
		....	....	....	....	....	....
		304.20	0.102	304.20	0.141	305.10	0.104
		....	....	....	....	....	....
2	FHC	365.2	0.221	....	....	....	....
		347.8	0.252	348.8	0.222	355.4	0.196
		....	....	....	....	....	....
		315.6	0.172	315.6	0.141	316.20	0.112
		....	....	....	....	....	....
3	6MEFHC	366.00	0.0638	....	....	....	....
		348.00	0.0765	349.20	0.149	356.40	0.169
		....	....	....	....	....	....
		....	....	....	0.122	....	....
		....	....	....	....	....	....
4	6OHFHC			....	....	....	....
		....	....	....	....		....
				338.61	....	Broad band at 340–352 nm	....
				....	....	....	....
				....	....	....	....
5	$6NO_2FHC$	376.40	0.0200	....	....	....	....
		358.20	0.0240	358.20	0.164	363.40	0.107
		....	....	....	....	....	....
		301.0	0.0280	309.60	0.178	310.00	0.126
		....	....	....	....	....	....
6	6ClFHC	371.00	0.150	....	....	....	....
		354.20	0.170	353.80	0.214	360.40	0.251
		....	....	....	....	....	....
		327.80	0.119	325.40	0.156	....	....
		....	....	....	....	....	....

which in turn affects the ESIPT, has been taken as the reference method for the study of ESICT effect by the substitution at the 6th position.

However, the effect of substitution in benzoylic part of 3HC has not been explored except a few reports.[15–17,22] Demchenko *et al.* have studied the effect of OCH_3 group, an electron rich chromophore, at the 7th position on both the absorption and emission spectra.[16] Interestingly, the effect of this electron rich substituent produces an opposite effect to that of substituents at the 2nd position on the electron density of the 4-carbonyl group.

Here, in the studied derivatives of 3HC, substitution has been made at the 6th position with electron donor groups (EDG) like that of CH_3, OH and electron withdrawing group (EWG) like that of NO_2. The effect of Cl group, which has negative inductive effect and positive resonance effect, has also been included. Role of these substitutions at the 6th position on the electron density of 4-carbonyl group has been interpreted from the changes brought in their absorption spectra.

Broadly, there are all types of absorption bands in the case of all 3HCs as observed in **FHC** as shown in figures 3 and 4. Spectrum of OH substituent (**6OHFHC**) could not be recorded in cyclohexane because of its immiscibility in cyclohexane. For all the other five 3HCs, the range of the band due to benzoylic part of the molecule varies between 240 nm to 250 nm. The significant blue shift (about 10 nm, along with the decrease in intensity) among these 3HCs is for NO_2 substituent (**6NO$_2$FHC**), while the position of this band for other 3HC derivatives remains the same in all the solvents. It seems that NO_2 being a strong EWG decreases the electron density in the benzoylic part of the molecule and hence the observed blue shift and decreased intensity of this band.

Among the absorption bands in set I, the n-π^* transition due to 'O' of 3-OH group, which is only observed using cyclohexane as the solvent, is not significantly changed by substitutions. The effect, whatever it may be, can be better studied from the ESIPT effect in the emission spectra. The n-π^* transition due to 'O' of 4-carbonyl group at 365 nm, which also only appears in cyclohexane as a solvent in all **3HCs** (**2-6**), varies between 365 to 377 nm. In **FHC**, it is red shifted by more than 11 nm as compared to **3HF**. Among the derivatives of FHC, the significant red shift, which is more than 10 nm, is only observed by going from **FHC** to **6NO$_2$FHC**.

Similarly, the position of the π-π^* transitions due to 4-carbonyl group varies from 340 to 360 nm in both cyclohexane and ACN and the range in MeOH is from 344 to 364 nm, which is slightly red shifted. There is a significant red shift of about 8 to 10 nm in going from 3HF to **FHC** and about 10 nm by going from **FHC** to **6NO$_2$ FHC** in all the solvents.

Range of the absorption band due to double bond (2–3 bond) in the 'C' ring is from 301 to 330 nm for all **3HCs** (**1** to **6**) in all the solvents. There is a red shift of about 10 nm by going from **3HF** to **FHC**

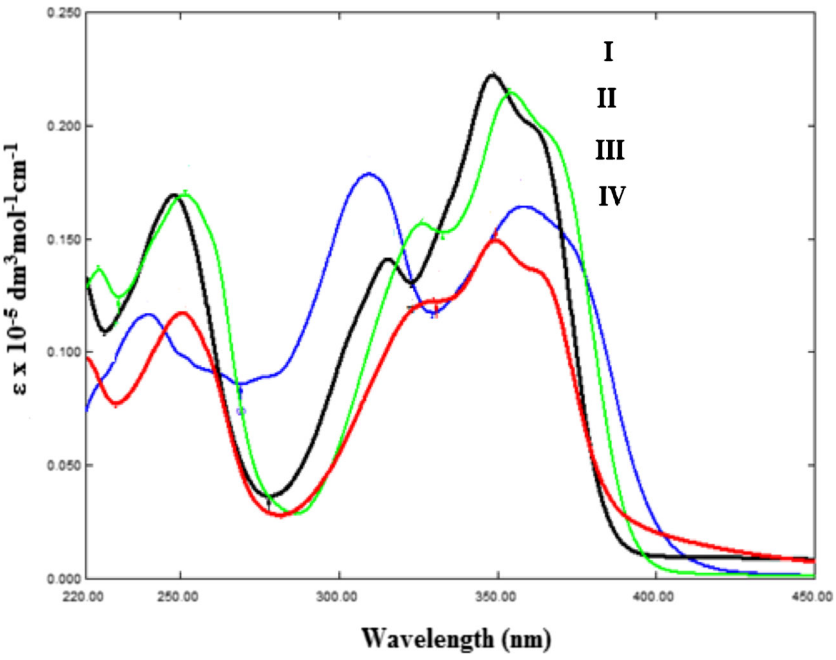


Figure 3. UV/VIS absorption spectra of various substituted derivatives of 3HC in acetonitrile. I, II, III and IV are **2**, **6**, **5** and **3** respectively.

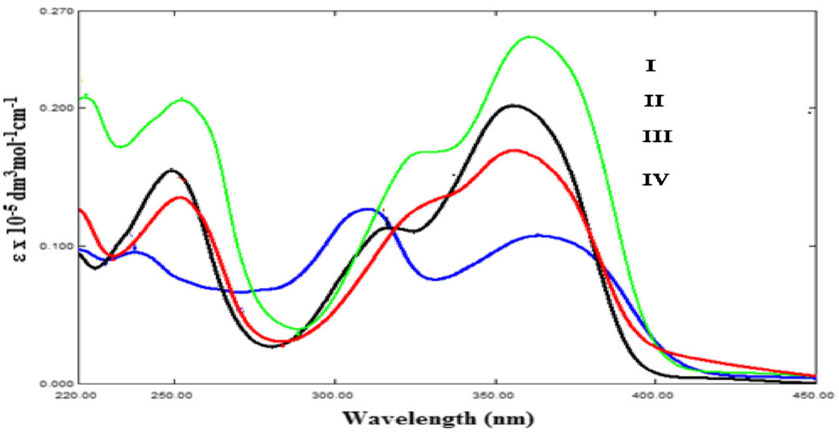


Figure 4. UV/VIS absorption spectra of various substituted derivatives of 3HC in methanol. I, II, III and IV are **6, 2, 3** and **5** respectively.

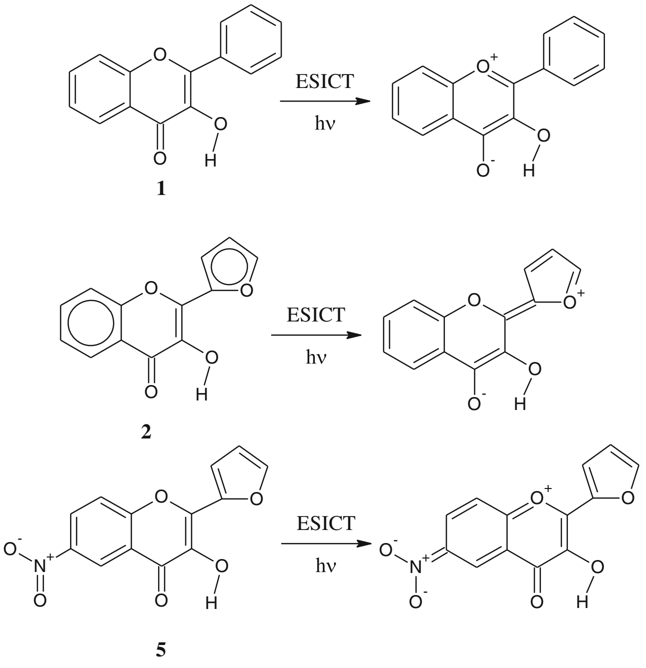
and a further red shift of about 12 nm by going from **FHC** to **6MEFHC** and **6ClFHC**. In OH substitution (**6OHFHC**) the shift is so high, that the two π-π^* absorption bands, one in the ‘C’ ring (2–3 double bond) another due to the 4-carbonyl group merge to form a broad band between 340 to 352 nm in methanol. However, there is a blue shift of about 15 nm in cyclohexane and 6 nm in ACN and MeOH in going from **FHC** to **6NO$_2$ FHC**. It is an obvious result that EDG at the 6th position increases the electron density at the ‘C’ ring which causes the red shift like that of furyl at the 2nd position and EWG (NO$_2$) has the opposite effect.

Although the substitution at the 6th position affects all the absorption bands by smaller or greater extent by changing the electron density or dipole moment of the molecule but the effect on the electron density/dipole moment of the π-π^* band due to the 4-carbonyl group mainly participates in the ESIPT process. Electron donating group (EDG) at the 6th position makes a blue shift and electron withdrawing group (EWG) shows a red shift in this band. Furthermore, the gap in energy between π-π^* transitions due to 4-carbonyl group and at 2–3 position of ‘C’ ring remains nearly the same in 3HF and FHC. While here, with EDG at the 6th position this gap is decreased and with EWG, there is a significant increase in this gap (table 1).

All this data shows that the behaviour of various substituents at the 6th position is different from that of substituent at the 2nd position. The electromeric effect of this kind of substitution on 2–3 double bond in the ‘C’ ring is similar but the effect on the double bond of 4-carbonyl group is opposite.

The effect of substitution is actually due to two parameters, in individual or in combination, one because of the change in electron density and second because of the change in the overall polarity of the molecule as has been reported.[16,17] Here, the substitution at the 2nd position primarily changes the electron density directly at the 4-carbonyl group and substitution at the 6th position changes the electron density of the ‘C’ ring directly, which strongly increases the overall dipole moment of the molecule, which in turn changes the electron density at 4-carbonyl group (scheme 2).

Figures 5 and 6 show the effect of substituent on the emission spectra. The red shift and increased I_{N*}/I_{T*} in **FHC** as compared to **3HF** is on the lines of already reported results.[14,15] The only significant effect of substitution at the 6th position is on the position of the N* band and on the I_{N*}/I_{T*} ratio in polar solvents. Position of N* band shows a red shift of 5 nm in NO$_2$ substituent



Scheme 2. Effect of substitution on ESICT.

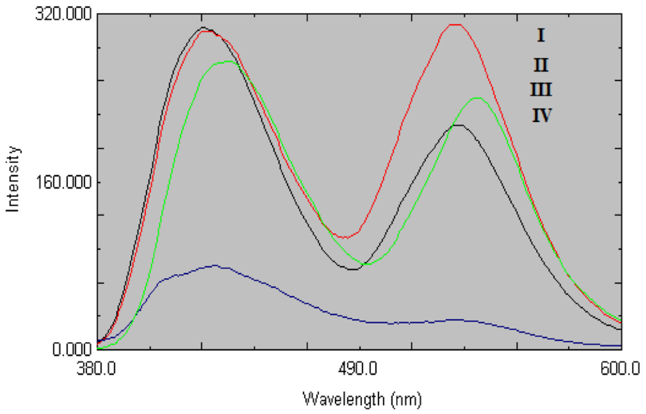


Figure 5. Fluorescence spectra of various substituted derivatives of 3HC in methanol. I, II, III and IV are for **3**, **6**, **2** and **5** respectively. Exciting wavelength, 359 nm.

(**5**) and a blue shift of 5nm in OH substituent (**4**) in methanol only along with significant increase (2 times) in I_{N*}/I_{T*} ratio in former and decrease (2 times) in the latter case as compared to **FHC** (table 2).

In the case of Cl substituent, the effect on the emission bands is more pronounced than in the absorption spectra. There is red shift in both the N* and T* bands along with the significant (3 times) increase in I_{N*}/I_{T*} in ACN. ESIPT may be affected either by the change in electron density at 4-carbonyl group or/and by the increased dipole moment of the molecule. Klymchenko *et al.* have studied the effect of charged substituents at 6th position on absorption and emission spectra as compared to its neutral analogues. It has been shown that absorption and emission spectra are shifted to longer wavelength with respect to its neutral analogues. The attached positively charged ammonium group also dramatically increases the I_{N*}/I_{T*} ratio in all the solvents.[17] Here, our results on the absorption and emission spectra are also on the same lines. The increase and decrease in dipole moment by substitution at the 6th position with EWG and EDG stabilizes and destabilizes the N* state in the polar solvents respectively. The difference in the present studies and the earlier observations is that the substituents have increased the dipole moment of the molecule directly but here, the change is brought about by the ESICT effect.

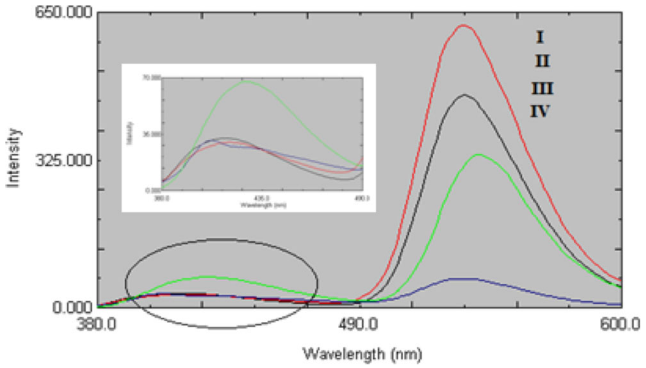


Figure 6. Fluorescence spectra of various substituted derivatives of 3HC in acetonitrile. I, II, III and IV are for **3**, **6**, **2** and **5** respectively. Exciting wavelength 359 nm.

Table 2. Wavelength maxima of emission from N* and T* of the substituted 3-hydroxychromones in three solvents.

Solvent	Compounds	$\lambda^{N*}_{max/nm}$	$\lambda^{T*}_{max/nm}$	I_{N*}/I_{T*}
Cyclohexane	1	....	527	....
	2	....	534	....
	3	....	533	....
	4	....	....	....
	5	....	550	....
	6	....	....	....
Acetonitrile	1	400**	527	0.0266
	2	415**	534	0.0695
	3	416**	534	0.0483
	4	417**	534	0.0681
	5	407(peak), 424 (shoulder)	535	0.4857
	6	426	539	0.2015
Methanol	1	407	531	0.3634
	2	425	530	1.4313
	3	426	531	0.9809
	4	420	525	0.6540
	5	407(shoulder), 430 (peak)	530	2.8079
	6	435	540	1.1456

λ^{N*}_{max} and λ^{T*}_{max} are the position of the emission maxima of the N* and T* forms, respectively. I_{N*}/I_{T*} are intensity ratios of two emission maxima.
** indicate the broad band.

4. Conclusions

Behaviour of the substitution in the benzoylic moiety is different from the substitution at 2nd position in 3HC molecules. Both these kinds of substitutions affect the electron density at the 4-carbonyl group of the molecule. Substitution of groups with different electromeric effect at the 6th position changes the electron density indirectly by changing the dipole moment of the 'C' ring, instead of directly affecting the charge density at 4-carbonyl group, unlike the substitution at the 2nd position which directly changes the electron density at 4-carbonyl group.

Supplementary Information

The proton NMR /D_2O data for various synthesized compounds (**2** to **6**) have been assigned in the figures S1–S12.

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