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# Synthesis and optical properties of coumarins and iminocoumarins: Estimation of ground- and excited-state dipole moments from a solvatochromic shift and theoretical methods



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# 1. Introduction

# The coumarin (2-H-chromen-2-one) moiety is often found in natural products [1]. In view of the ubiquity of this fragment in a variety of biologically active compounds, the synthesis of various <sup>2</sup>H-chromen-2-one analogs is important in gaging their potential as a source of chemotherapeutics [2]. They have been shown to inhibit the replication of HIV and thus exhibit a therapeutic potential [3]. A large number of structurally novel coumarin derivatives have been reported to show substantial cytotoxic and anti-HIV activities in vitro and in vivo [4,5]. Coumarins have been extensively studied due to their practical applications [6–10], which include uses as biological and chemical sensors, fluorescent probes and laser dyes [11–14].

In the present work, we designed and synthesized a 2-imino-<sup>2</sup>H-chromene-3-carbonitrile 3a, 7-hydroxy-2-imino-<sup>2</sup>H-chromene-3-carbonitrile 3b, 2-oxo-<sup>2</sup>H-chromen-3- carbonitrile 4a and 7-hydroxy-2-oxo-<sup>2</sup>H-chromen-3- carbonitrile 4b (Scheme 1).

All these compounds are described in the literature [15]. Using conventional heating, we have realized that these products under

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# ABSTRACT

The optical properties of coumarin and iminocoumarin were investigated in different solvents by UV/vis absorption and fluorescence spectroscopy at room temperature (298 K). These compounds were characterized by UV-vis, FT-IR, mass spectroscopy and NMR. A bathochromic shift is observed in absorption and fluorescence spectra of our molecules with increasing solvent polarity. Solvatochromic correlations were used to obtain the ground-state and excited-state dipole moments. The excited-state dipole moments for all the molecules were found to be larger than the corresponding ground-state dipole moments.

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microwave irradiation and reaction give excellent yield, have short reaction times and were carried out in environmentally friendly conditions: which means less solvent, less added acid, and less energy consumed for heating. All compounds were characterized with NMR, IR and mass spectroscopy.

The photophysics and spectral properties of these compounds (Scheme 1) were investigated in different solvents.

# 2. Experimental

# 2.1. Apparatus

Melting points were determined by an electrothermal Stuart scientific SPM3 apparatus fitted with a microscope and are uncorrected. IR spectra (KBr) were recorded on a FTIR – Perkin Elmer (Spectrum One). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in deuteriochloroform solutions and with DMSO-d<sub>6</sub> with TMS as internal standard on a BRUKER Avance 300, carbon: 75.47 MHz, proton: 300.13 MHz, and the chemical shifts are expressed in  $\delta$  (ppm). <sup>13</sup>C assignments were made using dept 135 and the mass spectra were recorded on a MicroTOF-Q de Bruker Daltonics.

All spectrophotometric measurements were conducted at ambient temperature. UV/vis absorption spectra were recorded on a Varian

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R=H: 3a,4a, R= OH: 3b,4b

(i)NaHCO3,RT;(ii)MW irradiation,300W,9min,HCI 2N

Scheme 1. Synthesis of coumarins and iminocoumarins

CARY 50 conc. The estimated experimental error was 2 nm on the band maximum and 5% on the molar extinction coefficient. Fluorescence work was performed on a Varian CARY Eclipse spectrofluorometer. All excitation and emission spectra were corrected. The fluorescence quantum yields were determined using fluorescein disodium salt ( $\Phi = 0.9$ ) as standard.

The fluorescence quantum yields  $(\Phi)$  were determined using the classical formula:

$$\Phi_{X} = \left( \Phi_{s.} A_{s.} F_{x.} n_{x}^{2} \right) / \left( A_{x.} F_{s.} n_{s}^{2} \right).$$

Where "A" is absorbance at the excitation wavelength, "F" is the area under the fluorescence curve and "n" is the refractive index of the solvents used. Subscripts "s" and "x" refer to the standard and to the sample of unknown quantum yield, respectively. The excitation source was a long life Xenon flash lamp.

# 2.2. Materials

For synthesis, salicylaldehyde, malonitrile, and 2,4-dihydroxy benzaldehyde were purchased from Aldrich. The solvents used in the present study, namely acetonitrile, dimethylsulfoxide, chloroform, ethyl acetate, cyclohexane and tetrahydrofurane were of HPLC and spectroscopic grade (purchased from Fluka and Labosi). The required solutions were prepared at a fixed solute concentration  $(3.2 \cdot 10^{-5} \text{ M})$ .

# 3. Results and discussion

## 3.1. UV/vis absorption spectra

The UV/vis absorption spectra of all the compounds 3a-b and 4a-b (concentration  $3.2 \times 10^{-5}$  M) were recorded immediately after dissolution of the products and filtration through paper. The magnitudes of Stokes shift vary between 3369 and 5248 cm<sup>-1</sup>. The values of the Stokes shift are also indicative of the charge transfer transition.



Fig. 1. (a-d): Absorption spectrum of all compounds (a) 3a, (b) 4a, (c) 3b and (d) 4b in different solvents.



Fig. 2. Emission spectrum of all compounds 3a, 4a, 3b and 4b in different solvents.

The absorption spectrum of all the compounds in tetrahydrofurane, chloroform, acetonitrile, cyclohexane, ethyl acetate and dimethyl-sulfoxide displays two distinct bands (Fig. 1(a)-(d)).

The absorption spectrum exhibited a band at around 290–300 nm, attributed to the  $n-\pi^*$  transition and associated with the imine and carbonyl groups. A large band at long wavelengths lying around 347, 355,

#### Table 1

Spectroscopic and photophysical characteristics of the derivatives of compounds 3(a-b) and 4(a-b) in different solvents.

Compounds	(Solvent)	$\lambda_{abs} (nm)$	$\epsilon  (M^{-1}  cm^{-1})$	$\lambda_{ex} (nm)$	$\lambda_{em} (nm)$	$(\overline{v}_a \text{-} \overline{v}_f) (cm^{-1})$	$\Phi_{\rm f}$
3a	DMSO	347	22,405		406	4187.90	$1.24 \cdot 10^{-3}$
	Acetonitrile	348	22,231		407	4165.61	$1.19 \cdot 10^{-3}$
	THF	350	10,496	273	409	4121.55	$6.81 \cdot 10^{-2}$
	Ethyl acetate	351	5581		410	4099.78	$8.42 \cdot 10^{-2}$
	Chloroform	352	7974		411	4078.19	$9.46 \cdot 10^{-2}$
4a	DMSO	334	17,307		405	5248.76	$2.20 \cdot 10^{-3}$
	Acetonitrile	336	9246		407	5191.88	$1.82 \cdot 10^{-3}$
	THF	338	8387	265	409	5135.92	$2.06 \cdot 10^{-2}$
	Ethyl acetate	339	7455		410	5108.28	$9.61 \cdot 10^{-2}$
	Chloroform	340	7440		411	5080.86	$0.58 \cdot 10^{-2}$
	Cyclohexane	342	6433		412	4967.92	$2.07 \cdot 10^{-2}$
3b	DMSO	355	13,549		409	3719.13	$2.20 \cdot 10^{-3}$
	Acetonitrile	356	11,275		408	3580.08	$8.60 \cdot 10^{-3}$
	THF	360	10,829	314	412	3505.93	$2.62 \cdot 10^{-2}$
	Ethyl acetate	362	13,087		414	3469.72	$7.20 \cdot 10^{-2}$
	Chloroform	364	18,036		415	3376.14	$3.42 \cdot 10^{-2}$
4b	DMSO	351	58,565		401	3552.37	$1.23 \cdot 10^{-3}$
	Acetonitrile	352	50,206		402	3533.46	$0.59 \cdot 10^{-3}$
	THF	355	19,771	311	405	3477.57	$1.02 \cdot 10^{-3}$
	Ethyl acetate	356	32,765		406	3459.34	$5.97 \cdot 10^{-2}$
	Chloroform	359	14,407		408	3345.35	$5.09 \cdot 10^{-2}$
	Cyclohexane	361	30,435		411	3369.93	$1.05 \cdot 10^{-2}$

 $\lambda_{abs}$ : Absorbance wavelength;  $\varepsilon$ : corresponding molar extinction coefficient;  $\lambda_{ex}$ : maximum excitation wavelength;  $\lambda_{em}$ : maximum emission wavelength and shoulders;  $\overline{v}_a - \overline{v}_f$ : Stokes shift; and  $\Phi_f$ : fluorescence quantum yield with excitation at the maximum absorption wavelength.



Fig. 3. Schematic representation of the different <sup>2</sup>H-chromene derivatives including their rotamers. Adopted nomenclatures are presented.

334 and 351 nm for 3a, 3b, 4a and 4b, in different solvents associated with the  $\pi$ - $\pi$ <sup>\*</sup>, the latter being associated with the cyano group.

This band can be attributed to the charge transfer that occurs between the electron donor group (the hydroxyl group) and the electrowithdrawing pole, constituted by the carbonyl, imino and the cyano groups that reinforce the electron-attracting strength on this side of these molecules.

# 3.2. Fluorescence spectra

The fluorescence of compounds 3a–b and 4a–b in all solvents used above  $(3.2 \times 10^{-5} \text{ M})$  was observed at room temperature.

#### 3.2.1. Steady-state emission spectra

For all compounds, the shape and position of the emission spectra were independent of the excitation wavelength, which confirms that only one species emits in each solution.

The emission spectra underwent a strong blue shift when the polarity of the solvent increased.

The peak moved from 406 in DMSO to 407 nm in acetonitrile to 409 nm in THF and to 411 nm in chloroform for compound 3a (Fig. 2). The emission spectra for compound 3b (Fig. 2) showed wavelength bands at 409 nm in DMSO, at 410 nm in chloroform and at 415 nm in CHCl<sub>3</sub>.

However large variations were found in the shape of the spectra according to the medium. For all the compounds, the intensity of the peak increased with the polarity of the solvent.

The fluorescence quantum yields were measured (Table 1). It ranges from  $10^{-2}$  to  $10^{-3}$  being divided by ten when passing from cyclohexane to DMSO. Our results are comparable to those described in the literature [14,16] where the authors have shown that the quantum yield of the chromene dye varies between  $10^{-2}$  and  $10^{-3}$ . 2-Imino-<sup>2</sup>H-chromene-3-carbonitrile 3a, 7-hydroxy-2-imino-<sup>2</sup>H-chromene-3-carbonitrile 4a and 7-hydroxy-2-oxo-<sup>2</sup>H-chromen-3-carbonitrile 4b are characterized by good fluorescence efficiency in aprotic apolar media.

# 3.3. Theoretical calculations of ground-state dipole moments

#### 3.3.1. Computational methods

The B3LYP [17,18] density functional method as implemented in the Gaussian 03 package [19] was used throughout the whole study. All structures were fully optimized by using the 6-31 + G (d,p) basis set. The harmonic vibrations were also calculated in order to characterize the structures of rotameric forms of different chromene derivatives and thermodynamic properties. Solute–solvent interaction was evaluated by the use of the conductor-like polarizable continuum model (CPCM) [20], in which the cavity was built up using the united atom topological model (UATM). The CPCM calculations were performed as single points on the gas phase geometries. The different solvents were modeled using their dielectric constant.

#### Table 2

Relative energies  $\Delta E_{(2PVE)}$  (kcal/mol) in the gas phase, relative energies  $\Delta E_0$  in solvent phases, and dipole moment (Debye) calculated at the B3LYP / 6–31 + G(d,p) level of theory.

Compounds	Gas phase ( $\epsilon = 1.000$ )		DMSO ( $\epsilon = 46.82$	6)	Acetonitrile ( $\epsilon = 1$	35.688)	Chloroform ( $\epsilon = 4.7113$ )	
	$\Delta E_{(ZPVE)}$	μ	$\Delta E_0$	μ	$\Delta E_0$	μ	$\Delta E_0$	μ
2-Imino- <sup>2</sup> H-chromene-3-co	arbonitrile 3a							
Molecule-3a <sub>1</sub>	01.23	06.35	01.91	09.05	01.83	09.01	0.003	08.37
Molecule-3a <sub>2</sub>	00.00	07.48	00.00	10.61	00.00	10.59	00.00	09.83
7-Hydroxy-2-imino- <sup>2</sup> H-chr	omene-3-carbonitrile 3	b						
Molecule-3b <sub>1</sub>	00.06	08.72	00.00	12.71	00.00	12.69	00.00	11.70
Molecule-3b <sub>2</sub>	00.00	07.63	00.07	11.00	00.07	10.98	0.0002	10.15
Molecule-3b <sub>3</sub>	00.80	06.05	01.81	08.73	01.73	08.70	01.45	08.05
Molecule-3b <sub>4</sub>	01.15	07.94	01.75	11.59	01.72	11.56	01.54	10.67
2-0xo- <sup>2</sup> H-chromene-3-car	bonitrile 4a							
Molecule-4a1	-	08.34	-	11.85	-	11.81	-	10.98
7-Hydroxy-2-oxo- <sup>2</sup> H-chromene-3-carbonitrile 4b								
Molecule-4b <sub>1</sub>	00.36	09.89	00.00	14.36	00.00	14.32	00.14	13.24
Molecule-4b <sub>2</sub>	00.00	08.20	00.03	11.81	00.01	11.78	00.00	10.90

# 3.3.2. Results and discussion

3.3.2.1. Relative stability. Fig. 3 depicts the schematic representation of the different <sup>2</sup>H-chromene derivatives including their rotamers when they exist. Relative energies for different rotamers computed at the B3LYP / 6-31 + G(d,p) level are summarized in Table 2. An inspection of the relative energies of rotamers reported in Table 2 shows a relative-ly small difference between rotamers and reveals that the variation of the spatial orientation of the -OH and/or =NH groups in different <sup>2</sup>H-chromenes has an insignificant effect on the relative stabilities. The very low relative rotamer energies suggest that many rotamers are present in the samples at room temperature.

Probably one of the most crucial factors determining the rotamer distribution is the environment. The study of interaction between solute and solvent is normally a complicated process. A CPCM allows one to take into account long-range interactions between solute and solvent. The continuum model is computationally efficient for the prediction of stability trends in the liquid phase. The energetic parameters of the rotamer forms in different solvents calculated at the B3LYP / 6-31 + G(d,p) level of theory are also listed in Table 2. Except for 2-imino-<sup>2</sup>H-chromene-3-carbonitrile, the introduction of solvent in 7-hydroxy-2-imino-<sup>2</sup>H-chromene-3-carbonitrile and 7-hydroxy-2-oxo-<sup>2</sup>H-chromene-3-carbonitrile modifies the hierarchy between rotamers. It is worth mentioning that the relative energies of rotamers remain very small. The molecular radius a0 (A°) of the spherical cavity obtained for optimized geometries for different chromenes are calculated at the B3LYP/6-31+G(d,) (Table 3).

3.3.2.2. Dipole moment. Dipole moment reflects the degree of charge distribution in a molecule. Habitually it is used to clarify a variety of physical and chemical properties. The dipole moments of different chromene derivatives have been computed at the B3LYP/6–31 + G(d,p) level of theory in different environments and are shown in Table 2. As can be seen, there is an important variation in dipole moment, while going from gaseous to solvent phase environments. Dipole moments of the studied compound have higher values in the solvent phase. This is due to the interactions between the molecules of solvents and the dipolar molecule of compounds. The value of the dipole moments increases with dielectric constant in the following order:

#### DMSO>acetonitrile>chloroform>gas phase.

In the case of chromenes having different rotamers it can be seen that, under the liquid phase, there is a direct correlation between the dipole moment and the order of stability. Polar rotamers have a larger dipole moment in a polar solvent, and consequently the stability of the molecular system is increased.

# 3.4. Determination of dipole moments in the excited-state in several solvents using the solvatochromic method

The dipole moment of a molecule in the excited-state is determined by the effect of electric field (internal or external) on its spectral band position. The solvent dependence of the absorption and fluorescence band maxima is used to estimate the excitation-state dipole

#### Table 3

Molecular radius  $a_0$  (Å) of the spherical cavity obtained for optimized geometries for different chromenes calculated at the B3LYP / 6–31 + G(d,p) level of theory. We considered only the most stable rotamers obtained in the liquid phase.

Compounds	$a_0$ (Å) molecular radius
2-Imino- <sup>2</sup> H-chromene-3-carbonitrile 3a	4.53
7-Hydroxy-2-imino- <sup>2</sup> H-chromene-3-carbonitrile 3b	4.45
2-Oxo- <sup>2</sup> H-chromene-3-carbonitrile 4a	4.60
7-Hydroxy-2-oxo- <sup>2</sup> H-chromene-3-carbonitrile 4b	4.46

#### Table 4

Summary of solvent properties and calculated values of solvent polarity parameters  $f(\epsilon,n)$  and  $\Phi(\epsilon,n)$ .

No.	Solvent	μ	3	n	f(ɛ,n)	$\Phi(\epsilon,n)$
1	Dimethylsulfoxide	3.9	46.7	1.478	0.841	1.488
2	Acetonitrile	3.45	37.5	1.344	0.863	1.331
4	Tetrahydrofurane	1.75	7.58	1.407	0.5492	1.102
5	Ethyl acetate	1.88	6.02	1.372	0.489	0.996
6	Chloroform	1.15	4.81	1.446	0.371	0.972
7	Cyclohexane	0.00	2.02	1.426	-0.003	0.575

moments of different molecules. The equations [Eqs. (1) and (2)] that afford the best results in the change of dipole moments of an excited molecule were suggested by A. Kawski and P. Bojarski [21–23]: The difference  $\overline{v}_a - \overline{v}_f$ :

$$\overline{\nu}_{a} - \overline{\nu}_{f} = S_{1} f(\epsilon, n) + \text{const.}$$

$$\tag{1}$$

And the sum  $\overline{\nu}_{a} + \overline{\nu}_{f}$ :

$$\overline{\nu}_{a} + \overline{\nu}_{f} = -S_{2}\Phi(\epsilon, n) + \text{const.}$$

$$(2)$$

Where

$$\Phi(\varepsilon, \mathbf{n}) = f(\varepsilon, \mathbf{n}) + 2g(\mathbf{n}). \tag{3}$$

And

$$g(n) = \frac{3}{2} \frac{n^4 - 1}{\left(n^2 + 2\right)^2}.$$
(4)

In these Eqs.,  $\overline{v}_a$  and  $\overline{v}_f$  are the absorption and fluorescence maxima  $(cm^{-1})$ , respectively, and n and  $\varepsilon$  are the refractive index and the dielectric constant of solvents, respectively.

Table 5

Spectroscopic and photophysical characteristics of 3a-b and 4a-b in different solvents.

Solvent	$\overline{\nu}_a \ (cm^{-1})$	$\overline{v}_{f}$ (cm <sup>-1</sup> )	$\overline{v}_a$ - $\overline{v}_f$ (cm <sup>-1</sup> )	$\overline{v}_a + \overline{v}_f \; (cm^{-1})$
DMSO				
3a	28,818.44	24,630.54	4187.90	53,448.98
4a	29,940.12	24,691.36	5248.76	54,631.48
3b	28,169.01	24,449.88	3719.13	52,618.89
4b	28,490.03	24,813.89	3552.37	53,427.68
Acetonitrile				
3a	28,735.63	24,449.88	4165.61	53,305.66
4a	29,673.59	24,509.80	5191.88	54,331.93
3b	28,089.88	24,570.02	3580.08	52,599.69
4b	28,490.03	24,875.62	3533.46	53,284.71
THF				
3a	28,653.29	24,390.24	4121.55	53,021.31
4a	29,585.80	24,449.88	5135.92	54,035.68
3b	27,624.31	24,570.02	3505.93	52,049.62
4b	28,248.59	24,570.02	3477.57	52,860.37
Ethyl acetate				
3a	28,571.43	24,271.84	4099.78	52,880.27
4a	29,498.52	24,330.90	5108.28	53,888.78
3b	27,548.21	24,509.80	3469.72	51,778.89
4b	28,169.01	24,570.02	3459.34	52,720.43
Chloroform				
3a	28,409.09	24,213.07	4078.19	52,739.99
4a	29,411.76	24,330.90	5080.86	53,742.66
3b	27,548.21	24,271.84	3376.14	51,568.91
4b	28,169.01	24,449.88	3345.35	52,364.96
Cyclohexane				
3a	28,248.59	-	-	-
4a	29,239.76	24,271.84	4967.92	53,511.61
3b	27,397.26	-	-	-
4b	28,089.89	24,154.59	3369.93	52,031.73

The expressions for the solvent parameters  $f(\varepsilon,n)$  and  $\Phi(\varepsilon,n)$  are given by A. Kawski and colleagues [21–23]:

$$f(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[ \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right]$$
(5)

$$\Phi(\varepsilon, \mathbf{n}) = \left(\frac{2n^2 + 1}{(n^2 + 2)} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right) + \frac{3(n^4 - 1)}{(n^2 + 2)^2}\right). \tag{6}$$

The calculated values of solvent polarity parameters  $f(\varepsilon,n)$  and  $\Phi(\varepsilon,n)$  are given in Table 4.

Table 4 summarizes solvent properties and calculated values of solvent polarity parameters  $f(\varepsilon,n)$  and  $\Phi(\varepsilon,n)$ .

From Eqs. (1) and (2) the expression for slopes  $S_1$  and  $S_2$  are given by:

$$S_{1} = \frac{2\left(\mu_{e} - \mu_{g}\right)^{2}}{hca_{0}^{3}}$$
(7)

$$S_2 = \frac{2\left(\mu_e^2 - \mu_g^2\right)}{hca_0^3}.$$
 (8)

Where  $\mu_g$  and  $\mu_e$  are ground- and excited-state dipole moments of the solute molecule. The symbols h and c are Planck's constant and the light velocity in vacuum, respectively.  $a_0$  is the Onsager cavity radius of the solute molecule and the values were calculated from the

molecular volume of dye molecules according to Suppan's equation [24,25]:  $a_0 = (3M/4\pi\delta N)^{1/3}$ , where  $\delta$  is the density of the solute molecule, M is the molecular weight of solute and N is Avogadro's number.

The ground- and excited-state dipole moments are estimated by means of Eqs. (9)-(11). Based on Eqs. (7) and (8) and assuming that the symmetry of the investigated solute molecules remains unchanged upon electronic transition and the ground- and excited-state dipole moments are parallel, one obtains:

$$\mu_{g} = \frac{|S_{2}-S_{1}|}{2} \left(\frac{hca_{0}^{3}}{2S_{1}}\right)^{1/2}$$
(9)

$$\mu_{e} = \frac{|S_{2} + S_{1}|}{2} \left(\frac{hca_{0}^{3}}{2S_{1}}\right)^{1/2}$$
(10)

$$\frac{\mu_e}{\mu_g} = \frac{|S_2 + S_1|}{|S_2 - S_1|} \text{ Slope S2>Slope S1.}$$
(11)

The slopes  $S_1$  and  $S_2$  were graphically determined by plotting Stokes shifts  $(\overline{\nu}_a - \overline{\nu}_f)$  and  $(\overline{\nu}_a + \overline{\nu}_f)$  versus the bulk solvent polarity functions  $f(\epsilon,n)$  and  $\Phi(\epsilon,n)$  respectively, for different solvents.

Solvent properties and polarity values  $f(\epsilon,n)$  and  $\Phi(\epsilon,n)$  for various solvents used in this study are presented in Table 1. The absorption and emission maxima, Stokes shift  $(\overline{\nu}_a - \overline{\nu}_f)$  and arithmetic mean of Stokes shift  $(\overline{\nu}_a + \overline{\nu}_f)$  for all the molecules in different solvents are given in Tables 5. Typical absorption and emission spectra of the compounds are given in Table 1.



Fig. 4. (a–d): The variation of Stokes shift with  $f(\epsilon,n)$  by using Eq. (1) in different solvents: (a) 3a, (b) 4a, (c) 3b and (d) 4b.



Fig. 5. (a–f): The variation of arithmetic sums of Stokes shift with  $\Phi(\epsilon,n)$  by using Eq. (2) in different solvents: (a) 3a, (b) 4a, (c) 3b and (d) 4b.

Figs. 4(a)–(f) and 5(a)–(d) show the graph of  $(\overline{\nu}_a + \overline{\nu}_f)$  versus  $f(\epsilon,n)$  and  $(\overline{\nu}_a + \overline{\nu}_f)$  versus  $\Phi(\epsilon,n)$  and the slopes S<sub>1</sub> and S<sub>2</sub> are obtained from these graphs, respectively.

The correlation coefficients, slopes and intercepts of the fitted lines are given in Table 6. Good correlation coefficient was obtained for all cases. The excited-state dipole moments  $\mu_e$  of four compounds have been estimated by computing the values of  $\mu_g$  obtained by Eqs. (9)–(10) and the values are presented in Table 7. The higher values of  $\mu_e$  and  $\mu_g$  and the variation in the dipole moment for all compounds may be understood in terms of their possible resonance structures as shown in Fig. 6. The carbonitrile substituent in 3a and 4a compounds does not produce a considerable change in the  $\pi$  electron mobility. Upon excitation the carbonyl group becomes a strong electron donor. Hydroxyl atom contributes better to the resonance of the mobility of  $\pi$  electrons. This explains the higher value of dipole moment in both excited states during the charge transfer process; the OH group may become more polar relative to the S<sub>0</sub> state.

Table 6	
Statistical treatment of the correlations of solvent spectral shifts of 3a-b and 4a	a–b.

Compounds	Slope	Intercept cm <sup>-1</sup>	Correlation coefficient	Number of data
Eq. (1) correlation	on			
3a	202.56701	4004.47968	0.97	5
4a	289.74356	4972.73407	0.94	6
3b	530.52448	3199.87424	0.90	5
4b	230.66489	3336.76768	0.88	6
Eq. (2) correlation	on			
3a	1293.3488	51,555.93578	0.92	5
4a	1242.71372	52,684.87309	0.97	6
3b	2036.43365	49,724.68844	0.96	5
4b	1628.97352	51,026.69919	0.97	6

The discrepancies between the experimental and theoretical excited dipole moments result from Kawski et al. [21–23] and all equations used for the treatment of the solvatochromic effect (Table 7) and at the B3LYP / 6-31 + G(d,p) level of theory in different environments (Table 2) may explain that the dipole moment of organic molecules depends on the transfer process within the molecule. These fluorescent probes show that they are more polar in the excited state than the ground state.

# 4. Conclusion

In the present study, we described the solvent effect on the absorption and emission spectra of 2-imino-<sup>2</sup>H-chromene-3-carbonitrile 3a, 7-hydroxy-2-imino-<sup>2</sup>H-chromene-3-carbonitrile 3b, 2-oxo-<sup>2</sup>H-chromen-3-carbonitrile 4a and 7-hydroxy-2-oxo-<sup>2</sup>H-chromen-3-

Table 7	
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Dipole moments in the ground and excited states and correlation coefficient of 3a-b a	nd
4a–b using $a_0$ calculated with ChemOffice (i) and $a_0$ calculated with B3LYP (ii).	

Molecules	Radius (A°)		$\mu_{g}\left(D\right)^{a}$		$\mu_{e}\left(D\right)^{b}$		$\Delta \mu (D)^{c}$		$\mu_e/\mu_g{}^d$	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
3a	3.79	4.53	12.04	10.82	16.51	14.84	4.47	4.02	1.37	1.37
4a	3.70	4.60	8.41	11.66	13.52	18.75	5.11	7.089	1.61	1.61
3b	3.75	4.45	8.83	11.42	15.06	19.46	6.22	8.04	1.70	1.70
4b	3.67	4.46	11.95	16.00	15.89	21.29	3.94	5.28	1.33	1.33

Debye =  $3.33564 \times 10^{-30}$  C·m =  $10^{-18}$  esu C·m. i, a<sub>0</sub> calculated with ChemOffice. ii, a<sub>0</sub> calculated with B3LYP.

<sup>a</sup> Experimental ground-state dipole moment calculated from Eq. (9).

<sup>b</sup> Experimental excited-state dipole moments calculated from Eq. (10).

<sup>c</sup> Change of dipole moment calculated from Eq. (7).

<sup>d</sup> Ratio of  $\mu_e$  and  $\mu_g$  is calculated from Eq. (11).



Fig. 6. Schematic representation of the resonance structures for the 7-hydroxy-<sup>2</sup>H-chromene derivatives.

carbonitrile 4b and estimated their dipole moments. A bathochromic shift is observed upon increasing the polarity of the solvent for all the molecules indicating a  $\pi$ - $\pi$ \* transition. We found that all molecules possess higher dipole moment values in the excited-state than in the ground-state and the dipole moment of the 2-imino-<sup>2</sup>H-chromene-3- carbonitrile 3a was higher than the other derivatives. This could be attributed to the intense electron resonance effect of substituents carbonile and imine in the excited singlet state. The interactions between systems  $\pi$  and chromophores CN lead to a strong delocalization of the excited state that makes molecules much more polar, thus resulting in greater values of dipole moments. The same is true for the mesomeric donor effect of the hydroxyl function which shows the same effect.

Furthermore, the dipole moments  $\mu_g$  and  $\mu_e$  were greater for molecule 3a, which presents the higher Onsager radius calculated by ChemOffice, which noted that the measured values of  $\mu_g$  and  $\mu_e$ for the four dyes differ from each other and this may be due to the structural differences between them. The higher values of the dipolar moments obtained for compounds 3a, 4a, 3b and 4b are also confirmed by the theoretical calculations (B3LYP) and evolve in the same order except for compound 3a.

2-Imino-<sup>2</sup>H-chromene-3-carbonitrile 3a, 7-hydroxy-2-imino-<sup>2</sup>H-chromene-3-carbonitrile 3b, 2-oxo-<sup>2</sup>H-chromen-3-carbonitrile 4a and 7-hydroxy-2-oxo-<sup>2</sup>H-chromen-3-carbonitrile 4b are characterized by good fluorescence efficiency even in aprotic apolar media as shown in the literature [26] for <sup>2</sup>H-chromene derivatives.

3a, 4a, 3b and 4b could be the building blocks for a new generation of fluorescent probes, combining the excellent optical properties of <sup>2</sup>H-chromene derivatives with the simplicity of their synthesis. They could be of interest in biochemistry and molecular diagnostic fields.

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