Journal of Molecular Structure 1012 (2012) 73-86

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Photophysical study of some 3-benzoylmethyleneindol-2-ones and estimation of ground and excited states dipole moments from solvatochromic methods using solvent polarity parameters

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ARTICLE INFO

Article history: Received 13 June 2011 Received in revised form 26 December 2011 Accepted 27 December 2011 Available online 4 January 2012

Keywords: Excited state Dipole moment Stokes shift ESIPT ICT

ABSTRACT

3-Benzoylmethyleneindol-2-ones, isatin based chalcones containing donor and acceptor moieties that exhibit excited-state intramolecular charge transfer, have been studied in different solvents by absorption and emission spectroscopy. The excited state behavior of these compounds is strongly dependent on the nature of substituents and the environment. These compounds show multiple emissions arising from a locally excited state and the two states due to intramolecular processes viz. intramolecular charge transfer (ICT) and excited state intramolecular proton transfer (ESIPT). Excited-state dipole moments have been calculated using Stoke-shifts of LE and ICT states using solvatochromic methods. The higher values of dipole moments obtained lead to support the formation of ICT state as one of the prominent species in the excited states of all 3-benzoylmethyleneindol-2-ones. The correlation of the solvatochromic Stokes-shifts with the microscopic solvent polarity parameter (E_T^N) was found to be superior to that obtained using bulk solvent polarity functions. The absorption and florescence spectral characteristics have been also investigated as a function of acidity and basicity (Ho/pH) in aqueous phase.

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1. Introduction

Chalcones, the bichromophoric molecules separated by a ketovinyl chain, form a remarkable class of compounds that are known to be effective photosensitive materials and have been of considerable photophysical and photochemical interest. Chalcones, both natural and synthetic, are known to exhibit various biological activities. They have been reported to possess antioxidant [1,2], antimalarial [3,4], antileishmanial [5], antitumor [6], antituberculosis [7] and antibacterial [8,9] activities. The presence of a reactive α,β -unsaturated keto functional group in chalcones is found to be responsible for their biological active properties, which may be altered depending on the type and position of substituent on the aromatic rings.

Benzoylmethyleneindol-2-one, an isatin based chalcone, has been identified as the essential synthetic building block for the synthesis of a wide variety of spiro derivatives [10,11] and biologically active compounds [12–14]. Benzoylmethyleneindol-2-one derivatives have been investigated for their pharmaceutical properties [15–17].

* Corresponding author. Fax: +91 11 27662618. E-mail address: rcrastogi@chemistry.du.ac.in (R.C. Rastogi). The biological activities of any compound are primarily a function of its molecular structure. It is known that the spectral behavior of an organic molecule is strongly related to its structure in both the ground and excited states. Considering that the solvent can significantly influence the chemical and physical properties of the solute, investigation of solvent–solute interactions is very important [18,19]. The solvent-induced changes in the electronic transitions of solutes are related to the nature and extent of solute–solvent interactions developed locally in the immediate vicinity of solutes.

Solvatochromism is caused by solvation of the ground and excited states of the light-absorbing molecule and thus provides a convenient tool to study the photophysical properties and determine the excited state dipole moments [20–26]. The knowledge of excited state charge distributions and dipole moments is important in understanding photochemical [27,28] and biological processes [29].

In this study, we present and discuss photophysical properties of benzoylmethyleneindol-2-one derivatives by means of steady state absorption and fluorescence spectroscopy. We have applied solvatochromic shift methods to estimate the excited-state dipole moments of a series of substituted benzoylmethyleneindol-2-ones (see Fig. 1). We have also investigated the absorption and fluorescence spectral characteristics as a function of acidity and basicity (Ho/pH) in aqueous phase.





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Fig. 1. (a) Structures of 3-benzoylmethyleneindol-2-ones. (b) Optimized geometry of BMI in ground state.

2. Experimental

2.1. Materials

Isatin (98%, Spectrochem), acetophenone (99.5%, SRL, India), phydroxyacetophenone (98%, Spectrochem), p-methylacetophenone (97%, Spectrochem), 3,4-dimethylacetophenone (98%, Spectrochem), p-methoxyacetophenone (99%, Spectrochem), 2,4-dimethoxyacetophenone (98%, S.D. Fine, India), p-chloroacetophenone (98%, SRL, India), 2,4-dichloroacetophenone (99%, S.D. Fine, India) and p-nitroacetophenone (98%, Spectrochem) were used without further purification for the synthesis of benzoylmethyleneindol-2-one and its derivatives.

All solvents, methanol (99.7%, Merck), 1-butanol (99.8%, Merck), 2-propanol (99.7%, Merck), acetonitrile (99.8%, Merck), tert-butanol (99.5%, Merck), N,N-dimethylformamide (99.8%, Merck), dichloromethane (99.5%, Merck), ethyl acetate (99.5%, Merck), 1,4-dioxane (99.8%, Merck), cyclohexane (99.7%, Merck) and n-Hexane (99.5%, Merck) used were of spectroscopic grade and were checked for the absence of absorbing or fluorescent impurities within the scanned spectral ranges. Triple distilled water was used.

Analytical grade sulfuric acid (98%, Rankem), hydrochloric acid (35.4%, S.D. Fine, India) and sodium hydroxide (98%, BDH, India) and triple distilled water were used to prepare acidic and basic solutions. HCl-H₂O mixture and NaOH-H₂O mixture were used to prepare pH solutions from pH 1–14, and H₂SO₄-H₂O mixture was used for solutions below pH = 1 according to Hammett's acidity scale (Ho) [30].

2.2. Instrumentation

Absorption and fluorescence spectra were recorded by using SHIMADZU UV-2501 PC spectrophotometer and SHIMADZU RF-5301 PC spectrofluorometer, respectively. All measurements were done in a 1 cm quartz cuvette. The slit widths used were 1 nm and 5 nm for absorption and fluorescence spectra, respectively. The pH values in the range of 1–14 were measured on Eutech make cyberscan pH meter.

| Table 1 |
|---|
| Calculated values of solvent polarity parameters. |

| Solvent | E_T^N | $F_1(D,n)$ | $F_2(D,n)$ |
|---------------|---------|------------|------------|
| n-Hexane | 0.009 | -0.003 | 0.254 |
| Cyclohexane | 0.006 | -0.003 | 0.287 |
| 1,4-Dioxane | 0.164 | 0.041 | 0.307 |
| Ethyl acetate | 0.228 | 0.489 | 0.497 |
| DCM | 0.309 | 0.590 | 0.583 |
| DMF | 0.386 | 0.835 | 0.709 |
| tert-Butanol | 0.389 | 0.688 | 0.607 |
| Acetonitrile | 0.460 | 0.859 | 0.663 |
| 2-Propanol | 0.546 | 0.778 | 0.645 |
| 1-Butanol | 0.586 | 0.750 | 0.646 |
| Methanol | 0.762 | 0.854 | 0.651 |
| Water | 1.000 | 0.912 | 0.683 |
| | | | |

Freshly prepared solutions were used for all the studies. Concentration of all the solutions was kept 4×10^{-5} M and 1×10^{-5} M for absorption and fluorescence spectra, respectively for all the studies. The absorption band maximum A2 was used as excitation wavelength to record emission spectra of BMI derivatives (Table 2). Excitation wavelength used to record the fluorescence spectra in different acidic and basic media was 350 nm for all studied derivatives.

2.3. Synthesis

The benzoylmethyleneindol-2-one derivatives were synthesized according to the standard procedures from literature [31,32] and their purity was confirmed by TLC, IR and ¹H NMR.

2.3.1. 3-Benzoylmethyleneindol-2-one (BMI)

A mixture of indoline-2,3-dione (0.01 mol), acetophenone (0.01 mol), diethylamine (3-4 drops) and ethanol (30 ml) was refluxed on oil bath for 2-3 h at 78 °C and the progress of reaction was monitored by TLC in 50% ethyl acetate and 50% petroleum ether solvent. The reaction mixture was kept overnight at room temperature to give intermediate (3-hydroxy-3-benzoylmethyleneindol-2-one), which separated as a precipitate. The compound thus obtained was recrystallized from chloroform by adding petroleum ether. The intermediate product was then refluxed with 1, 4dioxane (30 ml) and concentrated H₂SO₄ (1-2 drops) for 1-2 h on oil bath at 100 °C. After completion of reaction, the reaction mixture was poured into crushed ice with vigorous stirring. The solid thus separated was extracted with ethyl acetate and the moisture was removed by adding Na₂SO₄(s). After filtration, ethyl acetate was evaporated. The solid thus obtained was recrystallised from chloroform by adding petroleum ether. The separated orange-red



Fig. 2. (a) Electronic absorption spectra of BMI in different solvents. (b) Fluorescence emission spectra of BMI in different solvents.

crystals were characterized by IR and ¹H NMR whose spectral data are given in the next section. Other derivatives were also synthesized using the same procedure.

2.4. Spectral data

2.4.1. 3-Benzoylmethyleneindol-2-one (BMI)

Yield: 76% M.p.: 192–194 °C IR (KBr, cm⁻¹): 3426 v(NH), 3155, 1712, 1655 v(C=O), 1605 v(C=O) (amide), 1460, 1330; ¹H NMR

Table 2

Absorption maxima of 3-benzoylmethyleneindol-2-one and its derivatives in different solvents.

| Solvent ^a | BMI | | OHBN | 11 | MeBN | II | DiMel | BMI | OMeB | MI | DiOM | eBMI | CIBMI | | DiClBI | MI | NBMI | |
|----------------------|----------------------------|-------------------|----------------------------|-------------------|----------------------------------|-----|----------------------------------|-----|----------------------------------|-----|----------------------------------|------|----------------------------------|-----|----------------------------------|-----|----------------------------------|-----|
| | λ_{A1}/λ_{A} | ₂ (nm) | λ_{A1}/λ_{A} | ₂ (nm) | $\lambda_{A1}/\lambda_{A2}$ (nm) | | $\lambda_{A1}/\lambda_{A2}$ (nm) | | $\lambda_{A1}/\lambda_{A2}$ (nm) | | $\lambda_{A1}/\lambda_{A2}$ (nm) | | $\lambda_{A1}/\lambda_{A2}$ (nm) | | $\lambda_{A1}/\lambda_{A2}$ (nm) | | $\lambda_{A1}/\lambda_{A2}$ (nm) | |
| n-Hexane | 257 | 333 | 258 | 331 | 259 | 332 | 258 | 333 | NS ^b | NS | 259 | 333 | 258 | 334 | 258 | 334 | 266 | 340 |
| Cyclohexane | 259 | 335 | 258 | 333 | 258 | 333 | 259 | 335 | NS | NS | 259 | 334 | 259 | 335 | 259 | 336 | 267 | 341 |
| 1,4-Dioxane | 259 | 335 | 260 | 334 | 260 | 334 | 261 | 335 | 259 | 337 | 260 | 336 | 261 | 335 | 259 | 337 | 267 | 343 |
| Ethyl acetate | 257 | 335 | 259 | 334 | 259 | 334 | 260 | 335 | 259 | 339 | 261 | 334 | 260 | 335 | 259 | 335 | 267 | 342 |
| DCM | 259 | 337 | 259 | 336 | 259 | 337 | 259 | 336 | 258 | 339 | 261 | 331 | 260 | 338 | 259 | 339 | 269 | 344 |
| DMF | - | 337 | - | 337 | 265 | 338 | - | 338 | - | 344 | 266 | 338 | 266 | 337 | - | 340 | - | 344 |
| tert-Butanol | 261 | 339 | 259 | 336 | 260 | 337 | 260 | 338 | 259 | 345 | 262 | 338 | 261 | 339 | 260 | 339 | 267 | 347 |
| Acetonitrile | 259 | 334 | 259 | 332 | 259 | 332 | 259 | 333 | 257 | 335 | 260 | 328 | 262 | 332 | 259 | 334 | 267 | 341 |
| 2-Propanol | 260 | 339 | 259 | 338 | 260 | 337 | 260 | 338 | 259 | 345 | 262 | 338 | 261 | 339 | 260 | 339 | 266 | 345 |
| 1-Butanol | 260 | 340 | 260 | 337 | 260 | 338 | 260 | 338 | 259 | 345 | 262 | 340 | 261 | 339 | 259 | 341 | 267 | 346 |
| Methanol | 261 | 340 | 258 | 336 | 259 | 339 | 257 | 341 | 257 | 343 | 265 | 343 | 264 | 340 | 259 | 339 | 274 | 346 |
| Water | 257 | 336 | 257 | 338 | 259 | 338 | 261 | 338 | 254 | 347 | 265 | 330 | 258 | 341 | 259 | 340 | NS | NS |

^a Solvents are listed in order of increasing dielectric constant values.

^b Not soluble in this solvent.

| Table 3 | |
|--|--------------------------------|
| Fluorescence maxima of 3-benzoylmethyleneindol-2-one and its derivatives in different solvents (Ex. wa | avelength is λ_{A2}). |

| Solvent ^a | BMI | | | OHB | MI | | MeB | MI | | DiM | eBMI | | OMe | BMI | | DiO | ЛеВМ | I | CIBN | 1I | | DiCl | BMI | | NBM | [] ^d | |
|----------------------|-----------------------------|----------------------------------|------|-----------------------------|---------|------|-----------------------------|---------|-----|-----------------------------|--------------------------------|------|-----------------------------|---------|-----|-----------------------------|--------------|------|-----------------------------|--------------------------------|------|--------------------------------|--------------------------------|------|-----------------------------|--------------------------------|------|
| | λ_{F1}/λ | . _{F2} /λ _{F3} | | λ_{F1}/λ | F2/λF3 | | λ_{F1}/λ | F2/λF3 | | λ_{F1}/λ | _{F2} /λ _{F3} | | λ_{F1}/λ | F2/λF3 | | λ_{F1}/λ | F2/λF3 | | λ_{F1}/λ | _{F2} /λ _{F3} | | λ_{F1}/λ | _{F2} /λ _{F3} | | $\lambda_{\rm F1}/\lambda$ | _{F2} /λ _{F3} | |
| | λ_{LE}/λ (nm) | ict/λes) | SIPT | λ_{LE}/λ (nm) | ict/λes | SIPT | λ_{LE}/λ (nm) | ict/λes | ПРТ | λ_{LE}/λ (nm) | ict/λes) | SIPT | λ_{LE}/λ (nm) | ict/λes | IPT | λ_{LE}/λ (nm) | ict/λes) | SIPT | λ_{LE}/λ (nm) | ict/λes) | SIPT | λ_{LE}/λ (nm) | ict/λes) | SIPT | λ_{LE}/λ (nm) | ict/λes) | SIPT |
| n-Hexane | 374 | 402 | 486 | 382 | 405 | 541 | 376 | 400 | 545 | 387 | - | 545 | NS ^b | NS | NS | 385 | 406 | 479 | 382 | 408 | 577 | 384 | 410 | 518 | NF ^c | NF | NF |
| Cyclohexane | 374 | 402 | 485 | 384 | 411 | 535 | 377 | 398 | 545 | 387 | - | 547 | NS | NS | NS | 379 | 407 | 487 | 382 | 406 | 577 | 387 | 419 | 518 | NF | NF | NF |
| 1,4-Dioxane | 396 | 430 | - | 399 | 434 | - | 392 | 417 | - | 397 | 430 | - | 373 | 407 | - | 424 | 446 | - | 394 | 424 | - | 399 | 438 | - | NF | NF | NF |
| Ethyl acetate | 394 | 432 | - | 398 | 432 | - | 398 | 439 | - | 395 | 426 | - | 375 | 403 | - | 425 | 443 | - | 395 | 429 | - | 403 | 440 | - | NF | NF | NF |
| DCM | 398 | 438 | - | 400 | 434 | - | 399 | 441 | - | 418 | 449 | - | 411 | 439 | - | 403 | 432 | - | 394 | 431 | - | 398 | 444 | - | NF | NF | NF |
| DMF | 404 | 447 | - | 401 | 439 | - | 408 | 455 | - | 417 | 454 | - | 375 | 402 | - | 422 | 431 | - | 398 | 426 | - | 411 | 450 | - | NF | NF | NF |
| tert-Butanol | 407 | 442 | - | 406 | 445 | - | 412 | 458 | - | 400 | 443 | - | 381 | 408 | - | 416 | 454 | - | 405 | 436 | - | 414 | 449 | - | NF | NF | NF |
| Acetonitrile | 398 | 444 | - | 401 | 441 | - | 409 | 458 | - | 413 | 448 | - | 372 | 402 | - | 412 | 464 | - | 398 | 434 | - | 407 | 457 | - | NF | NF | NF |
| 2-Propanol | 412 | 446 | - | 407 | 448 | - | 411 | 455 | - | 403 | 443 | - | 378 | 423 | - | 411 | 450 | - | 404 | 434 | - | 415 | 453 | - | NF | NF | NF |
| 1-Butanol | 411 | 452 | - | 407 | 444 | - | 412 | 458 | - | 401 | 444 | - | 378 | 412 | - | 411 | 442 | - | 405 | 437 | - | 415 | 450 | - | NF | NF | NF |
| Methanol | 412 | 454 | - | 408 | 446 | - | 411 | 459 | - | 399 | 443 | - | 380 | 419 | - | 420 | 457 | - | 406 | 439 | - | 415 | 458 | - | NF | NF | NF |
| Water | 424 | 464 | - | 424 | 464 | - | 412 | 462 | - | 409 | 447 | - | 407 | 439 | - | 411 | 463 | - | 410 | 459 | - | 427 | 491 | - | NS | NS | NS |

^a Solvents are listed in order of increasing dielectric constant values.

^b Not soluble in this solvent.

^c No fluorescence observed in this solvent.

 $^{\rm d}\,$ Not used in dipole moment calculation.



Fig. 3. (a) Fluorescence spectra of OHBMI in different solvents. (b) Fluorescence spectra of MeBMI in different solvents.

(300 MHz, DMSO-d₆, ppm): δ 6.84 (d, J = 6 Hz, 1H, Ar–H), 7.03 (t, 1H, Ar–H), 7.31 (t, 1H, Ar–H), 7.80 (s, 2H, Ar–H), 7.49 (d, J = 9 Hz, 2H, Ar–H), 8.04 (d, J = 9 Hz, 2H, Ar–H), 8.33 (d, J = 6 Hz, 1H, Ar–H), 10.45 (s, 1H, –NH).



Fig. 4. Deconvoluted fluorescence emission spectra of BMI in methanol, acetonitrile and n-hexane.

2.4.2. 3-(4-Hydroxybenzoyl)methyleneindol-2-one (**OHBMI**) Yield: 61% M.p.: 140–142 °C IR (KBr, cm⁻¹): 3441 v(NH), 3200– 2900 v(OH), 1711, 1657 v(C=O), 1608 v(C=O) (amide), 1460, 1329;



Fig. 5. (a) Possible resonance structures of BMI and its derivatives. (b) ESIPT mechanism for the BMI and its derivatives. (c) Charge separated mesomeric form of BMI and its derivatives.

¹H NMR (300 MHz, DMSO-d₆, ppm): δ 6.78 (s, 1H, -OH), 6.82-7.98 (m, 8H, Ar-H), 7.69 (1H, S, -CO-CH=), 10.80 (s, 1H, -NH).

2.4.3. 3-(4-Methylbenzoyl)methylene-indol-2-one (MeBMI)

Yield: 80% M.p.: 204–206 °C IR (KBr, cm⁻¹): 3433 v(NH), 3200, 1712, 1656 v(C=O), 1609 v(C=O) (amide), 1459, 1329; ¹H NMR (300 MHz, DMSO-d₆, ppm): δ 2.41 (s, 3H, –CH₃), 6.86 (d, J = 9 Hz, 1H, Ar–H), 6.92 (t, 1H, Ar–H), 7.31 (t, 1H, Ar–H), 7.40 (d, J = 9 Hz, 1H, Ar–H), 7.70 (s, 1H, –CO–CH=), 7.96 (m, 4H, Ar–H), 10.80 (s, 1H, –NH).

2.4.4. 3-(3,4-Dimethylbenzoyl)methyleneindol-2-one (DiMeBMI)

Yield: 63% M.p.: 174–176 °C IR (KBr, cm⁻¹): 3434 ν(NH), 3161, 1709, 1656 ν(C=O), 1609 ν(C=O) (amide), 1461, 1337; ¹H NMR (300 MHz, DMSO-d₆, ppm): δ 2.33 (s, 6H, 2xCH₃), 6.80–7.98 (m, 7H, Ar–H), 7.70 (s, 1H, –CO–CH=), 10.81 (s, 1H, –NH).

2.4.5. 3-(4-Methoxybenzoyl)methyleneindol-2-one (OMeBMI)

Yield: 82% M.p.: 238–240 °C IR (KBr, cm⁻¹): 3435 v(NH), 3197, 1713, 1622 v(C=O), 1618 v(C=O) (amide), 1462, 1337, 1173; ¹H NMR (300 MHz, DMSO-d₆, ppm): δ 3.83 (s, 3H, -OC**H**₃), 6.86 (d, J = 6 Hz, 1H, Ar–**H**), 6.89 (t, 1H, Ar–**H**), 7.08 (d, J = 9 Hz, 2H, Ar–**H**),

7.28 (t, 1H, Ar–*H*), 7.68 (s, 1H, –CO–*CH*=), 7.96 (d, *J* = 9 Hz, 1H, Ar–*H*), 8.04 (d, *J* = 9 Hz, 2H, Ar–*H*), 10.45 (s, 1H, –N*H*).

2.4.6. 3-(2,4-Dimethoxybenzoyl)-methyleneindol-2-one (DiOMeBMI)

Yield: 79% M.p.: 164–166 °C IR (KBr, cm⁻¹): 3423 v(NH), 3158, 1716, 1655 v(C=O), 1615 v(C=O) (amide), 1464, 1330, 1139; ¹H NMR (300 MHz, DMSO-d₆, ppm): δ 3.84 (s, 6H, 2xOCH₃), 6.65– 6.68 (m, 2H, Ar–H), 6.83 (d, *J* = 9 Hz, 1H, Ar–H), 6.88 (t, 1H, Ar–H), 7.25 (t, 1H, Ar–H), 7.63 (s, 1H, –CO–CH=), 7.78 (d, *J* = 9 Hz, 1H, Ar–H), 8.08 (d, *J* = 9 Hz, 1H, Ar–H), 10.62 (s, 1H, –NH).

2.4.7. 3-(4-Chlorobenzoyl)methyleneindol-2-one (CIBMI)

Yield: 81% M.p.: 208–210 °C IR (KBr, cm⁻¹): 3431 v(NH), 3158, 1719, 1659 v(C=O), 1622 v(C=O) (amide), 1461, 1330, 889; ¹H NMR (300 MHz, DMSO-d₆, ppm): δ 7.68 (s, 1H, -CO-C**H**=), 6.84–8.10 (m, 8H, Ar-**H**), 10.91 (s, 1H, -N**H**).

2.4.8. 3-(2,4-Dichlorobenzoyl)methyleneindol-2-one (DiClBMI)

Yield: 90% M.p.: 224–226 °C IR (KBr, cm⁻¹): 3449 v(NH), 2924, 1723, 1662 v(C=O), 1602 v(C=O) (amide), 1461, 1331,744; ¹H NMR (300 MHz, DMSO-d₆, ppm): δ 6.83 (d, *J* = 10 Hz, 1H, Ar–*H*), 7.23 (t, 1H, Ar–*H*), 7.83 (s, 1H, –CO–C*H*=), 7.41 (t, 1H, Ar–*H*),



Fig. 6. Energy-reaction coordinate diagram of ground and excited state processes proposed for the interpretation of the photophysical behavior of donor–acceptor BMI and its derivatives, where **FC** = Franck Condon state, **LE** = locally excited state, **ICT** = intramolecular charge transfer, **ESIPT** = excited state intramolecular proton transfer and **A** = BMI and its derivatives.

7.60–7.63 (m, 1H, Ar—*H*), 7.80–7.84 (m, 2H, Ar—*H*), 8.31 (d, *J* = 9 Hz, 1H, Ar—*H*), 10.85 (s, 1H, —N*H*).

2.4.9. 3-(4-Nitrobenzoyl)-methyleneindol-2-one (**NBMI**)

Yield: 79% M.p.: 246–248 °C IR (KBr, cm⁻¹): 3326 ν(NH), 3170, 1722, 1666 ν(C=O), 1605 ν(C=O) (amide), 1518, 1461, 1334, 1145; ¹H NMR (300 MHz, DMSO-d₆, ppm): δ 7.74 (s, 1H, -CO-C**H**=), 6.89–8.45 (m, 8H, Ar-**H**), 10.83 (s, 1H, -N**H**).

2.5. Methods: dipole moment calculation

The dipole moment of a molecule in the excited state is determined by the effect of electric field (internal or external) on the position change of the absorption and fluorescence bands. Two methods depending on the internal electric field (solvatochromism) were employed in the present study.

In the first method, by employing the simplest quantummechanical second order perturbation theory and taking into account Onsager's model, Kawski et al. [33–40] have obtained the following expressions for $(\bar{v}_a - \bar{v}_f)$ and $1/2(\bar{v}_a + \bar{v}_f)$:

$$\bar{v}_a - \bar{v}_f = S_1 F_1(D, n) + C_1 \tag{1}$$

$$1/2(\bar{v}_a + \bar{v}_f) = S_2 F_2(D, n) + C_2 \tag{2}$$

where \bar{v}_a and \bar{v}_f are the absorption and fluorescence maxima, *n* and *D* are the refractive index and the dielectric constant of the solvents, respectively. The slopes S_1 and S_2 are expressed as

$$S_1 = \frac{2(\mu^* - \mu)^2}{hca^3}$$
 and $S_2 = \frac{-2(\mu^{*2} - \mu^2)}{hca^3}$ (3)

where μ^* and μ are respectively excited and ground state dipole moments of the solute molecule and '*a*' is the Onsager cavity radius. $F_1(D,n)$ and $F_2(D,n)$ are taken as

$$F_1(D,n) = \left[\frac{D-1}{D+2} - \frac{n^2 - 1}{n^2 + 2}\right] \times \frac{2n^2 + 1}{n^2 + 2}$$
(4)

$$F_2(D,n) = \frac{1}{2}F_1(D,n) + \frac{3/2(n^4 - 1)}{(n^2 + 2)^2}$$
(5)

Plots of the Stokes-shifts $(\bar{v}_a - \bar{v}_f)$ and $1/2(\bar{v}_a + \bar{v}_f)$ against the bulk solvent polarity functions $(F_1(D, n) \text{ and } F_2(D, n))$ for different solvents yield the slopes S_1 and S_2 , respectively. Assuming that the

Table 4

| The solution of the solution o | Absorbance and fluorescence | maxima as | ssignment o | f different | prototropic | species in H | lo/pH range | -5 to 14 |
|--|-----------------------------|-----------|-------------|-------------|-------------|--------------|-------------|----------|
|--|-----------------------------|-----------|-------------|-------------|-------------|--------------|-------------|----------|

| Ho/ | BMI | | | | OHBMI | | | | СІВМІ | | | |
|-----|----------------------------------|---------------------|---|------------------------------------|----------------------------------|---------------------|---|------------------------------------|----------------------------------|---------------------|--|------------------------------------|
| рН | Absorband | ce | Fluorescenc | e ^b | Absorband | ce | Fluorescer | nce | Absorban | ce | Fluorescer | nce |
| | $\lambda_{A1}/\lambda_{A2}$ (nm) | Assigned species | $\lambda_{\rm LE}/\lambda_{\rm ICT}$ (nm) | Assigned species ^a | $\lambda_{A1}/\lambda_{A2}$ (nm) | Assigned species | $\lambda_{\rm LE}/\lambda_{\rm ICT}$ (nm) | Assigned species | $\lambda_{A1}/\lambda_{A2}$ (nm) | Assigned species | $\frac{\lambda_{\text{LE}}}{\lambda_{\text{ICT}}}$ | Assigned species |
| -5 | 258, 369 | С | 470 | С | 256, 366 | С | 480 | С | 265, 359 | С | 485 | С |
| -4 | 259, 362 | С | 466 | С | 254, 363 | С | 478 | С | 265, 359 | С | 472 | С |
| -3 | 261, 360 | С | 466 | С | 256, 360 | С | 478 | С | 263, 354 | С | 472 | С |
| -2 | 265, 358 | С | 466 | С | 257, 357 | С | 476 | С | 266, 352 | С | 468 | С |
| -1 | 265, 358 | С | 466 | С | 258, 357 | С | 476 | С | 265, 345 | С | 460 | С |
| 1 | 263, 350 | С | 424 ^{sh} , 502 | N _{LE} + HB | 261, 352 | С | 472 | С | 266, 344 | С | 460 | С |
| 2 | 265, 346 | С | 424 ^{sh} , 502 | N _{LE} + HB | 262, 349 | С | 472 | С | 267, 344 | С | 415 ^{sh} , 460 | N _{LE} + C |
| 3 | 266, 344 | С | 424 ^{sh} , 502 | N _{LE} + HB | 262, 349 | C | 424 ^{sh} , 470 | N _{LE} + C | 267, 344 | С | 415 ^{sh} , 460 | N _{LE} + C |
| 4 | 264, 340 | Ν | 424, 454, 500 ^{sh} | N_{LE} + N_{ICT} | 262, 340 | Ν | 424, 455 | N_{LE} + N_{ICT} | 266, 340 | Ν | 415, 460 | N_{LE} + N_{ICT} |
| 5 | 266, 340 | Ν | 424, 454 | N _{LE} + N _{ICT} | 262, 340 | Ν | 424, 456 | N _{LE} + N _{ICT} | 266, 340 | Ν | 415, 450 | N _{LE} + N _{ICT} |
| 6 | 266, 340 | Ν | 424, 454 | $N_{LE} + N_{ICT}$ | 262, 340 | Ν | 424, 456 | $N_{LE} + N_{ICT}$ | 266, 340 | Ν | 415, 450 | $N_{LE} + N_{ICT}$ |
| 7 | 264, 340 | Ν | 424, 454 | $N_{LE} + N_{ICT}$ | 260, 340 | Ν | 424, 456 | $N_{LE} + N_{ICT}$ | 266, 340 | Ν | 415, 450 | N _{LE} + N _{ICT} |
| 8 | 267, 340 | N | 424, 454 | N _{LE} + N _{ICT} | 262, 340 | Ν | 424, 456 | N _{LE} + N _{ICT} | 266, 340 | Ν | 415, 450 | N _{LE} + N _{ICT} |
| 9 | 266, 340 | N | 424, 454 | N _{LE} + N _{ICT} | 261, 340 | Ν | 424, 456 | N _{LE} + N _{ICT} | 266, 340 | Ν | 415, 450 | N _{LE} + N _{ICT} |
| 10 | 266, 340 | N | 424, 454 | N _{LE} + N _{ICT} | 262, 340 | Ν | 424, 456 | N _{LE} + N _{ICT} | 265, 340 | Ν | 415, 450 | N _{LE} + N _{ICT} |
| 11 | 266, 340 | Ν | 424, 454 | N _{LE} + N _{ICT} | 261, 340 | Ν | 424, 456 | N _{LE} + N _{ICT} | 261, 340 | Ν | 415, 450 | N _{LE} + N _{ICT} |
| 12 | 265, 340 | Ν | 424, 458 | N _{LE} + N _{ICT} | 261, 340 | Ν | 424, 456 | N _{LE} + N _{ICT} | 264, 340 | Ν | 415, 450 | N _{LE} + N _{ICT} |
| 13 | 270, 346 | Α | 406 | Α | 273, 344 | А | 407 | Α | 264, 366 | А | 395 | А |
| 14 | 274, 350 | А | 406 | А | 275, 344 | А | 407 | А | 266, 377 | А | 395 | А |

^a Species assigned as N = neutral, C = cation, A = anion and HB = intramolecular hydrogen bonding in cationic species.
 ^b Excitation wavelength used to record the fluorescence spectra is 350 nm.



Fig. 7. (a) Absorbance spectra of BMI in water at selected Ho/pH. (b) Absorbance spectra of OHBMI in water at selected Ho/pH. (c) Absorbance spectra of CIBMI in water at selected Ho/pH.



Fig. 8. (a) Fluorescence spectra of BMI in water at selected Ho/pH (Ex. 350 nm). (b) Fluorescence spectra of OHBMI in water at selected Ho/pH (Ex. 350 nm).

angle between μ and μ^* is small and the cavity radius 'a' is same in both the ground and the excited states and using the Eqs. (1)–(3), the ratio of the dipole moments in the excited and ground states is given by the equation:

$$\frac{\mu^*}{\mu} = \frac{|S_1 - S_2|}{|S_1 + S_2|} \tag{6}$$

It may be noted that most theories [41–46] of the solvent effect on the location of the absorption (\bar{v}_a) and fluorescence (\bar{v}_f) bands lead, in spite of different assumptions, to similar expressions for $\bar{v}_a - \bar{v}_f$ and $1/2(\bar{v}_a + \bar{v}_f)$ (Eqs. (1) and (2)) with the difference, however, that the applied solvent polarity parameters ($F_1(D, n)$ and $F_2(D, n)$), differ significantly.

In the second method [47], the problem associated with the error in estimating the Onsager radius 'a' is minimized, since the ratio of two Onsager radii (a_B/a) is involved Eq. (7). The excited-state dipole moment is determined by

$$\Delta \bar{v}_{af} = 11307.6[(\Delta \mu / \Delta \mu_B)^2 (a_B / a)^3] E_T^N + \text{constant}$$
(7)

where $\Delta \bar{v}_{af}$ is the Stokes-shifts and E_T^N is the solvent-polarity parameter proposed by Reichardt [48] that correlates better than the traditionally used bulk solvent polarity functions. E_T^N is based on the absorption wavenumber of a standard betaine dye in the solvent. Its value for different solvents is given in Table 1 and is expressed as

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})}$$
(8)

 $\Delta \mu_B$ (=9 D) and R_B (=6.2 Å) are the dipole-moment changes upon excitation and the Onsager cavity radius, respectively, of betaine

dye [48], whereas $\Delta \mu$ and 'a' are the corresponding quantities for the molecule of interest (isatin chalcones). Thus, the plot of $\Delta \bar{v}_{af}$ (Stokes-shifts) versus E_T^N (Eq. (7)) can be used to obtain the change in the dipole moment ($\Delta \mu$) upon excitation.

The Onsager cavity radii of all molecules have been taken to be 40% of the longest axis in the optimized geometry of the molecule [49], obtained by using semiempirical calculations. Thus, by knowing ground state dipole moment ' μ ' from theoretical calculations, excited state dipole moment, μ^* can be determined.

2.6. Theoretical calculations

Parametric Method 3 (PM3) semiempirical molecular-orbital calculations were carried out to estimate the ground state and excited-state dipole moments. The Onsager cavity radii of all the molecules were determined theoretically using the optimized geometry. The quantum chemical package HyperChem Release 5.1 Pro [50] was used for the theoretical calculations reported here.

3. Results and discussion

3.1. Absorption and emission properties

Absorption and fluorescence spectra of benzoylmethyleneindol-2-ones were studied in twelve solvents of different polarity. Absorption and fluorescence spectra of BMI in different solvents are shown in Fig. 2 and the corresponding spectral data of BMI and its derivatives are summarized in Tables 2 and 3.

3.1.1. Absorption spectra

Absorption spectra of BMI and its derivatives exhibit two main bands in all the solvents (Table 2). The first band (band A1) is located in the range 250–270 nm and does not show any change towards the polarity of the solvent as well as the various substituents on the phenyl ring. The second band (band A2, 330–350 nm) is slightly structured and shows moderate sensitivity (3–6 nm) towards both solvent polarity and the substituents as compared to band A1. From this it can be concluded that the substitution as well as solvent effects are almost negligible in the ground state of the molecules.

Apart from the two strong absorption peaks (A1 and A2), one low intensity broad band has also been observed around 420 nm (Fig. 2a). For the assignment of absorption bands, the absorption spectrum of BMI was compared with the absorption spectra of isatin. This low-intensity broad band (~420 nm) may be assigned to the characteristic band of --NH--CO- functional group, as this is similar in shape and position to isatin absorption spectra, and stems from the transition in the --NH--CO- functional group. Evidently, isatin displays three bands, ~241 nm and ~311 nm due to the presence of benzene ring, and ~417 nm due to NH--CO--CO-functional group [51].

Attention was focused on the absorption band A2 showing a slight bathochromic shift from nonpolar to polar solvent. This band has been assigned to a charge transfer from the high-energy, occupied orbital of the substituted phenyl-donor group to the low-energy, unoccupied orbital of the acceptor carbonyl group (i.e. $\pi_{\rm Ph} \rightarrow \pi^*_{\rm C=0}$, [52,53]) of the molecule.

3.1.2. Fluorescence spectra

The wavelength of absorption band (A2) was used as excitation wavelength to record the emission spectra of BMI and its derivatives. Fluorescence spectra of BMI and its derivatives split into two bands in all the solvents (Fig. 2b, Fig. 3a and b). Exceptionally, along with the dual emissive bands a long wavelength band has also been observed to exist in cyclohexane and n-hexane. Hence,



Fig. 9. Protonation and deprotonation phenomena followed by BMI derivatives in ground and excited state in Ho/pH range from -5 to 14.

the fluorescence spectra seem to result from more than one form of excited state. In order to quantify these changes, fluorescence spectra have been fitted as a sum of two Gaussian curve-fitting programs. Fig. 4 displays the deconvoluted spectra of BMI in methanol, acetonitrile and n-hexane. The wavelengths of the maxima from deconvolution are compiled in Table 3.

For ease of explanation of results, emission spectra of BMI and its derivatives may be divided into three regions. The nearest (band F1), intermediate (band F2) and the longest wavelength (band F3) bands are in the range of 370–400 nm, 400–440 nm and 540– 580 nm (Table 3), respectively (Figs. 2b and 3a and b).

The emission maxima of bands F1 and F2 show large bathochromic shifts with increase in solvent polarity. The shorter wavelength band (F1) has less bathochromic shift (~20-50 nm, Table 3) as compared to the band F2 (\sim 20-80 nm, Table 3) from nonpolar to polar solvents and can be assigned to emission from the locally excited state (LE). The marked red shift of the fluorescence band, F2 is due to large difference in the electron distribution (originating from charge transfer) of ground and excited states of the molecule which makes the molecule highly polar in excited state resulting in significant interaction with polar solvents. Such behavior indicates that the emission takes place not only from the initially populated excited state (locally excited state, LE), but also from a more polar state with a charge transfer character (intramolecular charge transfer state, ICT). Therefore, bands F1 and F2 arise from two different states termed as locally excited (LE) state and the intramolecular charge-transfer state (ICT), respectively.

Assignment of the bands as LE and ICT can be further confirmed by the fact that the intensity of ICT emission (F2, more polar state) increases with increase in polarity of the solvent while the LE emission (F1, less polar state) shows an opposite dependence on polarity of the solvent. This is because ICT and LE show strong and weak solute-solvent interactions with the polar solvent, respectively [54].

The structure and nature of the ICT can be clearly depicted from the possible resonance states, **II** and **II**' (Fig. 5a), where the carbonyl group has been considered to be the electron acceptor while the rest of the molecule to be the donor. The close vicinity of strong electron donating phenyl group towards electron accepting carbonyl group facilitates the formation of resonance structure **II** in the excited state, explaining the substantial charge separation upon excitation.

However, the possibility of resonance structure **II**' to ICT is ruled out. The ICT state (band F2) is strongly favorable in all BMI derivatives due to the greater electron donating power of phenyl ring attached to the carbonyl group, which leads to the formation of coplanar (quinoid) structure (resonance structure **II** in Fig. 5).

Since BMI derivatives contain the essential —CO—NH— group for proton transfer, they can undergo the lactum–lactim tautomerism as in the case of isatin [55–58]. Even though the molecules are fully conjugated in ICT state (Fig. 5b, resonance structure **II**), intramolecular proton transfer can easily take place in excited state to provide more energy stabilization (Fig. 5b, resonance structure **III**) [59,60]. But the formation of this lactim form (structure III in Fig. 5b) is possible only in highly nonpolar solvents (n-hexane



Fig. 10. (a) Possible tautomerization, protonation and deprotonation mechanism of BMI derivatives in ground and excited states (LE + ICT) in Ho/pH range from -5 to 14 where, N_{cs} = neutral ground state, A_{cs} = anionic species in ground state, C_{cs} = cationic species in ground state, N_{LE} = neutral locally excited state, N_{ICT} = neutral intramolecular charge transfer excited state, A_{LE} = anionic species in locally excited state, C_{LE} = cationic species in locally excited state, A_{ICT} = intramolecular charge transfer in anionic species. (b) Intramolecular hydrogen bonding in BMI in excited state in acidic medium.

and cyclohexane) due to absence of strong solute-solvent interaction in comparison to all other solvents.

By considering the equilibrium Lactum \leftrightarrow Lactim (II \leftrightarrow III), in solvents of varying polarity, it has been found that increase in solvent polarity shifts the equilibrium towards the Lactum form. This form (Lactum) is more dipolar than hydroxyl-form (Lactim) due to the contribution of the charge-separated mesomeric form (Fig. 5c, IV). While in nonpolar solvents such as cyclohexane and n-hexane both tautomers exist in comparable amounts, the tautomeric equilibrium is shifted entirely in favor of the lactum form in polar solvents such as water. Thus, it is well-established that the longest wavelength band, F3 corresponds to emission of the excited state intramolecular proton transfer (ESIPT) [48].

Therefore, a mechanism followed by BMI derivatives in excited state can be proposed on the basis of fluorescence results and nature of the emitting states (shown in Fig. 6) [19,61]. As is clear from the explanation, excitation leads to population of Frank-Condon (FC) state that seems to decay by three competing pathways: (1) fluorescence to the ground state (LE), (2) relaxation of LE state to a closely lying ICT state and (3) ICT state to ESIPT state (Fig. 6). Consequently, the fluorescence bands (F1, F2 and F3) considered to arise from these three states are termed as the locally excited (band F1, LE) state, the intramolecular charge transfer state (band F2, ICT) [62] and the excited state intramolecular proton transfer state (band F3, ESIPT) [59] observed only in nonpolar solvents (see Table 3).

The foregoing results show that the equilibria among the LE (band F1), ICT (band F2) and ESIPT (band F3) states determine their relative contributions to the emission band, which depends

strongly on the solvent polarity as well as the acceptor strength of the carbonyl group.

NBMI is non-fluorescent owing to greater electron withdrawing capacity of nitro group. The lack of fluorescence in nitro derivative can be explained on the basis of the strong electron-withdrawing capacity of the nitro group (Table 3). Aromatic nitro compounds are in general only weakly fluorescent or completely non-fluorescent, due to the efficient nonradiative decay processes such as singlet–triplet intersystem crossing and internal conversion [63].

3.1.3. Effect of pH

The effect of pH on absorption and fluorescence spectra of three selected 3-benzoylmethyleneindol-2-one derivatives namely, BMI, OHBMI and CIBMI has been studied in water at the Ho/pH range from -5 to 14. The relevant data are compiled in Table 4. The absorption spectra and fluorescence spectra of BMI and OHBMI at selected Ho/pH are shown in Figs. 7 and 8, respectively.

The outlays of protonation and deprotonation phenomena followed by the BMI derivatives and possible tautomerization, protonation and deprotonation mechanisms in Ho/pH range of -5 to 14 are shown in Figs. 9 and 10, respectively. Neutral BMI derivatives show the presence of two excited states: the neutral LE and ICT denoted as N_{LE} and N_{ICT}. In acidic and basic medium, BMI derivatives show the formation of cation and anion (C_{LE}, A_{LE}, C_{ICT} and A_{ICT}) for both LE and ICT neutral states. In highly acidic condition C_{ICT} state is more dominant in comparison to the C_{LE} state as evident from their fluorescence spectra (discussed latter).

It is clear from the absorption spectral data (Table 4) that the spectral characteristics of BMI, OHBMI and CIBMI in the pH range



Fig. 11. (a) Stokes-shifts for LE band of 3-benzoylmethyleneindol-2-one versus the solvent polarity functions $F_1(D,n)$, $F_2(D,n)$ and E_T^N . (b) Stokes-shifts for ICT band of 3-benzoylmethyleneindol-2-one versus the solvent polarity functions $F_1(D,n)$, $F_2(D,n)$ and E_T^N .

Table 5

Correlation coefficients for the fits of Stokes-shifts of BMI and its derivatives versus the solvent polarity functions, E_1^n , $F_1(D, n)$ and $F_2(D, n)$ for both LE and ICT states.

| Molecule | Correlatio | n coefficien | ts | | | | |
|----------|---------------------|----------------------|----------------------|-----------------------|-------------|--------------|--|
| | $F_1(D,n)_{\rm LE}$ | $F_1(D,n)_{\rm ICT}$ | $-F_2(D,n)_{\rm LE}$ | $-F_2(D,n)_{\rm ICT}$ | $E_T^N(LE)$ | $E_T^N(ICT)$ | |
| BMI | 0.847 | 0.908 | 0.940 | 0.936 | 0.926 | 0.927 | |
| OHBMI | 0.822 | 0.970 | 0.902 | 0.943 | 0.966 | 0.976 | |
| MeBMI | 0.916 | 0.959 | 0.983 | 0.965 | 0.922 | 0.959 | |
| DiMeBMI | 0.849 | 0.867 | 0.963 | 0.868 | 0.979 | 0.976 | |
| OMeBMI | 0.919 | 0.972 | 0.811 | 0.807 | 0.846 | 0.987 | |
| DiOMeBMI | 0.880 | 0.943 | 0.895 | 0.895 | 0.804 | 0.912 | |
| CIBMI | 0.849 | 0.882 | 0.943 | 0.882 | 0.979 | 0.981 | |
| DiClBMI | 0.962 | 0.943 | 0.908 | 0.976 | 0.958 | 0.993 | |
| | | | | | | | |

 \sim 4–9 is due to the neutral species because the data is similar to what is obtained in the non-aqueous solvents. The absorption spectra of BMI, OHBMI and CIBMI show a red shift in band A2 at pH value 13 and above (Table 4). The red shifted band indicates the formation of a monoanion because of deprotonation from >NH moiety in BMI derivatives as in the case of isatin [64].

With decrease in pH there is also a red shift observed in absorption band maxima, A2 (from 340 nm to 350 nm). This shift indicates the formation of monocation in ground state. Further red

shift with the increase of acidity up to Ho = -5 suggests the complete formation of cationic species. Similar behavior is observed for the other BMI derivatives (OHBMI and CIBMI). Thus in BMI derivatives two equilibria (Monocation \leftrightarrow Neutral and Neutral \leftrightarrow Monoanion) exist in the ground state.

Fluorescence spectra of BMI, OHBMI and CIBMI were recorded in water at excitation wavelength, 350 nm in different acidic and basic media. The fluorescence spectra of various prototropic species formed in different pH range are explained by taking into account the existence of molecule in both LE and ICT states and their interactions.

In the acidic range Ho = -5 to -1, a single band is observed, which can be attributed to the monocationic species for all the BMI derivatives studied. The site of protonation of BMI monocation has two possibilities in the indole ring at carbonyl oxygen and at the nitrogen atom. The protonated species is formed by the protonation of carbonyl oxygen rather than the nitrogen atom. This is because if the protonation occurred at nitrogen, a blue shift will be expected in absorption and fluoresce spectra, as this center represents amino group. This is also supported by previous studies for the protonation of the similar derivatives of thiosemicarbazone [65], 2-indolinone [66] and 2-quinoxalinone [67].

For BMI derivatives in the range pH 1–3, a long wavelength band at \sim 502 nm is observed along with a new band at

Table 6

| Comparison of (μ | $(\mu)^{a}$ obtained from | n the solvatochro | omic method with | the computed valu | ies. | |
|-----------------------|---------------------------|-------------------|------------------|---------------------------|-------------|---------|
| Molecule | $S_{1(LE)}^{a}$ | $S_{1(ICT)}^{a}$ | $-S_{2(LE)}^{b}$ | $-S_2 (ICT)^{\mathbf{b}}$ | μ^{c}/D | μ^* |
| BMI | 1544 | 2227 | 3547 | 3376 | 3.85 | 5.4 |
| OHBMI | 989 | 1950 | 2025 | 2761 | 2 74 | 45 |

| Molecule | $S_{1(LE)}$ ^d | $S_{1(ICT)}^{a}$ | $-S_{2(LE)}^{D}$ | $-S_2 (ICT)^{D}$ | μ ^c /D | μ* ^c /D | $(\mu^*/\mu)_{LE}^{a}$ | $(\mu^*/\mu)_{ICT}^{u}$ | $(\mu^*/\mu)^e$ |
|--------------|--------------------------|------------------|------------------|------------------|-------------------|--------------------|------------------------|-------------------------|-----------------|
| BMI | 1544 | 2227 | 3547 | 3376 | 3.85 | 5.44 | 2.54 | 4.87 | 1.41 |
| OHBMI | 989 | 1950 | 2025 | 2761 | 2.74 | 4.57 | 2.91 | 5.81 | 1.67 |
| MeBMI | 1509 | 2836 | 3136 | 4206 | 3.86 | 5.37 | 2.86 | 5.14 | 1.39 |
| DiMeBMI | 918 | 702 | 1887 | 1035 | 3.63 | 5.17 | 2.89 | 5.22 | 1.42 |
| OMeBMI | 669 | 1367 | 1353 | 1830 | 4.88 | 6.11 | 2.96 | 6.90 | 1.25 |
| DiOMeBMI | 1867 | 2424 | 3692 | 3228 | 4.11 | 5.38 | 3.05 | 7.02 | 1.31 |
| CIBMI | 1052 | 1393 | 2309 | 2095 | 4.00 | 5.79 | 2.67 | 4.97 | 1.45 |
| DiCIBMI | 1073 | 2016 | 2246 | 3011 | 3.81 | 5.81 | 2.83 | 5.05 | 1.52 |
| | | | | | | | | | |

^a Calculated from the plots of Stokes-shifts versus $F_1(D,n)$ using Eq. (1).

^b Calculated from the plots of Stokes-shifts versus $F_2(D,n)$ using Eq. (2).

^c Theoretical values of ground-state and excited state dipole moments obtained using PM3 method.

Calculated using Eq. (6) from experimental values of S₁ and S₂ of LE and ICT states.

^e Calculated using theoretical values of ground-state and excited state dipole moments.

Table 7 Comparison of the changes in dipole moments $(\Delta \mu)^{\rm b}$ obtained from the solvatochromic method with the computed values.

| Molecule | Cavity radius ^a (a/Å) | IP ^b (eV) | Slope, $m_{(LE)}^{c}$ | Slope, $m_{(ICT)}^{c}$ | $\Delta \mu_{(\mathrm{LE})}^{\mathrm{d}}$ (D) | $\Delta \mu_{(ICT)}^{d}$ (D) | $\Delta \mu^{e}$ (D) |
|----------|--|-------------------------|--------------------------|---------------------------|---|------------------------------|-------------------------|
| BMI | 4.48 | 9.24 | 2119 | 4401 | 2.39 | 3.44 | 1.59 |
| OHBMI | 4.54 | 8.49 | 2899 | 3818 | 2.86 | 3.28 | 1.83 |
| MeBMI | 4.71 | 8.83 | 2643 | 4138 | 2.88 | 3.61 | 1.51 |
| DiMeBMI | 4.96 | 8.56 | 2298 | 3676 | 2.90 | 3.67 | 1.54 |
| OMeBMI | 5.07 | 8.22 | 2217 | 4193 | 2.94 | 4.05 | 1.31 |
| DiOMeBMI | 5.04 | | 1761 | 4414 | 2.60 | 4.12 | 1.27 |
| CIBMI | 4.66 | 9.07 | 2104 | 3974 | 2.53 | 3.47 | 1.79 |
| DiCIBMI | 4.68 | 9.10 | 2242 | 4464 | 2.83 | 3.70 | 2.00 |

^a Onsager cavity radius (40% of the longest axis in the optimized geometry of the molecule) obtained by using semiempirical calculations [49]

^b Ionization energies (IP) of gas-phase molecules of substituted benzene ring.

^c Slope (*m*) = 11307.6[$(\Delta \mu / \Delta \mu_B)^2 (a_B / a)^3$], calculated from the plot of Stokes-shifts versus E_T^N using Eq. (7).

Calculated using Eq. (7).

Calculated using theoretical values of ground-state and excited state dipole moments.

 \sim 424 nm. The band at \sim 502 nm is attributed to intramolecular hydrogen bonding between OH group (formed due to protonation) and the carbonyl group (present in chalcone moiety) in cationic species (Fig. 10b). This band is not observed at pH < 1, because of the increase in number of H⁺ ions which solvate the carbonyl oxygen restricting hydrogen bonding with -OH proton.

Two bands are observed at 424 nm and 454 nm in the range of neutral species from pH = 5 to pH = 12. While the lower wavelength fluorescence band is due to the LE state, the higher wavelength fluorescence band is due to the ICT interaction in neutral BMI. This has been previously confirmed by the pronounced red shift of ICT maximum on increasing the solvent polarity (see section 3.1.2). A large blue shifted band is observed at ${\sim}406\,\text{nm}$ on further increasing the pH value to 14, which is attributed to the anionic species formed due to the deprotonation at >NH group.

Almost similar behavior has been observed for OHBMI and CIBMI because the basic structures are same except for the presence of OH and Cl groups on the benzene ring, which enhances the process of ICT making it a dominant state. Similar to BMI in highly acidic medium (Ho = -5 to pH = 3), a long wavelength band is observed at 480 nm and 485 nm, respectively for cationic species of OHBMI and ClBMI. On increasing pH, the fluorescence from cationic species disappears and two bands are observed for neutral LE and neutral ICT in the range of pH value \sim 4–12. Formation of anion takes place in basic medium after pH \sim 12.

The only difference in their fluorescence behavior as compared to the BMI is the absence of fluorescence band at 502 nm in pH range 1-3 as shown by the intermediate species. This is because of the inductive effect of the OH and mesomeric effect of Cl group, which make the carbonyl oxygen rich in electron density. This high electron density enhances the phenomenon of solvation of carbonyl oxygen by H⁺ ions present in acidic solution restricting the interaction of oxygen with its own proton on -OH group (i.e. intramolecular hydrogen bonding).

3.2. Excited state dipole moments

Solvatochromic shifts caused by general (non-specific) solvent effects are often described by solvatochromic methods, which relate the energy difference between absorption and emission maxima to the dielectric constant and refractive index.

For estimation of the excited state dipole moments, Stokesshifts have been calculated for all the molecules from their absorption and fluorescence maxima i.e. the wavelengths corresponding to the band A2 (Table 2) and for both LE and ICT (Table 3) states in different solvents, respectively. The shift in emission peaks with variation in solvent polarity is more pronounced than that in the absorption peaks. This indicates that $\Delta \mu (=\mu^* - \mu)$ is positive for all the systems studied here i.e. the dipole moment increases on excitation.

Fig. 11 shows the plots of Stokes-shifts for BMI versus solvent polarity functions, $F_1(D,n)$, $F_2(D,n)$ and E_T^N for LE and ICT states. The calculated values of correlation coefficients from the linear least squares fit analysis of the Stokes-shifts versus bulk solvent polarity functions $F_1(D,n)$ and $F_2(D,n)$ as well as microscopic solvent polarity parameter (E_T^N) , are summarized in Table 5 for both LE and ICT states.

The ground state (μ) and excited state (μ^*) dipole moments and Onsager cavity radii 'a' have been calculated theoretically for all the systems and are given in Tables 6 and 7, respectively. Table 7 contains the $\Delta \mu$ values derived from the slopes obtained from the plots of Stoke-shifts versus E_T^N using Eq. (7). The slopes S_1 and S_2 were obtained from the plots of Eqs. (1) and (2) and the ratios of dipole moments (μ^*/μ) calculated using Eq. (6) are summarized in Table 6. The changes in dipole moment, $\Delta \mu$ values derived from the slopes (m) obtained from the plots of Stokes-shifts versus E_T^N using Eq. (7), are given in Table 7.

There is an increase in excited-state dipole moments ($\Delta \mu$ and μ^*/μ values, Tables 6 and 7) in comparison to the theoretically calculated excited state. This suggests considerable amount of charge transfer from the donor to the carbonyl acceptor moieties, which leads to an increase in the polarity of the excited state and consequently, the intensification of the donor-acceptor interaction. $\Delta \mu$

values are positive and quite significant for all the systems studied here. When $\Delta \mu_{(ICT)}$ and $\mu^*/\mu_{(ICT)}$ are compared with $\Delta \mu_{(LE)}$ and $\mu^*/\mu_{(LE)}$ values, it is clearly seen that the dipole moments for ICT states are larger than those of LE states for all BMI derivatives, indicating stronger electronic interaction for the former structures (ICT state, resonance structure II in Fig. 5). These results are in agreement with the fact that the band F1 arises from LE state with the similar electronic arrangement as in ground state and band F2 shows the presence of possible dipolar resonance forms termed as ICT state in all BMI derivatives.

The increase in the dipole moment upon excitation for BMI derivatives can be reasonably explained on the basis of resonance structures as shown in Fig. 5, and the nature of emitting states. All BMI derivatives studied here promote the resonance structure of type **II** in the excited state as ICT, explaining the substantial charge separation upon excitation.

The trend observed in the change in dipole moments of BMI derivatives reflects the nature of the substituents and is in accordance with the ionization potential (IP) trend of the substituted benzene ring for both LE and ICT states [68]. This indicates that both states are affected by solvent polarity in the same manner. BMI shows the lowest $\Delta\mu_{(ICT)}$ and $\mu^*/\mu_{(ICT)}$ values in comparison to the highest $\Delta\mu_{(ICT)}$ and $\mu^*/\mu_{(ICT)}$ values of OMeBMI and DiOMe-BMI derivatives.

4. Conclusions

The study of excited state dipole moments of benzoylmethyleneindol-2-one systems has brought into focus the presence of three emitting states (LE, ICT and ESIPT) in these molecules. These emitting states are affected by the change in solvent polarity as well as the substituted-phenyl moieties.

The experimentally calculated $\Delta \mu$ and μ^*/μ values of probes reveal an increase in the excited state dipole moment. Moreover, experimentally calculated values are significantly larger than the semiempirical computational (PM3) estimates justifying the ICT as the main character of the excited state.

Prototropic reaction has found the existence of three species monocation, neutral and monoanion in BMI derivatives. Therefore, two equilibria exist in these derivatives, Monocation \leftrightarrow Neutral and Neutral \leftrightarrow Monoanion in the range Ho/pH of -5 to 14 in ground state as well as excited state (LE and ICT). Anion and cation are formed due to the deprotonation from NH group and protonation on carbonyl group, respectively.

The valuable information so obtained about the nature of the emitting state opens the possibility of examination of various theoretical models for the electronic structure of the excited states. These solvatochromic studies provide insights for further applications of benzoylmethyleneindol-2-one derivatives as environment-sensitive probes.

Acknowledgements

The financial support from University of Delhi under the Scheme "To strengthen R&D Doctoral Research Program" is gratefully acknowledged. Manju K. Saroj is thankful to the University Grants Commission (UGC), New Delhi for the financial assistance.

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