Synthesis and comparative solvatochromic studies of simple and donor acceptor benzimidazole incorporated naphthyridine systems

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Benzimidazo[1,2-a]benzo[g]-1,8-naphthyridine (NB-1) and its donor-acceptor analog, 11-morpholino-benzimidazo[1,2-a]benzo(g)-1,8-naphthyridine-6-carbonitrile, (NB-2) have been synthesized and investigated for their optical and solvatochromic properties. Absorption and emission maxima of the push-pull chromophore, NB-2 were red shifted in comparison to NB-1 lacking in donor-acceptor motif. Both systems are highly fluorescent (φ = 0.74-0.84) and exhibit positive solvatochromism. Using solvatochromic shift method, we estimated 2 fold higher dipole moment in the excited state for NB-2 over NB-1. High degree of electronic charge redistribution in NB-2 seems to be responsible for its optical spectral red shifts and higher dipole moments compared to NB-1.

Keywords: Benzimidazole fused naphthyridines, synthesis, solvatochromic studies, dipole moments, intramolecular charge transfer

Conjugated organic molecular systems are under active investigations for applications in electronics and photonic fields. It is well known that donor-acceptor (D-A) systems facilitate electronic delocalization, leading to intramolecular charge transfer (ICT) interaction1-3. This phenomenon is markedly influenced by solvent polarity, causing perturbations in the ground and excited state energy levels. This in turn results in altered absorption and emission properties known as solvatochromism4-6. Study of solvatochromic shifts and evaluation of dipole moments provide key information about the altered nature of ground and excited states profiles of chromophores under different conditions7. Positive solvatochromism is typically conferred on D-A chromophores in which the dipole moment in the excited state is larger than in the ground state8. In continuation of our interest in the optoelectronic properties of D-A chromophores9-15, we now report on the synthesis and photophysical properties of benzimidazo[1,2-a]benzo[g]-1,8-naphthyridine, NB-1 and 11-morpholino-benzimidazo[1,2-a]benzo(g)-1,8-naphthyridine-6-carbonitrile, NB-2. While, NB-1 represents a basic heterocyclic core devoid of D/A groups, on the other hand NB-2 carries a donor, morpholino group and an acceptor, –CN acceptor group being in direct electronic conjugation through the heterocyclic backbone. Accordingly, it was of interest to evaluate and compare the ground and excited state dipole moments of NB-1 and NB-2.

Results and Discussion

Estimation of ground (µg) and excited state dipole moment (µe) are based on the solvent effects on the absorption and emission energies and Stokes shifts. A linear correlation is carried out between the wave numbers (in cm⁻¹) of ground and excited state maxima and solvent polarity function. Following equations16-20 provide the estimate of µg and µe, where υa and υf are absorption and fluorescence band shifts in solvents of varying permittivities (ϵ) and refractive indexes (n) relative to the band position of solute molecule.

\[ \frac{\overline{U}_a}{\overline{U}_f} + \overline{U}_f = m_1 F_1 \text{ Lippert – Mataga (} \epsilon, n) + \text{ constant... 1} \]

\[ \frac{\overline{U}_a}{\overline{U}_f} = m_2 F_2 \text{ Kawasaki – Chamma – Viallet (} \epsilon, n) + \text{ constant... 2} \]

The bulk solvent polarity parameter F (ϵ, n) of the solvent are given by eqs 3 (Ref 21) and 4 (Ref 22).

\[ F_{\text{Lippert-Mataga}}(\epsilon, n) = \frac{\epsilon + 1}{2 \epsilon + 1} - \frac{n^2 + 1}{2n^2 + 1} \text{ ... (3)} \]
F₂ Bakshiev (ε, n) = \frac{2n^2+1}{n^2+2} \left( \frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+1} \right) \ldots 4

Using equations 3 and 4, the plots of (ӯa-ӯf) versus F₁(ε,n) and \frac{U_a+U_f}{2} versus F₂(ε,n) are linear with slopes m₁ and m₂, respectively.

where,

\begin{align*}
m₁ &= \frac{2(\mu_x - \mu_y)^2}{fca^3} \quad \ldots 5 \\
m₂ &= \frac{2(\mu^2_y - \mu^2_x)}{fca^3} \quad \ldots 6
\end{align*}

The symbol \( \mathbb{A} \) and c are Planck’s constant and speed of light under vacuum, respectively and \( \alpha \) is Onsager cavity radii. Provided the \( \mu_y \) and \( \mu_x \) are considered parallel, the following equations are obtained

\begin{align*}
\mu_x &= \frac{m_x - m_y}{2} \left( \frac{hca^3}{2m_i} \right) \frac{1}{3} \quad \ldots 7 \\
\mu_y &= \frac{m_x + m_y}{2} \left( \frac{hca^3}{2m_i} \right) \frac{1}{3} \quad \ldots 8
\end{align*}

Synthesis of NB-1 and NB-2 was carried as shown in Scheme I. Condensation of 2-chloro-3-formyl quinoline 1 with 2-methyl benzimidazole 2 was carried out in N-methyl pyrrolidone solvent at elevated temperature. Purification of crude product by SiO₂ column chromatography afforded NB-1 as a light yellow solid in 60% yield. Similarly, the condensation of 2,6-dichloro-3-formylquinoline 3 with 2-cyanomethyl benzimidazole 4 afforded chloro derivative 5. For the synthesis of NB-2, compound 5 was heated with excess of morpholine in N-methylpyrrolidone solvent at 160°C for 10 h. Aqueous work up, followed by purification over neutral alumina led to the isolation of NB-2 in overall yield of 37% yield. NB-1 in chloroform displayed two absorption bands of nearly equal intensities at 338 and 391 nm, which are assignable to \( \pi-\pi^* \) and intramolecular charge transfer transitions (ICT), respectively. In contrast, NB-2 revealed a maximum at 456 nm with essentially no absorption appearing at shorter wavelengths. This observation implies that unlike NB-1 lacking in D-A interaction, the push-pull chromophore NB-2 exhibits electronic excitation originating mainly from the ICT transition²³. UV-Vis spectra of NB-1 and NB-2 in different solvents \((2.8 \times 10^{-3} \text{ M})\) are shown in Figure 1 and Figure 2, respectively.

Scheme I — Synthetic routes towards NB-1 and NB-2
As shown in Figure 3 and Figure 4, excitation of NB-1 and NB-2 (CHCl₃, 2.83 × 10⁻⁵ M) at their absorption maxima at 391 and 456 nm, respectively produced emission bands centered at 461 and 526 nm, respectively. Quantum yield φ for NB-1 and NB-2 were determined to be 0.74 and 0.84, respectively with reference to integrated fluorescence spectra of anthracene (0.27 in ethanol) and Rhodamine 6G (0.95 in ethanol), respectively. High quantum yields of NB-1 and NB-2 could be attributable to their coplanar,π-conjugated ring-fused structures.

For comparative evaluation of dipole moments of NB-1 and NB-2, we recorded their absorption and emission spectra in solvents of different polarities, and the results are collected in Table I. These chromophores exhibited varying degree of red shift in solvents of increasing polarity. Absorption and emission red shifts for NB-1 in going from nonpolar cyclohexane to highly polar DMSO were found to be 7 and 11 nm, respectively. On the other hand, absorption and emission red shifts for NB-2 in corresponding solvents are markedly higher at 27 and 68 nm, respectively. Owing to its predominant ICT character, NB-2 exhibits greater degree of electronic polarization in solvents of higher polarity such as DMSO. From these results, we can infer that NB-2 exhibits relatively more pronounced positive solvatochromism compared to NB-1.

In order to estimate the ground and excited state dipole moments of NB-1 and NB-2, the required parameters, namely solvent polarity functions f(ε,η),
\[ f(\varepsilon, n) + 2g(n) \], wave numbers of absorption and emission maxima along with refractive index \( n \) and dielectric constant \( \varepsilon \) are tabulated in Table II. The plot of spectral shifts \( (\nu_a - \nu_f) \) against solvent polarity functions \( f(\varepsilon, n) \) and the plot of \( (\nu_a + \nu_f) \) versus \[ f(\varepsilon, n) + 2g(n) \] in seven different solvents for NB-1, are shown in Figure 5 and Figure 6, respectively. The corresponding plots for the case of NB-2 are shown in Figure 7 and Figure 8, respectively. From linear regression, the data were fitted to straight lines, and the values of \( m_1 \) and \( m_2 \) were extracted from the slopes of the plots.

The magnitude of Stokes shifts for NB-1 varies between 4063 to 4116 cm\(^{-1}\), whereas for NB-2, which is a D/A system, the Stokes shifts ranged between 2380 to 3576 cm\(^{-1}\). The large magnitude of the Stokes shift in NB-2 implies that its excited state geometry could be vastly different from that of the ground state. In general, an increase in the Stokes shift with increasing solvent polarity signifies an increase in the dipole moment in the excited states. For NB-2, increase in solvent polarity causes both absorption and emission bands to undergo appreciable bathochromic shifts, leading to the highly dipolar-excited state.

Assuming the molecules to be spherical in shape, the Onsager cavity radii ‘a’ for NB-1 and NB-2, calculated using Edward’s method\(^{25}\) were estimated to be 3.8Å and 4.2Å respectively. The ground and excited state dipole moments, \( \mu_g \) and \( \mu_e \) were calculated using eqs. 7 and 8, respectively. The values of \( \mu_g \), \( \mu_e \) and ‘a’ along with the slopes ‘\( m_1 \)’ and ‘\( m_2 \)’for NB-1 and NB-2 are summarized in Table III.

In the case of NB-2, the non-bonding electrons residing on the the morpholino group contributes towards the mobility of the \( \pi \) electrons on the heteroaromatic ring system. Upon excitation of NB-2, it is assumed that the cyano group at the C-6 position becomes highly electrophilic, whereas the ‘nitrogen’ of the morpholino group, being tertiary in nature becomes a
strong electron donor. The variations in the dipole moment values of NB-2 can be understood in terms of its possible resonance structures. As shown in Scheme II, the lone pair of morpholino nitrogen is delocalized all the way to the cyano group throughout the heterocyclic core. This push-pull interaction explains why the values of $\mu_e/\mu_g$ for NB-2 are relatively higher compared to weakly charge transfer system, NB-1.

**Experimental Section**

Chemicals and solvents used were purchased from Sigma-Aldrich, India. UV-Visible spectra were recorded using Shimadzu spectrophotometer, model no. UV-2401PC. Fluorescence studies were carried out using Shimadzu spectrofluorometer, model no. RF-5301PC. IR spectra were recorded using Perkin-Elmer FT-IR spectrometer and pellets were made by using KBr. NMR spectra were recorded on Bruker Advance II 300 instrument running at 300 MHz.

**Benzimidazo[1,2-a]benzo(g)-1,8-naphthyridin, NB-1**

2-Chloroquinoline-3-carboxaldehyde (1) (191 mg, 1 mmol) and 2-methyl benzimidazole (2) (132 mg, 1 mmol) were dissolved in 5 mL of dry N-methyl-2-pyrrolidone. The reaction mixture was stirred and heated in an oil bath maintained between 140-150°C under N$_2$ atmosphere for 5 h. After the completion of the reaction, it was poured over saturated NaHCO$_3$ solution. The precipitated brown solid was filtered, washed well with water and air dried. Purification of the crude product over neutral alumina column chromatography with CHCl$_3$: MeOH (99:1) as eluent yielded a fluorescent yellow solid NB-1 in 60% yield (161 mg), m.p.229-31°C (Lit. m.p.230-31°C) (Ref 28). IR (KBr): 3060, 1658, 1614, 1456, 1399 and 742 cm$^{-1}$; $^1$H NMR (DMSO-d$_6$): $\delta$ 7.4-7.8 (4H, m), 7.9 (2H, m), 8.0 (1H, d, $J = 7.6$ Hz), 8.2 (1H, d, $J = 7.8$ Hz.), 8.3 (1H, d, $J = 7.8$ Hz), 9.0 (1H, s), 9.3 (1H, d, $J = 8.1$ Hz). MS: m/z 268.71. Anal. Calcd for C$_{18}$H$_{11}$N$_3$: C, 80.28; H, 4.12; N, 15.60. Found: C, 79.87; H, 4.21; N, 15.76%.

**11-Chloro-benzimidazo[1,2-a]benzo(g)-1,8-naphthyridine-6-carbonitrile, 5**

The reaction of 7-chloro-2-chloroquinoline-3-carbaldehyde (3) (226 mg, 1 mmol) and 2-cyanomethylbenzimidazole (Ref 27) (191 mg, 1 mmol) and 2-methyl benzimidazole (2) (132 mg, 1 mmol) were dissolved in 5 mL of dry N-methyl-2-pyrrolidone. The reaction mixture was stirred and heated in an oil bath maintained between 140-150°C under N$_2$ atmosphere for 5 h. After the completion of the reaction, it was poured over saturated NaHCO$_3$ solution. The precipitated brown solid was filtered, washed well with water and air dried. Purification of the crude product over neutral alumina column chromatography with CHCl$_3$: MeOH (99:1) as eluent yielded a fluorescent yellow solid NB-1 in 60% yield (161 mg), m.p.229-31°C (Lit. m.p.230-31°C) (Ref 28). IR (KBr): 3060, 1658, 1614, 1456, 1399 and 742 cm$^{-1}$; $^1$H NMR (DMSO-d$_6$): $\delta$ 7.4-7.8 (4H, m), 7.9 (2H, m), 8.0 (1H, d, $J = 7.6$ Hz), 8.2 (1H, d, $J = 7.8$ Hz.), 8.3 (1H, d, $J = 7.8$ Hz), 9.0 (1H, s), 9.3 (1H, d, $J = 8.1$ Hz). MS: m/z 268.71. Anal. Calcd for C$_{18}$H$_{11}$N$_3$: C, 80.28; H, 4.12; N, 15.60. Found: C, 79.87; H, 4.21; N, 15.76%.
The crude product obtained on work-up was purified over neutral alumina using CHCl₃: MeOH (99:5) as eluent to yield 5 as a yellow solid in 75% yield (246 mg) m.p. 282-83°C. IR (KBr): 3052, 2232, 1685, 1606, 1065 and 770 cm⁻¹; ¹H NMR (DMSO- d₆): δ 7.6-7.7 (2H, m), 7.8 (1H, dd, J = 8.7 Hz and 1.4 Hz), 8.0 (1H, d, J = 8.5), 8.3 (1H, d, J = 8.7), 8.5 (1H, d, J = 1.4 Hz), 8.91 (1H, s), 9.2 (1H, s) and 9.4 (1H, d, J = 7.1). MS: m/z 327.71.

Anal. Calcd for C₁₉H₉N₄Cl: C, 69.41; H, 2.76; N, 17.04; Cl, 10.78. Found: C, 69.30; H, 2.98; N, 16.87; Cl, 10.55%.

Synthesis of 11-morpholino-benzimidazo[1,2-a]benzo-(g)-1,8-naphthyridine-6-carbonitrile, NB-2

Compound 5 (328 mg, 1 mmol) and distilled morpholine (2 mL) were dissolved in dry N-methyl-2-pyrrolidone (5 mL), and the resulting solution was heated in an oil bath maintained around 140°C for 3 h. After the completion of the reaction, the reaction mixture was cooled to RT and poured over ice water. The precipitated product was filtered, washed with water and air-dried. Purification of the crude over neutral alumina column chromatography using CHCl₃ as eluent yielded NB-2 as a fluorescent bright orange solid in 56% yield (0.265g). m.p. >300°C. IR (KBr): 2960, 2223, 1625, 1600, 1456, 1397, 1178, 764 cm⁻¹; ¹H NMR (TFA-d): δ 4.4 (4H, t, J = 6.7 Hz), 4.7 (4H, t, J = 6.7 Hz), 8.0-8.2 (4H, m), 8.4 (1H, d, J = 8.6 Hz), 8.8 (1H, d, J = 8.7 Hz), 9.6 (1H, s), 9.73 (1H, s), 9.94 (1H, d, J = 7.2 Hz). MS: m/z 380.40.

Anal. Calcd for C₂₃H₁₇N₅O: C, 72.81; H, 4.51; N, 18.46. Found: C, 72.59; H, 4.66; N, 18.22%.

Conclusions

Benzimidazole fused naphthyridine system, NB-1 and its D/A analog, NB-2 were synthesized and investigated for their solvatochromic properties. Both systems displayed high fluorescent (φ = 0.74-0.84) as well as positive solvatochromism. In contrast to NB-1, the absorption and emission maxima of the push-pull chromophore, NB-2 were considerably red shifted presumably owing to its predominant ICT character. Solvatochromic shift data revealed 2 fold higher excited state dipole moment for NB-2 over NB-1. This observation is consistent with the high degree of electronic charge redistribution in the push pull chromophore, NB-2, a feature which is absent in the case of NB-1. Work to extend the range of donor-acceptor benzimidazole fused naphthyridine systems to study their photophysical properties and potential applications in nonlinear optics is in progress.

Acknowledgement

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References


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Scheme II — Photoinduced intramolecular charge transfer in NB-2
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