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Synthesis and fluorescence study of 3-aminoalkylamidonapthalimides

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ABSTRACT

A new series of fluorescent 3-aminoalkylamidonapthalimides were synthesized starting form 1,8-naphthalic anhydride. The structure of these compounds was characterized by ^{1}H NMR, ^{13}C NMR, IR and Mass spectral analysis. The solvent effect on ^{1}H and ^{13}C NMR of these compounds was studied in $CDCl_3$, $CDCl_3$:DMSO-d_6 (7:3, v/v) and DMSO-d_6. NMR chemical shift of the ortho and para protons and meta carbons of naphthalene ring showed maximum variation on moving from $CDCl_3$ to DMSO-d_6. In $CDCl_3$ solvent naphthalene ring may exist in slightly puckered form while in DMSO-d_6 it attains maximum planar configuration. Fluorescent properties of the title compounds and their precursors were investigated in different solvents like chloroform, ethanol, acetonitrile, acetone, DMSO and water. 3-Aminoalkylamidonapthalimides exhibited improved fluorescence than their precursors. Cyclic amino derivatives yielded higher fluorescence quantum efficiency in protic solvents, ethanol and water. Acylic amino derivatives yielded high fluorescence quantum efficiency in chloroform solvent. The maximum fluorescence quantum yield up to 0.14 was found for butyl amine derivative in chloroform solvent. In general proton accepting nucleophilic solvents like acetone and DMSO quenched the fluorescence.

1. Introduction

1,8-Naphthalimide (NI) derivatives received considerable attention for both their spectroscopic properties and potential applications in biology because of their anticancer activity [1–4]. 1,8-Naphthalimide has high photostability, a large Stokes shift, strong fluorescence and therefore has a wide range of applications in the areas of polymers [5], optical storage [6], photo physical dyads [7], nucleic acid intercalators [8], DNA photo cleavage [9], yellow daylight fluorescent pigments, fluorescent dichroic dyes in liquid crystal displays and fluorescent brighteners in detergents, textiles, papers, plastics and paints [10–14]. Due to its favorable characteristics and numerous applications, naphthalimide based fluorescent chemosensors have been developed by several research groups [15–25]. In the presence of metal ion in different solvents, 1,8-naphthalimides were used as optical switches [26,27]. Owing to the immense importance of naphthalimides, in this paper, we report the synthesis of a few 3-aminoalkylamidonapthalimides along with their fluorescence properties. While investigating the nuclear magnetic resonance spectral studies for structure determination of these 3-aminoalkylamidonapthalimides, we have noticed interesting solvent effects. Hence, we present the effect of $CDCl_3$, $CDCl_3$:DMSO-d_6 (7:3, v/v) and DMSO-d_6 on the ^{1}H NMR and ^{13}C NMR spectra of a few napthalimides.

2. Experimental

2.1. Materials

1,8-Naphthalic anhydride and other starting compounds were purchased from Aldrich chemicals and were used without further purification. All the chemicals and solvents used were of spectroscopic grade purchased from Sigma–Aldrich Chemicals.

2.2. Instrumentation

^{1}H NMR and ^{13}C NMR spectra were performed on 400 MHz and 100 MHz Bruker Ultra shield (Avance-III) Nano Bay spectrometer. All the spectra were recorded at 298 K. ^{1}H NMR data are reported as follows: s: singlet, d: doublet, t: triplet, bs: broad singlet. TLC analysis was carried out using silica gel 60 F_{254} plates. Infrared spectra were obtained employing Bruker FT-Infrared, Tensor-27 using KBr pellets. The melting points reported were uncorrected and determined in Polmon instrument (model No. MP-96). Mass spectroscopy was performed on VG Micro mass 7070 H (ESI-MS). Elemental composition was determined by elemental analyzer, Elementar, Vario EL model. Steady state fluorescence was investigated on RF-5301PC Shimadzu spectrofluorophotometer, with 5 nm excitation and emission slit widths at 18 °C employing 1 cm^3 quartz cell.

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pH 7.4 was adjusted with dilute aqueous NaOH and measured by Global digital pH meter.

2.3. Synthesis of 3-aminoalkylamidonapthalimides and their intermediates

2.3.1. N-Aminonapthalimide (NMI)

2 g (10.10 mmole) of 1,8-naphthalic anhydride (NA) was taken in 80 ml of chloroform and stirred at room temperature for 15 min. To this, 0.97 ml of hydrazine hydrate (20.20 mmole) was added. The reaction mixture was refluxed for 4 h monitoring with TLC. After cooling, a yellow solid obtained was separated by filtration. Then the product was dried in oven at 100 °C. The compound was characterized by IR, NMR and Mass spectral and elemental analysis data.

Yield (91.74%), m.p. 262–264 °C. yellow color, ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.51 (d, 2H, naphthalene, J = 7.2 Hz), 8.46 (d, 2H, naphthalene, J = 8 Hz), 7.88 (t, 2H, naphthalene, J^{1-2} = 8 Hz), 5.80 (s, 2 NH, D_2O exchange). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 160.9(CO), 134.9, 131.7, 131.2, 127.7, 126.4, 122.1. IR (KBr): 3311, 3234, 3065, 1706, 1696, 1650, 1584 cm^{-1}. Elemental analysis (%) for $C_{12}H_8N_2O_2$ (212): calcd C 67.92, H 3.80, N 13.20, observed C 67.85, H 3.62, N 13.34, MS: M+1 m/z 213.

2.3.2. 3-Chloroalkylamidonapthalimides (NMICl) (4)

1 g (4.716 mmole) of 2-amino-benzo[de]isoquinoline-1,3-dione (NMI) was taken in 50 ml of dry chloroform solvent, to this, 1.62 g (11.79 mmol) K_2CO_3 was added and cooled to 0 °C. To this, 0.90 ml (9.43 mmole) of chloropropionyl chloride was added drop wise and then allowed to room temperature and refluxed for 12 h. After cooling the reaction mixture, it was poured on to crushed ice to obtain solid. This solid was filtered under vacuum. The solid product was dried in oven at 100 °C. The compound was characterized by UV–vis, IR, NMR and Mass spectral and elemental analysis data.

Yield (88.48%), m.p. 230–234 °C. white color, ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.56–8.53 (m, 4H, naphthalene), 7.92 (t, 2H, naphthalene, J^{1-2} = 7.6 Hz), 3.87(t, 2H, J^{1-2} = 6.4 Hz), 2.91(t, 2H, J^{1-2} = 6.4 Hz), 10.91 (s, 1H, NH, D_2O exchange). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 168.50(CO), 161.91(CO), 135.40, 132.05, 131.77, 127.73, 122.32, 37.02. IR (KBr): 3242, 3031, 2925 1723, 1693, 1678, 1586, 1537 cm^{-1}. Elemental analysis (%) for $C_{15}H_{11}ClN_2O_3$ (302): calcd C 59.52, H 3.66, N 9.25, observed C 59.26, H 3.54, N 9.07, MS: M+1 m/z 303.

2.3.3. 3-Pyrrolidinepropylamidonapthalimide (7f)

General procedure: 0.1 g (0.33 mmole) of 3-chloro-N-(1,3-dioxo-1H,3H-benzo[de]isoquinolin-2-yl)-propionamide was taken in 15 ml of N,N-dimethylformamide solvent, to this, 0.069 ml (0.82 mmol) pyrrolidine was added drop wise and stirred at room temperature for overnight (12 h). The N,N-dimethylformamide was removed under vacuum by rotavapour and washed with hexane to obtain solid product. The compound was characterized by UV–vis, IR, NMR and Mass spectral and elemental analysis data.

Yield (96%), m.p. 175–178 °C. brown color, ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.55 (d, 4H, naphthalene, J = 7.6 Hz), 7.928 (t, 2H, naphthalene, J^{1-2} = 8 Hz), 2.96(t, 2H,), 2.85–2.60 (m, 6H) 1.63–1.85 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 169.98(CO), 162.01(CO), 135.44, 132.08, 131.78, 127.77, 122.35, 53.65, 50.98, 32.47, 23.59. IR (KBr): 3376, 2938, 1725, 1698, 1670, 1590, 1572 cm^{-1}. Elemental analysis (%) for $C_{19}H_{19}N_3O_3$ (337): calcd C 67.64, H 5.68, N 12.46, observed C 67.39, H 5.50, N 12.14, MS: M+1 m/z 338.49.

2.3.4. 3-Piperidinpropylamidonapthalimide (7a)

Yield (87.27%), m.p. 175–178 °C. brown color, ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.54–8.52 (m, 4H, naphthalene), 7.92 (t, 2H, naphthalene, J^{1-2} = 7.6 Hz), 4.8 (s, NH), 2.63–2.51 (m, 6H), 1.54–1.49 (m, 6H), 1.45–1.36 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 170.95(CO), 162.01(CO), 135.27, 132.05, 131.65, 127.71, 122.48, 54.58, 54.06, 32.02, 26.05, 24.45. IR (KBr): 3382, 2941, 1727, 1696, 1673, 1589, 1567 cm^{-1}. Elemental analysis (%) for $C_{20}H_{21}N_3O_3$ (351): calcd C 68.36, H 6.02, N 11.96, observed C 68.21, H 5.89, N 11.82, MS: M+1 m/z 352.

2.3.5. 3-Piperazinpropylamidonapthalimide (7b)

Yield (85.83%), m.p. 230–232 °C. brown color, ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.543 (d, 4H, naphthalene, J = 7.6 Hz), 7.927 (t, 2H, naphthalene, J^{1-2} = 7.6 Hz), 3.127–3.08 (m, 6H), 2.74–2.67 (m, 5H), 2.56 (t, 2H), 10.8 (s, 1H, NH, D_2O exchange). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 170.42(CO), 162.05(CO), 135.40, 132.11, 131.75, 127.76, 122.40, 53.36, 49.40, 43.43, 31.94. IR (KBr): 3241, 3006, 1722, 1694, 1670, 1584 cm^{-1}. Elemental analysis (%) for $C_{19}H_{20}N_4O_3$ (352): calcd C 64.76, H 5.72, N 15.90, observed C 64.60, H 5.49, N 15.84, M+1 m/z 353.35.

2.3.6. 3-(4-Methyl-piperazin)-propylamidonapthalimide (7c)

Yield (90.90%) m.p. 135–140 °C. brown color, ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.545 (d, 4H, naphthalene, J = 7.6 Hz), 7.928 (t, 2H, naphthalene, J^{1-2} = 7.6 Hz), 2.55–2.81 (m, 15H), 10.73 (s, 1H, NH, D_2O exchange). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 170.20(CO), 162.05(CO), 135.44, 132.10, 131.78, 127.77, 122.36, 53.00, 52.74, 49.66, 43.07, 31.64. IR (KBr): 3248, 2973, 1722, 1695, 1667, 1582, 1512 cm^{-1}. Elemental analysis (%) for $C_{20}H_{22}N_4O_3$ (366): calcd C 65.56, H 6.05, N 15.29, observed C 65.29, H 5.76, N 15.01, M+1 m/z 367.

2.3.7. 3-(4-Ethyl-piperazin)-propylamidonapthalimide (7d)

Yield (86.4%), m.p. 220–224 °C. brown color, ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.544 (m, 4H, naphthalene), 7.926 (t, 2H, naphthalene, J^{1-2} = 7.6 Hz), 2.95–3.10 (m, 6H), 2.74–2.82 (m, 7H), 2.60(t, 2H), 1.21 (t, 3H), 10.8 (s, 1H, NH, D_2O exchange). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 170.23(CO), 162.04(CO), 135.42, 132.11, 131.77, 127.76, 122.38, 52.82, 51.24, 50.84, 49.75, 31.68, 9.60. IR (KBr): 3259, 2962, 1724, 1690, 1586, 1514 cm^{-1}. Elemental analysis (%) for $C_{21}H_{24}N_4O_3$ (380): calcd C 66.30, H 6.36, N 14.73, observed C 66.16, H 6.02, N 14.59, M+1 m/z 381.

2.3.8. 3-Morpholinpropylamidonapthalimide (7e)

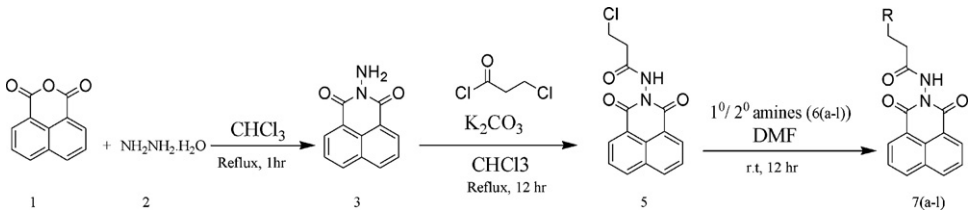
Yield (88.2%), m.p. 225–230 °C. brown color, ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.54 (m, 4H, naphthalene), 7.926 (t, 2H, naphthalene, J^{1-2} = 7.6 Hz), 3.75–4.00 (m, 6H), 2.95–3.10 (m, 6H), 11.14 (s, 1H, NH, D_2O exchange). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 168.67(CO), 161.99(CO), 135.54, 132.12, 131.87, 127.79, 122.26, 63.92, 52.40, 51.83, 28.45. IR (KBr): 3362, 2986, 1732, 1690, 1643, 1591, 1514 cm^{-1}. Elemental analysis (%) for $C_{19}H_{19}N_3O_4$ (353): calcd C 64.58, H 5.42, N 11.89, observed C 64.29, H 5.27, N 11.65, MS: M+1 m/z 354.47.

2.3.9. 3-Cyclopentylaminopropylamidonapthalimide (7g)

Yield (88.5%), m.p. 255–260 °C. brown color, ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.55 (d, 2H, naphthalene, J = 7.6 Hz), 7.93 (t, 2H, naphthalene, J^{1-2} = 7.6 Hz), 3.49 (t, 2H), 3.04 (t, 2H), 2.1–2.0 (m, 2H), 1.70–1.83 (m, 4H), 1.54–1.68 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 168.78(CO), 162.00(CO), 135.58, 132.13, 131.88, 127.82, 122.25, 59.19, 59.11, 42.22, 29.63, 24.00. IR (KBr): 3410, 3186, 2956, 1726, 1687, 1588, 1507 cm^{-1}. Elemental analysis (%) for $C_{20}H_{21}N_3O_3$ (351): calcd C 68.36, H 6.02, N 11.96, observed C 68.09, H 5.82, N 11.71, MS: M+1 m/z 352.35.

2.3.10. 3-Propylaminopropylamidonapthalimide (7h)

Yield (96.8%), m.p. 230–235 °C. grey color, ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.55 (dd, 4H, naphthalene, J^{1-2} = 2 Hz, J^{1-3} = 8.4 Hz), 7.931 (t, 2H, naphthalene, J^{1-2} = 7.6 Hz), 3.19 (t, 2H),



Scheme 1. Synthesis of 3-aminoalkylamidonapthalimides.

2.94–2.88 (m, 4H), 1.70–1.60 (m, 2H), 0.935 (t, 3H), 8.98 (brs, 1H, NH, D_2O exchange), 11.12 (brs, 1H, NH, D_2O exchange). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 168.81(CO), 161.94(CO), 135.49, 132.12, 131.81, 127.77, 122.30, 48.91, 43.10, 30.06, 19.34, 11.36. IR (KBr): 3407, 2974, 1728, 1692, 1588, 1460 cm^{-1}. Elemental analysis (%) for $C_{18}H_{19}N_3O_3$ (325): calcd C 66.45, H 5.89, N 12.91, observed C 66.33, H 5.62, N 12.78, MS: M+1 *m*/*z* 326.29.

2.3.11. 3-Isopropylaminopropylamidonapthalimide (7i)

Yield (92.6%), m.p. 250–255 °C. cream color, ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.544 (d, 4H, naphthalene, J = 7.6 Hz), 7.923 (t, 2H, naphthalene, J^{1-2} = 8 Hz), 3.42–3.38 (m, 1H), 3.18 (t, 2H, J^{1-2} = 7.6 Hz), 2.93 (t, 2H, J^{1-2} = 8 Hz), 1.27 (d, 6H, J = 6.8 Hz), 8.98 (brs, 1H, NH, D_2O exchange), 11.09 (brs, 1H, NH, D_2O exchange). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 168.63(CO), 162.01(CO), 135.69, 131.96, 127.91, 127.66, 122.11, 49.95, 30.04, 30.08, 20.84, 19.07. IR (KBr): 3326, 2930, 1709, 1668, 1606, 1580, 1518 cm^{-1}. Elemental analysis (%) for $C_{18}H_{19}N_3O_3$ (325): calcd C 66.45, H 5.89, N 12.91, observed C 66.20, H 5.72, N 12.65, MS: M+1 *m*/*z* 326.29.

2.3.12. 3-Butylaminopropylamidonapthalimide (7j)

Yield (91.3%), m.p. 225–230 °C. white color. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.55 (dd, 4H, naphthalene, J^{1-2} = 2.4 Hz, J^{1-3} = 8.4 Hz), 7.933 (t, 2H, naphthalene, J^{1-2} = 8 Hz), 3.19 (t, 2H), 2.95–2.90 (m, 4H), 1.65–1.57 (m, 2H), 1.40–1.31 (m, 2H), 0.91 (t, 3H), 8.96 (brs, 1H, NH, D_2O exchange), 11.11 (brs, 1H, NH, D_2O exchange). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 168.81(CO), 161.94(CO), 135.50, 132.11, 131.80, 127.77, 122.29, 47.03, 43.12, 30.08, 27.93, 19.73, 13.72. IR (KBr): 3313, 2923, 1705, 1666, 1609, 1587, 1514 cm^{-1}. Elemental analysis (%) for $C_{19}H_{21}N_3O_3$ (339): calcd C 67.24, H 6.24, N 12.38, observed C 67.08, H 6.13, N 12.06, MS: M+1 *m*/*z* 340.44.

2.3.13. 3-Isobutylaminopropylamidonapthalimide 7(k)

Yield (92.6%), m.p. 240–245 °C. brown color, ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.55 (d, 4H, naphthalene, J = 8 Hz), 7.935 (t, 2H, naphthalene, J^{1-2} = 7.6 Hz), 3.21 (t, 2H, J^{1-2} = 7.6 Hz), 2.95 (t, 2H, J^{1-2} = 7.6 Hz), 2.82 (d, 2H, J = 7.2 Hz), 2.02 (m, 1H), 0.978 (d, 6H, J = 6.8 Hz), 8.84 (s, 1H, NH, D_2O exchange), 11.11 (s, 1H, NH, D_2O exchange). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 168.77(CO), 162.04(CO), 135.74, 132.0, 127.94, 127.71, 122.12, 54.30, 43.46, 29.71, 25.89, 20.50. IR (KBr): 3319, 2926, 1702, 1668, 1604, 1585, 1512 cm^{-1}. Elemental analysis (%) for $C_{19}H_{21}N_3O_3$ (339): calcd C 67.24, H 6.24, N 12.38, observed C 67.03, H 6.06, N 12.14, MS: M+1 *m*/*z* 340.44.

2.3.14. 3-Hexylaminopropylamidonapthalimide (7l)

Yield (89.67%), m.p. 210–215 °C. white color, ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 8.55 (d, 4H, naphthalene, J = 8 Hz), 7.93(t, 2H, naphthalene, J^{1-2} = 8 Hz), 3.19 (t, 2H), 2.98–2.88 (m, 4H), 1.70–1.59 (m, 2H), 1.36–1.23 (m, 4H), 0.88 (t, 3H), 8.95 (s, 1H, NH, D_2O exchange), 11.07 (s, 1H, NH, D_2O exchange). ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6, 25 °C): δ 168.39(CO), 161.28(CO), 134.23, 131.13, 131.06, 127.26, 126.35, 121.47, 47.54, 43.13, 30.44, 29.61, 25.55, 25.30, 21.66, 13.28. IR (KBr): 3326, 2929, 1724, 1690, 1586 cm^{-1}. Elemental analysis calcd (%) for $C_{19}H_{21}N_3O_3$ (367): calcd C 68.64, H 6.86, N 11.44, observed C 68.45, H 6.58, N 11.10, MS: M+1 *m*/*z* 367.

3. Results and discussion

3.1. Synthesis of 3-aminoalkylamidonapthalimides

Synthesis of 3-aminoalkylamidonapthalimides was carried out starting from naphthalene monoanhydride in good yields as shown in Scheme 1.

6a-l: piperidine, piprazine, n-methyl piperazine, n-ethyl piperazine, morpholine, pyrrolidine, cyclopentyl amine, propyl amine, isopropyl amine, n-butyl amine, isobutyl amine and n-hexyl amine.

Naphthalene monoanhydride (NMA, 1) was treated with hydrazine monohydrate in chloroform solvent to yield N-aminonapthalimide (NMI, 3) and it was characterized by IR, NMR and Mass spectral data. The proton NMR spectrum of NMI confirms its formation. In the NMR spectra, two hydrogens attached to the nitrogen of imide exhibited a signal at 5.8 ppm in DMSO-d_6. These protons were exchanged with deuterium in D_2O solvent.

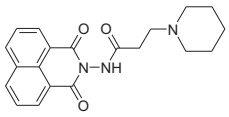
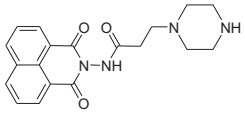
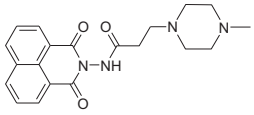
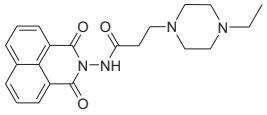
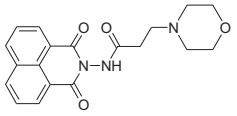
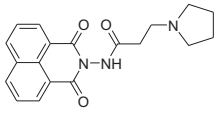
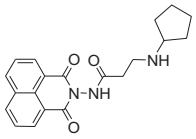
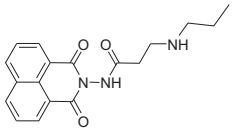
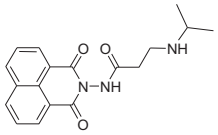
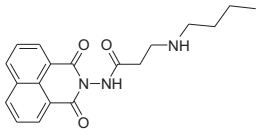
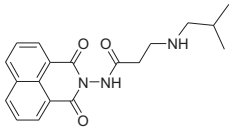
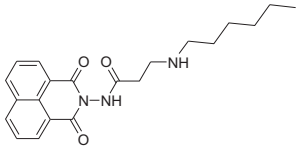
The chloroform solution of NMI was charged with anhydrous K_2CO_3 and chloropropionylchloride at 0 °C and stirred to reach room temperature. The resulting reaction mixture was refluxed for about 1 h, then poured onto crushed ice to get 3-chloroalkylamidonapthalimides (NMICl). The evidence for the structure of NMICl was derived from IR, NMR and Mass spectral data. In proton NMR, the proton attached to the nitrogen of amide exhibited a signal at 10.52 ppm in $CDCl_3$ + DMSO-d_6. This proton was exchanged with deuterium in D_2O solvent. The chlorine attached methylene protons showed as a triplet signal at 3.80 ppm and its adjacent methylene protons exhibited a triplet signal at 2.88 ppm.

NMICl was treated with different primary and secondary amines in DMF and stirred at room temperature overnight to produce 3-aminoalkylamidonapthalimides. This nucleophilic substitution reaction was carried without any added base as the reactant amine itself acted as a base. A series of 3-aminoalkylamidonapthalimides were prepared by employing different amines. The DMF solution of NMICl was treated with piperidine and then stirred the reaction mixture overnight at room temperature. Subsequently the DMF was removed under vacuum and the residue was washed with hexane to obtain the solid product. In ^1H NMR spectrum of the above product, 7a, the acyclic carbon attached protons gave a triplet signal at 2.80 ppm and its adjacent carbon attached protons and piperdine nitrogen attached carbon protons gave a multiplet signal between 2.68 and 2.58 ppm. Other piperidine ring protons gave a multiplet at 1.68–1.50 ppm. A list of the compounds prepared is given in Table 1.

3.2. Structure variation-NMR studies

^1H NMR spectrum of NMI, NMICl and amino derivatives of NMICl was recorded in $CDCl_3$, $CDCl_3$:DMSO-d_6 (7:3, v/v) and DMSO-d_6 solvents. The ^1H NMR spectra of all these compounds in $CDCl_3$ and $CDCl_3$:DMSO-d_6 (7:3, v/v) exhibited two signals separately around 8.30 and 8.61 ppm for ortho and para aromatic protons

Table 1
Synthesis of 3-aminoalkylamidonapthalimides.

Compound number	Product	Yield (%)	M.p. (°C)
7a		87.27	175–178
7b		85.83	230–232
7c		90.90	226–229
7d		86.4	220–224
7e		88.2	225–230
7f		96.6	175–178
7g		88.5	255–260
7h		96.8	230–235
7i		92.6	250–255
7j		91.3	225–230
7k		92.6	235–238
7l		89.67	210–215

of naphthalene ring respectively. However, in case of NMICl and its amino derivatives, in DMSO-d_6 solvent the para and ortho protons of naphthalene ring were merged in to one signal exhibiting a chemical shift around 8.55 ppm. The merging of ortho and para protons signals of naphthalene ring in to a single signal can be considered as a diatropic shift to para protons while it is paratropic to ortho protons. The chemical shift values of aromatic protons of a few compounds in two different solvent media are given in Table 2.

From Table 2 it can be noticed that compound 3, NMI has given three signals in the three solvents each representing ortho, para and meta hydrogens of naphthalene ring. However, when the amino nitrogen of imide was substituted by a bulky group as in the case of NMICl and 7a to 7l, the aromatic protons of naphthalene ring behaved differently in DMSO-d_6 compared to NMI. The ortho and para protons of NMICl and 7a to 7l were merged and gave a single multiplet signal in DMSO while giving two separate signals in $CDCl_3$ and $CDCl_3$:DMSO-d_6 (7:3, v/v). The merging of two signals of ortho and para protons into one signal in DMSO-d_6 solvent may be associated with the structure variation. In $CDCl_3$:DMSO-d_6 (7:3, v/v) solvent the naphthalene ring may exist slightly in puckered configuration, making the three aromatic carbons i.e. ortho, meta and para carbons of naphthalene deviate from the single plane making the respective protons chemically non equivalent. However, in more polar solvent like DMSO-d_6, the naphthalene ring may assume planar geometry which probably assisted by the bulky substituent. This rearranged planar geometry stabilized by the surrounding polar medium may make the ortho and para hydrogens resonate at the same frequency exhibiting a single signal as shown in Table 2.

Similar structure and solvent dependent chemical shifts were also observed in ^{13}C NMR spectral studies of these compounds. In general all the carbons have experienced a paratropic shift in DMSO-d_6 compared to $CDCl_3$:DMSO-d_6 (7:3, v/v) solvent with some exceptions. It was observed that C_4 (ortho) and C_6 (para) carbons have given separate signals in both the solvents and have experienced variation in chemical shifts to a similar magnitude. However, C_5 (meta) carbons of the naphthalene ring had experienced significant variation in their chemical shifts on moving form $CDCl_3$:DMSO-d_6 (7:3, v/v) to DMSO-d_6. The greater variation in the chemical shifts of C_5 (meta) carbons may be due to change in the puckered geometry of these imido N-substituted compounds in $CDCl_3$:DMSO-d_6 (7:3, v/v) to a planar geometry in DMSO-d_6.

3.3. *Steady state fluorescence studies*

NMICl and its derivatives are the naphthalene derivatives and investigation of their fluorescent properties would enable their utility as fluoroprobes. The NMI is a weekly fluorescent molecule. But NMICl is showing appreciable fluorescence and all its amino derivatives are highly fluorescent. Fig. 1 shows the excitation and fluorescence spectra of NMI, NMICl and 7a in ethanol. From Fig. 1 it can be observed that the fluorescence spectra of NMI, NMICl and 7a are mirror images of their excitation spectrum. When the amino group in the NMI was converted to amide, the later became a fluorescent molecule with very small change in the excitation and emission wavelengths. Similarly when the chlorine in NMICl was substituted with amines, the amino derivatives have higher fluorescence than the NMICl with a small change in the excitation and emission wavelengths. The steady state fluorescence of all these compounds was studied in six different solvents. The fluorescence spectral data including Stokes shift is given Table 3. The solvents employed were chloroform, ethanol, acetonitrile, acetone, dimethylsulfoxide (DMSO) and water (pH 7.4). NMI showed weak fluorescence in the all solvents. NMICl is fluorescent less fluorescent in DMSO, in ethanol and in water it is more fluorescent. The order of NMICl fluorescence intensity in the solvents investigated

Table 2
^{1}H NMR chemical shifts of NMI, NMICl and amino derivatives of NMICl in $CDCl_3$:DMSO-d_6 (7:3, v/v) and DMSO-d_6 solvents.

Compound no.	^{1}H NMR chemical shift values (ppm)[a]						Difference in ^{1}H NMR chemical shift values (Hz)[b]		
	$CDCl_3$ + DMSO-d_6 or $CDCl_3$			DMSO-d_6			Ortho	Para	Meta
	Ortho	Para	Meta	Ortho	Para	Meta			
NMI	8.27	8.58	7.79	8.46	8.51	7.88	−76[c]	28	−36
NMICl	8.25	8.61	7.80	8.50	8.50	7.92	−99	25	−51
7a	8.26	8.64	7.78	8.53	8.53	7.92	−109	41	−55
7h	8.28	8.53	7.77	8.55	8.55	7.93	−108	8	−64
7i	8.32	8.58	7.82	8.53	8.53	7.92	−81	18	−42
7j	8.31	8.55	7.79	8.55	8.55	7.93	−96	0.8	−56
7l	8.25	8.55	7.74	8.55	8.55	7.93	−118	9.8	−74

[a] Approximately 6 mg of compound dissolved in 0.8 ml of solvent.
[b] Difference in the chemical shift value $= \delta_{DMSO-d_6} - \delta_{CHCl_3:DMSO-d_6\ (7:3,\ v/v)}$.
[c] Diatropic chemical shift.

is water > ethanol > acetonitrile > chloroform > acetone > DMSO. The relative fluorescence quantum efficiency, Φ_f, the ability of a molecule to emit absorbed light energy, was evaluated by employing 9,10-diphenyl anthracene as standard (Φ_f = 0.9) employing Eq. (1) and the results obtained are given in Table 4.

$$\Phi_{unk} = \Phi_{std}\left(\frac{I_{unk}}{I_{std}}\right)\left(\frac{A_{unk}}{A_{std}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \quad (1)$$

where, Φ_{unk}, Φ_{std}, I_{unk}, I_{std}, A_{std}, A_{unk}, η_{unk} and η_{std} are the fluorescence quantum efficiencies, the integral of the emission intensities, the absorbance at the excitation wavelength and the refractive indexes of the corresponding unknown and the standard samples respectively. The relative fluorescence quantum efficiency, Φ_f, of these compounds varied between 1.4×10^{-1} and 4.37×10^{-4}.

Among the cyclic amino derivatives, piperazine derivative, 7b showed higher quantum yield compared to all other cyclic amino compounds in ethanol. On the other side piperidine derivative, 7a has shown lower fluorescence quantum yield than all the cyclic amino derivatives. Among the piperazine series piperazine showed maximum quantum yield compared to the N-ethyl and N-methyl piperazines. In the acyclic amino substituted compounds butyl amine derivative showed maximum fluorescence quantum yield than the propyl, cyclopentyl, n-hexyl, isobutyl and isopropyl amino derivatives. The order of fluorescence of these compounds in chloroform solvent is 7j > 7h > 7k > 7l > 7g > 7b > 7e > 7i > 7d > 7c > 7f > 7a. The quantum efficiency of all the compounds is in the similar order and has not varied significantly in chloroform, ethanol, water and acetonirile. However in DMSO solvent, the Φ_f is the lowest among all the solvents investigated.

The fluorescence spectrum of 7j in different solvents is given in Fig. 2. From the above figure it can be noticed that 7j is more fluorescent in chloroform than in the remaining solvents. From Fig. 2 it can be observed that in chloroform, compound 7j has given an emission doublet maximum at 367 and 386 nm with a well developed shoulder at 407 nm and a subdued shoulder at 430 nm. When the fluorescence spectrum of 7j was taken in ethanol, the distinct doublet emission maxima at 367 and 386 nm merged into a diffused broad maxima centering at 385 nm while the shoulders at 407 and 430 nm have disappeared. Similar is the case with in DMSO, acetonitrile and acetone solvents. In water, 7j has given a broad emission doublet maximum similar to ethanol but a symmetrical doublet centering at 390 nm. The difference in the fluorescence spectra of these compounds in the more polar solvents and protic solvents compared to chloroform medium may be associated with the aggregation of these molecules like organic dyes. The shoulders at longer wavelengths in the emission spectrum of 7j in chloroform may not be due to the dual fluorescence as was assigned by Heagy et al. [28,29] as there are no substituents present in the naphthalene ring, therefore the new longer wavelength shoulders in chloroform at 407 and 430 nm are attributed to the excimer emission. These excimers were not found in more polar solvents like DMSO or proton donating solvents like ethanol and water. Therefore, it is appropriate to study the effect of DMSO or ethanol on the fluorescence spectra of 7j in chloroform. The effect of ethanol on the fluorescence of 7j in chloroform is given in Fig. 3. From Fig. 3 it can be noticed that with increase in the concentration of ethanol, the shoulders at 407 and 430 nm disappeared while the distinct doublet at 367 and 386 nm was changed to a diffused broad emission maximum at 385 nm. From Fig. 3 it can also be noticed that with increase in the amount of ethanol the intensity of the fluorescence emission maxima decreases attaining a minimum at its 50% (v/v) ratio then the additional increase in the amount of ethanol has increased the intensity in the 385 nm emission band. Further it can be noticed that at greater than 50% of ethanol volume, the shoulders at 407

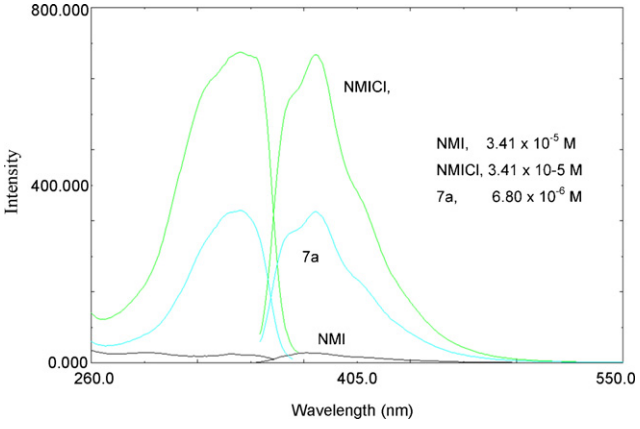


Fig. 1. Excitation and emission spectra of NMI, NMICl and 7a in ethanol.

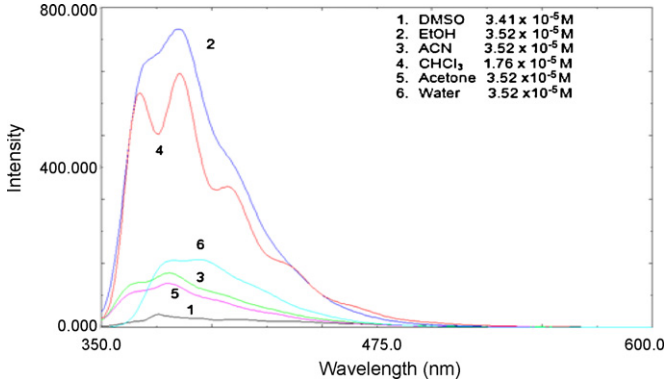


Fig. 2. Fluorescence spectra of 7j in different solvents.

Table 3
The fluorescence data of 3-aminoalkylamidonapthalimides in five different solvents.

Compound no	Solvents								
	Chloroform			Ethanol			Acetone		
	λ_{abs} max (nm)	λ_{em} max (nm)	Stokes shift	λ_{abs} max (nm)	λ_{em} max (nm)	Stokes shift	λ_{abs} max (nm)	λ_{em} max (nm)	Stokes shift
NMI	340	381, 410, 435	3163 5021 6423	337	377	3147	338	374 401	2847 4647
NMI-Cl	340	364, 381	3165	339	377	2972	346	362 378	1276 2445
7a	340	381, 410, 435	3163 5020 6421	342	383	3130	339	361, 377	1797 2972
7b	338	363, 382, 403	2031 3406 4771	340	383	3302	339	361, 378	1797 3042
7c	337	364, 382, 435	2200 3495 6684	342	383	3129	338	360, 376, 400	1807 2989 4857
7d	337	364, 381, 410, 436	2200 3426 5282 6737	342	384	3198	339	361, 377, 399, 423	1797 2972 4435 5857
7e	336	364, 378	2288 3304	340	385	3436	341	362 379	1700 2939
7f	339	381, 410, 435	3258 5107 6509	342	383	3130	339	361, 377	1797 2972
7g	341	367, 385, 407	2077 3350 4754	340	385	3436	344	382	2890
7h	342	367, 386, 407	1992 3333 4669	338	386	3678	341	380	3009
7i	340	381, 410, 435	3165 5021	342	383	3129	336	375 402	3093 4884
7j	340	367, 386, 407	2164 3505 4841	340	385	3436	341	380	3009
7k	340	367, 385, 407	2164 3437 4841	342	383	3129	336	375 402	3093 4884
7l	341	367, 386, 407	2077 3418 4754	341	384	3283	342	381	2992

Compound no	Solvents					
	Acetonitrile			DMSO		
	λ_{abs} max (nm)	λ_{em} max (nm)	Stokes shift	λ_{abs} max (nm)	λ_{em} max (nm)	Stokes shift
NMI	338	377 401	3060 4648	338	376 395 414 438	2984 4269 5431 6753
NMI-Cl	344	364 381	1596 2813	339	377	2972
7a	340	363, 379	1862 3025	338	376 411	2984 5254
7b	340	379	3025	325	395	5452
7c	339	379 401	3112 4560	338	376 414	2984 5430
7d	339	364, 379, 401	2025 3112 4560	338	376 411	2984 5254
7e	336	364, 378	2287 3304	338	376, 413	2984 5371
7f	340	363, 379	1862 3025	338	376 411	2984 5254
7g	341	381	3078	339	377 411	2972 5167
7h	342	382	3060	338	376 413	2989 5372
7i	339	379	3112	338	376 413	2989 5372
7j	340	381	3164	338	376 411	2989 5254
7k	339	379	3112	338	376 411	2984 5254
7l	341	381	3078	338	376 395 416	2984 4269 5546

Table 4
Fluorescence quantum efficiencies of 3-aminoalkylamidonapthalimides in six different solvents.

Compound no.	Solvents					
	Chloroform	Ethanol	Acetone	Acetonitrile	DMSO	Water (pH 7.4)
NMI	6.86×10^{-3}	3.07×10^{-3}	1.40×10^{-3}	5.41×10^{-3}	8.13×10^{-4}	1.39×10^{-6}
NMI-Cl	4.52×10^{-2}	7.10×10^{-2}	2.71×10^{-2}	6.85×10^{-2}	5.87×10^{-3}	1.20×10^{-1}
7a	6.20×10^{-3}	8.97×10^{-3}	8.64×10^{-4}	9.49×10^{-4}	4.37×10^{-4}	5.94×10^{-2}
7b	9.95×10^{-2}	1.11×10^{-1}	5.72×10^{-2}	7.28×10^{-2}	3.29×10^{-3}	6.20×10^{-2}
7c	5.05×10^{-2}	6.87×10^{-2}	1.26×10^{-2}	1.76×10^{-2}	0.81×10^{-3}	6.43×10^{-2}
7d	5.79×10^{-2}	7.59×10^{-2}	1.07×10^{-2}	1.53×10^{-2}	0.57×10^{-3}	6.50×10^{-2}
7e	9.85×10^{-2}	1.07×10^{-1}	5.28×10^{-2}	6.42×10^{-2}	2.38×10^{-3}	7.10×10^{-2}
7f	9.98×10^{-3}	1.13×10^{-2}	6.29×10^{-3}	7.61×10^{-3}	3.90×10^{-3}	2.38×10^{-2}
7g	1.0×10^{-1}	1.12×10^{-1}	6.10×10^{-2}	7.77×10^{-2}	5.24×10^{-3}	6.11×10^{-2}
7h	1.13×10^{-1}	1.05×10^{-1}	5.20×10^{-2}	6.39×10^{-2}	3.91×10^{-3}	7.47×10^{-2}
7i	9.68×10^{-2}	9.80×10^{-2}	5.77×10^{-2}	6.22×10^{-2}	5.23×10^{-3}	6.92×10^{-2}
7j	1.4×10^{-1}	1.28×10^{-1}	7.60×10^{-2}	8.57×10^{-2}	5.71×10^{-3}	7.28×10^{-2}
7k	1.12×10^{-1}	1.05×10^{-1}	6.84×10^{-2}	7.51×10^{-2}	4.55×10^{-3}	7.2×10^{-2}
7l	1.10×10^{-1}	1.02×10^{-1}	5.95×10^{-2}	7.52×10^{-2}	5.25×10^{-3}	6.11×10^{-2}

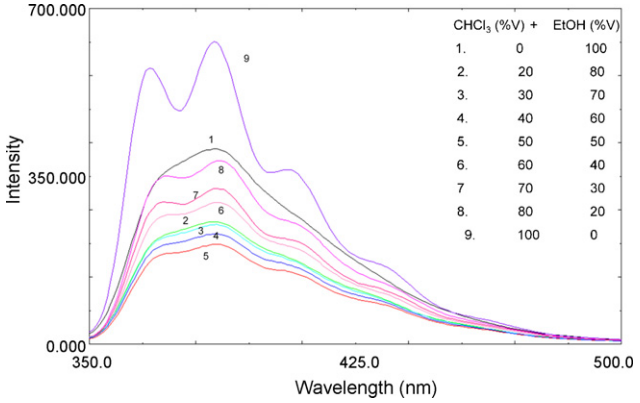


Fig. 3. Titration fluorescence spectra of 7j, 3.76×10^{-5} M in chloroform and ethanol.

and 430 nm are gradually disappearing and finally in pure ethanol the shoulders were missing. The change in the fluorescence spectrum with change in the solvent may not be considered as only due to solvatochromism but may be associated with the dissociation of the excimers that were found in a less polar aprotic solvent like chloroform.

The fluorescence of all the compounds is quenched in DMSO and acetone. The reason for quenching in these aprotic polar solvents is unknown and could be due to structural changes from a more rigid puckered form to a planar system as was observed in NMR spectral investigation. The rigid cyclic systems have a decreased non radiative deactivation of excited states over a planar system leading to higher emission efficiency in less polar chloroform medium and protic solvents.

4. Conclusion

We have reported an efficient synthesis of new fluorescent 3-aminoalkylamidonapthalimides starting from 1,8-naphthalene dicarboxylic anhydride involving NMI and NMICl as stable intermediates. All the compounds showed fluorescence. Acyclic amino substituted derivatives have exhibited higher fluorescence quantum yield than the cyclic amino derivatives exhibiting similar emission pattern. It was observed that the chemical shifts of aromatic protons of NMICl and amino derivatives of NMICl were solvent and structure dependent. In DMSO-d_6 solvent the meta carbons and bridged carbons are resonating at same frequency while in the $CDCl_3$ + DMSO-d_6 meta carbon and bridged carbon signal are well resolved. The variation in chemical shift values of aromatic protons and aromatic carbons in NMICl and its amino derivatives in DMSO-d_6 and quenching of their fluorescence in DMSO and acetone can be explained due to the variation in the structure in polar and non polar solvents.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.11.002.

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