DOI:10.7598/cst2017.1314
ISSN:2278-3458

Chemical Science Transactions
2017, **6(1),** 57-68

RESEARCH ARTICLE

Synthesis and Photophysical Properties of 5-Methoxy-naphtho[1,2-*d*]thiazole-2-carboxylic Acid

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Received 25 August 2016 / Accepted 3 September 2016

Abstract: Synthesis of 5-methoxynaphtho[1, 2-d]thiazole-2-carboxylic acid was developed from new synthetic route starting from using potassium ferricyanide as catalyst. The absorption and fluorescence properties of structurally related 4-methoxynaphthalene-1-ylamine **(4),** *N*-(4-methoxynaphthalene-1-yl)-oxalamic acid ethyl ester **(5),** 2-(4-methoxynaphthalene-1-ylamino)-2-thioxoacetic acid **(6)** and 5-methoxynaphtho[1,2-*d*]thiazole-2-carboxylic acid **(7)** were investigated in 4 different solvents. The absorption maxima of these compounds (except **7)** in the order C_6H_6 > cyclohexane >MeOH>EtOH+HCl. The spectral characteristics are solvent and compound specific. Fluorophores with electron withdrawing group have larger fluorescence quantum yields and greater solvatochromism than the compounds with electron donating groups. Protic solvents yielded higher fluorescence quantum efficiency. While no such relationship exists between the latter and electronic absorption maxima, fluorescence emission maxima, fluorescence quantum efficiency and Stokes shift.

Keywords: 4-Methoxynaphthyl amine**,** Naphthothiazole**,** Solvatochromism**,** Stokes shift**,** Fluorophore

Introduction

Functionalized benzimidazoles and benzothiazoles are very useful *N*-containing heterocyclic intermediates for the development of pharmaceutical molecules[1] and drugs of biological activities[2], such as antitumor, antiviral, anticancer, antihypertensive and antihistamines among others. They are important ligands for complexation with transition metals[3] and have also been applied in laser dyes[4], chemosensing[5], fluorescence and nonlinear organic materials[6]. Thiazoles are important nitrogen and sulfur-containing five membered heterocyclic compounds. Several thiazole derivatives possess important pharmacological activities. They are of interest as potential neuroprotective agents[7-9]. Epidemics of human trypanosomiasis in subsided to the present level of controlled endemicity largely due to thiazole chemotherapy[10,11]. Nevertheless, disease foci still exist and there is potential for new human epidemic[12]. Presently used trypanocides have serious drawbacks, such as toxicity or ineffectiveness in late-stage infection[13-15]. The interest in the fluorescent molecules has steadily increasing in recent years. Fluorescent biomarkers and probes provide

in-depth knowledge about biological system. Many scientific articles have focused on the absorption and emission properties of differently substituted benzoxazoles and benzothiazoles because of their high quantum yields. They have a wide range of applications as fluorescent probes and as intermediates for dyes[16–19]. The electronic absorption and emission studies revealed that the light absorbing and emitting chromophore is the naphthoxy moiety. There is no extensive delocalization of aromatic π-electrons in the active chromophore which exhibited lower quantum yields and lower Stokes shifts[20]. Based on the importance of naphthothiazoles in the pharmacological activity and electronic properties of naphthol moiety, therefore, in this paper, we report a facile method ofsynthesis of 5-methoxynaphtho[1,2-*d*]thiazole-2-carboxylic acid using potassium ferricyanide as catalyst along with tis photophysical properties in this paper.

Experimental

1-Napthol, dimethyl sulphate, glacial acetic acid, chloro-oxo-acetic acid ethyl ester, phosphorus penta sulfide and potassium ferricyanide and CAN were purchased from Aldrich and used without further purification. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates (Merck). All the solvents employed were of spectroscopic grade and used without any further purification. The relative fluorescence quantum yields of 4-methoxy-naphthalen-1-ylamine, *N*-(4-methoxy-naphthalene-1-yl)-oxalamic acid ethyl ester, (4-methoxy-naphthalene-1-ylamino)-thioxo-acetic acid ethyl ester and 5-methoxy-naphtho[1,2-d]thiazole-2-carboxylic acid were measured using 9,10-diphenyl anthracene as reference by following the eq.1.

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

The melting points reported were uncorrected and determined in Polmon instrument (model No. MP-96). The IR spectra were recorded on Bruker Infrared model Tensor-27. The ^{1}H NMR spectra were recorded on 400 MHz of Bruker Ultrashield (Avance-III) Nano Bay spectrometers using TMS as internal standard. The EI mass spectra were recorded on a VG micro mass 7070-H. UV–Vis spectra were recorded on Elico SL 159 UV–Vis spectrophotometer. Steady state fluorescence was investigated on Shimadzu RF-5301PC spectrofluorophotometer, with 5 nm excitation and emission slit widths at 18 ^{o}C employing 1 cm 3 quartz cell. Elemental composition was determined by elemental analyzer, Elementar, Vario EL model.

*Synthesis of 1-naphthyl methyl ether (**2**)*

To a mixture of 36 g of 1-napthol **(1)** 10.5 g of NaOH in 150 mL of water 31.5 g (23.5 mL) of dimethyl sulphate (DMS) was added whilst cooled in ice. Heated for 1 hour at 70-80 ^{o}C and allowed to cool. Extracted with chloroform, evaporated the chloroform and collected brick red liquid. The b.p. 135-137 ^{o}C and IR are coincide with the literature data[21].

*Synthesis of 1- methoxy-4 nitro naphthalene(**3**)*

A solution of 1-methoxy naphthalene **(2)** 4 g in 10 mL of glacial acetic acid was added drop wise to a super saturated solution of ceric ammonium nitrate in 10 mL of glacial acetic acid. The reaction mixture was heated on water bath at 70 $^\circ$C for 1 h. Then the mixture was cooled and 10 g of crushed ice was added. The nitration products were extracted with $CHCl_3$ and dried over anhydrous sodium sulphate and filtered. The $CHCl_3$ from the filtrate was removed under vacuum and the mixture was collected. The individual components were separated on

a pre-coated silica gel 20x20 cm plates with pet.ether-chloroform (50:50, v/v). The numbers of compounds obtained are six and one of the compounds was 1-methoxy-4-nitronaphthalene as reported earlier[21].

Reduction of a nitro group to a primary amine

*4-Methoxynaphthalene-1-ylamine (**4**)*

In a 50 mL RB flask fitted with a reflux condenser 1 g of 1-methoxy-4-nitro naphthalene **(3)** was placed and 2 g of granulated tin in 10 mL of conc. HCl was added with three equal portions and shaken thoroughly after each addition. After the vigorous reaction subsides, heated under reflux on a water bath until the nitro compound has completely reacted (20-30 min.). The reaction mixture was shaken well from time to time. The reaction mixture was cooled and 30% sodium hydroxide solution was added until the precipitate of tin hydroxide dissolved. Extracted with ethyl acetate and evaporated the ethyl acetate and collected the deep block-red residue **(4)**. Disappearance of $-NO_2$ group and appearance of NH_2 group is established by IR, H^1 NMR and mass spectra. m.p. 248-250 ^oC.

*Synthesis of N-(4-methoxynaphthalene-1-yl)-oxalamic acid ethyl ester (**5**)*

To a 4-methoxynaphthalene-1-ylamine **(4)** (0.25 mol; 2.78 mL), ethyl oxalyl chloride (0.25 mol) in $CHCl_3$ (10 mL) was dispensed drop by drop under stirring at < 10 ^oC. After the addition of acid chloride the RB flask was left overnight at room temperature for completion of reaction then the mixture poured into ice cold water (100 mL) and extracted with $CHCl_3$, the layer was washed with 5% $NaHCO_3$ solution followed by water and dried over anhydrous Na_2SO_4. Extract was concentrated under reduced pressure and subjected to column chromatography (silica gel 8 g) using pet ether as an eluent. Removal of solvent gives white colored compound. It was identified as *N*-(4-methoxynaphthalene-1-yl)-oxalamic acid ethyl ester **(5)**. Introduction of ethyl oxoloyl group at primary nitrogen was established by IR, H^1 NMR and mass spectra. m.p. 102-104 ^oC.

*Synthesis of 2-(4-methoxynaphthalene-1-ylamino)-2-thioxoacetic acid (**6**)*

N-(4-methoxynaphthalene-1-yl)oxalamic acid ethyl ester **(5)** (28 g., 0.106 mole) was dissolved in boiling xylene (560 mL) and phosphorus pentasulfide (8.4 g., 0.038 mole) was added slowly to the refluxing solution and the solution gradually turned black. Reflux was continued for 40 minutes. The reaction mixture was cooled and extracted with five 200 mL portions of 1 N sodium hydroxide. The basic extracts were filtered, cooled to 0 ^oC and acidified with concentrated hydrochloric acid washed with cold water maintained pH 1 to 2 filter and collect the orange-yellow compound **(6),** it was established by IR ^1H NMR, ^{13}C NMR and mass spectrum. m.p. 191-193 ^oC. This compound was used without further purification for the cyclization to the naphthothiazole.

*Synthesis of 5-methoxynaphtho[1,2-d]thiazole-2-carboxylic acid (**7**)*

30 g (0.113 mole) of 2-(4-methoxynaphthalene-1-ylamino)-2-thioxoacetic acid **(6)** was dissolved in 1 N sodium hydroxide (500 mL) and oxidized with potassium ferricyanide (135 g in 340 mL of water) by the slow addition of the thioamide to the ferricyanide solution keeping the temperature of the reaction mixture below 10 ^oC. After 20 minutes reflux the reaction mixture for 12 h after completion of the reaction filter, cool and acidify with conc.HCl, filter the reaction mixture when it is cooled condition and maintain the pH = 3 the mixture solution is converted from yellowish-brown to deep-green colour remove water and collect the compound cyclization to thiazole ring is established by IR, H^1 NMR ^{13}C NMR and mass spectra. m.p. 159-161 ^oC.

The structure of the intermediates and the final products was established by IR, NMR and mass spectra. The intermediate *N*-(4-methoxynaphthalene-1-yl)oxalamic acid ethyl ester **(5)** has been proved by ^{1}H NMR. Ethyl -CH_3 resonated at δ 1.48 (t) and CH_2 at δ 4.49 (m), NH peak at δ 9.2(br), the naphthyl *ortho*-CH and *meta*-CH gives at δ 7.81 and 6.83, OCH_3 peak at δ 4.01; In ^{13}C NMR CH_3 and CH_2 peak at δ 55.65 and 55.69, OCH_3 at δ 63.46, the naphthyl *ortho*-C and *meta*-C carbon gave at δ 120.80, 120.07, amide carbonyl and ester carbonyl carbon at δ 154.60 and 161.38. The mass spectrum of oxalamic acid ethyl ester compound exhibited the molcular ion peak at [M+1] 258, which is in agreement with its molcular formula $C_{15}H_{15}NO_3$. The intermediate 2-(4-methoxynaphthalene-1-ylamino)-2-thioxoacetic acid **(6)** has been proved by ^{1}H NMR. The NH peak at δ 9.28(br), OH peak at δ 11.1, OCH_3 peak at δ 4.07, the naphthyl *ortho*-CH and *meta*-CH gives at δ 7.81 6.91; ^{13}C NMR OCH_3 at δ 55.23. The naphthyl *ortho*-C and *meta*-C peak gave at δ 120.70 and 103.07 thia carbonyl and acid C=O peak at δ 128.09 and 153.66. The mass spectrum of 2-(4-methoxynaphthalene-1-ylamino)-2-thioxoacetic acid compound exhibited the molcular ion peak at [M+1] 262, which is in agreement with its molcular formula $C_{13}H_{11}NO_3S$. The final product of 5-methoxynaphtho[1,2-d]thiazole-2-carboxylic acid**(7)** has been proved by ^{1}H NMR. The carboxylic acid OH peak at δ 10.64, OCH_3 protons at δ 4.03, the naphthyl *meta*-CH peak gave at δ 7.33; ^{13}C NMR naphthyl *ortho*-C and *meta*-C peak gave at δ 98.51 and 131.88 The thiazole carbon at δ 152.08 C=O peak at δ 154.13. The mass spectrum of 5-methoxy-naphtho[1,2-d]thiazole-2-carboxylic acid exhibited a psudomolcular ion [M+1] peak 260 amu which is in agreement with its molcular formula $C_{13}H_9NO_3S$.

Spectral data

*4-Methoxy-naphthalene-1-ylamine (**4**)*

mp: 248-250 ^{o}C; ^{1}H NMR(400 MHz, DMSO-d6): δ 8.16 [m, 1H, HC(8)], 8.12 [m, 1H, H-C(5)], 7.50-7.45 [m, 2H, H-C(6), H-C(7)], 6.79 [d, 1H, 3J(H-C(3), H-C(2)) = 8.5, H-C(3)], 6.40 [d, 1H, 3J(H-C(2), H-C(3)) = 8.5, H-C(2)], 5.53 (bs, 2H, NH2), 3.87 (s, 3H, OCH3). 13C NMR (400 MHz, DMSO-d6): δ 146.7 [s, C(1)], 138.8 [s, C(4)], 126.2 [s, C(9)], 125.5 [d, 1J(C,H)=160, C(6)], 125.2 [d, 1J(C,H) = 158, C(7)], 124.9 [s, C(10)], 122.4 [d, 1J(C,H) = 127, C(8)], 122.1 [d, 1J(C,H) = 128, C(5)], 105.8 [d, 1J(C,H) = 158, C(3)], 103.2 [d, 1J(C,H) = 155, C(2)], 55.9 [dd, 1J(C,H) = 125, OCH3]. Mass (ES): *m/z* 173 $[M]^+$, 174 $[M+H]^+$.

*N-(4-Methoxy-naphthalene-1-yl)-oxalamic acid ethyl ester (**5**)*

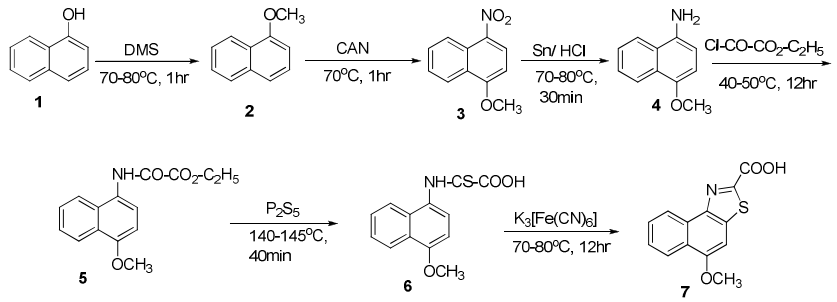
mp: 102-104 ^{o}C; IR (KBr, cm^{-1}): 3239, 3068, 2983, 2939, 2898, 2843, 2061, 1944, 1851, 1731, 1687, 1597, 1583, 1508, 1466, 1391, 1304, 1278, 1248, 1190, 1150, 1091, 1047, 1022;^{1}H NMR (400MHz, DMSO-d_6): δ 1.48 (t, 3H, *J* = 7.2Hz), 4.49 (q, 2H), 4.01 (s, 3H), 6.83 (d, 1H, *J* = 8.4Hz), 7.54 (t, 1H, *J* = 8.0Hz), 7.58 (t, 1H, *J* = 6.8Hz), 7.81 (d, 1H, J = 8.0Hz), 7.96 (d, 1H, *J* = 7.2Hz), 8.33 (d, 1H, *J* = 9.2Hz), 9.20 (bs, 1H); ^{13}C NMR (400MHz, DMSO-d_6): 55.65, 55.69, 63.46, 103.48, 120.07, 120.80, 122.97, 123.86, 125.51, 126.04, 127.17, 127.83, 154.16, 154.60, 161.38; Mass (ES): *m/z* 273 $[M]^+$, 274 $[M+H]^+$.

*2-(4-Methoxynaphthalene-1-ylamino)-2-thioxoacetic acid (**6**)*

mp: 191-193 ^{o}C; IR (KBr, cm^{-1}): 3240, 3093, 3076, 3010, 2963, 2935, 2839, 2066, 1970, 8152, 1825, 1779, 1755, 1688, 1628, 1584, 1535, 1508, 1458, 1426, 1391, 1356, 1333, 1279, 1252, 1230, 1170, 1096, 1060, 1021;^{1}H NMR (400MHz, DMSO-d_6): δ 4.07 (s, 3H,), 6.91 (d,1H, *J* =8.4Hz), 7.61 (t, 1H, *J* =1.2Hz), 7.67 (t, 1H, *J* =1.6Hz), 7.81 (d, 1H, *J* = 7.2Hz), 8.28 (d, 1H, *J* =8.4 Hz), 8.39 (d, 1H, *J* = 0.8Hz), 9.28 (bs, 1H), 11.10 (s, 1H); ^{13}C NMR (400MHz, DMSO-d_6): 55.23, 103.07, 120.70, 121.25, 121.66, 122.05, 122.13, 124.23, 124.92, 125.48, 126.42, 128.09, 153.66; Mass (ES): *m/z* 261 $[M]^+$, 262 $[M+H]^+$.

5-Methoxynaphtho[1,2-d]thiazole-2-carboxylic acid (7)

mp: 159-161 °C; IR (KBr, cm^{-1}): 3340, 2074, 1578, 1416, 1248, 1120, 1051, 1020, 928, 766, 655; ^{1}H NMR (400MHz, DMSO-d_6): δ 4.03 (s, 3H,), 7.64 (t,1H, J = 7.6Hz), 7.75 (t, 1H, J = 6.8Hz), 8.25 (d, 1H, J = 8Hz), 8.67 (d, 1H, J = 8Hz), 9.29 (s, 1H), 10.64 (s, 1H); ^{13}C NMR (400MHz, DMSO-d_6): 56.74, 56.83, 98.51, 122.82, 123.59, 125.08, 126.14, 128.02, 128.89, 131.88, 144.32, 152.08, 154.13; Mass (ES): *m/z* 259 $[M]^+$, 260 $[M+H]^+$.



Scheme 1. 5-Methoxynaphtho[1,2-d]thiazole-2-carboxylic acid

UV-Visible spectroscopic studies

The electronic absorption spectra of compound **4** in different solvents are shown in Figure 1. From the above spectrum it is evident that compound **4** exhibits the La and Lb transitions of naphthalene ring. Similar spectra are obtained for the compounds **5, 6** and **7** and data obtained is shown in Table 1-5. From the table it is evident that compound **5** gave the low energy transition at a longer wavelength than compound **4.** Compound **5** is a *N*-substituted derivative of compound **4** and the *n*-electrons on nitrogen is pulled away in the reverse direction thereby enhancing the delocalization of π/*n*-electrons and causing the lower energy transition red shifted. Compound **6** is a thiocarbonyl derivative of compound **5** and because of the larger size of the sulphur than oxygen there is an increased length of delocalization and it exhibited the absorption maxima at longer wavelength than compound **5**. Compound **7** is constructed as a result of angular thiazolidization. It absorbed at longer wavelength than all its precursors. The order of wavelength of occurrence of lower energy transition is **7 > 6 > 5 >4.**

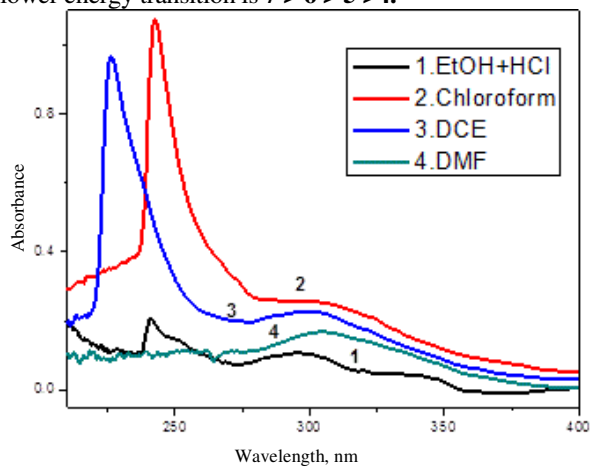


Figure 1. The electronic absorption spectrum of compounds **(4)** [$6.25x10^{-5}$] in EtOH + HCl, chloroform, DCE and DMF

Table 1. Physical properties of the compounds **4-7**

Compound No.	Time, min	Yield, %	m.p, ^{o}C	
			Observed	Literature[21]
4	20-30	92	248-250	248-250
5	Overnight	80	102-104	NA
6	40	79	191-193	NA
7	15	70	159-161	NA

Fluorescence study

The fluorescence spectra of compounds **4-7** is shown in Figure 3 in acidic ethanol medium. The stoke shift, the fluorescence emission maxima and quantum yield of compound **7** and its precursor molecule is given in Table 2 to 5. From the tables and Figure 3, it can be generalized that the napththiazole compound **7** is less fluorescing. The Stoke's shift and fluorescence quantum yield are affected by solvent polarity.

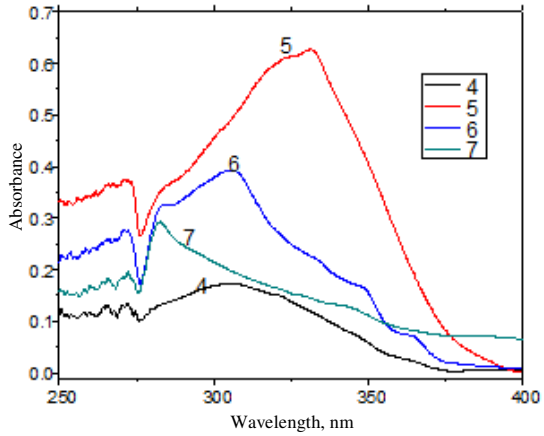


Figure 2. The electronic absorption spectrum of **(4)** [$6.25x10^{-5}$], **(5)** [$3.66x10^{-5}$], **(6)** [$3.46x10^{-5}$] and **(7)** [$3.85x10^{-5}$] in chloroform

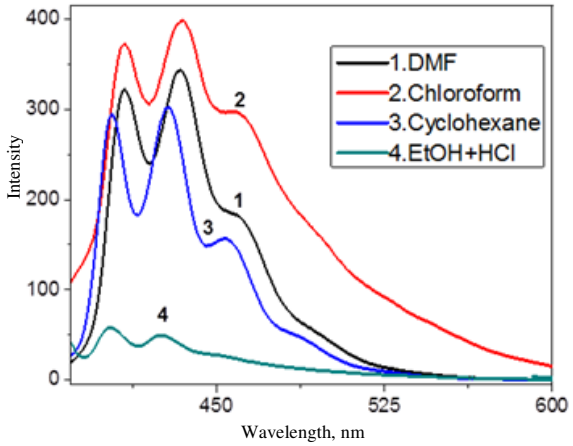


Figure 3. Fluorescence spectra of **(6)** [$6.92x10^{-6}$] in DMF, chloroform, cyclohexane and ethanol+HCl

The fluorescence of these naphthalene derivatives undergoes solvent specific interaction. The relative fluorescence quantum yield of these compounds was determined by employing equation (*c.f.* eq. 1) using 9,10-diphenylanthracene as standard in ten different solvents including aqueous medium and the data obtained is shown Tables 2-5**.** The compounds are moderately to appreciably fluorescing. The relative fluorescence quantum efficiency of these compounds are structure and solvent dependent and vary in between 0.00007 and 0.52. The cyclized thiazole compound **(7)** is less fluorescing than all of its precursor molecules. The reason for decrease in the fluorescence quantum efficiency of a cyclic rigid system than its precursor linear counterparts is not immediately known.

Table 2. Spectral characteristics of 4-methoxynaphthalene-1-ylamine (4)

S. No	Solvent	Solvent Polarity (dielectric constant)	$\lambda_{abs\cdot max,}$ nm ϵ,dm^2 mol^{-1}	$\lambda_{flu.max}$ nm	Stoke's Shift nm	Φ_f
1	Cyclohexane	2.02	241(21.78×10^3) 300(8.15×10^3)	338	38	3.49×10^{-1}
2	Benzene	2.28	272(7×10^3) 275(6.26×10^3) 306(9.1×10^3)	355	49	3.9×10^{-1}
3	Chloroform	4.81	242(56.47×10^3) 298(13.63×10^3)	342	44	4.043×10^{-1}
4	1,2-Dichloroethane	10.42	299(12×10^3)	433	134	0.798×10^{-1}
5	2-Propanol	20.80	254(9×10^3) 264(11.3×10^3) 300(11.73×10^3)	339	39	1.069×10^{-1}
6	Ethanol	25.3	216(13.78×10^3) 234(11.47×10^3) 241(18.73×10^3) 304(8.26×10^3) 307(8.3×10^3) 315(8×10^3) 322(7.6×10^3)	406	84	3.77×10^{-1}
7	Methanol	33.00	215(154.84×10^3) 299(10.9×10^3)	340	41	2.856×10^{-1}
8	Acetonitrile	36.64	299(10×10^3)	427	128	0.83×10^{-1}
9	*N,N*-Dimethylformamide	38.25	305(8.89×10^3)	409	104	0.76×10^{-1}
10	Ethanol+HCl		241(11×10^3) 296(5.68×10^3) 320(3×10^3) 333(2.47×10^3) 361(0.15×10^3)	405	44	0.034×10^{-1}

Table 3. Spectral characteristics of *N*-(4-methoxynaphthalene-1-yl)oxalamic acid ethyl ester(**5**)

S.No	Solvent	Solvent Polarity (dielectric constant)	$\lambda_{abs\cdot max,}$ nm, ϵ,dm^2 mol^{-1}	$\lambda_{flu.ma}$ nm	Stoke's Shift, nm	Φ_f
1	Cyclohexane	2.02	205(9.26×10^3) 217(10.2×10^3) 226(9.9×10^3) 244(49×10^3) 330(21.7×10^3)	338	8	2.97×10^{-1}
2	Benzene	2.28	331(20.9×10^3)	434	103	0.247×10^{-1}
3	Chloroform	4.81	245(64.26×10^3) 326(17.83×10^3) 332(17.83×10^3)	433	101	1.788×10^{-1}
4	1,2-Dichloroethane	10.42	316(17.2×10^3) 322(17.3×10^3)	356	34	1.211×10^{-1}
5	2-Propanol	20.80	265(9.1×10^3) 300(16.26×10^3) 309(16.36×10^3)	338	29	1.419×10^{-1}
6	Ethanol	25.3	231(11×10^3) 241(35.5×10^3) 312(15.2×10^3)	338	26	2.674×10^{-1}
7	Methanol	33.00	299(17.6×10^3) 307(17.2×10^3)	338	31	1.616×10^{-1}
8	Acetonitrile	36.64	234(62.4×10^3) 309(16.63×10^3)	339	30	2.58×10^{-1}
9	*N,N*-Dimethylformamide	38.25	310(16.33×10^3)	341	31	3.99×10^{-1}
10	Ethanol+HCl		241(20.96×10^3) 296(8.2×10^3) 306(7.66×10^3)	430	124	0.257×10^{-1}

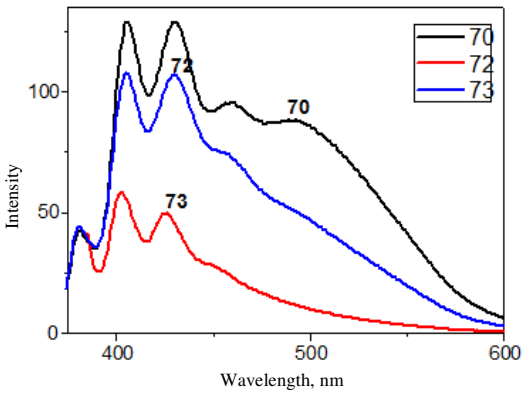


Figure 4. Fluorescence spectra of **(4)** [$1.25\text{x}10^{-5}$], **(5)** [$6.92\text{x}10^{-6}$] and **(7)** [$7.7\text{x}10^{-6}$] in ethanol+HCl

Table 4. Spectral characteristics of 2-(4-methoxynaphthalene-1-ylamino)-2-thioxoacetic acid (**6**)

S. No	Solvent	Solvent Polarity (dielectric constant)	$\lambda_{abs.max}$ nm ϵ,dm^2 mol^{-1}	$\lambda_{flu.max}$ nm	Stoke's Shift, nm	Φ_f
1	Cyclohexane	2.02	242(28×10^3) 262(16.87×10^3) 303(18×10^3) 346(8.8×10^3) 363(6.7×10^3) 376(5.2×10^3)	429	53	1.848×10^{-1}
2	Benzene	2.28	284(17.1×10^3) 305(20.68×10^3)	340	35	0.0679×10^{-1}
3	Chloroform	4.81	243(64.42×10^3) 286(18.42×10^3) 303(18.94×10^3)	435	132	2.05×10^{-1}
4	1,2-Dichloroethane	10.42	265(24.2×10^3) 294(24×10^3) 395(2.2×10^3)	433	38	0.327×10^{-1}
5	2-Propanol	20.80	236(17.89×10^3) 255(22.94×10^3) 265(35.1×10^3) 276 (33.84×10^3) 362(4×10^3)	405	43	0.846×10^{-1}
6	Ethanol	25.3	222(9.26×10^3) 228(9.42×10^3) 243(31.89×10^3) 264(30.73×10^3) 283(28.68×10^3)	338	55	4.88×10^{-1}
7	Methanol	33.00	212(53.73×10^3) 262(20.15×10^3) 299(20.47×10^3)	428	129	1.46×10^{-1}
8	Acetonitrile	36.64	261(18.78×10^3) 299(20×10^3)	409	110	4.785×10^{-1}
9	*N,N*-Dimethylformamide	38.25	305(17.26×10^3)	434	129	5.22×10^{-1}
10	Ethanol+HCl		261(7.1×10^3) 301(12.2×10^3) 319.2(6.2×10^3) 332(5.6×10^3) 361(0.6×10^3)	404	43	0.264×10^{-1}

Table 5. Spectral characteristics of 5-methoxynaphtho[1,2-d]thiazole-2-carboxylic acid (**7**)

S. No	Solvent	Solvent Polarity (dielectric constant)	$\lambda_{abs.max}$, nm, ϵ,dm^2 mol^{-1}	$\lambda_{flu.max}$, nm	Stoke's Shift, nm	Φ_f
1	Cyclohexane	2.02	241(3.8×10^3) 280(2×10^3) 287(2×10^3) 327(0.3×10^3)	428	100	5.1×10^{-3}
2	Benzene	2.28	283 (7.6×10^3)	343	60	2.5×10^{-3}
3	Chloroform	4.81	235(7.5×10^3) 242(21.4×10^3)	592	350	2.68×10^{-1}
4	1,2-Dichloroethane	10.42	252(9×10^3) 274(11.6×10^3)	547	273	3.14×10^{-1}
5	2-Propanol	20.80	279(2.3×10^3) 293(2.2×10^3) 312(1.8×10^3) 381(0.4×10^3) 395(1.37×10^3)	432	37	0.16×10^{-1}
6	Ethanol	25.3	243 (2.8×10^3) 276(1×10^3) 315(1.2×10^3) 319(1.2×10^3) 328(1.3×10^3) 339(1.3×10^3) 389(0.3×10^3)	404	15	0.188×10^{-1}
7	Methanol	33.00	267 (4.6×10^3) 339(1.4×10^3) 381(0.38×10^3) 395(0.5×10^3)	429	34	0.246×10^{-1}
8	Acetonitrile	36.64	337(1.58×10^3)	339	2	0.07×10^{-3}
9	*N,N*-Dimethylformamide	38.25	291(1.45×10^3) 322(1×10^3) 338(0.9×10^3)	434	96	0.194×10^{-1}
10	Ethanol+HCl		273(4.2×10^3) 320(1.9×103) 340(0.8×10^3) 361(1.8×10^3)	405	44	0.528×10^{-1}

Results and Discussion

Preparation of the compounds **4-7** was developed following the four component reaction by mixing different naphthyl derivatives in different ratios and different temperatures. This method was not only afforded the products in excellent yields but also avoids the problems associated with handling, safety and pollution. Thus, the 4-methoxy-naphthalene-1-ylamine, *N*-(4-methoxynaphthalene-1-yl)oxalamic acid ethyl ester, 2-(4-methoxynaphthalene-1-ylamino)-2-thioxoacetic acid and 5-methoxy-naphtho[1,2-d]thiazole-2-carboxylic acid prepared by employing different naphthyl derivatives are shown in (*c.f.* Scheme 1). The reaction was carried out under solvent conditions, clean products were obtained with traces

of impurities. These impurities were removed by either recrystalization from ethyl acetate and pet.ether mixture (1:2) or by column chromatography over silica gel (Merck 60-120 mesh) using ethyl acetate and pet.ether (2.5:7.5) as the mobile phase. The yields presented in Table 1 are the best results obtained.

Conclusion

5-Methoxynaptho[1,2-*d*] thiazole-2-carboxylic acid is prepared and its photo physical properties including solvatochromism in four different solvents is investigated. **4 < 5 ≈ 6>> 7.** An angular thiazole ring reduced the fluorescence lone pair electrons an nitrogen, when cross conjugated between ester and naphthalene ring enhanced the fluorescence and the high fluorescence.

Acknowledgement

Authors would like to thank theRegistrar, Osmania University and University Grants Commission for providing financial support under Faculty Development Program.

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