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Synthesis and absorption spectra of alkali clearable azo dyes of 5-aminoisophthalic acid

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ABSTRACT

The synthesis of novel, alkali clearable dyestuffs derived from the naphthanilides **(5a-h)** have been described. 3-carboxy-2-hydroxy naphthanilides **(4a-h)** were used as coupling agent, and 5-aminoisophthalic acid **(3)** as diazo component. The dyes were characterized by using FT-IR, ^{1}H and ^{13}C NMR spectroscopy. The absorption maxima of dyes in acidic and basic conditions in various solvents have been evaluated.

KEYWORDS

Alkali clearable azo dyes;
Aminoisophthalic acid;
3-carboxy-2-hydroxy naphthanilides;
Absorption spectra.

INTRODUCTION

Naphthaimides have been investigated in a number of ways to examine their use as intermediates for dyes to be applied on both synthetic and natural fabrics as well as on the other polymeric materials. Pioneering work on naphthalimide and their derivatives have been investigated to assess their role as intermediates for dye stuffs preparation[1-5]. Heterocyclic derivatives such as naphthlimides, phenylazo phthalimides and 1, 8-naphthalic anhydrides have been considered for the preparation of disperse dyestuffs for other polymer fibers, and dyestuffs for polymeric materials and dyestuffs[6,7]. It has been reported that benzene azonaphthalimide dyestuffs[8] prepared from 4-amino naphthalimide have a very intense color due to the polar forms which occur under normal conditions. Considerable attention has been reduced the impact of dyeing process on the environment through reduction in effluent discharge as well as in the use of energy and materials[9,10].

Keeping in view of the potential application of naphthalimide dyes and in view of obtaining more alkali clearable dyestuffs, in the present study a series of manoazo dyes have been obtained by 3-carboxy-2-hydroxy naphthanilides **(4a-h)** as coupling agent, and 5-aminoisophthalic acid **(3)** as diazo component. Thus the diazo component 5-aminophthalic acid **(3)** was prepared by reduction of 5-nitroisophthalic acid **(2)** which in turn was obtained by the nitration of isophthalic acid. The diazotization and coupling reactions were carried out in order to obtain the final dyestuffs. Again maximum yields were sought after and the reaction conditions were varied accordingly. The final dyestuffs were recrystalized in order to attain purity.

EXPERIMENTAL

General

IR spectra were recorded in the region of 4000

cm^{-1}- 400 cm^{-1} on a FTIR-8400s SHIMADZU spectrometer in KBr pellets. The UV-Visible absorption spectra were recorded in range of solvents, DMSO, DMF, methanol, THF, 0.1N NaOH methanol+0.1N HCl, and methanol+0.1N NaOH with a SHIMADZU UV-Visible 1650 spectrometer. The ^1H and ^{13}C-NMR spectra were recorded in DMSO-d_6 at 400 MHz using amx400 FT-NMR spectrometer with tetramethylsilane as an internal standard.

Synthesis of 5-nitroisophthalic acid (2)

Compound **(2)** was prepared from the documented procedure available in the literature[11] and characterized by comparing their melting point and spectral data with literature. [Aldrich, CAS No-618-88-2]

Coupling components (4a-h)

All the coupling components were purchased and they were further purified by recrystalization in ethanol.

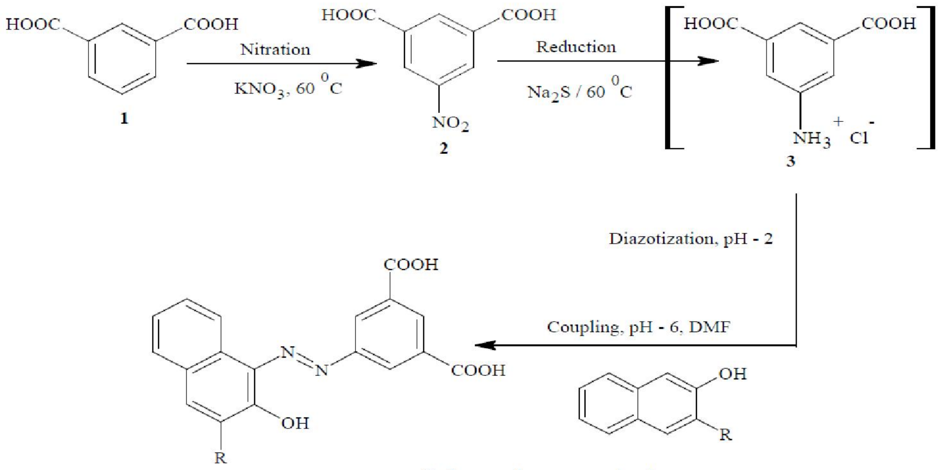
Synthesis of 5-aminoisophthalic acid (3)

The compound **(2)** (2.11 g, 0.01 mol) was added to a solution containing 50 ml of 5 % NaOH and $Na_2S.9H_2O$ (1.58 g, 0.02 mol) with constant stirring for 1 hr at 60 °C. Then the resulting mixture was allowed to cool to room temperature and filtered. The filtrate thus obtained was acidified with concentrated HCl and allowed to stand overnight and filter. Thus the filtrate obtained was subjected for the synthesis of dye stuffs.

5-(2-hydroxy-naphthalen-1-ylazo)-isophthalic acid (5a)

Diazotization

The filtrate containing 5-aminoisophthalic acid **(3a)** was cooled to 0-5 °C and an equimolar solution of aqueous $NaNO_2$ was added drop wise with constant stirring. After complete addition, the stirring was continued for 30 min. The excess $NaNO_2$ was destroyed by adding 1.5-2 g of urea and the *p*H of the reaction mixture was maintained 4-5 by adding chilled aqueous solution of sodium carbonate. To this solution the compound **(4a)** (1.44 g, 0.01 mol, taken in 20 ml DMF) was added in portions while keeping temperature 0-5 °C in the *p*H range of 4-5 for 2 hrs. The dye obtained was filtered, washed, dried, and recrystalized from appropriate solvent. The purity of the compound was checked by TLC. All other dyes **(5b-h)** were synthesized with similar method by using different coupling components **(4b-h)** as given in the Scheme 1.



5a - h

Scheme-1

4a - h

5a - R = H
5b - R = COOH
5c - R = CONH - C_6H_5
5d - R = CONH-2$CH_3C_6H_4$
5e - R = CON-2-CH_3-4-Cl-C_6H_3
5f - R = CONH-2$NO_2C_6H_4$
5g - R = CONH-1-$C_{10}H_7$
5h - R = CONH-2-$C_{10}H_7$

4a - R = H
4b - R = COOH
4c - R = CONH - C_6H_5
4d - R = CONH-2$CH_3C_6H_4$
4e - R = CON-2-CH_3-4-Cl-C_6H_3
4f - R = CONH-2$NO_2C_6H_4$
4g - R = CONH-1-$C_{10}H_7$
4h - R = CONH-2-$C_{10}H_7$

5-(2-hydroxy-naphthalen-1-ylazo)-isophthalic acid (5a)

IR (KBr)

3400-2800 cm^{-1} (OH), 1698 cm^{-1} (C=O), 1516 cm^{-1} (N=N), 1558 cm^{-1}, 1389 cm^{-1} (C-N). ^{1}H-NMR (dmso-d$_6$) ppm: 13.54 (br, s, 2H, COOH), 8.74 (s, 1H, ArH), 8.52 (s, 2H, ArH), 7.75 (s, 1H, ArH), 7.72-7.70 (d, 1H, ArH, J = 8.21), 7.65 (s, 1H, ArH), 7.41-7.43 (d, 1H, ArH, J = 7.28), 7.32-7.28 (t, 1H, ArH, J = 7.52, 14.28), 7.08-7.03 (t, 1H, ArH, J = 8.62, 15.78). ^{13}C-NMR (dmso-d$_6$) ppm: 165.2 (2C, COOH), 154.3 (C-OH), 134.5, 133.2, 131.2, 129.8, 128.8, 127.2, 126.5, 123.6, 117.7 (ArC), 112.5 (C-N).

5-(3-carboxy-2-hydroxy-naphthalen-1-ylazo)-isophthalic acid (5b)

IR (KBr)

3500-2800 cm^{-1} (OH, COOH), 1697 cm^{-1} (C=O), 1506 cm^{-1} (N=N), 1524 cm^{-1}, 1393 cm^{-1} (C-N). ^{1}H-NMR (dmso-d$_6$) ppm: 13.54 (br, s, 2H, COOH), 8.82 (s, 1H, ArH), 8.57-8.54 (m, 3H, ArH), 7.91-7.89 (d, 1H, ArH, J= 7.71) 7.64-7.57 (t, 1H, ArH, J = 7.10, 14.28), 7.38-7.32 (t, 1H, J = 7.0, 14.1). ^{13}C-NMR (dmso-d$_6$) ppm: 169.2 (COOH), 166.6 (COOH), 157.7 (C-OH), 137.5, 136.0, 132.9, 131.2, 129.8, 125.2, 123.6, (ArC), 122.2 (C-N=N).

5-(2-hydroxy-3-phenylcarbamoyl-naphthalen-1-ylazo)-isophthalic acid (5c)

IR (KBr)

3648-3613 cm^{-1} (OH), 3487-3445 cm^{-1} (NH), 1697 cm^{-1} (C=O), 1501 cm^{-1} (N=N), 1549cm^{-1}, 1379 cm^{-1} (C-N). ^{1}H-NMR (dmso-d$_6$) ppm: 16.02 (br, s, 1H, OH), 13.56 ((br, s, 2H, COOH), 11.22 (s, 1H, NH), 8.74 (s, 1H, ArH), 8.48 (s, 1H, ArH), 8.32 (s, 1H, ArH), 8.32-8.22 (d, 1H, ArH, J = 6.69), 7.96-7.91 (d, 1H, ArH, J = 6.74), 7.79-7.71 (m, 3H, ArH), 7.54-7.48 (t, 1H, ArH, J = 14.31), 7.34-7.41 (t, 2H, ArH, J = 7.58, 15.22), 7.16-7.09 (t, 1H, ArH, J = 7.25, 14.49). ^{13}C-NMR (dmso-d$_6$) ppm: 176.1 (CO), 166.6 (COOH), 161.3 (COOH), 146.7 (C-OH), 138.3 (C-NH), 142.7, 134.2, 133.3, 131.7, 131.2 130.1, 128.9, 127.6, 127.1, 126.4, 123.8, 121.7, 121.1 (ArC), 119.1 (C-N=N).

5-(2-hydroxy-3-o-tolyl carbamoyl-naphthalen-1-ylazo)-isophthalic acid (5d)

IR (KBr)

3500-3200 cm^{-1} (OH, NH), 1624 cm^{-1} (C=O), 1485 cm^{-1} (N=N), 1554 cm^{-1}, 1357 cm^{-1} (C-N). ^{1}H-NMR (dmso-d$_6$) ppm: 13.68 (br, s, 2H, COOH), 11.8 (s, 1H, NH), 8.91 (s, 1H, ArH), 8.45 (s, 2H, ArH), 7.98-7.94 (d, 2H, ArH, J = 7.93), 7.79-7.75 (d, 1H, ArH, J = 8.21), 7.55-7.48 (t, 1H, ArH, J = 7.11, 14.07), 7.38-7.21 (m, 3H, ArH), 7.15-6.99 (t, 1H, ArH, J = 6.91, 14.27). ^{13}C-NMR (dmso-d$_6$) ppm: 172.1 (COOH), 164.5 (C-OH), 136.3, 135.8, 131.4, 130.2, 129.9, 128.8, 128.2, 126.9, 126.2, 125.6, 124.8, 123.7, 123.3, 120.5 (ArC), 110.7 (C-N=N), 17.69 (CH$_3$).

5-[3-(4-chloro-2-methyl-phenylcarbamoyl)2-hydroxy-naphthalen-1-ylazo]-isophthalic acid (5e)

IR (KBr)

3310-3062 cm^{-1} (OH, NH), 1623 cm^{-1} (C=O), 1503 cm^{-1} (N=N), 1556 cm^{-1}, 1359 cm^{-1} (C-N). ^{1}H-NMR (dmso-d$_6$) ppm: 14.8 (br, s, 1H, OH), 13.55 (br, s, 2H, COOH), 11.84 (s, 1H, NH), 8.91 (s, 1H, ArH), 8.69 (s, 1H, ArH), 8.60 (s, 1H, ArH), 8.51 (s, 1H, ArH), 8.00-7.57 (d, 1H, ArH, J = 8.08), 7.79-7.76 (d, 1H, ArH, J = 8.17), 7.54-7.48 (t, 1H, ArH, J = 7.12, 15.65), 7.18-7.11 (m, 2H, ArH), 7.18-7.11 (m, 2H, ArH), 3.92 (s, 3H, CH$_3$). ^{13}C-NMR (dmso-d$_6$) ppm: 170.0 (2COOH), 162.9 (C=O), 152.3 (C-OH), 147.2, 135.9, 132.7, 129.0, 128.3, 127.1, 125.5, 124.2, 123.4, 122.9, 120.8, 119.1, 112.2 (ArC), 110.9 (C-N=N), 56.4 (CH$_3$).

5-[2-hydroxy-3-(3-nitro-phenyl carbamoyl)-naphthalen-1-ylazo]-isophthalic acid (5f)

IR (KBr)

3400-3067 cm^{-1} (OH, NH), 1679 cm^{-1} (C=O), 1492 cm^{-1} (N=N), 1597 cm^{-1} (NO$_2$), 1535 cm^{-1}, 1361 cm^{-1} (C-N). ^{1}H-NMR (dmso-d$_6$) ppm: 13.22 (br, s, 1H, COOH), 11.1 (s, 1H, ArH), 8.95 (s, 1H, ArH), 8.89 (s, 1H, ArH), 8.55 (s, 1H, ArH), 8.42 (s, 1H, ArH), 8.09-7.99 (d, 1H, ArH, J = 8.24), 7.88-8.06 (m, 4H, ArH), 7.72-7.58 (m, 3H, ArH). ^{13}C-NMR (dmso-d$_6$) ppm: 169.1 (COOH), 165.1 (C=O), 156.0 (C-OH), 148.6 (C-NO$_2$), 132.8, 131.7, 131.0, 130.7, 129.1, 129.6, 129.4, 128.7, 125.9, 124.2, 119.2 (ArC), 115.1 (C-N=N).

5-[2-Hydroxy-3-(naphthalene-1-ylcarbamoyl)-naphthalen-1-ylazo]-isophthalic acid (5g)

IR (KBr)

3288-3056 cm^{-1} (OH, NH), 1649 cm^{-1} (C=O), 1506 cm^{-1} (N=N), 1554 cm^{-1}, 1364 cm^{-1} (C-N). ^{1}H-NMR (dmso-d_6) ppm: 13.32 (br, s, 1H, COOH), 10.75 (s, 1H, NH), 8.93 (s, 1H, ArH), 8.72 (s, 1H, ArH), 8.54 (s, 1H, ArH), 8,45 (s, 1H, ArH), 7.98-7.86 (m, 4H, ArH), 7.81-7.77 (d, 2H, ArH, *J* = 8.5), 7.56-7.33 (m, 5H, ArH). ^{13}C-NMR (dmso-d_6) ppm: 171.1 (COOH), 163.2 (C=O), 153.7 (C=OH), 135.9 (1C), 135.7 (1C), 133.O, 130.4, 130.1, 128.6, 128.2, 128.0, 127.3, 126.8, 126.4, 125.7, 124.8, 123.7, 120.8, 122.0, 116.8(ArC), 110.5 (C-N=N).

5-[2-Hydroxy-3-(naphthalene-2-ylcarbamoyl)-naphthalen-1-ylazo]-isophthalic acid (5h)

IR(KBr)

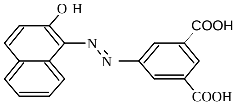
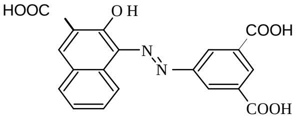
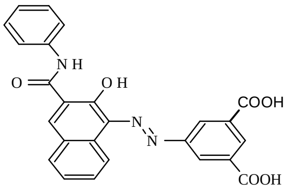
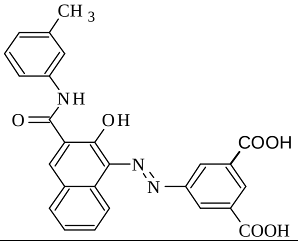
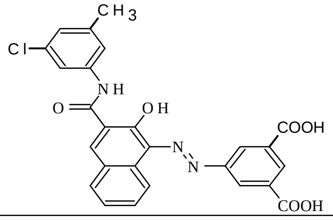
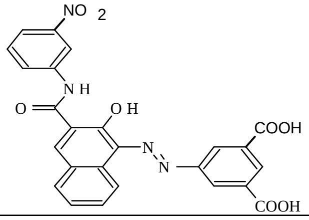
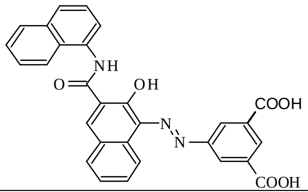
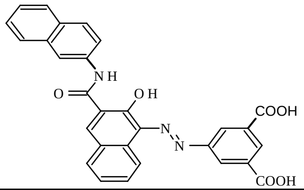
3307-3055 cm^{-1} (OH, NH), 1656 cm^{-1} (C=O), 1504 cm^{-1} (N=N), 1554cm^{-1}, 1361 cm^{-1} (C-N). ^{1}H-NMR (dmso-d_6) ppm: 13.58 (br, s, 1H, COOH), 11.9 (s, 1H, NH), 8.89 (s, 1H, ArH), 8.70 (s, 1H, ArH), 8.48 (s, 1H, ArH), 8.14-8.07 (t, 2H, ArH, *J* = 8.21, 18.71), 8.02-7.96 (t, 2H, ArH, *J* = 8.88, 17.59), 7.85-7.78 (dd, 2H, ArH, *J* = 8.22, 5.77 8.31), 7.64-7.50 (m, 4H, ArH), 7.43-7.36 (m, 2H, ArH). ^{13}C-NMR (dmso-d_6) ppm: 168.1 (COOH), 165.5 (C=O), 153.7 (C=OH), 136.0, 133.7, 133.3, 131.4, 128.9, 128.3, 127.7, 127.3, 127.1, 126.3, 126.3, 126.1, 125.8, 125.4, 123.8, 121.7, 121.0 (ArC), 110.7(C-N).

RESULTS AND DISCUSSION

The most convenient approach for the preparation of desire dyes involves the synthesis of aminoisophthalic acid, which was readily synthesized from easily avaible starting material i.e., isophthalic acid. Isophthalic acid upon nitration under appropriate experimental conditions gave 5-nitroisophthalic acid. The resulting 5-nitroisophthalic acid was converted into corresponding 5-aminoisophthalic acid in presence of aqueous sodium sulphide as reducing agent under the controlled reaction conditions. Thus continued efforts to isolate the aminoisophthalic acid was not successful due zwitterion effect, hence the diazotization and coupling reactions were carried out *in situ* with a series of 3-hydroxy-2-naphthanilides **(4a-h)** to obtain the corresponding dyes **(5a-h)** respectively. Their yield, solubility and color are summarized in the TABLE 1. The FT-IR, ^{1}H and ^{13}C-NMR data of these compounds are given in experimental section.

The FT-IR spectra of the compound **(5b)** exhibited a broad band in 3400-2800 cm^{-1} region was due to hydroxyl group and the intense strong band appeared at 1697 cm^{-1} was assigned to C=O of carboxylic groups. Further, a band at the region 1506 cm^{-1} was attributed to the azo group in the compound. The ^{1}H NMR spectra of **(5b)** (figure 3) showed a signal at δ: 13.54 ppm for the proton of the carboxylic acid, and there was no peak appeared for –OH proton might be due to solvent interaction; however it is confirmed in ^{13}C-NMR. Peaks obtained in the range of δ: 7.38 to 8.82 ppm were assigned to aromatic protons (Ar-H). The ^{13}C NMR spectra of compound **(5b)** (figure 4) shows 2 peaks at δ: 169.2 and 166.6 ppm due to carbon of carboxylic groups, and δ: 157.7 ppm due to the carbon of the attached to hydroxyl group (C-OH). The peak at δ: 122.2 ppm was due to carbon which was attached to nitrogen (ArC-N). The aromatic carbon peaks which were appeared in between δ: 123-137 ppm. The FT-IR spectra of the compound **(5c)** exhibited a broad band in 3648-3445 cm^{-1} region and could be attributed to -OH and –NH of amide group and an intense strong band at 1697 cm^{-1} could be assigned to C=O of carboxylic groups. Further, a band in the region 1501 cm^{-1} can be attributed to the azo group. The ^{1}H NMR spectra of 5c (figure 5) shows a broad band at δ: 16.02 ppm for the hydroxy protons and δ: 13.56 ppm for the carboxylic proton, at 11.22 ppm for amide proton. Peaks obtained in the range of δ: 7.09 to 8.74 ppm was assigned to aromatic protons (Ar-H). The ^{13}C NMR spectra of compound **(5c)** (figure 6) shows 3 peaks at δ: 176.1, 166.6 and 161.3 due to carbon of carbamide and carboxylic acid groups respectively. And δ: 146.7 ppm due to the carbon of the attached to hydroxyl group (C-OH). The peak at δ: 119.1 ppm can be assigned carbon which is attached to nitrogen (ArC-N=N). The aromatic carbon peaks which were appeared in between δ: 121-138 ppm.

TABLE 1: Physical characteristic table of the dyes (5a-h)

Compound	Mol. formula (Mol. wt)	Structure	Color	Solubility	Yield (%)
5a	$C_{18}H_{12}N_2O_5$ (336.29)		Dark Red	DMF, DMSO, methanol	56
5b	$C_{19}H_{12}N_2O_7$ (380.30)		Brick Red	DMF, DMSO, methanol	56
5c	$C_{25}H_{17}N_3O_6$ (455.41)		Red	DMF, DMSO methanol,Acetone,	68
5d	$C_{26}H_{19}N_3O_6$ (469.44)		Orange	Methanol, DMF, Acetone,	62
5e	$C_{26}H_{18}ClN_3O_6$ (503.89)		Crimson red	Methanol, DMF, Acetone,	76
5f	$C_{25}H_{16}N_4O_8$ (500.41)		Brown red	Methanol, DMF, Acetone,	64
5g	$C_{29}H_{19}N_3O_7$ (521.47)		yellow Orange	Methanol, DMF, Acetone,	71
5h	$C_{29}H_{19}N_3O_7$ (521.47)		Scarlet red	Methanol, DMF, Acetone,	56

Absorption spectra

Solvent effect

Absorption spectra of dyes **(5a-h)** were recorded in various solvents at the range of 10^{-3} to 10^{-4} molar concentration. The *p*H value of all the solutions used was in the range between acidic and basic conditions. The results show that absorption spectra of the dyes did not show regular variations with the polarity of the solvents, however absorption spectra recorded in basic *p*H showed relatively small absorption when compared to absorption spectra recorded in solvents at neutral and acidic *p*H may be due to the reason that phenolic and carboxylic acid groups present in dyes **(5a-h)** form a strong ionic bond which may retard the absorption maxima of the dyes. The results are summarized in TABLE 2.

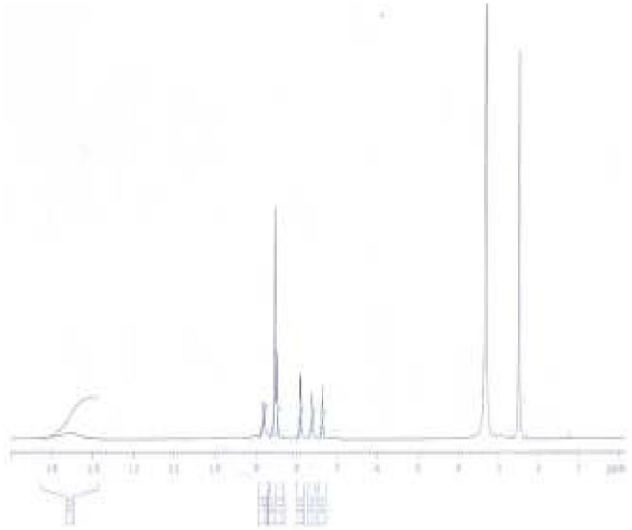


Figure 1 : ^{1}H-NMR of 5b

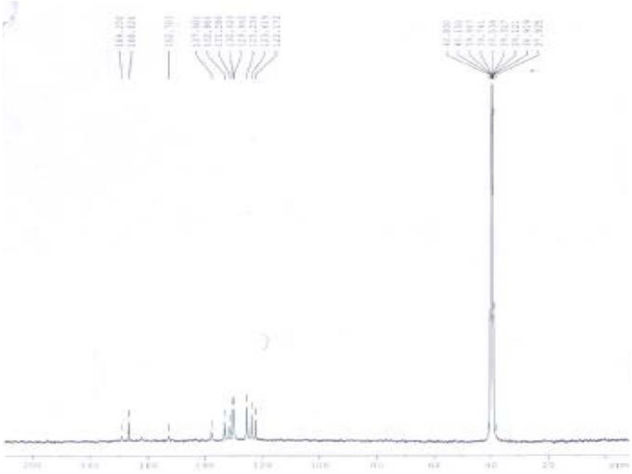


Figure 2 : ^{13}C-NMR of 5b

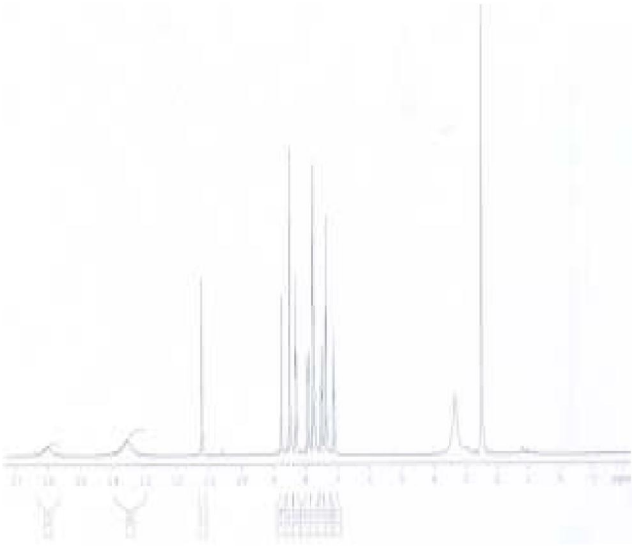


Figure 3 : ^{1}H-NMR of 5c

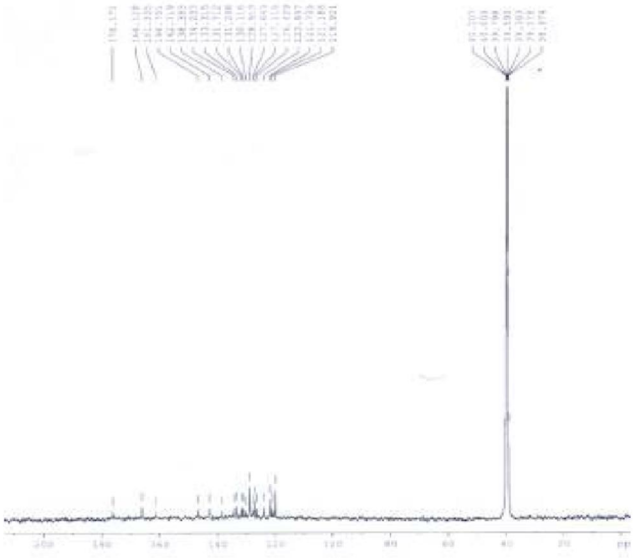


Figure 4 : ^{13}C-NMR of 5c

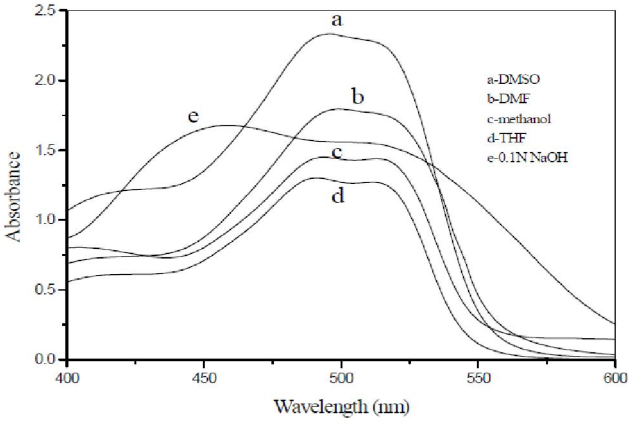


Figure 5 : Absorption spectra of 5c in various solvents

ABBREVIATIONS

S - Singlet
D - Doublet
T - Triplet
M - Multiplet.

TABLE 2 : Absorption maxima (nm) of dyes (5a-h) in various solvents

Compound	DMSO	DMF	Methanol	THF	0.1NaOH	0.1NaOH+ Methanol	0.1 HCl + Methanol
5a	493	474	520	486	390	448	476
5b	475	434	476	468	444	482	496
5c	425	498	495	453	477	460	514
5d	500	494	512	511	461	400	485
5e	494	498	514	488	396	397	507
5f	499	462	519	490	393	423	493
5g	496	458	520	514	385	397	443
5h	495	420	515	491	395	398	528

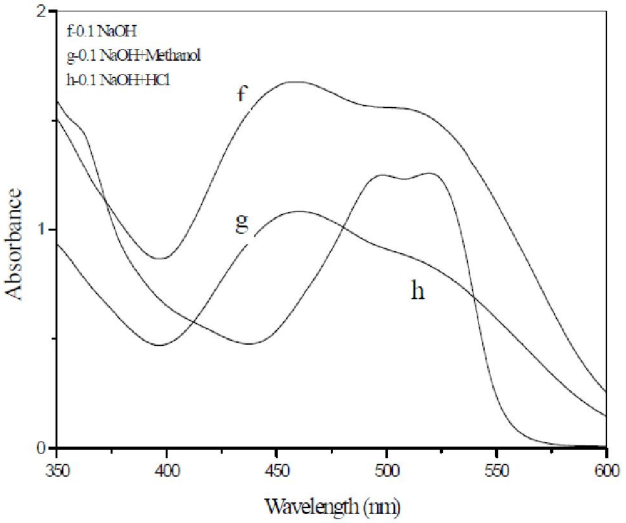


Figure 6 : Absorption spectra of 5c in acidic and basic solutions

CONCLUSION

We have established an efficient route for the synthesis of novel water soluble azo dyes of aminoisophthalic acid. It is interesting to note that the colors of the dyes were deepened and λ_{max} of these dyes lies in between 400-550 nm. Moreover these dyes were found to be highly soluble in water in their salt form due to the presence of more carboxylic acid groups.

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