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SPECTROSCOPIC PROPERTIES OF NOVEL AZO SCHIFF BASE DYES

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ABSTRACT

Novel aldehyde (**3**) was synthesized through azo coupling between 6-amino-2-mercaptopyrimidin-4-ol and 4-(dimethylamion) benzaldehyde. The new aldehyde was condensed with four different amines to give four new dyes (**5a-d**). The new dyes were characterised using spectroscopic methods such as I.R, ^{1}H and ^{13}C NMR. The electronic spectra of dye **3** was studied in solvents of varying polarity and displayed a bathochromic shift in the more polar solvents. The UV-visible spectra of the dyes **5 a-d** showed a red shift following extension of the chromophores in these new dyes.

KEYWORDS: azo dye; schiff base; pyrimidine; electronic spectra study.

INTRODUCTION

Dyes and pigments are among the most known products applied in modern life.[1-4] The influence of colour on mankind was shown a long time ago and in fact there are no places in our lives where the application of dyes and pigments cannot be seen.[5] Azo dyes comprise several classes of dyes with a diverse range of applications, including in liquid crystals, laser displays and ink jet printers.[6] Azo dyes have the widest range of application of all dyes, because the differences in chemical structure are easily achievable and application methods are not normally complex.[3] Heterocyclic diazo components with azo dyes have been widely investigated to make bright and strong colour shades ranging from red to greenish blue on synthetic fabrics.[8] Azo compounds are important molecules and have received much attention in the investigation of both their basic structure and applications.[1, 9-11] Spectral studies play an important role in studying the structure of these dyes.[7] Apart from their chemical interest, azomethine dyes are becoming ever more popular in the textile, plastic and

leather industries. The concentration of dye in the environment is increased according to the industrial significance of the particular azo dye and also in relation to the structure of the dye.[12-16] Azo dye compounds have many applications in industry including photosensitive, photodynamic therapy, electro photographic and photographic system applications and are predominant organic photo-conductive materials.[17,18]

Therefore, synthesis of aromatic azo compounds has attracted great attention.[3] This work has focused on the synthesis of amino pyrimidine **(1)** following the procedure of Taylor and Cheng.[19] The novel amino pyrimidine **(1)** was used to synthesise the novel aldehyde **(3)** via azo coupling.[20] Aldehyde **(3)** went through four condensation reactions with four different aromatic amines to generate four novel azo-Schiff base dyes **(3)** and **(5a-d).** All the new dyes **(3)** and **(5a-d)** were identified using proton and carbon NMR as well infrared spectroscopy. A UV-visible study was performed for the new dyes in order to specify the electronic transitions and their spectroscopic properties.

EXPERIMENTAL

General

All melting points were measured without correction on a Melting point/ SMP31. The reagents were purchased from commercial sources and used without further purification. Infrared Reflection Absorption Spectroscopy (IRRAS) (4000-400 cm^{-1}) was recorded using a Perkin Elmer tensor 27 as a thin film. NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. UV spectra were recorded on a LTD 90 plus instrument with a double beam using a crystal cell with a path length of 1 cm.

Synthesis of (Z)-4-(dimethylamino)-3-((6-hydroxy-2-mercaptopyrimidin-4-yl)diazenyl)benzaldehyde (3)

6-amino-2-mercaptopyrimidin-4-ol (1 gm, 6.28 mmole) was dissolved in a mixture of 4 ml concentrated hydrochloric acid and 4 ml distilled water at 0 ^{o}C in an ice bath. Sodium nitrite (0.23 gm, 6.28 mmol) was dissolved in cold water and added drop wise to the reaction mixture and stirred for 15 min. The diazonium salt was added to a solution of 4-(dimethylamion) benzaldehyde (1.12 gm, 6.28 mmol) in sodium hydroxide (10 ml, 10 %) in ice bath. The diazonium salt was added slowly over a 20 min period and the reaction mixture was stirred for 1 h. The precipitate was filtered and washed with methanol. The crude product was purified using column chromatography using ethyl acetate/ hexane (3:7) as eluent. The title compound **(3)**, was obtained in a yield of 1.24 gm (65 %), m.p. 77-79 ^{o}C; I.R (IRRAS):

3083, 2917, 2860, 1702, 1660, 1587, 1551, 1434, 1363, 1342, 1306, 1227, 1162, 1122, 1063, 998, 979, 940, 989, 867, 813, 802, 746, 730, 681, 672.; ^{1}H NMR ($CDCl_3$, 400 MHz), δ 8.34 (1H, s), 8.01 (1H, s), 7.78 (1H, d, J=8 Hz), 7.51 (1H, d, J= 8 Hz), 6.74 (1H, s), 6.58 (1H, s), 2.96 (6H, s); ^{13}C-NMR ($CDCl_3$) δ: 190.30, 162.08, 154.10, 152.96, 130.94, 129.88, 129.64, 127.81, 123.51, 119.40, 111.50, 40.13 and 40.09.

General procedures of synthesis azomethane compounds **(5a-d)**

Synthesis of 3-((E)-3-(dimethylamino)-4-((Z)-(6-hydroxy-2-mercaptopyrimidin-4-yl)diazenyl)benzylideneamino)benzoic acid **5a**

The aldehyde **(3)** (0.1 gm, 0.3 mmole) was dissolved in 10 ml dry absolute ethanol and an excess of Na_2SO_4. 3-amino-banzoic acid (0.05 gm, 0.3 mmole) was added to the stirred solution. The reaction mixture was refluxed for 2 hrs when TLC showed the reaction to be complete. The mixture was then filtered and the solvent was evaporated under reduce pressure. The crude product was re-crystallized from methanol to give the title compound **(5a)** (0.12 gm), in a yield of 86 %, m. p. 174-175 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ 9.61 (1H, s), 8.29 (1H, s), 7.80 (1H, s), 7.71 (1H, s), 7.69 (1H, d, J=8 Hz), 7.38 (1H, s), 7.35 (1H, s), 6.70 (1H, d, J= 8 Hz), 6.68 (1H, d, J = 8 Hz), 6.66 (1H, d, J=8 Hz), 6.64 (1H, s), 3.37 (1H, br s), 3.03 (3H, s), 3.01 (3H, s); I.R (IRRAS): 3061, 2886, 2804, 1663, 1603, 1549, 1363, 1240, 1166, 1065, 1027, 932, 812, 753, 725, 673, 626; ^{13}C-NMR ($CDCl_3$) δ:190.83, 169.01, 168.64, 161.88, 154.48, 146.32, 132.08, 132.08, 131.26, 130.69, 129.05, 128.97, 126.42, 126.13, 124.63, 121.51, 119.98, 116.05, 39.91, 39.86.

Using the same procedure to prepare compounds (5b-d)

Preparation of 1-(3-((E)-3-(dimethylamino)-4-((Z)-(6-hydroxy-2-mercaptopyrimidin-4-yl)diazenyl)benzylideneamino)phenyl)ethanone **(5b)**

Yield 80 % (0.11gm), m. p. 168-169 ^{o}C; I.R (IRRAS): 2902, 2820, 1668, 1606, 1578, 1550, 1525, 1433, 1409, 1357, 1315, 1301, 1268, 1232, 1165, 1123, 1069, 977, 957, 945, 887, 840, 817; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (1H, s), 7.93 (1H, s), 7.72 (1H, s), 7.71 (1H, d, J=8 Hz), 7.72-6.67 (3H, m), 7.18 (1H, m), 7.15 (1H, s), 3.47 (1H, s broad), 3.04 (3H, s), 3.01 (3H, s), 2.55 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 197.39, 190.81, 162.14, 156.94, 154.46, 152.90, 151.84, 133.54, 132.90, 130.77, 129.89, 127.26, 126.88, 123.12, 120.92, 113.38, 112.01, 110.85, 40.35, 39.79, 26.25.

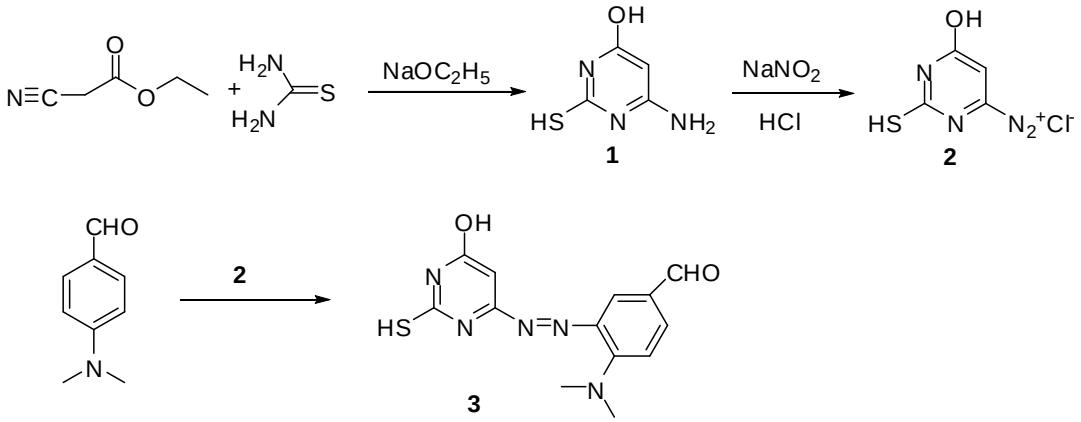
Preparation of 6-((Z)-(2-(dimethylamino)-4-((E)-(phenylimino)methyl) phenyl) diazenyl)-2-mercaptopyrimidin-4-ol (5c)

Yield 82 % (0.114 gm), m. p. 135-136^{o}C; I.R (IRRAS): 3029, 2892, 2851, 1585, 1524, 1488, 1440, 1361, 1315, 1230, 1160, 1066, 961, 942, 907, 873, 810, 756; ^{1}H NMR ($CDCl_3$, 400 MHz) 8.32 (1H, s), 7.81 (1H, s), 7.79 (1H, s, 7.39 (2H ,t, J=8 Hz), 7.22-7.16 (3H, m), 6.76 (2H, d, J= 8Hz), 3.06 (6H, s); ^{13}C-NMR ($CDCl_3$) δ 190.30, 160.16, 154.32, 152.67, 152.67, 146.32, 131.80, 130.78, 129.25, 129.03, 125.16, 125.11, 120.90, 118.52, 115.08, 111.59, 110.97, 4015, 40.05.

***Preparation of 6-((Z)-(2-(dimethylamino)-4-((E)-(3-hydroxyphenylimino) methyl)phenyl)diazenyl)-2-mercaptopyrimidin-4-ol* (5d)**

Yield 79 % (0.11gm, brown solid); m. p. 184-185^{o}C; I. R (IRRAS): 2917, 2854, 2795, 1658, 1577, 1530, 1472, 1434, 1415, 1370, 1340, 1314, 1291, 1279, 1230, 1163, 1140, 1122, 1064, 996, 979, 944, 888, 866, 813, 783, 724, 691, 661cm^{-1}; ^{1}H-NMR ($CDCl_3$) ppm: 8.20 (1H, s), 7.64 (1H, s), 7.62 (1H, s), 7.09 (1H, t, J = 8 Hz), 6.66 (2H, d, J = 8 Hz), 6.64 (3H, d, J=8 Hz, abscure o-proton next to amino group), 3.26 (1H, br s), 2.96 (6H, br s); ^{13}C NMR; 161.33, 157.37, 153.14, 152.63, 147.33, 132.09, 130.55, 129.89, 129.78, 112.47, 111.71, 111.42, 110.85, 108.07, 107.18, 105.93, 102.43, 39.82, 39.77.

RESULTS AND DISCUSSION

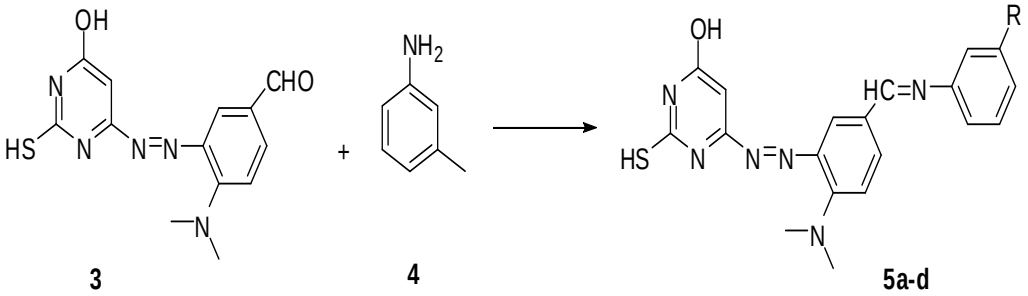


Scheme 1: Preparation of aldehyde (3).

6-amino-2-mercaptopyrimidin-4-ol **(1)** was prepared starting with ethyl 2-cyanoacetate according to the procedure described by Taylor and Cheng.[19] Amine **(1)** was converted into the corrisponding diazonium salt and coupled with 4-(dimethylamino) benzaldehyde, resulting in the formation of 4-(dimethylamino)-3-((6-hydroxy-2-mercaptopyrimidin-4-yl)diazenyl) benzaldehyde **(3)** Scheme 1, as bright yellow solid. This was purified by column

chromatography (eluting with ethyl acetate/hexane 3:7) to give pure aldehyde (**3**) in 65 % yield.[21]

The azoaldehyde **(3)** was condensed with four different aromatic amines in absolute ethanol in the presence of anhydrous Na_2SO_4. The novel compounds **(5a-d)** were purified by recrystallization from ethanol to give a good yield. (Scheme 2).[22]



5a-d

R, a= COOH, b= COMe, c=H, d=OH

5	R
a	COOH
b	COMe
c	H
d	OH

Scheme 2: Synthesis of dyes **(5a-d)**

Infra red study for the synthesized compounds

The infra red spectrum showing the position of the major band of the compounds prepared compared with the literature data[23-24] are given in the Table 1.

Table 1: Infrared of some functional groups of the prepared compounds

No	C=N	C=O	C=C	C-O	N=N
1	-	1660	1587	1227	1434
5a	1580	1663	1549	1231	1441
5b	1607	-	1576	1233	1457
5c	1606	-	1585	1232	1433
5d	1598	1665	1577	1232	1444

The formation of the new aldehyde **(3)** was confirmed by the infra red spectrum. The IR spectra showed a lack of absorbance above 3300 cm^{-1} belonging to NH group and absorbance at 1660 and 1434 cm^{-1} belonging to C=O and N=N groups respectively. The IR spectra of compounds **(5a-d)** showed the appearance of new absorbance in the range 1580 to 1607 cm^{-1} due to the azomethane group. The symmetric N=N group showed absorbance in the range

1433 to 1457 cm^{-1} for the stretching mode, while the stretching of the C-O group absorbed in the range 1227-1233 cm^{-1}. All spectra compounds **(5a-d)** showed a lack of absorbance at 1660 cm^{-1} which confirmed the disappearance of the carbonyl group in these compounds. Compound **(5a)** displayed broad absorbance at 2866 cm^{-1} belonging to the OH of the carboxylic group while compound **(5d)** showed absorbance at 2854 cm^{-1} also belonging to the hydroxyl group. Compound **(5b)** showed absorbance at 1665 cm^{-1} belonging to the carbonyl group of the aceyl group.

^{1}H NMR spectra

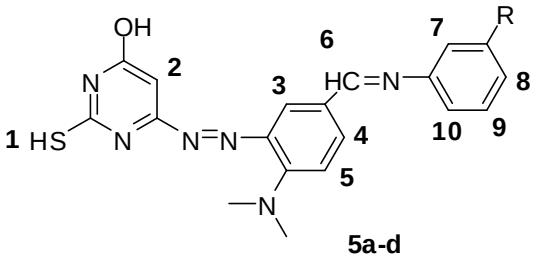


Figure 1: General structure of the prepared compounds (5a-d)

The proton NMR for aldehyde **(3)** was obtained under room temperature in $CDCl_3$. This displayed singlet signals at 8.34 and 8.01 ppm for the aldehyde proton and for the mercapto group respectively. The pyrimidine ring displayed a singlet at 6.58 for proton 2, while the protons, 3 and 5 (figure 1) were displayed as a doublet and a double doublet at 7.78 and 7.51 ppm. Compounds **(5a-d)** showed a signal between 8.20 and 8.32 ppm for the mercapto protons, while the azomethane protons **(6)** showed a signal between 7.94 to 7.64 ppm. The aromatic protons 7, 8, 9 and 10 resonated between 6-7 ppm. The methyl groups displayed a signal at 3.00 ppm. The carboxylic proton of compound **(5a)** resonated at 9.61 ppm and the acetyl group of compound **(5b)** showed a singlet at 2.55 ppm. The hydroxyl group of compound **(5d)** displayed a broad singlet at 3.26 ppm.

^{13}C NMR spectra

Aldehyde **(3)** showed absorbance at 190.34 for the carbonyl carbon, while the pyrimide ring carbons were displayed at 162.12 for the carbon next to the thiol group. The carbon next to the hydroxyl and azo groups were seen at 154.86 and 153.00 ppm respectively. Compound **(5a)** displayed absorbance at 190.83 ppm due to the carboxylic group, and at 196.01, 168.6 and 161.88 ppm due to the pyrimidine carbon and the Schiff base carbons respectively. Compound **(5b)** exhibited absorbance at 198.09 ppm due to the carbonyl carbon and at

162.14, 156.94 and 154.46 ppm due to the pyridine ring carbon and the Schiff base carbons respectively, as shown in the Table 2.

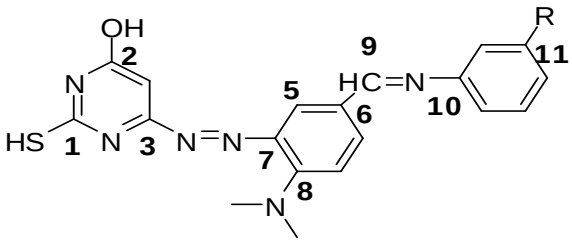


Table 2: Carbon 13 NMR of the azo Schiff base synthesised.

	Pyrimidine ring carbons			Middle ring carbons					
	1	2	3	8	5	6	8	11	10
4	162.34	154.86	153	148.98	109.03	115.41	131.99	129.92	127.85
5a	169.01	168.6	154.48	152.42	119.51	121.51	130.69	129.05	128.97
5b	162.14	156.94	152.90	151.84	110.85	120.38	130.77	129.96	127.26
5c	160.16	154.32	152.67	146.32	110.97	120.90	130.78	129.25	125.16
5d	161.28	154.48	153.18	152.63	110.88	123.24	130.58	129.82	124.24

The electronic spectra absorption

Comparison of the spectra of the prepared dyes showed the first UV absorbance between 280-290 nm can be appropriated to the ($\pi - \pi^*$) transition of the aromatic rings. The second absorbance is the 370-385 nm transition due to π-electrons of azo and azo methane groups. Changing the solvent to a more polar solvent (DMSO) gave a bathochromic shift, while changing pH to 5 gave an even greater bathochromic shift than the polar solvent, to 483 nm, figure 2.[25]

Table 3: UV-visible properties of azo-Schiff base synthesised.

Azo no.	λ_{max} /€	m.p.	Colour
3	251/ 34000 354/ 56000	77-79	Yellow
5a	307/ 50000 464/ 63000	174-175	Red
5b	284/ 57000 411/ 61000	168-169	Oxa red
5c	346/ 43000 507/ 53000	135-136	Dark red
5d	302/ 57000 514/ 63000	184-185	Red

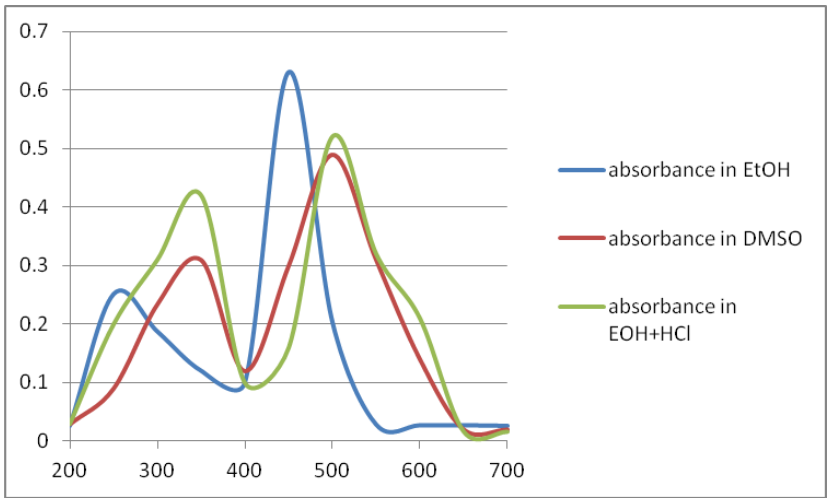


Figure 2: UV-vis absorbation of dye 3 in different solvents.

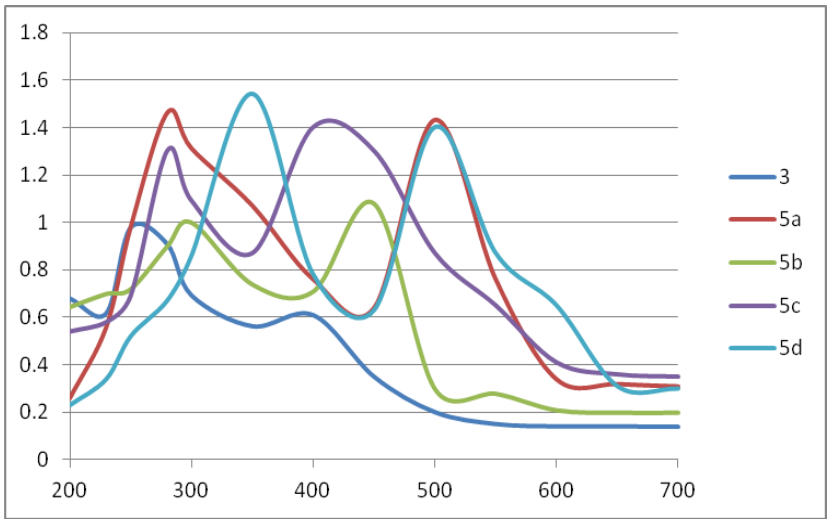


Figure 3: UV-vis absorbation of dyes (3) and (5a-d) in ethanol

The UV–visible spectra of the prepared dyes (**5a-d**) were recorded in solvents of different polarity in the region 200–700 nm. The absorbance band that appeared around 350 nm in ethanol is due to π–π * transition, figure 2. Since all the prepared dyes have n– π * and π – π * transitions in close proximity, the lower intensity n– π * transition is totally overlaid by the intensive π – π * transition.[24] In contrast with the unsubstituted parent azo Schiff base (5c), the maximum absorbance was blue shifted in the substituted Schiff bases **(5a), (5b)** and **(5d).** This may be due to the fact that the existence of substituents leads to an increase in the resonance interaction of the π electrons in the prepared dyes. In most of the azo-Schiff bases, the absorption spectrum depends greatly on the solvent polarity and red shift was observed in the dyes **(5a-d)** compared with azo aldehyde **(3)**. There was a bigger red shift in the maximum absorbance band in the dye **(5a)** (Table 3) which may be due to the extent of the π

system and the carboxylic group which have a greater interaction with ethanol. This was confirmed by comparing the absorbance band of azo aldehyde **(3)** with the other dyes **(5a-d)** since all of them give red shift in comparison with azo aldehyde **(3)**, figure 3**.**[26-28]

CONCLUSIONS

A series of heterocyclic azo-azo methane dyes compounds were synthsized containing using a coupling reaction between 6-amino-2-mercaptopyrimidin-4-ol and 4-(dimethylamion) benzaldehyde forming, 4-(dimethylamino)-3-((6-hydroxy-2-mercaptopyrimidin-4-yl)diazenyl) benzaldehyde. The next step was a condensation reaction between the aldehyde formed in the first step and 3-amino-banzoic acid, 1-(3-aminophenyl)ethanone, aniline and 3-aminophenol. The synthesized dyes were characterised by UV-visible, FT-IR, ^{1}H and ^{13}C NMR. Furthermore, the solvent effect on the UV-visible spectra was studied. It was noticed that the absorption of these dyes depends on the substituted group on the azo-methene group of the dye. On the other hand when the solvent effect was studied on the novel aldyhyde which was synthesized in this study the more polar solvent was found to give a more bathochromic shift.

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