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Microwave Assisted Synthesis of Amino-Thiophene Dyes and study of Solvent Effects on the UV-Visible Absorption Spectra

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ABSTRACT

New series of Amino-thiophene dyes 3 (a-g) were synthesized, with growing environmental concerns, developing greener approach for the synthesis of azo dyes is crucial. In present research we describe microwave (MW)-assisted protocol for rapid access to a variety of amino thiophene-azo dyes by coupling amino-thiophenecarboxylate with aromatic amines. After MW-assisted synthesis, Compounds were isolated by precipitation followed by recrystallization to obtain pure azodyes. Then newly synthesized thiophene dyes gave positive solvatochromism so that the absorption bands of the azodye, move towards longer wavelengths as the polarity of the solvent increases.

Keywords: Amino-thiophene dyes, microwave assisted synthesis, UV visible spectra.

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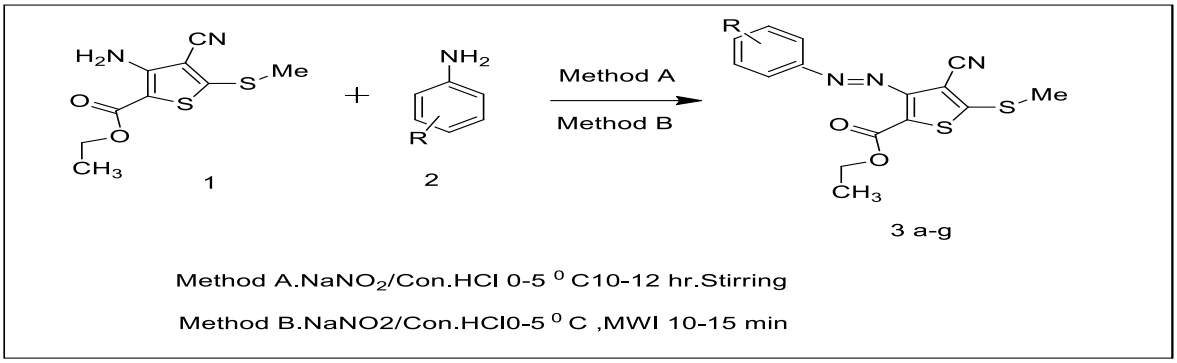
INTRODUCTION

Color plays a significant role in a wide range of industries particularly in printing, pharmaceutical, cosmetic, food, textile dyes are considered to be easy to use, relatively cheap and to provide clear, strong colours. In India there are approximately 2000 azo dyes available the market. Most of the Artificial dyes are used in the market. They are classified as Azo, Xanthene, Indigo, Tetrazine, Triphenylmethane etc. They are one of the most widely used chromophores in dye chemistry. Azo compounds are the compounds of both natural and manufactured chemicals that contain at least one azo group (N_2) in their structure. The atomic groups connected to the nitrogen atoms might be of any organic class, but the commercially relevant azo compounds, Which account for more than half of all commercial dyes, contain the benzene group or its derivatives as the attached groups. Although azo compounds come in a wide variety, pigments, and dyes are the most popular. Bismarck Brown, the first commercial azo dye, was introduced in 1863. [1-4] The field of heterocyclic azo dyes continues to be dynamic, driven by the need for brighter, more durable, and environmentally friendly dyes. The synthesis and application of heterocyclic azo dyes, especially in textiles, offer significant advantages in terms of color brilliance, fastness, and versatility. The development of novel dyes, including those with antimicrobial properties, is evidence of the constant innovation in this field. [5-6] .Azo compounds have broad fields of applications such as, antifungal, antibacterial [4], anti-inflammatory [5], anticancer and antioxidant [6]. Beside of it, it has many other applications like, coloring fiber [7], printing systems [8], photo electronics [9], analytical, polymer additive [10], optical recording [11] and storage [12], light and weather fastness [13] and resistance to solvents and water [14-16]. Most of the Azo dyes showed positive absorption spectra. [17-19]

MATERIALS AND METHOD

All the required reagents and chemical were brought from Merck and Sigma Aldrich without any additional purification. The progress of reaction were monitored by Thin layer chromatography carried out on 1.2 silica gel 60 F254 Merck plates using ultraviolet light for detection. Digital melting point apparatus were used to measure melting point. Products were recrystallized from ethanol.IR spectra recorded on Shimadzu FTIR-Tensor II spectrophotometer. Brucker 500 MHz spectrometer was used to measure ^{1}HNMR.Mass spectra were recorded on Shimadzu GC-MS mass spectrophotometer.

Synthesis of Amino thiophene dyes 3 (a-g)



Scheme 1 Synthesis of Amino Thiophene dyes

Method A Conventional Method

Ethyl-3-amino-4-cyano-5-(methyl-thio) thiophene-2-carboxylate 1 (0.242g,1mmol) was dissolved in 1 mL concentrated hydrochloric acid and cooled to 0-5ºC. A previously cooled solution of sodium nitrite (0.069g,1mmol) in distilled water(1mL) was added at0-5ºC. The solution was stirred for an hour. It was tested for positive test for nitrous acid on starch iodide paper; the excess of nitrous acid was removed by adding required amount of urea. Aniline (0.1 g, 1 mmol) was dissolved in concentrated HCl (0.5 mL), water (1 mL) and cooled below 0-5ºC. The diazotized compound 1 was added drop wise to the solution of aniline. The pH of reaction mixture was maintained at 5.5 to 6.0 by adding solution of sodium acetate (20% w/v). It was further stirred for 3 hours at 0-5ºC and at room temperature for 2 h. The solid was collected and recrystallized from ethanol afforded compounds.

Method B Non-Conventional Method

Aniline based thiophene-azo dyes 3 (a-g) were derived from the coupling of ethyl-3-amino-4-cyano-5-(methyl-thio) thiophene-2-carboxylate (1) with various aromatic amines (2) (a-g) given in Table 1) at 0-5°C in presence of conc. HCl and reaction mixture was irradiated at 300 W for 10-15 minutes at 20 interval of 20 sec. By maintaining pH at 5-6 solution of sodium acetate (20% w/v) added to reaction mixture. Thiopheneazo dyes compounds3(a-g) were obtained with 78-86% yield. The compounds synthesized were recrystallized from methanol. (Scheme 1)

Table 1: Practical Yield of Thiophene-azo dyes 3 (a-g)

Entry	R-	% yield Conventional	% yield MWI	M.P. ºC
3a	C_6H_5-NH_2	68	78	152
3b	3-Cl- C_6H_5	70	79	158
3c	4-Cl-C_6H_5	67	81	122
3d	2-Cl-6-CH_3-C_6H_5	65	82	175
3e	4-CH_3-C_6H_5	72	81	228
3f	2-OCH_3-C_6H_5	71	80	157
3g	4-NO_2-C_6H_5	73	83	148

RESULTS AND DISCUSSION

The structures of the newly synthesized compounds were established by spectroscopic interpretation as discussed above. Melting range of the synthesized compounds, percentage yield, were established (table 1)

Ethyl-3-(2-(4-amino-phenyl)-diazenyl)-4-cyano-5-(methy-lthio)-thiophene-2- carboxylate, (3a)

IR(KBr)$\bar{\nu}$cm^{1}:3425,3325(NH_2),3163(NH);3062(ArCH),2214(CN),1620(C=O),1404(N=N);^{1}HNMRCDCl_3): δ1.32-1.41 (t, *J*=7 Hz, 3H, CH_3),2.71 (s, 3H,SCH_3),4.26-4.32 (q, *J*=7&14Hz, 2H, OCH_2), 5.76 (s, 2H, NH_2), 6.73 (d, *J* = 8 Hz, 2H, Ar-H), 7.91 (d, *J* = 8 Hz, 2H, Ar-H); ESI-MS: *m/z* (%) = 369.06 [$C_{15}H_{14}N_4O_2S_2Na$, 100%].

Ethyl-3-(2-(5-methyl-2-amino-3-chloro-phenyl) diazenyl)-4-cyano-5-methylthio)-thiophene-2carboxylate, (3d)

IR(KBr)$\bar{\nu}$cm^{1}:3445,3335(NH_2),3128(NH);3069(ArCH),2218(CN),1628(C=O),1409(N=N);^{1}HNMR ($CDCl_3$):δ1.32-1.36(t, *J* =7Hz, 3H,CH_3), 2.29(s,3H, ArCH_3),2.65(s, 3H,SCH_3),4.26-4.32(q, *J*=7 &14Hz,2H,OCH_2),5.76(s, 2H,NH_2),7.68(d, *J* =1.8Hz,1H,Ar-H), 7.79 (d, *J* = 1.8 Hz,1H, Ar-H); ESI-MS: *m/z*(%) = 419.03 [M+2Na, 46%],417.02[M+Na,100%].

Spectroscopic properties

The ultraviolet absorption spectra of some newly synthesized thiopheneazo dyes derived from the coupling of ethyl-3-amino-4-cyano-5-(methyl-thio)-thiophene-2- carboxylate with various aromatic anilines were recorded in various solvents acetonitrile, dimethylformamide (DMF), methanol (MeOH), methanol plus one drop of hydrochloric acid (MeOH + HCl) and methanol plus one drop of 10% potassium hydroxide (MeOH + KOH) at the concentration of 10^{-4} -10^{-5} M in the range of 200- 800 nm. The maximum absorption (λmax) recorded, The electronic

Table 3: Spectroscopic properties of some Thiophene-azo dyes derivatives

Dyes	DMF		Acetonitrile		MeOH		MeOH+HCl		MeOH+KOH	
	λmax	log ε	λmax	log ε	λmax	log ε	λmax	log ε	λmax	log ε
3a	358	2.045	349	2.044	433	1.837	448.5	2.062	421.5	1.919
3c	338	1.867	351	1.982	349.5	2.021	352.5	1.982	340	2.021
3d	346	1.839	357	2.006	425.5	1.569	427.5	1.601	412	1.692
3e	400	2.041	350	2.024	393	1.968	395.5	1.96	410.5	2.046
3f	342	1.886	344	2.029	477	2.029	479	2.007	466	2.029

CONCLUSION

The absorption spectra of newly synthesized thiopheneazo-dyes derivatives were recorded in different solvents. The maximum absorption recorded. We have reported facile and efficient

protocol for the synthesis of (4-cyano-5-methyl-thio)-thiophene-2-carboxylate incorporated azo dyes under the green conditions with good yields. Particularly valuable features of the present method include, broad substrate scope, short reaction time, simple procedure and easy work up that facilitated 78–85% yield.

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