



Solvent effects on the UV-visible absorption spectra of some new (4-arylazothiophen-2-yl) (5-bromothiophen-2-yl) ketone dyes

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Received: 9/10/2019
Accepted: 17/10/2019

ABSTRACT: A facile synthesis of various (4-arylazothiophen-2-yl) (5-bromothiophen-2-yl) ketone dyes **4a-e** was described through heterocyclization of the precursor 2-arylazo-2-acetyl-thioacetanilides **3** with 5-bromo-2-(bromoacetyl)-thiophene. The effect of solvent polarity on absorption spectra was investigated, as was the relationship between dye structures and absorption in the UV-visible region. The absorption maxima of the tested arylazo-thiophene dyes ranged from 464 to 490 nm in ethanol, from 484 to 492 nm in DMF and from 494 to 496 nm in acetone.

Keywords: 2-Acetyl-2-arylazothioacetanilides, 5-Bromo-2-(bromoacetyl)-thiophene, dithiophen-2-yl ketones, UV-visible absorption, Solvent effect

1. Introduction

The wide range of azo dyes utilization is due to the variation in their chemical structures and application methods. Many azo dyes are utilized for dyeing natural and synthetic fibers such as cotton, silk, wool, polyesters, polyamides, acrylics and viscose rayon. They can be used for the coloring of paints, printing inks, plastics, rubber, cosmetics and foods [1]. A large number of heterocyclic azo dyes are introduced into the market to produce a full range of azo disperse dyestuffs based on various heteroaromatic diazo or coupling components [2]. Utilization of heterocyclic diazo components in the synthesis of dyes have received much attention due to their excellent brightness and high tinctorial power [3]. Nitrogen and/or Sulphur heterocyclic azo dyes have been utilized in different fields such as color formers, printing, electronic photography, laser technology and solar energy conversion [4]. Such compounds have potential use in optical communications, frequency doubling and integrated optics [5]. Arylazo dyes of different heterocyclic moieties have been reported in the recent literature as the subject of intense research by chemists [6] and dye manufacturers [7]. Arylazothiophene derivatives has received significant attentions since they are applied in dye-sensitized solar cells

and as efficient semiconducting materials [8–12]. In the present research article, we successfully synthesized a series of (4-arylazothiophen-2-yl) (5-bromothiophen-2-yl) ketone derivatives by heterocyclization of the precursors, 2-acetyl-2-arylazo-thioacetanilide derivatives with 5-bromo-2-(bromoacetyl)-thiophene.

2. Experimental

2.1. General:

Melting points were measured in degree centigrade on Gallenkamp apparatus and are uncorrected. The ultraviolet-visible absorption spectra were measured on a Shimadzu 1700 spectrophotometer in the region 200–600 nm. The infrared spectra (KBr) were explored on Thermo Scientific Nicolet iS10 FTIR spectrometer. ¹H NMR spectra were measured in DMSO-*d*₆ as a solvent at 500 MHz on JEOL's spectrometer. Perkin-Elmer 2400 analyzer has been used to determine the elemental analyses.

2.2. Synthesis of (5-bromothiophen-2-yl)(3-methyl-5-(phenylamino)-4-(arylazo)-thiophen-2-yl)methanone dyes **4a-e**:

Each derivative of 2-acetyl-2-arylazothioacetanilide **1** (1 mmol) was suspended in 30 mL

hot ethyl alcohol. 5-bromo-2-(bromoacetyl)-thiophene (0.28 g, 1 mmol) and 0.5 mL triethylamine were added to the hot solution. The reaction was proceeded by heating under reflux for 3 hours. The solid that formed on cooling to 25°C was filtered and dried to pick up the targeted arylazo-thiophene dyes **4a-e**.

2.3. (5-Bromothiophen-2-yl)(3-methyl-5-(phenylamino)-4-(phenylazo)thiophen-2-yl)methanone (**4a**):

Red solid, yield = 86%, m.p. = 184-186°C. IR (KBr): 3444 (N-H), 1592 cm^{-1} (C=O). ^1H NMR: δ 2.53 (s, 3H, CH_3), 7.27-7.33 (m, 2H, Ar-H), 7.39 (d, $J = 4.00$ Hz, 1H, thiophene- H_4), 7.45-7.53 (m, 6H, Ar-H), 7.75-7.77 (m, 3H, Ar-H and thiophene- H_3), 13.70 ppm (s, 1H, NH). Analysis for $\text{C}_{22}\text{H}_{16}\text{BrN}_3\text{OS}_2$ (481): Calculated: C, 54.77; H, 3.34; N, 8.71%. Found: C, 54.86; H, 3.39; N, 8.78%.

2.4. (5-Bromothiophen-2-yl)(3-methyl-5-(phenylamino)-4-(4-tolylazo)thiophen-2-yl)methanone (**4b**):

Red solid, yield = 90%, m.p. = 180-182°C. IR (KBr): 3443 (N-H), 1594 cm^{-1} (C=O). ^1H NMR: δ 2.35 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 7.25-7.28 (m, 1H, Ar-H), 7.32 (d, $J = 8.50$ Hz, 2H, Ar-H), 7.38 (d, $J = 4.00$ Hz, 1H, thiophene- H_4), 7.47-7.52 (m, 4H, Ar-H), 7.71 (d, $J = 8.50$ Hz, 2H, Ar-H), 7.75 (d, $J = 4.00$ Hz, 1H, thiophene- H_3), 13.43 ppm (s, 1H, NH). Analysis for $\text{C}_{23}\text{H}_{18}\text{BrN}_3\text{OS}_2$ (495): Calculated: C, 55.65; H, 3.65; N, 8.46%. Found: C, 55.81; H, 3.60; N, 8.57%.

2.5. (5-Bromothiophen-2-yl)(3-methyl-5-(phenylamino)-4-(4-anisylazo)thiophen-2-yl)methanone (**4c**):

Brown solid, yield = 67%, m.p. = 150-152°C. IR (KBr): 3441 (N-H), 1599 cm^{-1} (C=O). ^1H NMR: δ 2.58 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 7.08 (d, $J = 8.50$ Hz, 2H, Ar-H), 7.25-7.28 (m, 1H, Ar-H), 7.38 (d, $J = 4.00$ Hz, 1H, thiophene- H_4), 7.50-7.51 (m, 4H, Ar-H), 7.75 (d, $J = 4.00$ Hz, 1H, thiophene- H_3), 7.79 (d, $J = 9.00$ Hz, 2H, Ar-H), 12.84 ppm (s, 1H, NH). Analysis for $\text{C}_{23}\text{H}_{18}\text{BrN}_3\text{O}_2\text{S}_2$ (511): Calculated: C, 53.91; H, 3.54; N, 8.20%. Found: C, 53.80; H, 3.56; N, 8.12%.

2.6. (5-Bromothiophen-2-yl)(3-methyl-5-(phenylamino)-4-(4-nitrophenylazo)thiophen-2-yl)methanone (**4d**):

Red solid, yield = 62%, m.p. = 230-232°C. IR (KBr): 3443 (N-H), 1598 cm^{-1} (C=O). ^1H NMR: δ 2.35 (s, 3H, CH_3), 7.32 (t, $J = 7.25$ Hz, 1H, Ar-H), 7.40-7.42 (m, 3H, Ar-H and thiophene- H_4), 7.51-7.54 (m, 2H, Ar-H), 7.78 (d, $J = 2.50$ Hz, 2H, Ar-H), 7.79 (d, $J = 2.00$ Hz, 1H, thiophene- H_3), 8.29 (d, $J = 9.00$ Hz, 2H, Ar-H), 14.34 ppm (s, 1H, NH). Analysis for $\text{C}_{22}\text{H}_{15}\text{BrN}_4\text{O}_3\text{S}_2$ (526): Calculated: C, 50.10; H, 2.87; N, 10.62%. Found: C, 50.27; H, 2.81; N, 10.72%.

2.7. (5-Bromothiophen-2-yl)(3-methyl-5-(phenylamino)-4-(4-chlorophenylazo)thiophen-2-yl)methanone (**4e**):

Red Solid, yield = 81%, m.p. = 182-184°C. IR (KBr): 3435 (N-H), 1593 cm^{-1} (C=O). ^1H NMR: δ 2.53 (s, 3H, CH_3), 7.29 (t, $J = 7.25$ Hz, 1H, Ar-H), 7.38 (d, $J = 4.00$ Hz, 1H, thiophene- H_4), 7.47-7.56 (m, 7H, Ar-H), 7.75 (d, $J = 4.00$ Hz, 1H, thiophene- H_3), 7.82 (d, $J = 9.00$ Hz, 2H, Ar-H), 13.42 ppm (s, 1H, NH). Analysis for $\text{C}_{22}\text{H}_{15}\text{BrClN}_3\text{OS}_2$ (515): Calculated: C, 51.12; H, 2.93; N, 8.13%. Found: C, 51.26; H, 2.90; N, 8.22%.

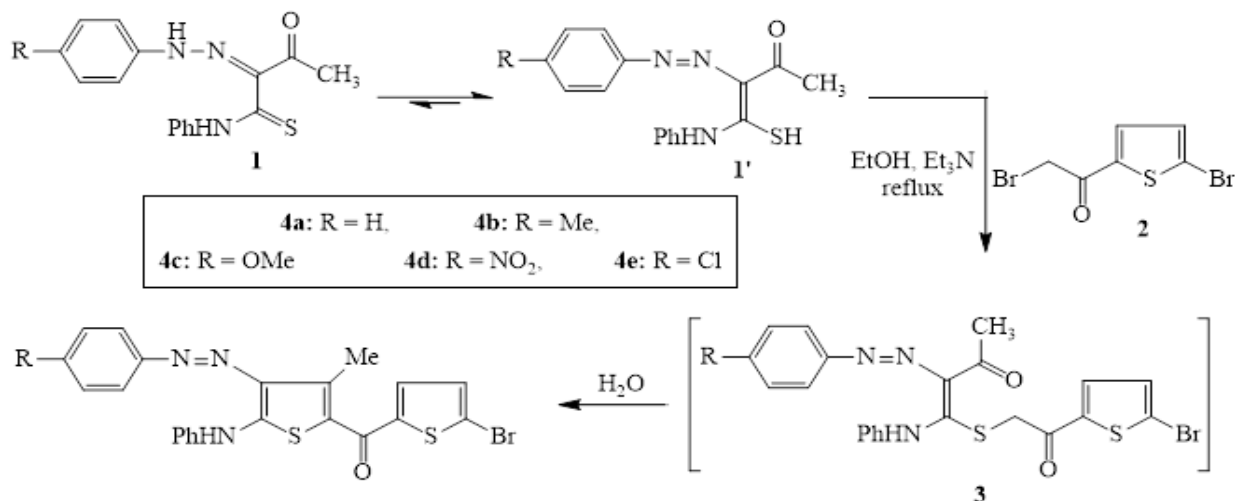
3. Results and discussion

2-Acetyl-2-arylazothioacetanilide derivatives **1** have been prepared in the light of the previously reported method [13]. They reacted through their thiol form **1'** with 5-bromo-2-(bromoacetyl)-thiophene in boiling ethyl alcohol containing triethylamine to give the corresponding (4-arylazothiophen-2-yl) (5-bromothiophen-2-yl) ketone dyes **4** (Scheme 1). The mechanistic scenario for the formation of these dithiophen-2-yl ketones involves initial alkylation of **1** with 5-bromo-2-(bromoacetyl)-thiophene to give the non-isolable thioether intermediates **3** followed by *in situ* heterocyclization through nucleophilic addition of methylene group to the carbonyl group and elimination of water molecule.

The chemical structures of dithiophen-2-yl ketones **4a-e** were secured based on their correct spectral analyses. The infrared spectra of the constructed dithiophen-2-yl ketones **4a-e** exhibited the characteristic absorption of N-H in the range 3444-3435 cm^{-1} . The characteristic absorption of carbonyl group was identified at lower wavenumber in the range of 1599-1592 cm^{-1} due to high conjugation with thiophene rings. The ^1H NMR spectrum of (5-bromothio-

phen-2-yl)-(4-phenylazothiophen-2-yl)methanone dye **4a** displayed singlet at δ 2.53 ppm for the protons of methyl group (thiophene-CH₃). The aromatic protons resonated as multiplet for two protons in the region 7.27-7.33 ppm, multiplet for six protons in the region 7.45-7.53

ppm and multiplet for three protons in the region 7.75-7.77 ppm (2Ar-H and thiophene-H₃). The proton of thiophene-C₄ was observed as doublet at 7.39 ppm. The singlet at 13.70 ppm referred to the proton of imine function (N-H).



Scheme (1)

3.1. The solvent effect on the UV-visible absorption spectra

The effect of solvent on the absorption maxima (UV-visible spectra) of (4-arylazothiophen-2-yl) (5-bromothiophen-2-yl) ketone dyes **4** was explored using different solvents with different polarities. In general, different colors of the synthesized dithiophen-2-yl dyes result from either alternation of the substituent in aryl-diazo components. Since the color of the prepared dyes varied from orange to red, a common technique of estimating the color of the dye was to examine the absorption spectra of their solutions.

The wavelength at maximum absorption of the prepared arylazo-dithiophen-2-yl ketone dyes **4a-e** were determined in three different types of solvents with various polarities (ethanol, acetone and dimethylformamide). The absorption maxima of the prepared arylazo-thiophene dyes in ethanol (table 1) ranged from 464 to 490 nm. They announced a narrow range from 484 to 492 nm in DMF and from 494 to 496 nm in acetone. Within the series of 4-arylazo-thiophene dyes investigated **4a-e**, the relationship between the change that occurred in the absorption maxima, and polarities of the substituents, may be summarized in the following points:

(a) In ethanol, the introduction of nitro group or chlorine atom in the phenyldiazo component affects shifting the absorption maxima to higher values (bathochromic shift) according to the following order: NO₂ (**4d**: λ_{\max} = 490) > Cl (**4e**: λ_{\max} = 488) > OMe (**4c**: λ_{\max} = 474) > Me (**4b**: λ_{\max} = 472) = H (**4a**: λ_{\max} = 472).

(b) In DMF, the absorption λ_{\max} values of the five arylazothiophene dyes **4a**, **4b**, **4c**, **4d** and **4e** were shifted to higher values than their corresponding values in ethanol.

(c) In acetone, the absorption λ_{\max} values of the five arylazothiophene dyes **4a**, **4b**, **4c**, **4d** and **4e** were very close to each other (494-496 nm).

(d) Acetone solvent caused more bathochromic shift than DMF and ethanol. The highest observed λ_{\max} value, through all measurements, was 496 nm in acetone.

Table (1): UV-visible absorption wavelength (λ_{\max} , nm) for the synthesized (4-arylazothiophen-2-yl) (5-bromothiophen-2-yl) ketone dyes **4a-e**.

Dye No.	EtOH	DMF	Acetone
4a	472	492	496
4b	472	484	494
4c	474	492	496
4d	490	492	496
4e	488	490	496

4. References:

1. R.J. Chudgar and J. Oakes. Azo Dyes Kirk-Othmer (2003). Encyclopedia of Chemical Technology, 9
2. L. Shuttleworth and M. A. Weaver. In: Waring D. R., G. Hallas, Eds. (1990). The Chemistry and Application of Dyes. New York: Plenum
3. J.S. Hunter, R.J. Lindsay, R.W. Kenyon and D. Trhrop. (1985). Heterocyclic disperse azo dyes. British Patent 2,151,611
4. G.S. Uscumlic, D.Z. Mijin, N.V. Valentic, V.V. Vajs and B.M. (2004). Susic. Substituent and solvent effects on the UV/Vis absorption spectra of 5-(4-substituted arylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridones. Chem. Phys. Lett., **397**, 148–53
5. M.M.M. Raposo, A.M.R.C. Sousa, A.M.C. Fonseca and G. Kirsch. Thienylpyrrole azo dyes: (2005). Synthesis, solvatochromic and electrochemical properties. Tetrahedron, **61**, 8249–56
6. K. Takagi, A. Mizuno, H. Iwamoto, S. Kawashima, S. Nishida and T. Hashikawa. (1994). Syntheses and absorption spectra of new azo dyes containing an azulene ring. Dyes Pigments, **26**, 51–60
7. Y.M. ElKholi and S.A. Abd El-Hafiz. (1994). Polyfunctionally pyrazole azo dyes: Synthesis and application. Pigment Resin Technol., **23**, 3–5
8. A. Mishra, C.Q. Ma and P. Bauerle. (2009). Functional oligothiophenes: Molecular design for multi-dimensional nano-architectures and their applications. Chem. Rev., **109**, 1141-1276
9. M.C. Gather, A. Kohnen and K. Meerholz. (2011). White organic light-emitting diodes. Adv. Mater., **23**, 233-248
10. A.S. Radwan, M.M. Makhlof and E. Abdel-Latif. Azothiophene dyes nanotubes structure based thin films: (2016). Synthesis, structural and optical characterization toward application in dye-sensitized solar cells. Dyes Pigment, **134**, 516-525
11. M. Nazim, S. Ameen, M.S. Akhtar and H.-S. Shin. D- π -A- π -D type thiazolo[5,4-*d*]-thiazole-core organic(2018). chromophore and graphene modified PEDOT:PSS buffer layer for efficient bulk heterojunction organic solar cells. Solar Energy, **171**, 366-373
12. A. Mahmood, J. Hu, A. Tang, F. Chen, X. Wang and E. Zhou(2018). A novel thiazole-based acceptor for fullerene-free organic solar cells. Dyes Pigments, **149**, 470-474
13. F.A. Amer, A. Harhash and M.L. Awad. (1978). Synthesis of 2-methyl-1-phenylthiocarbamoyl glyoxal arylhydrazones and diethyl (arylozo)(phenylthiocarbamoyl)-malonate and their reactions with hydrazines. Z. Naturforsch., **33b**, 660–662