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Part 1: Synthesis and Visible Absorption Spectra of Some New Monoazo Dyes Derived from Ethyl 2-amino-4-(4'-substitutedphenyl)thiophenes

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Abstract

Series of monoazo dyes from some ethyl 2-amino-4-(4'-substitutedphenyl) thiophenes were prepared and characterized. The structure of the substances was confirmed by FT-IR, ¹H-NMR and mass spectroscopic techniques. The relationship among the structure of the dyes, their absorption characteristics and the solvatochromic and halochromic behaviors of the dyes were investigated. Introduction of electron-accepting substituent into the diazo moiety results in large bathochromic shifts in all solvents used. The dyes exhibited positive solvatochromism and their solvatochromic properties were discussed in relation to tautomerism.

Keywords: Azo dyes, Thiophene, Absorption spectra, Solvent effect, Substituent effect, Halochromism

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Introduction

Arylazo heterocycles are a versatile class of colored organic compounds that have recently attracted the interest of many research groups due to their diverse applications, not only as conventional synthetic dyes and pigments but also as solvatochromic probes and thermally stable organic second-order nonlinear optical (NLO) chromophores [1-3]. They also play a significant role in many applications such as optical data storage devices, liquid crystals [2-5], dye-sensitized solar cells (DSCC), photovoltaic and fluorescent devices, acid-base and metal sensors [6,7] and so on.

Numerous heterocyclic dyes are now marketed as disperse azo dyes based on heteroaromatic diazo or coupling components. Thus, the shade especially blues and greens have become obtainable more economically and properties such as high tinctorial strength and excellent brightness have become attainable and are commercially competitive with the more expensive anthraquinone dyes. [8, 9]. 2-Aminothiophene derivatives have been used as diazo components for the synthesis of disperse azo dyes for a long time because of their bathochromic effect [10-14]. In addition, it has been reported that thiophene rings lead to excellent sublimation fastness on fibers and better dye ability because of their small molecular structure [14, 15].

Numerous reports on the synthesis of hetarylazo dyes based on thiophene have appeared. Most of these dyes have been prepared from carbocyclic coupling components and 2aminothiophene derivatives as diazo components [14-24]. Although thiophene derivatives have rarely been reported as coupling components for disperse dyes, some examples obtained from the coupling moieties of 2-aminothiophenes have been reported [25]. We have previously reported the synthesis of new heterocyclic azo dyes containing pyridone [26,27], 8-hydroxyquinoline [28], and indol [29-31] moiety with hetarylazo or phenylazo groups. These new π -conjugated systems exhibit remarkable solvatochromic and halochromic behaviors. In recent years a number of new thienylazo disperse dyes have been prepared from 2-N-substituted aminothiophenes as coupling components and these dyes exhibit different spectroscopic properties with substitution of 3- and/or 4-position of the thiophene ring [32-35]. Although the hetarylazo dyes based on thiophene have been known for many years, relatively little is known about the dyes prepared from a primary amino group consisting thiophene ring as coupling components [36-38]. Also, influence of substituent on visible

absorption spectra and solvatochromic and halochromic behaviours of these dyes have not been discussed in depth yet. In addition, amino group have a contribution the affinity of the dye molecules onto fabric with intermolecular H-bond between the fabric and the dye molecule [39,40].

Consequently, we reported here the synthesis of three series of new heterocyclic monoazo dyes derived from 2-amino-3-carboetoxy-4-(4'-substitutedphenyl)thiophenes as coupling components and discussed the correlation between the dye structure and spectral properties. Azo-hydrazone tautomerism, solvatochromic and halochromic properties of the dyes were also investigated.

Experimental

Materials and instrumentation

The chemical used in the synthesis of all dyes were obtained from Aldrich Chemical Company (USA) and were used without further purification. Benzene was freshly distillated and the other solvents were used spectroscopic grade.

IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer (Gazi University Department of Chemistry, Turkey) in KBr (v, in cm⁻¹). ¹H NMR spectra were recorded on a Bruker-Spectrospin Avance DPX 400 MHz Ultra-Shield (Hacettepe University Department of Chemistry, Turkey) in DMSO- d_6 with TMS as the internal reference. Chemical shifts were expressed in δ units (ppm). Ultraviolet-visible (UV-vis) absorption spectra were recorded on an Analytikjena Specord 200 Spectrophotometer (Gazi University Department of Chemistry, Turkey) at the wavelength of maximum absorption (λ_{max} , in nm) in range of solvents, i.e. Dimethylsulphoxide (DMSO, ϵ , 46.45), methanol (ϵ , 32.66), acetic acid (ϵ 6.17) and chloroform (ϵ , 4.81). All melting points were uncorrected and in ^oC (Electrothermal 9200 melting point apparatus). Mass analyses were performed on a Waters LCT Premier XE (TOF MS) (Gazi University Laboratories, Department Pharmacological Sciences).

Synthesis of coupling components

Ethyl 2-cyano-3-phenylbut-2-enoate derivatives (I-a, I-b and I-c) were synthesized by Knoevenagel condensation with 4-substituted acetophenones and ethyl cyanoacetate as starting materials [41]. Ethyl 2-amino-4-phenylthiophene-3-carboxylate derivatives (II-a, II-b and II-c) were synthesized according to the method described in the literature by Gewald reaction [42, 43] (Scheme 1). Compound II-a was synthesized from compound I-a and sulphur at presence of triethylamine according to the literature [43]. It was recrystallized from ethanol to give yellow crystals (65 % yield, m.p: 98-99 °C ; Lit. values m.p.: 98 °C, 62 % yield).

Compound II-b was synthesized from I-b in a similar manner described above for compound II-a and recrystallized from ethanol to give dark yellow crystals (41 % yield, m.p.:81 °C; melting point and yield of II-b was not found in literature) [44].

Similarly, compound II-c was synthesized from I-c, purified from column chromatography (Ethyl acetate/n-Heksane, 1:1 (v/v)) and recrystallized from ethanol to give light yellow crystals (48 % yield , m.p. : 98 °C; Lit. values m.p.: 98-100 °C, 60 % yield) [45].

Scheme 1 is here

Preparation of ethyl 2-amino-5-(4-substitutedphenyldiazenyl)-4-(4'-substitutedphenyl) thiophene-3-carboxylate derivatives (1-15)

Diazotization of various carbocyclic amines was affected with HCl and NaNO₂. A typical procedure was described below and all compounds (1-15) were prepared in a similar manner (Scheme 2). The yields of the dyes were in the range of 56-97% and these yields were obtained after two times recrystallization from ethanol. The purity of the compounds was confirmed by ¹H-NMR data and the reaction was controlled by TLC. Characterization data were given below, melting points and nomenclature of compounds were given in Table 1.

Scheme 2 and Table 1 are here

General procedure for preparation of substituted thienylazo dyes [46]

P-Substituted aniline (2.0 mmole) was dissolved in hydrochloric acid (1.5 mL conc. HCl in 4 mL water). The solution was then cooled to 0-5 °C with stirring. Sodium nitrite (0.15 g, 2.0 mmole) in water (3 mL) was gradually added to this solution over 15 min period at 0-5 °C with stirring. The mixture was stirred for an additional 1 hour while maintaining at temperature of 0-5 °C. Excess nitrous acid was destroyed by addition of urea, and the solution was filtered. The resulting clear diazonium salt was used immediately in the coupling reaction. Ethyl 2-amino-4-(4'-substitutedphenyl)thiophene-3-carboxylate (2.0 mmole) was dissolved in acetic acid/propionic acid (4 mL, ratio 3:1) and cooled to 0-5 °C in a salt/ice bath. The cold diazonium salt solution was added to this cooled solution over 20 min with vigorous stirring in a drop wise manner, while maintaining the pH at 4-6 by addition of saturated sodium carbonate solution. The mixture was further stirred for 1 hour at 0-5 °C and resulting solid was filtered, washed with cold water, dried, and recrystallized two times in ethanol.

Preparation of ethyl 2-amino-5-(phenyldiazenyl)-4-phenylthiophene-3-carboxylate (dye 1)

This dye was obtained from aniline and ethyl 2-amino-4-phenylthiophene-3-carboxylate as brick red crystals. IR (KBr) v_{max} (cm⁻¹) : 3371, 3254 (N-H), 3049 (aromatic C-H), 2980 (aliphatic C-H), 1664 (C=O), 1272 (C-O), 1574 (C=C), 503 (C-S); ¹H NMR (DMSO-*d*₆); δ 8.55 (br, 2H, -NH₂), 7.28-7.44 (m, 10H), 3.90 (q, 2H, -COO<u>CH₂CH₃</u>, *J*= 7.10 Hz), 0.85 (t, 3H, -COOCH₂CH₃, *J*= 7.10 Hz). TOF MS (*m*/*z*) : 352.1 (100%) (M-H)^{+.}

Preparation of ethyl 2-amino-5-(4-methylphenyldiazenyl)-4-phenylthiophene-3-carboxylate (dye 2)

This dye was obtained from 4-methylaniline and ethyl 2-amino-4-phenylthiophene-3carboxylate as orange crystals. IR (KBr) v_{max} (cm⁻¹) : 3380, 3261 (N-H), 3021 (aromatic C-H), 2978 (aliphatic C-H), 1659 (C=O), 1272 (C-O), 1572 (C=C), 505 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.48 (br, 2H, -NH₂), 7.40 (s, 5H), 7.33 (d, 2H, *J*= 8.29 Hz), 7.21 (d, 2H, *J*= 8.29 Hz), 3.95 (q, 2H, -COO<u>CH₂CH₃</u>, *J*= 7.12 Hz), 2.30 (s, 3H, -CH₃), 0,85 (t, 3H, -COOCH₂<u>CH₃</u>, *J*= 7.08 Hz). TOF MS (*m*/*z*) : 366.1 (100%) (M-H)^{+.}

Preparation of ethyl 2-amino-5-(4-methoxyphenyldiazenyl)-4-phenylthiophene-3-carboxylate (*dye 3*)

This dye was obtained from 4-methoxylaniline and ethyl 2-amino-4-phenylthiophene-3carboxylate as brown crystals. IR (KBr) v_{max} (cm⁻¹) : 3366, 3245 (N-H), 3066 (aromatic C-H), 2978, 2935 (aliphatic C-H), 1662 (C=O), 1241 (C-O), 1599, 1578 (C=C), 547 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.40 (br, 2H, -NH₂), 7.40 (d, 2H, *J*= 8.98 Hz), 7.37 (s, 5H), 6.95 (d, 2H, *J*= 9.02 Hz), 3.95 (q, 2H, -COO<u>CH₂CH₃</u>, *J*= 7.10 Hz), 3.75 (s, 3H, -O<u>CH₃</u>), 0.80 (t, 3H, -COOCH₂<u>CH₃</u>, *J*= 7.10 Hz). TOF MS (*m*/*z*): 382.2 (100%) (M-H)^{+.}

Preparation of ethyl 2-amino-5-(4-cyanophenyldiazenyl)-4-phenylthiophene-3-carboxylate (*dye 4*)

This dye was obtained from 4-cyanoaniline and ethyl 2-amino-4-phenylthiophene-3carboxylate as red crystals. IR (KBr) v_{max} (cm⁻¹) : 3391, 3286, 3251 (N-H), 3055 (aromatic C-

H), 2985 (aliphatic C-H), 2220 (C=N), 1678 (C=O), 1255 (C-O), 1608 (C=C), 553 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.85 (br, 2H, -NH₂), 7.80 (d, 2H, *J*= 8.59 Hz), 7.48 (d, 2H, *J*= 8.59 Hz), 7.40 (s, 5H), 3.95 (q, 2H, -COO<u>CH₂CH₃</u>, *J*= 7.09 Hz), 0.82 (t, 3H, -COOCH₂<u>CH₃</u>, *J*= 7.09 Hz). TOF MS (*m*/*z*) : 377.1 (100%) (M-H)^{+.}

Preparation of ethyl 2-amino-5-(4-nitrophenyldiazenyl)-4-phenylthiophene-3-carboxylate (*dye 5*)

This dye was obtained from 4-nitroaniline and ethyl 2-amino-4-phenylthiophene-3carboxylate as black crystals. IR (KBr) v_{max} (cm⁻¹) : 3447, 3305, 3247 (N-H), 3052 (aromatic C-H), 2985 (aliphatic C-H), 1669 (C=O), 1594 (C=C), 1507,1373 (NO₂), 1244 (C-O), 490 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.96 (br, 2H, -NH₂), 8.23 (d, 2H, *J*= 9.09 Hz), 7.53 (d, 2H, *J*= 9.07 Hz), 7.43 (s, 5H), 4.00 (q, 2H, -COO<u>CH₂CH₃</u>, *J*= 7.07 Hz), 0.85 (t, 3H, -COOCH₂<u>CH₃</u>, *J*= 7.08 Hz). TOF MS (*m*/*z*): 395.0 (100%) (M-H)^{-.}

Preparation of ethyl 2-amino-5-(phenyldiazenyl)-4-(4'-nitrophenyl) thiophene-3-carboxylate (*dye 6*)

This dye was obtained from aniline and ethyl 2-amino-4-(4'-nitrophenyl)thiophene-3carboxylate as light red crystals. IR (KBr) v_{max} (cm⁻¹) : 3411, 3298, 3250 (N-H), 3061 (aromatic C-H), 2963 (aliphatic C-H), 1671 (C=O), 1589 (C=C), 1509, 1337 (NO₂), 1233 (C-O), 543 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.63 (br, 2H, -NH₂), 8.27 (d, 2H, *J*= 8.77 Hz), 7.73 (d, 2H, *J*= 8.77 Hz), 7.39-7.46 (m, 4H), 7.31-7.36 (m, 1H), 4.00 (q, 2H, -COO<u>CH₂CH₃</u>, *J*= 7.07 Hz), 0.90 (t, 3H, -COOCH₂<u>CH₃</u>, *J*= 7.07 Hz). TOF MS (*m*/*z*): 395.0 (100%) (M-H)⁻⁻

Preparation of ethyl 2-amino-5-(4-methylphenyldiazenyl)-4-(4'-nitrophenyl) thiophene-3-carboxylate (dye 7)

This dye was obtained from 4-methylaniline and ethyl 2-amino-4-(4'-nitrophenyl) thiophene-3-carboxylate as dark red crystals. IR (KBr) v_{max} (cm⁻¹) : 3416, 3296, 3253 (N-H), 3026 (aromatic C-H), 2984 (aliphatic C-H), 1672 (C=O), 1593 (C=C), 1503, 1336 (NO₂), 1236 (C-O), 600 (C-S); ¹H NMR (DMSO- d_6): δ 8.56 (br, 2H, –NH₂), 8.26 (d, 2H, *J*= 8.79 Hz), 7.71 (d, 2H, *J*= 8.79 Hz), 7.35 (d, 2H, *J*= 8.28 Hz), 7.22 (d, 2H, *J*= 8.24 Hz), 4.00 (q, 2H, -

 $COOCH_2CH_3$, J= 7.09 Hz), 2.30 (s, 3H, -CH₃), 0.90 (t, 3H, -COOCH₂CH₃, J= 7.10 Hz). TOF MS (m/z) : 409.1 (100%) (M-H)^{-.}

Preparation of ethyl 2-amino-5-(4-methoxyphenyldiazenyl)-4-(4'-nitrophenyl) thiophene-3carboxylate (**dye 8**)

This dye was obtained from 4-methoxylaniline and ethyl 2-amino-4-(4'-nitrophenyl) thiophene-3-carboxylate as brown crystals. IR (KBr) v_{max} (cm⁻¹) : 3453, 3323 (N-H), 3103 (aromatic C-H), 2983 (aliphatic C-H), 1673 (C=O), 1586 (C=C), 1504, 1337 (NO₂), 1103 (C-O), 556 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.49 (br, 2H, -NH₂), 8.25 (d, 2H, *J*= 8.77 Hz), 7.70 (d, 2H, *J*= 8.74 Hz), 7.43 (d, 2H, *J*= 8.98 Hz), 6.98 (d, 2H, *J*= 9.01 Hz), 4.00 (q, 2H, -COO<u>CH₂CH₃</u>, *J*= 7.08 Hz), 3.80 (s, 3H, -O<u>CH₃</u>), 0.85 (t, 3H, -COOCH₂<u>CH₃</u>, *J*= 7.09 Hz). TOF MS (*m*/*z*) : 425.0 (100%) (M-H)^{-.}

Preparation of ethyl 2-amino-5-(4-cyanophenyldiazenyl)-4-(4'-nitrophenyl) thiophene-3-carboxylate (dye 9)

This dye was obtained from 4-cyanoaniline and ethyl 2-amino-4-(4'-nitrophenyl) thiophene-3carboxylate as red crystals. IR (KBr) v_{max} (cm⁻¹) : 3487, 3413, 3370 (N-H), 3099 (aromatic C-H), 2985 (aliphatic C-H), 2221 (C=N), 1692 (C=O), 1588 (C=C), 1513, 1346 (NO₂), 1190 (C-O), 557 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.93 (br, 2H, -NH₂), 8.28 (d, 2H, *J*= 8.78 Hz), 7.84 (d, 2H, *J*= 8.59 Hz), 7.73 (d, 2H, *J*= 8.76 Hz), 7.51 (d, 2H, *J*= 8.58 Hz), 4.00 (q, 2H, -COO<u>CH₂CH₃, *J*= 7.08 Hz), 0.90 (t, 3H, -COOCH₂<u>CH₃</u>, *J*= 7.07 Hz). TOF MS (*m*/*z*) : 422.1 (100%) (M-H)^{-.}</u>

Preparation of ethyl 2-amino-5-(4-nitrophenyldiazenyl)-4-(4'-nitrophenyl) thiophene-3-carboxylate (dye 10)

This dye was obtained from 4-nitroaniline and ethyl 2-amino-4-(4'-nitrophenyl) thiophene-3carboxylate as black crystals. IR (KBr) v_{max} (cm⁻¹) : 3453, 3370, 3311 (N-H), 3079 (aromatic C-H), 2979 (aliphatic C-H), 1671 (C=O), 1585 (C=C), 1513, 1346 (NO₂), 1252 (C-O), 584 (C-S); ¹H NMR (DMSO-*d*₆): δ 9.03 (br, 2H, –NH₂), 8.29 (d, 2H, *J*= 8.64 Hz), 8.24 (d, 2H, *J*= 8.98 Hz), 7.75 (d, 2H, *J*= 8.63 Hz), 7.57 (d, 2H, *J*=8.96 Hz), 4.00 (q, 2H, -COO<u>CH₂CH₃, *J*= 7.10 Hz), 0.90 (t, 3H, -COOCH₂<u>CH₃</u>, *J*= 7.09 Hz). TOF MS (*m/z*) : 440.0 (100%) (M-H)⁻⁻</u>

Preparation of ethyl 2-amino-5-(phenyldiazenyl)-4-(4'-methoxyphenyl) thiophene-3carboxylate (**dye 11**)

This dye was obtained from aniline and ethyl 2-amino-4-(4'-methoxyphenyl) thiophene-3carboxylate as orange crystals. IR (KBr) v_{max} (cm⁻¹) : 3361, 3211 (N-H), 3054 (aromatic C-H), 2975 (aliphatic C-H), 1667 (C=O), 1574 (C=C), 1248 (C-O), 509 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.52 (br, 2H, -NH₂), 7.35 (d, 2H, *J*= 8.70 Hz), 7.36-7.47 (m, 5H), 6.96 (d, 2H, *J*= 8.72 Hz), 4.00 (q, 2H, -COO<u>CH₂CH₃</u>, *J*= 7.10 Hz), 3.80 (s, 3H, -O<u>CH₃</u>), 0.95 (t, 3H, -COOCH₂<u>CH₃</u>, *J*= 7.07 Hz). TOF MS (*m/z*) : 382.1 (100%) (M-H)^{+.}

Preparation of ethyl 2-amino-5-(4-methylphenyldiazenyl)-4-(4'-methoxyphenyl) thiophene-3carboxylate (**dye 12**)

This dye was obtained from 4-methylaniline and ethyl 2-amino-4-(4'-methoxyphenyl) thiophene-3-carboxylate as orange crystals. IR (KBr) v_{max} (cm⁻¹) : 3368, 3276 (N-H), 3018 (aromatic C-H), 2981 (aliphatic C-H), 1665 (C=O), 1574 (C=C), 1238 (C-O), 584 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.45 (br, 2H, -NH₂), 7.40 (d, 2H, *J*= 8.16 Hz), 7.35 (d, 2H, *J*= 8.60 Hz), 7.22 (d, 2H, *J*= 8.41 Hz), 6.95 (d, 2H, *J*= 8.74 Hz), 4.00 (q, 2H, -COO<u>CH₂CH₃</u>, *J*= 7.14 Hz), 3.80 (s, 3H, -O<u>CH₃</u>), 2.30 (s, 3H, -CH₃), 0.95 (t, 3H, -COOCH₂CH₃, *J*= 7.11 Hz). TOF MS (*m/z*) : 396.1 (100%) (M-H)^{+.}

Preparation of ethyl 2-amino-5-(4-methoxyphenyldiazenyl)-4-(4'-methoxyphenyl) thiophene-3-carboxylate (**dye 13**)

This dye was obtained from 4-methoxyaniline and ethyl 2-amino-4-(4'-methoxyphenyl) thiophene-3-carboxylate as orange crystals. IR (KBr) v_{max} (cm⁻¹) : 3368, 3250 (N-H), 3000 (aromatic C-H), 2928 (aliphatic C-H), 1663 (C=O), 1577 (C=C), 1242 (C-O), 548 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.38 (br, 2H, -NH₂), 7.43 (d, 2H, *J*= 8.97 Hz), 7.34 (d, 2H, *J*= 8.68 Hz), 7.00 (d, 2H, *J*=9.00 Hz), 6.94 (d, 2H, *J*= 8.74 Hz), 4.00 (q, 2H, -COO<u>CH₂CH₃</u>, *J*= 7.13 Hz), 3.53 (s, 3H, -O<u>CH₃</u>), 3.54 (s, 3H, -O<u>CH₃</u>), 0.93 (t, 3H, -COOCH₂<u>CH₃</u>, *J*= 7.11 Hz). TOF MS (*m*/*z*) : 410.1 (100%) (M-H)^{-.}

Preparation of ethyl 2-amino-5-(4-cyanophenyldiazenyl)-4-(4'-methoxyphenyl) thiophene-3carboxylate (**dye 14**)

This dye was obtained from 4-cyanoaniline and ethyl 2-amino-4-(4'-methoxyphenyl)thiophene-3-carboxylate as black crystals. IR (KBr) v_{max} (cm⁻¹) : 3434, 3285, 3240 (N-H), 3000 (aromatic C-H), 2932 (aliphatic C-H), 2217 (C=N), 1668 (C=O), 1591 (C=C), 1248 (C-O), 553 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.85 (br, 2H, -NH₂), 7.80 (d, 2H, *J*= 8.51 Hz), 7.50 (d, 2H, *J*= 8.52 Hz), 7.35 (d, 2H, *J*= 8.62 Hz), 6.95 (d, 2H, *J*= 8.67 Hz), 4.00 (q, 2H, -COO<u>CH₂CH₃, *J*= 7.10 Hz), 3.80 (s, 3H, -O<u>CH₃), 0.95 (t, 3H, -COOCH₂CH₃, *J*= 7.10 Hz), 3.80 (s, 3H, -O<u>CH₃), 0.95 (t, 3H, -COOCH₂CH₃, *J*= 7.10 Hz). TOF MS (*m*/*z*) : 405.1 (100%) (M-H)^{-.}</u></u></u>

Preparation of ethyl 2-amino-5-(4-nitrophenyldiazenyl)-4-(4'-methoxyphenyl) thiophene-3carboxylate (**dye 15**)

This dye was obtained from 4-nitroaniline and ethyl 2-amino-4-(4'-methoxyphenyl) thiophene-3-carboxylate as black crystals. IR (KBr) v_{max} (cm⁻¹) : 3444, 3296, 3247 (N-H), 3099 (aromatic C-H), 2984 (aliphatic C-H), 1670 (C=O), 1596 (C=C), 1507, 1374 (NO₂), 1242 (C-O), 588 (C-S); ¹H NMR (DMSO-*d*₆): δ 8.91 (br, 2H, -NH₂), 8.22 (d, 2H, *J*= 8.97 Hz), 7.52 (d, 2H, *J*= 8.96 Hz), 7.37 (d, 2H, *J*= 8.64 Hz), 6.95 (d, 2H, *J*= 8.67 Hz), 4.00 (q, 2H, -COO<u>CH₂CH₃, *J*= 7.10 Hz), 3.80 (s, 3H, -O<u>CH₃</u>), 0.95 (t, 3H, -COOCH₂<u>CH₃</u>, *J*= 7.10 Hz). TOF MS (*m*/*z*) : 425.1 (100%) (M-H)⁻⁻</u>

Results and Discussion

Ethyl 2-amino-4'-substitutedphenylthiophene-3-carboxylate derivatives (II a-c) were synthesized by Gewald reaction according to the method described in the literature [43-45] with 4-substituted acetophenones and ethyl cyanoacetate as starting materials, as shown in Scheme 1.

As shown in Scheme 2, three series of some new thienylazo dyes (1-15) based on 4substituted anilines as diazo components with coupling components, ethyl 2-amino-4phenylthiophene-3-carboxylate, ethyl 2-amino-4-(4'-nitrophenyl)thiophene-3-carboxylate and ethyl 2-amino-4-(4'-methoxyphenyl)thiophene-3-carboxylate compounds were prepared by

the same general procedure as described in the Experimental section. **Dyes 1-15** were obtained generally in high yields (56-97 %). The characterization of these thienylazo dyes (1-15) was made by FT-IR, ¹H-NMR, UV-Vis spectra and TOF-MS measurements (see Exp. Sec.). Physical data of the dyes are given in Table 1.

Scheme 3 is here

Azo-hydrazone tautomerism in disperse azo dyes is one of the most interesting research fields because it is very important for their optical stability and fastness properties. Hence, we considered the possible tautomeric structures of the dyes while discussing the spectroscopic properties of the dyes. The dyes can exist in three possible tautomeric forms, but two of them may relatively stable, namely amino-azo and imine-hydrazone forms as shown in Scheme 3. The imineazo-enol form of the dyes was not existed in both solid state and solution because OH stretching band was not observed in FT-IR spectra and there was no signal of OH proton in ¹H-NMR spectra of the dyes. Additionally, the other forms were stabilized with intramolecular H-bonding. The deprotonation of the tautomers leads to common cation (Scheme 4 and Scheme 5).

Scheme 4 and 5 are here

Characterization of the dyes by ¹H NMR and FT-IR (1-15)

The IR spectra of dyes 1-15 (in KBr) showed two strong broad band within the range 3487-3361 cm⁻¹ and 3413-3211 cm⁻¹ due to NH₂ stretching vibration and a characteristic absorption band of ester carbonyl group at 1692-1659 cm⁻¹. It can be suggested that these dyes exist in amino-azo form or imine-hydrazone form in the solid state. And also, it showed that the dyes prepared are not in diazoamino structures because it is expected that only one NH stretching band are observed for diazoamino structers. Other v_{max} values at 3103-3000 cm⁻¹ (aromatic C-H) and at 2985-2928 cm⁻¹ (aliphatic C-H) were recorded. For **dyes 4**, **9** and **14** an intense band within the range 2217-2221 cm⁻¹ assignable to the CN stretching was recorded. In addition, **dyes 5**, **10** and **15** showed absorption at 1507, 1513, 1504 and 1373, 1346, 1337cm⁻¹ for the NO₂ group, respectively.

The ¹H-NMR spectra (DMSO- d_6) of dyes 1-15 showed a broad singlet at δ 9.03-8.38 ppm (2H) assigned to the NH₂ group, a triplet at δ 0.80-0.95 ppm (3H) and a quartet at δ 3.90-4.00 ppm (2H) for the ethoxy group. The dyes also showed signals at δ 6.94-8.29 ppm which were assigned to the aromatic protons of phenyl rings. Detailed spectral data are given in the Experimental section.

¹H-NMR spectra gave an evidence of the presence of the amino-azo tautomeric form. A broad singlet (2H) at 9.03-8.38 ppm was observed due to the NH₂ group and there was no hydrazone NH signal. It is well known that the hydrazide protons of the hydrazone form for azo dyes are observed at ~ 14-15 ppm [47, 48]. The observed value for the dyes in DMSO-*d*₆ is a clear indication of the NH₂ protons, which was confirmed by the two stretching frequency values $3487-3361 \text{ cm}^{-1}$ and $3413-3211 \text{ cm}^{-1}$ in the FT-IR spectra. The shift in the second stretching band and its broadening provide further evidence for the H-bonding. These spectral results suggested that dyes 1-15 exist as the amino-azo form both the solid state and in the solution.

Substituent effect on absorption spectra of dyes

The λ_{max} values of the dyes (1-15) in chloroform, acetic acid, methanol and DMSO were summarized in Table 2. As far as absorption maxima are concerned, λ_{max} values are directly proportional to the electronic effect of the substituent in a benzenoid system.

Table 2 is here

A comparison of the position of the absorption maxima in the three series in relation to substitution on the diazo component (dyes 1-5, dyes 6-10 and dyes 11-15) generally shows the same decreasing order NO₂ > CN > OCH₃ > CH₃ > H in each solvent, indicating the more conjugation of the 4-nitrosubstituted dyes except dye 1 in acetic acid. Also, λ_{max} values of some dyes did not changed with substitution, for example dye 11 and dye 12 in DMSO. In particular, these shifts are greatest in DMSO (Fig. 1).

Figure 1 is here

From the viewpoint of absorption maxima, electronic spectral data for the variously substituted thienylazo dyes show that there is a general tendency for the visible absorption band to move bathochromically with increasing of the electron-withdrawing strength of the substituent in the 4-position of the diazo component, in accordance with the donor-acceptor chromogens, as known for azo dyes [7]. These results also confirmed that the dyes prepared exist in one tautomeric form (amino-azo) in solution.

The introduction of the nitro group in the 4-position into the diazo component results in large bathochromic shifts in all solvents used (for dye 5 $\Delta \lambda_{max} = 61$ nm in DMSO, $\Delta \lambda_{max} = 56$ nm in methanol, $\Delta \lambda_{max} = 35$ nm in acetic acid, $\Delta \lambda_{max} = 67$ nm in chloroform relative to λ_{max} of dye 1 in the same solvents). This bathochromic shift is attributed to the stronger electron-acceptor character of the nitro group, thus enhancing electron delocalization in the dye molecule. In contrast, introduction of the nitro group in the 4-position into the phenyl ring of the thienyl group (dye 6) did not significantly change the λ_{max} values of the dyes (for dye 6 $\Delta\lambda_{max} = 1$ nm in DMSO, $\Delta\lambda_{max} = 3$ nm in methanol, $\Delta\lambda_{max} = 10$ nm in acetic acid, $\Delta\lambda_{max} = 14$ nm in chloroform relative to the λ_{max} of dye 1 in the same solvents). Moreover, the introduction of electron-donor or electron-acceptor substituent into the phenyl ring at the coupling component showed nearly the same effect and the spectra obtained showed little, if any, shift compared to unsubstituted dye 1 in all solvents used. Dye 1 absorbs at 468 nm, dye 6 (X: NO2) and dye 11 (X: OCH3) absorb at 469 nm in DMSO. Hence, the influence of substitution in this position is negligible. The failure of 4-substituents on the phenyl ring of the coupling component effect to the color shifts in thienylazo dyes may result from the inability of these substituents to enter effectively into the resonance of the donor-acceptor part of the dye molecule. In addition, introduction of nitro groups in both positions of the dye (dye 10) did not significantly change the λ_{max} values of the dyes either (for **dye 10** $\Delta\lambda_{max} = 61$ nm in DMSO, $\Delta \lambda_{max} = 49$ nm in methanol, $\Delta \lambda_{max} = 37$ nm in acetic acid and $\Delta \lambda_{max} = 66$ nm in chloroform relative to the λ_{max} of dye 1 in the same solvents) and these observed results do not differ significantly from that of dye 5. A similar behavior was apparent in 4-CN-substituted dye (dye 4) which resulted in bathochromic shifts of 33 nm in DMSO, 34 nm in methanol, 18 nm in acetic acid and 39 nm in chloroform compared to dye 1. Furthermore, it was found that electron-donor substituents (methyl and methoxy groups) in the 4-position of the diazo component had only a slight influence on the absorption maxima as compared to those of electron-acceptor substituents. For example, the $\Delta\lambda_{max}$ values are +1 nm in DMSO, +3 nm in

methanol, -6 nm in acetic acid and +23 nm in chloroform for dye 2 relative to dye 1. The same effect is also observed for dye 3 (Table 2). The largest bathochromic shift in comparison with the visible spectra of the three series is observed for dye 15 (X: OCH₃, R: NO₂). This dye absorbs at 535 nm in DMSO, 511 nm in methanol, 501 nm in acetic acid and 505 nm in chloroform.

Judging from these results, it can be concluded that the color of the dyes prepared is not affected by substituents in the phenyl ring in 3-position of the thienyl ring but the largest bathochromic effect is obtained when a stronger electron-donor substituent in 4-position of the phenyl ring of the coupling component and a stronger electron-acceptor substituent in 4-position of the phenyl ring of the diazo component are present in the dye molecule. These results are in agreement with resonance theory.

Solvent effect on absorption spectra of dyes

Since the tautomeric equilibrium strongly depend on the nature of the media, the solvatochromic properties of the dyes in solvents of different polarities were studied. For this purpose, the absorption spectra of the dyes were recorded in solvents of different polarities at a concentration of approximately $10^{-6} - 10^{-8}$ M. These are run at different concentrations because of solubility problems and the results are given in Table 2. The absorption spectra of **dye 9** in solvents with different polarities are shown in Fig. 2 as typical example of the three series investigated. Their visible absorption spectra in all solvents used revealed in each case one characteristic absorption maximum in the region 430-535 nm. Such an absorption pattern is similar to that reported for the azo compounds that exist in a single tautomeric form. It can be seen in Fig. 2 and Table 2 that the dyes exist in one tautomeric form, namely the amino-azo form since the absorption difference pattern of the dyes was not changed with solvents. The dyes generally show bathochromic shifts as the polarity of the solvents is increased in the order DMSO > methanol ~ acetic acid > chloroform. The observed positive solvatochromism is consistent with a transition having a significant charge transfer character.

Fig. 2 is here

To provide conclusive evidence for the tautomeric structure of the compounds (1-15), the effects of acid and base on their absorption spectra were investigated. For this purpose, the

spectra of the dyes were recorded in acidic and basic media. It was observed that the absorption curves of the dyes were not sensitive to bases. The absorption maxima of the dyes did not change when various amounts of 0.1 M KOH was added to their methanolic solutions, except **dyes 5**, **10** and **15** (Table 3). This result indicates that these compounds exist in one tautomeric form in alkaline media and the absence of any dissociation.

Fig. 3 and Table 3 are here

As shown in Table 3 and Fig. 3, in the case of **dyes 5, 10** and **15**, with the addition of 0.1 M KOH to their methanolic solutions, the intensity of the absorption band decreased and a new band appeared at longer wavelengths which were assigned to the common anion form relatable to resonance stabilization. This indicates that these dyes exist in a partly dissociated state in methanolic KOH solutions. This is confirmed by the observation of one isosbestic point in the different basic solutions (Fig. 3). The relative ease of the formation of the common anions from these dyes may be attributed to the additional resonance contribution of the nitro groups. Also, to determine the base effect on absorption spectra of the dyes in other solvents, a small amount of piperidine was added to solutions of **dyes 1-5** in DMSO. As shown in Table 4, the similar effect was observed with their methanolic KOH solutions. When piperidine was added to the dye solutions in DMSO, the λ_{max} of **dyes 1-3** did not change whereas the λ_{max} of **dyes 4** and **5** showed second maximums at longer wavelengths (for **dye 4** λ_{max} : 578 nm and for **dye 5** λ_{max} : 644 nm) which was attributed to a common anion form.

Table 4 is here

The λ_{max} values of some dyes showed large bathochromic shifts when various amounts of 0.1 M HCl were added to their methanolic solutions. As can be seen in Table 3, the largest bathochromic shift of the absorption maxima was observed for **dye 8** ($\Delta\lambda_{\text{max}} = + 86 \text{ nm}$), which possesses the methoxy group in diazo component and the nitro group in coupling component. As an example of these dyes, the absorption spectra of **dye 7** are given in Fig. 4. In contrast, the **dyes 4**, **5**, **10**, **14** and **15**, having an electron accepting group in diazo component exhibited hypsochromic shifts. The largest hypsochromic shift of the λ_{max} was observed for **dye 15** ($\Delta\lambda_{\text{max}} = -42 \text{ nm}$) which possesses the strong electron-accepting nitro group in diazo component and the methoxy group in coupling component. Additionally, in the case of **dye 9** (X: NO2; R: CN) the λ_{max} value did not changed and **dye 8** exhibited small bathochromic shift. As apparent in Table 3, the introduction of electron-donating substituent

in the p-position of diazo component results in bathochromic shifts whereas the introduction of electron-accepting substituent in the same position of diazo component results in hypsochromic shifts. From this view, it can be seen that the absorption maxima of the cationic form of dyes prepared were affected with substitution of the diazo component.

Fig. 4 is here

In acidic media, protonation of the dyes can occur either at the terminal amino group to give the ammonium tautomer or at the β -nitrogen atom of the azo group to give the azonium tautomer [50-52]. The protonation of terminal -NH₂ group prevents mesomeric interaction of the lone pair of electrons with π -electronic system, thus its absorption is expected at shorter wavelength than the neutral dye. We observed that in acidic media the some dyes prepared absorbed at longer wavelength than the neutral dyes. This showed that dyes observed at longer wavelength existed in azonium tautomer which contains a delocalized positive charge. In contrast, the dyes containing electron accepting substituents such as **dye 14** and **dye 15** showed hypsochromic shifts (**dye 14**: $\Delta\lambda_{max} = -18$ nm; **dye 15**: $\Delta\lambda_{max} = -42$ nm in methanolic HCl solutions). Also, absorption maximum of **dye 9** did not change in acidic medium. To show the relationship between Hammett substituent constants and the wavelength difference, $\Delta\lambda_{max}$ values of the dyes in acidic methanolic solutions relative to neutral methanolic solutions of the dyes are graphed. $\Delta\lambda_{max}$ values of the dyes showed nearly linear correlation with Hammett substituent constants, except Fig. 6 (Fig. 5-7). These result also suggested that the dyes exist one tautomeric form, namely azonium tautomer in acidic medium.

Fig. 5-7 is here

Conclusion

Three series of monoazo dyes consisting primer amino group were synthesized from ethyl 2amino-4-(4'-substitutedphenyl) thiophenes and their UV-Vis absorption spectral properties were investigated. It was observed that the dyes exist in one tautomeric form (azo-amino) in all solvents used. The largest bathochromic shift was observed by the nitro substituted dyes in the diazo component in DMSO.

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Figure captions

Fig. 1. Absorption spectra of dyes 6-10 in DMSO.

Fig. 2. Absorption spectra of dye 9 in various solvents.

- Fig. 3. Absorption spectra of dye10 in basic solutions of methanol.
- Fig. 4. Absorption spectra of dye 7 in acidic solutions of methanol.
- Fig. 5. Relationship between Hammett substituent constants with $\Delta \lambda_{max}$ values of the dyes 1-5 ($\Delta \lambda_{max}$: The difference between the azonium and neutral forms of the dyes in methanol).
- Fig. 6. Relationship between Hammett substituent constants with $\Delta\lambda_{max}$ values of the dyes 6-10 ($\Delta\lambda_{max}$: The difference between the azonium and neutral forms of the dyes in methanol).
- Fig. 7. Relationship between Hammett substituent constants with $\Delta\lambda_{max}$ values of the dyes 11-15 ($\Delta\lambda_{max}$: The difference between the azonium and neutral forms of the dyes in methanol).

Scheme captions

Scheme 1. Synthesis of coupling components (II a-c) by Gewald reaction.

Scheme 2. Synthesis of dyes (1-15).

Scheme 3. Possible tautomeric forms of dyes in different solvents.

Scheme 4. Possible anionic forms in basic media.

Scheme 5. Possible cationic forms in acidic media.

Table captions

Table 1 Structures of dyes (1-15).

Table 2 Influence of solvent on λ_{max} (nm) of dyes (1-15).

Table 3 Hammett substituent constants (σ_p) and absorption maxima of dyes (1-15) in methanolic solution.

Table 4 Absorption maxima of dyes (1-5) with piperidine in DMSO.

ÇP



Fig. 1. Absorption spectra of dyes 6-10 in DMSO.



Fig. 2. Absorption spectra of dye 9 in various solvents.



Fig. 3. Absorption spectra of dye10 in basic solutions of methanol.



Fig. 4. Absorption spectra of dye 7 in acidic solutions of methanol.



Fig. 5. Relationship between Hammett substituent constants with $\Delta\lambda_{max}$ values of the dyes 1-5

($\Delta\lambda_{max}$:The difference between the azonium and neutral forms of the dyes in methanol).



Fig. 6. Relationship between Hammett substituent constants with $\Delta\lambda_{max}$ values of the dyes

6-10 ($\Delta\lambda_{max}$: The difference between the azonium and neutral forms of the dyes in

methanol).



Fig. 7. Relationship between Hammett substituent constants with $\Delta \lambda_{max}$ values of the dyes 11-15 ($\Delta \lambda_{max}$: The difference between the azonium and neutral forms of the dyes in methanol).



Scheme 1. Synthesis of coupling components (II a-c) by Gewald reaction.



Scheme 2. Synthesis of dyes (1-15).





Scheme 4. Possible anionic forms in basic media.



Table 1

Structures of dyes (1-15).

				x	CH ₃ CH ₂ O O NH ₂
				R	N
Dye No	х	R	% Yield	Melting point (°C)	Nomenclature
1	Н	н	90	127-129	Ethyl 2-amino-5-(phenyldiazenyl)-4-phenylthiophene-3- carboxylate
2	Н	CH ₃	91	150-154 (dec.) ^ª	Ethyl 2-amino-5-(4-methylphenyldiazenyl)-4 phenylthiophene-3-carboxylate
3	Н	OCH₃	82	135-138	Ethyl 2-amino-5-(4-methoxyphenyldiazenyl)-4 phenylthiophene-3-carboxylate
4	н	CN	98	204-205	Ethyl 2-amino-5-(4-cyanophenyldiazenyl)-4 phenylthiophene-3-carboxylate
5	Н	NO ₂	94	232-235	Ethyl 2-amino-5-(4-nitrophenyldiazenyl)-4 phenylthiophene-3-carboxylate
6	NO ₂	н	91	204-205	Ethyl 2-amino-5-(phenyldiazenyl)-4-(4'- nitrophenyl)thiophene-3-carboxylate
7	NO ₂	CH ₃	62	231-233	Ethyl 2-amino-5-(4-methylphenyldiazenyl)-4-(4'- nitrophenyl)thiophene-3-carboxylate
8	NO ₂	OCH₃	62	125-127	Ethyl 2-amino-5-(4-methoxyphenyldiazenyl)-4-(4'- nitrophenyl)thiophene-3-carboxylate
9	NO ₂	CN	97	256-257	Ethyl 2-amino-5-(4-cyanophenyldiazenyl)-4-(4'- nitrophenyl)thiophene-3-carboxylate
10	NO ₂	NO ₂	91	275-276	Ethyl 2-amino-5-(4-nitrophenyldiazenyl)-4-(4'- nitrophenyl)thiophene-3-carboxylate
11	OCH ₃	Н	79	154-156	Ethyl 2-amino-5-(phenyldiazenyl)-4-(4'- methoxyphenyl)thiophene-3-carboxylate

-	12	OCH₃	CH ₃	72	167-168	Ethyl 2-amino-5-(4-methylphenyldiazenyl)-4-(4'- methoxyphenyl)thiophene-3-carboxylate
-	13	OCH ₃	OCH₃	56	164-165	Ethyl 2-amino-5-(4-methoxyphenyldiazenyl)-4-(4'- methoxyphenyl)thiophene-3-carboxylate
-					224-230	Ethyl 2-amino-5-(4-cyanophenyldiazenyl)-4-(4'-
_	14	OCH ₃	CN	72	(dec.) ^a	methoxyphenyl)thiophene-3-carboxylate
	15	OCH ₃	NO ₂	79	197-200	Ethyl 2-amino-5-(4-nitrophenyldiazenyl)-4-(4'- methoxyphenyl)thiophene-3-carboxylate
	^a dec.:	decompos	ition			

Table 2

Influence	of solvent on \hat{a}	λ_{\max} (nm) of dyes (:	1-15).	
Dvo No	λ _{max} (nm)	λ _{max} (nm)	λ _{max} (nm)	λ _{max} (nm)
Dye NO	(DMSO)	(Methanol)	(Acetic acid)	(Chloroform)
1	468	448	461	430
2	469	451	455, 501(s) ^a	453
3	469	455	459, 528(s) ^a	457
4	501	482	479	469
5	529	504	496	497
6	469	451	451	444
7	475	454	454	450
8	481	462	463	462
9	505	481	481	469
10	529	497	498	496
11	469	452	458	435
12	469	453	456, 502(s) ^a	448
13	478	457	462, 530(s) ^a	460
14	508	487	481	487
15	535	511	501	505

^a s: shoulder

Table 3

Hammett substituent constants (σ_p) and absorption maxima of dyes (1-15) in methanolic solution.

Substituent(Dye	λ	λ _{max} (nm)	$\Delta \lambda_{max}$	λ _{mav} (nm)
R)	σ _p ď	No	(Methanol)	(Methanol+HCl)	(nm)	(Methanol+KOH)
Н	0	1	448	487	+ 39	448
CH ₃	-0,17	2	451	501	+ 50	451
OCH ₃	-0,27	3	455	472(s) ^b ,525	+ 70	455
CN	+0,66	4	482	476	- 6	483
NO ₂	+0,78	5	504	479	- 25	504, 599
Н	0	6	451	486	+ 35	451
CH ₃	-0,17	7	454	500	+ 46	454
OCH₃	-0,27	8	462	468(s) ^b , 548	+86	462
CN	+0,66	9	481	481	0	481, 572(s) ^b
NO ₂	+0,78	10	497	486	- 11	498, 605
Н	0	11	452	486	+ 34	452
CH ₃	-0,17	12	453	503	+ 50	454
OCH ₃	-0,27	13	457	528	+ 71	457
CN	+0,66	14	487	469	- 18	487
NO ₂	+0,78	15	511	469	- 42	510, 598

 ${}^{a}\sigma_{p}$ constants can be found in Ref [49].

^b s: shoulder

Table 4

Absorption maxima of dyes (1-5) with piperidine in DMSO.

No. No.	λ _{max} (nm)	λ _{max} (nm)
Dye No	(DMSO)	(DMSO + piperidine)
1	468	468
2	469	469
3	469	469
4	501	501, 578
5	529	500, 644
		6.

Graphical abstract



HIGHLIGHTS

- The dyes consisting primer amino group from thiophene derivatives were synthesized. •
- Effects of substituent, solvent and pH on absorption spectra of dyes were studied. •
- Tautomeric behavior of the dyes was investigated by spectroscopic techniques. •

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