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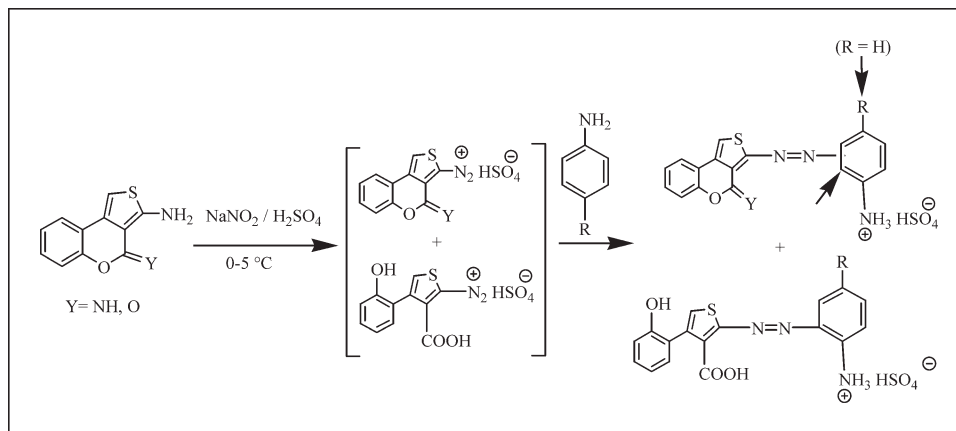
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Dedicated to the memory of Professor Zacharias TANEE FOMUM.



The coupling reactions of two diazotized 3-aminothieno[3,4-c]coumarins were investigated. Compounds **1a,b** both react with sodium nitrite in concentrated sulphuric acid at 0–5°C to give the diazotized intermediates **2** and **3**, the latter resulting from the acid-catalyzed hydrolysis of the lactonic ring of **2**. The *in situ* formed diazonium salts react with aromatic amines (**4**) to afford a series of arylazothiophenes dyes in the form of their ammonium sulfate salts. With diazotized aniline, besides the normally expected phenylazothiophene **10** from the reaction with compound **1a**, the corresponding product of acid hydrolysis **11** was also isolated. In at least one of the cases, the thienyl diazonium salt **2** undergoes a Gomberg–Bachmann arylation reaction with *p*-nitroaniline to give the 2-arylthiophene **9**. The direct hydrolysis of compounds **1a,b** by concentrated sulphuric acid and subsequent oxidative dimerization of the primary product of acid hydrolysis led to compound **12**.

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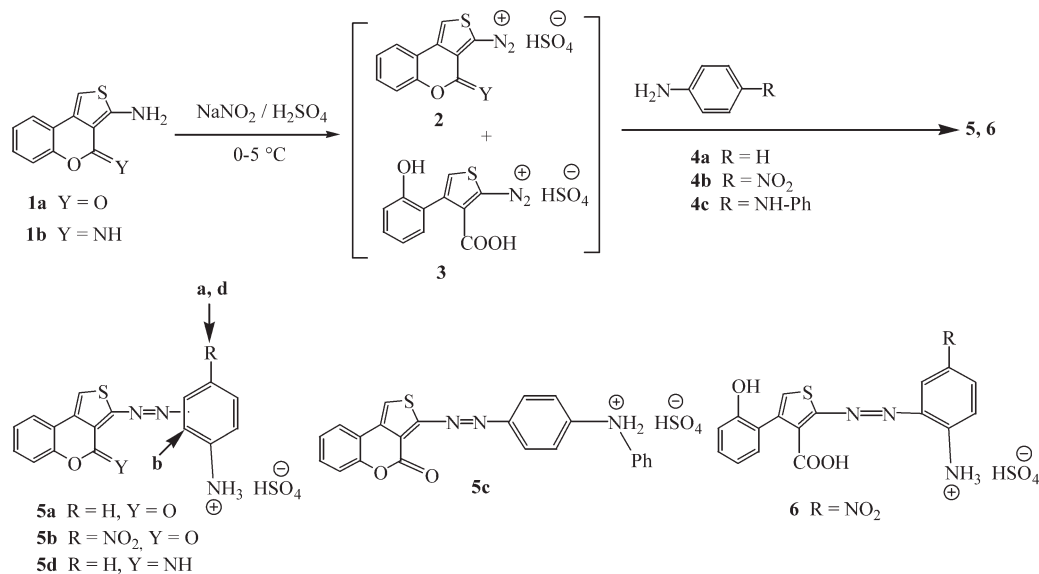
INTRODUCTION

The versatility of azo dyes in general is demonstrated by their wide applications in industry and photodynamic therapy as well as photosensitive species in photographic or electrophotographic systems. They are organic photoconductive materials [1] and have also found applications in cosmetics [2] and have shown a variety of interesting biological activities including antibacterial

[3–8], anti-inflammatory [9–11], anti-fungal [4], and pesticidal activities [12]. Azo compounds containing naphthalene rings have been reported to possess antimicrobial [13,14], HIV-1 integrase inhibitory effects [15], inhibitions of protein tyrosine kinases [16], and inactivation of enveloped viruses [17].

The chemistry of 2-aminothiophenes has received much attention due to their facile availability through

Scheme 1



the versatile Gewald's synthesis [18]. The importance of azothiophene dyes is demonstrated by the high number of publications and patents [19–21] dealing in one way or another with that class of dyestuffs. Besides their highly interesting dyeing properties, namely their high degree of brightness compared with azo dyes derived from anilines [22] and their excellent brightness of shade, 2-aminothiophene-based azo dyes are gaining more and more attention from medicinal chemists for their high pharmacological potentiality. [23] In this article, we report the reactions of diazonium sulfates generated from two 2-aminothieno[3,4-*c*]coumarins (**1a,b**) with some arylamines, as well as the reactions of diazotized aniline with compounds **1a,b**.

RESULTS AND DISCUSSION

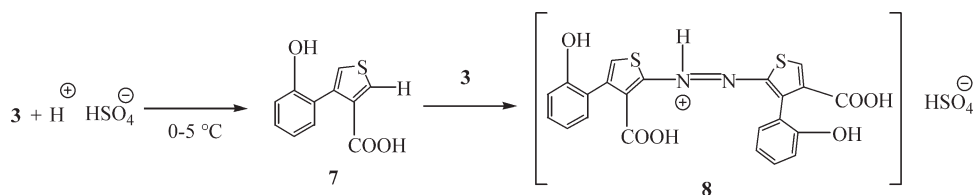
The synthesis of the thienocoumarins **1a,b** from the multicomponent condensation of ketones, cyanoacetate, and elemental sulfur was originally published by Ried and Nyiondi-Bonguen [24]. Diazotization in concentrated acid is used for the preparation of the diazo component, because hydrolysis of the diazonium salt occurs in dilute acid. Here, the acid of choice was concentrated sulphuric acid. The amine component was diazotized

satisfactorily at 0–5°C. The end point of diazotization was checked by thin layer chromatography (TLC), to detect the presence of unreacted amine in the diazotization mixture. Both thienocoumarins **1a,b** led to the diazonium salt solutions of **2** and **3**, respectively. Subsequent coupling reactions took place readily on adding arylamines such as aniline (**4a**), *p*-nitroaniline (**4b**), and diphenylamine (**4c**), affording compounds **5** and **6** (Scheme 1) in good yields. In concentrated sulphuric acid, the imino function of **1b** undergoes hydrolysis in some cases to yield compound **1a**, which is then further hydrolyzed and diazotized to afford the intermediary compounds **2** and **3**. These intermediates subsequently react with the aromatic amines to give the isolated products.

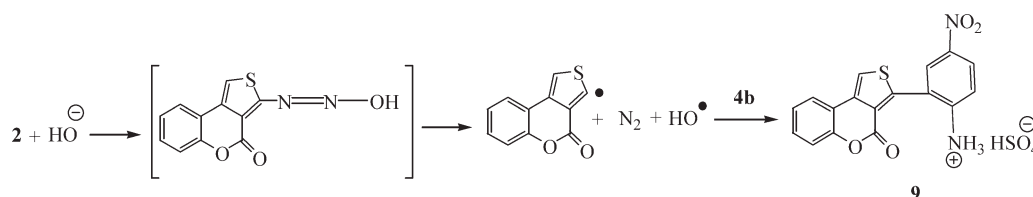
On attempting to induce a reaction between **2** or **3** with β -naphthol, it was found that no coupling reaction occurred as anticipated between the two components. Instead, the symmetrical product **8** was isolated from this reaction, probably from a two-step process between two molecules of **3** as displayed in Scheme 2.

The structure of compound **8** is supported by a characteristic ion fragment on the HREIMS at *m/z* 247 corresponding to C₁₁H₇O₃N₂S. The presence of the COOH groups is confirmed in the ¹³C-NMR spectrum by a low

Scheme 2



Scheme 3



field signal at 184.16 ppm. The spectrum also contains 10 other signals among which five (120.00, 114.80, 128.89, 125.45, and 117.12 ppm) could be assigned to tertiary C—H aromatic carbons and the other five to the quaternary carbon atoms by comparing the measured values with the simulated ones.

Structure **8** and the structures of all the other hydrolysis products containing free phenolic —OH groups were further confirmed by a positive ferric chloride phenol-enol test [25,26], showing the presence of free phenolic hydroxyl groups in the molecules.

Compound **5a** crystallizes with a molecule of sulphuric acid. The presence of two characteristic doublets at $\delta_{\text{H}} = 8.83$ (d, $J = 6.39$ Hz) and $\delta_{\text{H}} = 8.09$ (d, $J = 6.40$ Hz) on the ^1H -NMR spectrum suggests that the coupling reaction took place at the *para*-position of aniline.

The reaction of diazotized **1a** with **4b** gave the coupling product **5b** (Scheme 1) and the Gomberg–Bachmann [27] arylation product **9** (Scheme 3). The aromatic region (7.4–8.8 ppm) of the ^1H -NMR spectrum of compound **5b** contains four sets of multiplets with the integral ratio 3:2:2:1 corresponding to the eight available aromatic protons. The presence of a singlet at 8.73 ppm suggests that the coupling reaction occurs at the *ortho*-position of the amine function. The signals of the HSO_4^- and NH_3^+ protons could be seen as D_2O -exchangeable broad singlets around 14.34 and 7.88 ppm, respectively. The ^{13}C -NMR spectrum contains exactly 17 relevant signals out of which eight (116.98, 118.14, 125.33, 125.44, 127.14, 128.93, 135.29, and 135.53 ppm) were assigned to the tertiary aromatic C—H based on the DEPT-90/135 experiments. The remaining nine signals were assigned without ambiguity to the nine quaternary C-atoms by comparing the measured values with the calculated ones.

The decomposition that often accompanied the coupling reaction could explain the formation of the Gomberg–Bachmann product **9** as a result of a thienyl-aryl coupling via the diazonium salt **2** (Scheme 3).

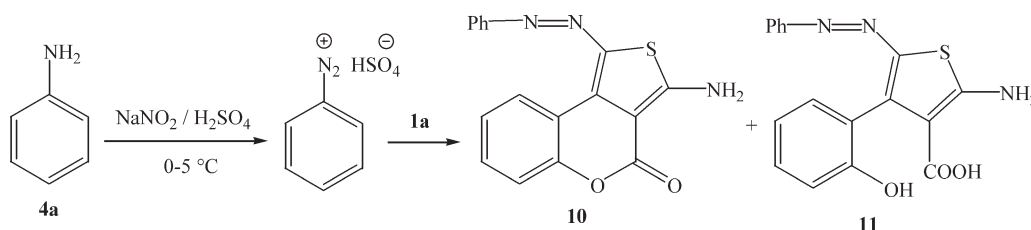
The structure of compound **9** is strongly supported by its elemental analysis and its HREIMS, which shows the molecular ion peak at $m/z = 436$. The absence of the diazo bridge in **9** was further confirmed on the FTIR spectrum by the absence of the characteristic —N=N— stretching bands in the range 1500–1400 cm^{-1} . On the ^1H -NMR spectrum, besides the set of four multiplets appearing between 7.47 and 8.75 ppm attributable to the eight aromatic protons, two broad D_2O -exchangeable signals were observed around 14.35 and 3.36 ppm and assigned to the HSO_4^- and NH_3^+ protons, respectively.

The presence of two doublets around 8.73 and 7.86 ppm in the ^1H -NMR spectrum of compound **5c**, clearly indicates that the electrophilic substitution took place at the *para*-position of **4c**. Here too the characteristic signals of the HSO_4^- and NH_3^+ protons could be seen as D_2O -exchangeable broad singlets around 14.34 and 8.22 ppm, respectively. Between 6.81 and 7.49 ppm were observed a broad base D_2O -exchangeable massif combined with four sets of multiplets that could be assigned to the thiophenic and the other nine aromatic protons.

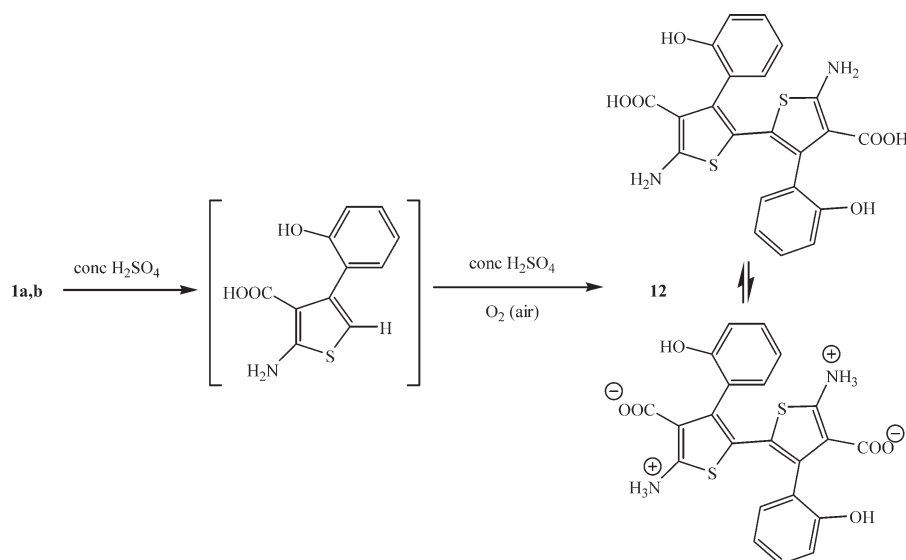
The structures of compounds **5d** and **6** were assigned based on their analytical and spectral data similarly as above.

Diazotized aniline (**4a**) reacted with compound **1a** to give two products identified as **10** and **11** (Scheme 4); their structures were in agreement with their analytical and spectral data. Compound **10** was reported earlier by other authors [28], as resulting from the coupling of the phenyl diazonium chloride and **1a**.

Scheme 4



Scheme 5



The absence of the characteristic 5-H thiophenic singlet around 6.80 ppm in the ^1H -NMR spectrum was an undeniable proof that in the formation of these compounds, the coupling took place at the unsubstituted 5-position of the thiophene ring.

From the coupling reactions of the diazotized intermediates **2** and **3**, a compound **12** was isolated. Its structure (Scheme 5) was assigned based on the spectroscopic data.

The coexistence of the two tautomeric forms in the solid state was proven in the solid state FTIR spectrum by the presence of the stretching band of the carbonyl function of the free COOH group at $\nu = 1759\text{ cm}^{-1}$ and that of the associated COO^- at $\nu = 1693\text{ cm}^{-1}$. The combined stretching frequencies of both free and combined $-\text{OH}$, $-\text{NH}-$, and COOH functions appeared as a complex band between 2664 and 3254 cm^{-1} . In solution, however, the compound exists solely in the covalent form. The sample homogeneity is evidenced by the ^1H and ^{13}C (^1H)-NMR experimental data. The amino protons resonated as a broad D_2O -exchangeable singlet around 8.64 ppm, besides the signals of the aromatic protons displayed as a set of multiplets (8.21–8.38, 8.61–8.67, and 9.49–9.55). The ^{13}C (^1H)-NMR experiment exhibited exactly 11 signals, among which a downfield signal at 184.18 ppm is assigned to the two COOH groups. The presence of the eight tertiary aromatic CH carbon atoms was confirmed by the DEPT-90/135 experiments, which showed four signals at 117.10, 125.44, 128.83, and 135.55 ppm. The mass spectrum of compound **12** showed fragments ions at m/z 379.2; 347.2; 331.3; 301.3 and 299.2, which could be assigned to $\text{M}^+ + \text{H} - 2\text{CO}_2 - \text{H}_2$; $\text{M}^+ + \text{H} - 2\text{CO}_2 - \text{H}_2\text{S}$; M^+

$-\text{C}_6\text{H}_5\text{O}-\text{CO}_2$; $\text{M}^+ - \text{C}_6\text{H}_5\text{O}-\text{CO}_2-\text{H}_2-\text{N}_2$ and $\text{M}^+ - \text{C}_6\text{H}_5\text{O}-\text{CO}_2-2\text{NH}_2$, respectively.

CONCLUSIONS

Diazotization of compounds **1** under concentrated sulphuric acid conditions is often accompanied with the hydrolysis of the imino function (**1b**) into the oxo functionality (in **1a**) followed in both cases by the hydrolysis of the lactonic ring to afford a mixture of 4 (2-hydroxyphenyl)-thiophene-3-carboxylic acid and the corresponding thienyl diazonium sulfate. Subsequent coupling of these intermediates with arylamines or their diazonium sulfates led to symmetric or mixed azo dyes. The formation of thienyl-aryl products in some cases is the evidence that couplings are usually accompanied by alternative reaction. On the 2-aminothiophenes' components, the substitution was regiospecifically oriented on the unsubstituted 5-position of the thiophene ring, whereas on the arylamines' components, the orientation of the regiospecific substitutions followed the Hollemann rules [29].

EXPERIMENTAL

All melting points are uncorrected and were determined with a Reichert Thermovar Microscope and a Büchi 530 melting point apparatus. The IR spectra were measured with a SHIMADZU FTIR-8400S and a Perkin Elmer FTIR 2000 spectrometers. The UV spectra were recorded with a Beckman U-640 spectrophotometer. Combustion analyses were carried with Yanaco CHN corder MT-6 (Yanaco Analytical Instruments, Kyoto, Japan). HREIMS and EIMS (direct inlet 70 eV) were

measured on Jeol JMS AX-500 and AX-700 spectrometers. ^1H and ^{13}C -NMR spectra were recorded in DMSO- d_6 with a Jeol JNM ECA-600 and AL-400 spectrometers with TMS and/or the residual solvent signals as internal references. Coupling constants J in brackets are reported in Hertz. Simulated ^1H and ^{13}C (^1H)-NMR spectra were performed with an ACD-NMR-spectra simulation programme and with Chemdraw software.

Reagents and starting materials. All the reagents mentioned in this work were purchased from Aldrich and Fluka and were used without further purification. Starting materials **1a,b** have been prepared according to literature procedures as published earlier [18,30–32].

Preparation of diazonium salt solution. Dry sodium nitrite (2.07 g, 3 mmol) was slowly added over a period of 30 min to concentrated sulphuric acid (10 mL) with occasional stirring. The solution was cooled to 0–5°C. Compounds **1a,b** and **4a** were dissolved in DMSO (10 mL) and cooled to 0–5°C. The nitrosyl sulphuric acid solution was added to the solution of **1a,b** and **4a**, and the temperature was maintained to 0–5°C. The clear diazonium salt solution thus obtained was used immediately in the coupling reactions.

(4H)-2-(p-Aminophenylazo)thieno[3,4-c]chromen-4-one hydrogen sulfate (5a). Aniline (0.279 g; 3 mmol) was cooled in an ice-bath at 0–5°C. The diazonium solution **2** previously prepared was added drop wise over 1 h, and then 15 mL sodium acetate solution (10%) was added in the mixture. The solid material was collected on a filter and crystallized from methanol to give the title compound **5a** (13.6 mg, 11%) as a red powder mp 244–246°C; IR (potassium bromide): 3936, 3880, 3830, 3674, 2966, 2925, 1772, 1627, 1488, 1419 cm^{-1} ; λ_{max} (THF) (log ϵ) 203 (4.36), 213 (4.35), 237 (4.77), 267 (4.84), 283 (4.75), 302 (4.07), 359 nm (3.88); ^1H -NMR (DMSO- d_6 , 300 MHz) δ 8.83 (d, 2H, 2'-H and 6H, $J = 6.4$ Hz), 8.09 (d, 2H, 3'-H and 5'-H, $J = 6.4$ Hz), 8.09 (broad s, 3H, NH_3^+ , deuterium oxide-exchangeable), 7.98 (s, 1H, 1-H), 7.39 (d, 1H, 9-H, $J = 8.2$ Hz), 7.28 (dd, 1H, 8-H, $J = 6.4, 8.2$ Hz), 7.19 (dd, 1H, 7-H, $J = 6.4, 7.3$ Hz), 7.13 (d, 1H, 6-H, $J = 8.2$ Hz); ms: (EI) m/z (%) 540 (5), 499 (3), 457 (27), 398 (5), 339 (10), 291 (1), 259 (7), 120 (49). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_6\text{S}_2$: C, 48.68; H, 3.12; N, 10.02. Found C, 48.76; H, 3.28; N, 9.98.

(4H)-2-(p-Amino-5-nitrophenylazo)thieno[3,4-c]chromen-4-one hydrogen sulfate (5b). *Para*-nitroaniline (414 mg, 3 mmol) was dissolved in DMSO (10 mL) and then cooled in an ice-bath at 0–5°C. The diazonium solution **2** previously prepared was added dropwise over 1 h, and then 15 mL sodium acetate solution (10%) was added to the mixture. The solid material that was formed was crystallized from hot water to give the title compound **9** (601 mg, 46 %) as a red powder. Crystallization of the solid residue from aqueous ethanol gave the title compound **5b** (465 mg, 33%) as orange powder, mp 233–234°C; IR (potassium bromide) 3552, 3533, 3012, 2825, 2802, 2717, 2538, 1726, 1679, 1498 cm^{-1} ; λ_{max} (THF) (log ϵ) 203 (4.45), 213 (4.44), 235 (4.80), 273 (4.83), 282 (4.84), 325 (4.38), 382.0 (4.13), 387 (4.11), 471 nm (3.44); ^1H -NMR (DMSO- d_6 , 300 MHz) δ 14.34 (broad s, 1H, HSO_4^- , deuterium oxide-exchangeable), 8.73 (d, 1H, 4'-H, $J = 8.2$ Hz), 8.73 (s, 1H, 6'-H), 7.99 (d, 1H, 3'-H, $J = 8.2$ Hz), 7.88 (broad s, 3H, NH_3^+ , deuterium oxide-exchangeable), 7.83 (ddd, 1H, 7-H, $J = 1.8, 6.4, 7.3$ Hz), 7.82 (dd, 1H, 9-H, $J = 1.8, 8.2$ Hz), 7.79 (dd, 1H, 6-H, $J = 1.8, 5.5$ Hz), 7.56 (s, 1H, 1-H), 7.52 (ddd, 1H, 8-H, $J = 1.8, 6.4, 8.2$ Hz); ^{13}C (^1H)-NMR (DMSO-

d_6 , 300 MHz) δ 163.6 (C-4), 156.7 (C-9b), 154.9 (C-3a), 152.72 (C-5a), 147.86 (C-5'), 135.53 (C-3), 135.29 (C-2'), 128.93 (C-7), 128.93 (C-9a), 128.93 (C-3'), 127.14 (C-9), 127.14 (C-1'), 125.45 (C-8), 125.33 (C-4'), 125.33 (C-6'), 118.14 (C-6), 116.98 (C-1); ms: (EI) m/z (%) 530 (1), 477 (1), 449 (5), 402 (1), 367 (1), 321 (1), 291 (2), 255 (1). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{12}\text{N}_4\text{O}_8\text{S}_2$: C, 43.96; H, 2.60; N, 12.06. Found C, 44.07; H, 2.58; N, 12.19.

(4H)-2-(p-N-Phenylaminophenylazo)thieno[3,4-c]chromen-4-one hydrogen sulfate (5c). Diphenylamine (507 mg, 3 mmol) was dissolved in DMSO (10 mL) and then cooled in an ice-bath at 0–5°C. The diazonium solution **3** previously prepared was added dropwise over 1 h, and then 15-mL sodium acetate solution (10%) was added to the mixture. Crystallization from methanol gave the title compound **5c** (564 mg, 37%) as a yellow powder, mp 236–238°C; IR (potassium bromide): 3371, 3259, 3205, 3176, 2731, 2135, 1965, 1755, 1733, 1672, 1494, 1446, 1406 cm^{-1} ; λ_{max} (THF) (log ϵ) 204 (4.24), 213 (4.26), 235 (4.61), 272 (4.65), 282 (4.65), 325 (4.16), 389 nm (3.88); ^1H -NMR (DMSO- d_6 , 300 MHz) δ 14.34 (broad s, 1H, HSO_4^- , deuterium oxide-exchangeable), 8.73 (d, 2H, 2'-H and 6'-H, $J = 7.3$ Hz), 8.68 (d, 2H, 2''-H and 6''-H, $J = 7.8$ Hz), 8.22 (broad s, 1H, NH_2^+ , deuterium oxide-exchangeable), 7.86 (d, 2H, 3'-H and 5'-H, $J = 7.3$ Hz), 7.50 (d, 1H, 9-H, $J = 8.2$ Hz), 7.21 (dd, 2H, 3''-H and 5''-H, $J = 6.4, 7.3$ Hz), 7.21 (dd, 1H, 4''-H, $J = 7.3, 6.4$ Hz), 7.10 (dd, 1H, 8-H, $J = 9.1, 9.2$ Hz), 7.04 (m, 7-H, 1H), 6.82 (d, 1H, 6-H, $J = 8.2$ Hz), 6.80 (s, 1-H, 1H); ms: (EI) m/z (%) 356 (11), 337 (22), 296 (7), 240 (7), 205 (1), 183 (100). *Anal.* Calcd. for $\text{C}_{23}\text{H}_{17}\text{N}_3\text{O}_6\text{S}_2$: C, 55.75; H, 3.46; N, 8.48. Found C, 55.81; H, 3.53; N, 8.41.

(4H)-4-Imino-2-(p-aminophenylazo)thieno[3,4-c]chromen hydrogen sulfate (5d). The reaction mixture of the diazonium sulfate of **1b** with **4a** was worked up as above to afford the title compound **5d** (349 mg, 27%) as a red powder, mp > 230°C; IR (potassium bromide): 3652, 3203, 3178 (NH), 3047 (arom. C—H), 2918, 1448, 1404 cm^{-1} ; λ_{max} (THF) (log ϵ) 204 (4.23), 217 (4.26), 236 (4.64), 269 (4.71), 283 (4.66), 474 nm (3.76); ^1H -NMR (DMSO- d_6 , 300 MHz) δ 9.30 (broad s, 1H, =NH, deuterium oxide-exchangeable), 8.96 (broad s, 1H, HSO_4^- , deuterium oxide-exchangeable), 7.75 (s, 1H, thiophenic proton), 7.62 (m, 2H, aromatic protons), 7.45 (m, 2H, aromatic protons), 7.40 (m, 2H, aromatic protons), 7.25 (m, 2H, aromatic protons), 7.17 (broad s, 3H, NH_3^+ , deuterium oxide-exchangeable); ms: (EI) m/z (%) 512 (1), 418 (M+, 1), 402 (7), 367 (7), 330 (11), 301 (2), 243 (4), 169 (1). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_5\text{S}_2$: C, 48.80; H, 3.35; N, 13.40. Found C, 49.02; H, 3.45; N, 13.54.

2-(2-Amino-5-nitrophenylazo)-4-(2-hydroxyphenyl)-thiophene-3-carboxylic acid hydrogen sulfate (6). *para*-Nitroaniline (414 mg; 3 mmol) was dissolved in DMSO (10 mL) and then cooled in an ice-bath at 0–5°C. The diazonium solution **3** previously prepared was added dropwise over 1 h, and then 15-mL sodium acetate solution (10%) was added to the mixture. Crystallization of the resulted solid material from aqueous ethanol gave the title compound **6** (144 mg, 10%) as a red powder, mp 190–192°C; IR (potassium bromide): 3290, 3269, 3236, 2914, 2804, 2705, 2667, 1733, 1676, 1602, 1444 cm^{-1} ; λ_{max} (THF) (log ϵ) 203 (4.53), 213 (4.52), 239 (5.04), 268 (4.99), 286 (4.98), 325 (5.18), 448 (4.16), 553 nm (3.48); ^1H -NMR (DMSO- d_6 , 300 MHz) δ 8.92 (dd, 1H, 4''-H, $J = 1.4,$

1.3 Hz), 7.66 (s, 1H, 6''-H), 7.64 (broad s, 3H, NH_3^+ , deuterium oxide-exchangeable), 7.30 (d, 1H, 6'-H, $J = 1.2$ Hz), 7.27 (dd, 1H, 4'-H, $J = 1.2, 6.7$ Hz), 7.24 (dd, 1H, 5'-H, $J = 1.2, 6.3$ Hz), 7.23 (d, 1H, 3'-H, $J = 1.2$ Hz), 7.22 (d, 1H, 3''-H, $J = 1.2$ Hz), 7.19 (s, 1H, 5-H); ^{13}C (^1H)-NMR (DMSO- d_6 , 300 MHz) δ 184.3 (COOH), 154.9 (C-2'), 153.4 (C-3), 153.4 (C-2''), 147.3 (C-4), 135.4 (C-5''), 135.2 (C-2), 128.9 (C-4'), 128.9 (C-6'), 125.4 (C-5), 125.4 (C-4''), 125.4 (C-6''), 125.3 (C-1'), 119.9 (C-1''), 117.1 (C-5'), 116.9 (C-3''), 114.9 (C-3'); ms: (FAB+) m/z (%) 384 (1), 383 (1), 307 (60), 429 (11), 248 (100), 154 (91). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_9\text{S}_2$: C, 42.32; H, 2.92; N, 11.61. Found: C, 42.25; H, 3.01; N, 11.69.

Azo bis[4-(2-hydroxyphenyl)-thiophene-3-carboxylic acid-2-yl](8). β -Naphthol (0.384 g; 3 mmol) was dissolved in DMSO (10 mL) and then cooled in an ice-bath at 0–5°C. The diazonium solution **3** previously prepared was added dropwise over 1 h, and then 15 mL of sodium acetate solution (10%) was added in the mixture. The solid precipitate was filtered and crystallized from methanol to give the title compound **8** (31.3 mg, 20%) as yellow powder mp > 230°C; IR (potassium bromide): 3807, 3484, 2299, 1750, 1726, 1444; λ_{max} (THF) (log ϵ) 203 (4.60), 215 (4.59), 234 (4.92), 276 (4.94), 281 (4.96), 325 (4.61), 385 nm (4.34); ^1H -NMR (DMSO- d_6 , 300 MHz) δ 14.38 (broad s, 1H, COOH, deuterium oxide-exchangeable); 8.70 (dd, 1H, 3'-H, $J = 0.9$ and 6.00 Hz); 8.05 (broad s, 1H, NH, deuterium oxide-exchangeable); 7.85 (ddd, 1H, 4'-H, $J = 0.9, 5.4$ and 6.3 Hz); 7.60 (s, 2H, 5-H), 7.51 (ddd, 2H, 5'-H, $J = 0.9, 5.4, 10.8$ Hz), 7.31 (d, 2H, 6'-H, $J = 6.6$ Hz), 6.98 (broad s, 2H, OH, deuterium oxide-exchangeable); ^{13}C (^1H)-NMR (DMSO- d_6 , 300 MHz) δ 184.1 (COOH), 154.9 (C-2'), 153.8 (C-3), 153.4 (C-1'), 147.7 (C-4), 135.5 (C-2), 128.8 (C-6'), 125.4 (C-5), 120.0 (C-5'), 117.1 (C-3'), 114.8 (C-4'); ms: (EI) m/z (%) 364 (2), 402 (1), 248 (12), 247 (100), 231 (40), 214 (12), 203 (14), 189 (24), 144 (28), 77 (10). *Anal.* Calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_{10}\text{S}_3$: C, 46.80; H, 2.86; N, 4.96. Found C, 46.65; H, 2.88; N, 4.80.

(4H)-2-(2-Amino-5-nitrophenyl) thieno [3,4-c]chromen-4-one hydrogen sulfate(9). mp 238–239°C; IR (potassium bromide) 3556, 3351, 3105, 3001, 2794, 2700, 2690, 2599, 1728, 1679 cm^{-1} ; λ_{max} (THF) (log ϵ) 203 (4.39), 213 (4.38), 239 (4.90), 267 (4.85), 286 (4.84), 324 (4.86), 383 nm (4.44); ^1H -NMR (DMSO- d_6 , 300 MHz) δ 14.35 (broad s, 1H, HSO_4^- , deuterium oxide-exchangeable), 8.02 (d, 1H, 4'-H, $J = 1.1$ Hz), 8.01 (d, 1H, 3'-H, $J = 1.5$ Hz), 7.85 (ddd, 1H, 7-H, $J = 1.5, 8.3, 11.8$ Hz), 7.78 (ddd, 1H, 8-H, $J = 1.5, 9.4, 11.9$ Hz), 7.78 (d, 1H, 6-H, $J = 9.5$ Hz), 7.55 (s, 1H, 6'-H), 7.49 (d, 1H, 9-H, $J = 1.1$ Hz), 7.46 (s, 1H, 1-H), 3.36 (3H, NH_3^+ , deuterium oxide-exchangeable); ms: (EI) m/z (%) 436 (1), 425 (51), 392 (1), 362 (7), 310 (11), 268 (76), 235 (1), 228 (82), 201 (43), 186 (1), 121 (6), 157 (13). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_8\text{S}_2$: C, 46.79; H, 2.77; N, 6.42. Found: C, 46.69; H, 2.68; N, 6.51.

Preparation of 10 and 11. Compound **1a** (0.651 g; 3 mmol) was dissolved in DMSO (10 mL) and then cooled in an ice-bath at 0–5°C. The diazonium solution of **4a** previously prepared was added dropwise over 1 h, and then 15-mL sodium acetate solution (10%) was added to the mixture. The solid material that was formed, was filtered, and crystallized from hot water to afford the title compound **11** (370 mg, 26%) as a red powder. The solid residue was crystallized from methanol to yield the title compound **10** (388 mg, 40%) as a red powder.

(4H)-3-Amino-1-phenylazo-1-thienof[3,4-c]chromen-4-one(10). mp 238–239°C [lit. [28] 232–234°C from DMF/ethanol (5:3)]; IR (potassium bromide): 3207, 3107, 3062, 2896, 2875, 2845, 2580, 1874, 1731, 1683, 1488, 1404 cm^{-1} ; λ_{max} (THF) (log ϵ) 211 (3.67), 253 (4.11), 291 (3.89), 336 (3.66), 478 nm (4.12); ^1H -NMR (DMSO- d_6 , 300 MHz) δ 8.84 (dd, 1H, H-9, $J = 7.9, 1.4$ Hz), 7.74 (d, 1H, H-2' and H-6', $J = 7.4$ Hz), 7.59 (ddd, 1H, H-7, $J = 1.5, 7.7, 7.7$ Hz), 7.54 (dd, 1H, H-3' and H-5', $J = 7.5, 8.0$ Hz), 7.40 (d, 1H, H-4', $J = 7.4$ Hz), 7.45 (ddd, 1H, H-8, $J = 1.1, 7.7, 7.6$ Hz), 7.35 (dd, 1H, H-6, $J = 7.4, 8.3$ Hz); ^{13}C (^1H)-NMR (DMSO- d_6 , 300 MHz) δ 168.2 (C-3), 158.2 (C-4a), 152.6 (C-1' and C-8a), 151.9 (C-2), 134.9 (C-9), 133.0 (C-8b), 131.5 (C-7), 129.4 (C-3' and C-5'), 129.0 (C-6), 128.8 (C-8), 125.1 (C-4'), 121.7 (C-2' and C-6'), 117.2 (C-5), 117.0 (C-2a); ms: (EI) m/z (%) 321 (6), 280 (22), 247 (22), 208 (100), 190 (24). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$: C, 63.54; H, 3.45; N, 13.08. Found C, 63.43; H, 3.50; N, 13.15.

2-Amino-4-(2-hydroxyphenyl)-5-phenylazothiophene-3-carboxylic acid(11). mp 150°C; IR (potassium bromide): 3425, 3315, 3143, 3056, 3028, 1741, 1676, 1483, 1460 cm^{-1} ; λ_{max} (THF) (log ϵ) 203 (3.87), 212 (3.78), 220 (3.91), 247 (4.47), 258 (4.48), 288 (4.33), 345 (4.02), 461 (4.52), 471 nm (4.54). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_3\text{S}$: C, 60.18; H, 3.83; N, 12.39. Found: C, 60.05; H, 3.71; N, 12.46.

5,5'-Diamino-3,3'-bis-(2-hydroxyphenyl)-[2,2']bithiophenyl-4,4'-dicarboxylic acid (12). The reaction mixture of the diazonium sulfate of **1a** and **1b** was worked up as above to afford the title compound **12** (340 mg, 24%). Crystallization from methanol gave the title compound **12** as a brown powder, mp > 283°C; IR (potassium bromide): 3658, 3253, 3137, 2991, 2948, 2831, 2198, 1976, 1928, 1758, 1693 cm^{-1} ; λ_{max} (THF) (log ϵ) 204 (4.15), 213 (4.17), 234 (4.49), 274 (4.53), 281 (4.54), 301 (3.86), 364 (3.67), 527 nm (4.24); ^1H -NMR (DMSO- d_6 , 300 MHz) δ 15.20 (broad s, 2H, OH, deuterium oxide-exchangeable), 13.49 (broad s, 2H, COOH, deuterium oxide-exchangeable), 9.51 (dd, 2H, H-5', $J = 1.50, 8.10$ Hz), 8.64 (broad s, 2H, NH_2 , deuterium oxide-exchangeable), 8.32 (2H, ddd, J 1.0, 8.5, 5.4 Hz, H-3'), 8.29 (d, 2H, H-6', $J = 8.3$ Hz), 7.85 (dd, 2H, H-4', $J = 5.4, 6.3$ Hz), 7.60 (broad s, 2H, OH, deuterium oxide-exchangeable); ^{13}C (^1H)-NMR (DMSO- d_6 , 300 MHz) δ 184.2 (COOH), 154.9 (C-2'), 153.9 (C-2), 153.5 (C-5), 147.8 (C-4), 135.5 (C-6'), 128.8 (C-4'), 125.4 (C-5'), 120.0 (C-3), 117.1 (C-3'), 114.9 (C-1'); ms: (EI) m/z (%) 347 (1), 331 (1), 300 (2), 285 (1), 255 (4), 247 (12), 231 (1), 211 (3), 181 (4), 167 (7). *Anal.* Calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_6\text{S}_2$: C, 56.40; H, 3.44; N, 5.98. Found C, 56.49; H, 3.53; N, 5.85.

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