

SYNTHESIS OF AZO-DISPERSED DYES DERIVED FROM 2-(2-CYANOACETAMIDO)-4,5,6,7-TETRAHYDROBENZO- [b]THIOPHENE-3-CARBOXAMIDE

M.A. Gouda^{1,2}, H.F. Eldien¹, M.M. Girges¹, M.A. Berghot¹

¹ Department of Chemistry, Faculty of Science, Mansoura University, El-Gomhoria Street, Mansoura, 35516, Egypt.

² Department of Chemistry, Faculty of Science and Arts, Ulla, Taibah University, KSA
e-mail: dr_mostafa_chem@yahoo.com

Coupling of 2-(2-cyanoacetylamino)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxamide (**3**) or 2-[2-(5-oxo-3-phenylthiazolidin-2-ylidene)]-2-cyanoacetamido-4,5,7-tetrahydrobenzo[b]thiophene-3-carboximide (**6**) with various diazotized aryl amines in pyridine gave the corresponding aryl hydrazonopropionitrile derivatives. Some of the synthesized dyes were applied to polyester fabrics as dispersed dyes in which their colour measurements and fastness properties were evaluated.

Key words: *azo-dispersed dyes, thiophene-3-carboxamide, aryl diazonium chlorides, colour measurement and fastness properties.*

INTRODUCTION

2-Aminothiophenes have demonstrated a broad spectrum of uses including pharmaceuticals [1–3], dyes and agrochemical applications. Traditionally, poly-substituted 2-aminothiophenes are prepared *via* the Gewald reaction [4]. Furthermore, substituted cyanoacetamides are important intermediates in the synthesis of a variety of agrochemicals, dyes and pharmacologically active compounds [5]. In recent years, efforts have been made to replace certain an-thraquinone dyes with technically equivalent azo dyes for both the environmental and economic reasons [6]. In view of the above-mentioned findings and as continuation of our efforts [7, 8] to identify new candidates that may be of value in designing new azo-dispersed dyes, we report herein the synthesis of some new azo-dispersed dyes derived from 2-(2-cyanoacetamido)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxamide [9].

EXPERIMENTAL

All melting points were determined on *Gallenkamp* electric melting point apparatus. TLC analysis was carried out on silica gel 60 F₂₅₄ precoated aluminum sheets. Infrared spectra were recorded on *Mattson 5000* FTIR spectrometer (λ , cm^{-1}) using potassium bromide *Wafer* technique at the Microanalytical Unit, Faculty of Science, Mansoura University. The ¹H NMR spectra were determined on a *Varian XL* 200 MHz apparatus at the Microanalytical Center (Cairo University, Giza, Egypt) using CDCl_3 or DMSO as solvents and TMS as an internal standard. The mass spectra (EI) were recorded at 70 eV with *Kratos MS* equipment at the Microanalytical Center (Cairo University, Giza, Egypt). Elemental analysis (C, H and N) data were found to agree favorably with the calculated values and these analyses were carried out at

the Microanalytical Center (Cairo University, Giza, Egypt). The dyeing assessment, fastness tests, colour measurements were carried out in El-Nasr Company for Spinning and Weaving El-Mahalla El-Kubra, Egypt. Thiophene derivatives **6**, **7b** and **8** were prepared according to the previously reported methods [9].

Synthesis of 2-(2-cyanoacetylarnino)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide (3). A mixture of compound **1** (2.7 g, 14 mmol) and 3-(3,4-dimethyl-1*H*-pyrazol-1-yl)-3-oxopropanenitrile (2.39 g, 14 mmol) in benzene (20 ml), was refluxed for 5 h. The solvent was evaporated under vacuum and the residue was crystallized from ethanol to give carboxamide **3** white powder; yield 90%; m.p. 172 °C [7], m.p. 175 °C.

Synthesis of 2-(2-arylhydrazone)-2-cyanoacetamido)-4,5,7-tetrahydrobenzo[*b*]thiophene-3-carboximides (4a-4e) and 2-[2-(4-(arylhydrazone)-5-oxo-3-phenylthiazolidin-2-ylidene)-2-cyanoacetamido)-4,5,7-tetrahydrobenzo[*b*] thiophene-3-carboximides (7a-7e)

General procedure. A well-stirred solution of aromatic amine (0.005 mol) in 1.2 ml of concentrated HCl and 2 ml of H₂O was cooled in ice bath and diazotized with the solution of 0.4 g of NaNO₂ (0.0058 mol) in 2 ml of H₂O. The cold diazonium solution was added slowly to a well-stirred solution of compound **3** (2.63 g) or **6** (2.248 g) in pyridine (15 ml). The reaction mixture was stirred for another 2 h. The crude product was filtered off, dried well and recrystallized from EtOH/benzene to give carboxamides **4a-4e** and **7a-7e**.

Compound **4c** was prepared by another route using *p*-anisidine (0.615 g, 0.005 mole) as aromatic amine and compound **8** (1.99 g, 0.005 mol) instead of compound **3**.

2-(2-Phenylhydrazone)-2-cyanoacetamido)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide (4a). Yellow powder; yield 2 g (95%); m.p. 306 °C; IR spectrum (KBr): ν/cm^{-1} = 3401; 3316; 3227; 3193 (NH₂, 2NH); 2232 (CN); 1662; 1631 (CO), 1496 (N=N). ¹H NMR spectrum (200 MHz, DMSO-*d*₆) δ (ppm): 1.68–1.76 (m, 4H, C₅-2H, C₆-2H); 2.65–2.76 (m, 4H, C₄-2H, C₇-2H); 7.13–7.68 (m, 7H, Ar-H, NH₂); 12.28 (br, s, 1H, NHCO); 12.93 (br, 1H, NH, hydrazo).

MS (EI, 70 ev) *m/z* (%) = 369 (M⁺+2; 3.4); 368 (M⁺+1; 10.5); 367 (M⁺, 44.3); 351 (5.5); 350 (23.7); 321 (8.2); 307 (1.7); 294 (3.1); 258 (6.0); 245 (18.2); 206 (11.7); 179 (30.0); 151 (14.8); 116 (6.1); 105 (33.0); 92 (27.9);, 77 (100.0); 65 (36.0).

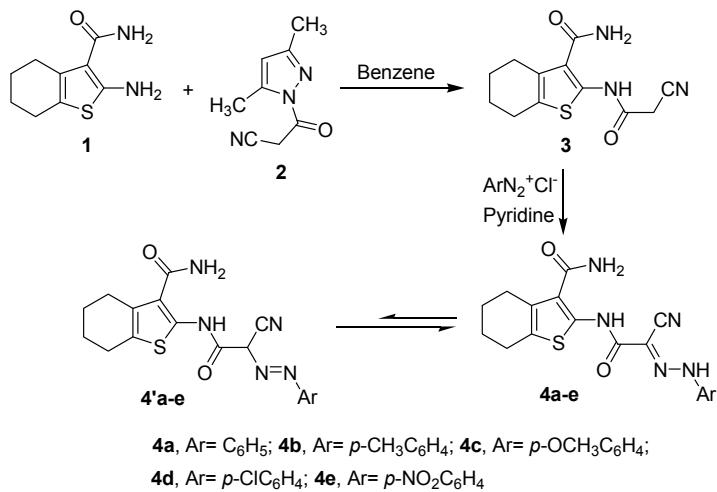
Elemental analysis data. Calculated for C₁₈H₁₇N₅O₂S (367.11), %: C, 58.84; H, 4.66; N, 19.06. Found, %: C, 58.91; H, 4.72; N, 19.13.

2-(2-(2-*p*-Tolylhydrazone)-2-cyanoacetamido)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide (4b). Yellow crystals; yield 1.9 g (90%); m.p. 285°C; IR spectrum (KBr), ν , cm^{-1} = 3355; 3309; 3226; 3191 (NH₂, 2NH); 2213 (CN); 1656; 1645 (2CO); 1486 (N=N). ¹H NMR spectrum (200 MHz, DMSO-*d*₆) δ (ppm): 1.66–1.81 (m; 4H; C₅-2H; C₆-2H); 2.30 (s, 3H, CH₃); 2.63–2.76 (m, 4H, C₄-2H, C₇-2H); 7.18–7.58 (m, 6H, Ar-H, NH₂); 12.52 (br, s, 1H, NHCO); 12.90 (br, 1H, NH, hydrazo).

MS (EI; 70 ev) *m/z* (%) = 383 (M⁺+2; 2.6); 382 (M⁺+1; 8.1); 381 (M⁺, 33.4); 364 (22.9); 331 (5.1); 321 (2.0); 308 (1.9); 293 (0.7); 280 (0.4); 245 (7.2); 223

(1.8); 206 (8.7); 179 (24.7); 151 (10.7); 119 (20.1); 106 (23.9); 91 (100.0); 77 (22.6); 65 (9.9).

Elemental analysis data. Calculated for $C_{19}H_{19}N_5O_2S$ (381.13), %: C, 59.82; H, 5.02; N, 18.36. Found: C, 59.87; H, 5.11; N, 18.46%.



Scheme 1. Synthesis of 2-arylhyclazo cyanoacetamides **4a–e**.

2-(2-(4-Methoxyphenyl)hydrazone)-2-cyanoacetamido-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxamide (4c). Brown powder; yield 1 g (83%); m.p. 247 °C; IR spectrum (KBr), ν , cm^{-1} = 3391; 3324; 3197 (NH₂, 2NH); 2218 (CN); 1646 (br, 2CO); 1464 (N=N). ¹H NMR spectrum (200 MHz, DMSO-*d*₆) δ (ppm): 1.69–1.75 (m, 4H, C₅-2H, C₆-2H); 2.63–2.74 (m, 4H, C₄-2H, C₇-2H); 3.79 (s, 3H, OCH₃); 6.95–7.64 (m, 6H, Ar-H, NH₂); 12.22 (br, s, 1H, NHCO); 12.89 (br, 1H, NH, hydrazone).

MS (EI, 70 ev) m/z (%) = 399 (M⁺+2; 1.5); 398 (M⁺+1; 4.2); 397 (M⁺; 12.1); 380 (16.9); 369 (8.8); 358 (9.4); 339 (8.6); 313 (8.2); 294 (6.7); 274 (5.5); 258 (6.7); 246 (11.2); 223 (94.0); 206 (61.1); 195 (4.1); 179 (57.4); 151 (49.7); 135 (100.0); 123 (50.6); 108 (73.6); 96 (68.5); 77 (53.7); 65 (44.1).

Elemental analysis data. Calculated for $C_{19}H_{19}N_5O_3S$ (397.12), %: C, 57.42; H, 4.82; N, 17.6%. Found, %: C, 57.33; H, 4.80; N, 17.57%.

2-(2-(4-Chlorophenyl)hydrazone)-2-cyanoacetamido-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxamide (4d). Brown powder; yield 1.2 g (80%); m.p. 307 °C; IR spectrum (KBr), ν , cm^{-1} = 3312; 3233; 3191; 3163 (NH₂, 2NH); 2219 (CN); 1659; 1645 (2CO); 1483 (N=N); 708 (C-Cl). ¹H NMR spectrum (200 MHz, DMSO-*d*₆) δ (ppm): 1.69–1.75 (m, 4H, C₅-2H, C₆-2H); 2.63–2.75 (m, 4H, C₄-2H, C₇-2H); 7.38–7.80 (m, 6H, Ar-H, NH₂); 12.38 (br, s, 1H, NHCO); 12.97 (br, 1H, NH, hydrazone).

MS (EI, 70 ev) m/z (%) = 403 (M⁺+2; 4.1); 402 (M⁺+1; 11.5); 401 (M⁺; 46.4); 384 (35.8); 351 (6.3); 342 (5.4); 328 (1.7); 306 (0.6); 293 (1.3); 275 (0.5); 258 (11.2); 245 (25.9); 230 (4.4); 206 (21.3); 194 (1.9); 179 (40.0); 151 (21.5); 139 (43.9); 113 (32.0); 111 (100.0); 91 (22.6); 79 (29.3); 65 (11.5).

Elemental analysis data. Calculated for $C_{18}H_{16}ClN_5O_2S$ (401.07), %: C, 53.80; H, 4.01; N, 17.43. Found, %: C, 53.85; H, 4.07; N, 17.49.

2-(2-(4-Nitrophenyl)hydrazone)-2-cyanoacetamido-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxamide (4e). Brown powder; yield 1.1 g (92%); m.p. 289 °C; IR spectrum (KBr), ν , cm^{-1} = 3411; 3316; 3264; 3208 (NH₂, 2NH); 2223 (CN); 1670; 1643 (2CO); 1515 (N=N); 1450; 1346 (NO₂). ¹H NMR spectrum (200 MHz, DMSO-*d*₆) δ (ppm): 1.70–1.75 (m, 4H, C₅-2H, C₆-2H); 2.63–2.75 (m, 4H, C₄-2H, C₇-2H); 7.82–8.27 (m, 6H, Ar-H, NH₂); 12.35 (br, s, 1H, NHCO); 13.15 (br, 1H, NH, hydrazo).

MS (EI, 70 ev) m/z (%) = 414 (M⁺+2; 5.2); 413 (M⁺+1; 16.5); 412 (M⁺; 67.7); 395 (52.1); 382 (2.5); 362 (8.7); 339 (2.7); 320 (3.0); 293 (1.3); 258 (29.2); 245 (39.2); 230 (9.4); 217 (10.9); 206 (28.8); 190 (4.2); 179 (32.4); 150 (26.8); 138 (6.6); 122 (100.0); 106 (10.7); 91 (28.2); 76 (13.8); 64 (20.3).

Elemental analysis data. Calculated for C₁₈H₁₆N₆O₄S (412.1), %: C, 52.42; H, 3.91; N, 20.38. Found, %: C, 52.51; H, 3.96; N, 20.47%.

2-(2-(4-Phenylhydrazone)-5-oxo-3-phenylthiazolidin-2-ylidene)-2-cyanoacetamido-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxamide (7a). Brown crystals; yield 0.5 g (70%); m.p. 218 °C; IR spectrum (KBr), ν , cm^{-1} = 3326; 3251; 3205; 3187 (NH₂, 2NH); 2200 (CN); 1726; 1641 (3CO); 1494 (N=N). ¹H NMR spectrum (200 MHz, DMSO-*d*₆) δ (ppm): 1.71–1.74 (m, 4H, C₅-2H, C₆-2H); 2.62–2.89 (m, 4H, C₄-2H, C₇-2H); 7.02–8.0 (m, 12H, Ar-H, NH₂); 11.35 (br, s, 1H, NHCO); 12.40 (br, 1H, NH, hydrazo).

MS (EI, 70 ev) m/z (%) = 538 (M⁺–4H; 1.3); 524 (1.0); 514 (1.6); 476 (2.6); 471 (3.8); 459 (2.0); 438 (8.9); 396 (4.8); 379 (4.4); 367 (30.6); 350 (18.3); 318 (17.0); 263 (8.9); 246 (21.1); 229 (17.8); 222 (75.0); 206 (34.9); 194 (14.3); 179 (100.0); 160 (10.0); 151 (71.5); 135 (94.4); 123 (93.7); 110 (50.4); 93 (41.9); 80 (17.0); 66 (46.5).

Elemental analysis data. Calculated for C₂₇H₂₂N₆O₃S₂ (542.12), %: C, 59.76; H, 4.09; N, 15.49. Found, %: C, 59.82; H, 4.16; N, 15.57.

2-(2-(4-(4-Methoxyphenyl)hydrazone)-5-oxo-3-phenylthiazolidin-2-ylidene)-2-cyanoacetamido-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxamide (7c). Reddish brown powder; yield 0.7 g (92%); m.p. 210 °C; IR spectrum (KBr), ν , cm^{-1} = 3382; 3336; 3249; 3216; 3193 (NH₂, 2NH); 2206 (CN); 1726, 1641 (3CO); 1494 (N=N). ¹H NMR spectrum (200 MHz, DMSO-*d*₆) δ (ppm): 1.69–1.73 (m, 4H, C₅-2H, C₆-2H); 2.63–2.89 (m, 4H, C₄-2H, C₇-2H); 3.73 (s, 3H, OCH₃); 6.93–7.95 (m, 11H, Ar-H, NH₂); 11.3 (br, s, 1H, NHCO); 12.35 (br, 1H, NH, hydrazo).

MS (EI, 70 ev) m/z (%) = 575 (M⁺+3; 0.4); 565 (0.8); 547 (3.5); 533 (1.3); 521 (1.1); 491 (3.1); 459 (6.5); 417 (5.5); 379 (5.3); 368 (9.8); 352 (6.3); 324 (6.4); 319 (12.7); 279 (14.3); 235 (12.6); 222 (36.9); 204 (12.4); 194 (17.7); 179 (66.4); 167 (37.9); 149 (95.1); 132 (12.7); 122 (49.9); 103 (16.3); 93 (93.9); 71 (69.8); 57 (80.3); 43 (100.0).

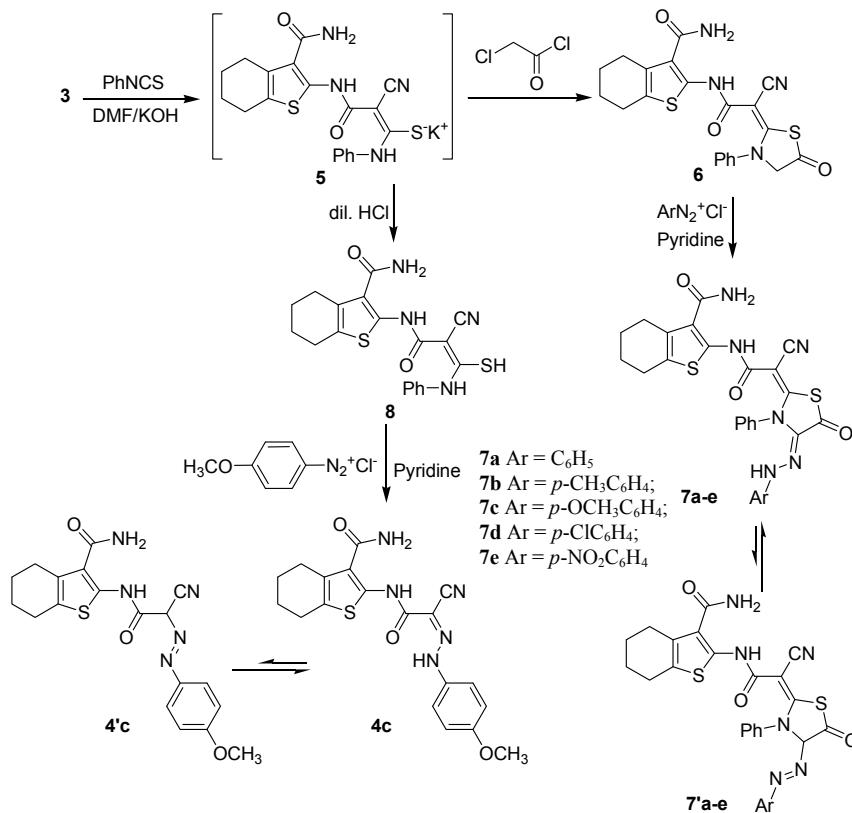
Elemental analysis data. Calculated for C₂₈H₂₄N₆O₄S₂ (572.13), %: C, 58.73; H, 4.22; N, 14.68. Found, %: C, 58.65; H, 4.17; N, 14.62%.

2-(2-(4-(4-Chlorophenyl)hydrazone)-5-oxo-3-phenylthiazolidin-2-ylidene)-2-cyanoacetamido-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxamide (7d). Reddish brown powder; yield 0.7 g (97%); m.p. 226 °C; IR spectrum (KBr), ν , cm^{-1} = 3401; 3309; 3254; 3227; 3159 (NH₂, 2NH); 2197 (CN); 1640, 1607 (3CO); 1483 (N=N). ¹H NMR spectrum (200 MHz, DMSO-*d*₆) δ (ppm):

1.69–1.74 (m, 4H, C₅-2H, C₆-2H); 2.67–2.89 (m, 4H, C₄-2H, C₇-2H); 7.31–7.94 (m, 11H, Ar-H, NH₂); 11.41 (br, s, 1H, NHCO); 12.78 (br, 1H, NH, hydrazo).

MS (EI, 70 ev) *m/z* (%) = 576 (M⁺ 0.3); 563 (0.3); 548 (0.3); 522 (0.3); 467 (0.3); 458 (0.5); 439 (0.5); 426 (0.6); 408 (0.4); 401 (5.8); 384 (5.4); 342 (1.1); 312 (6.5); 298 (10.9); 279 (9.8); 246 (6.4); 222 (15.5); 206 (16.7); 194 (6.8); 179 (22.3); 167 (31.3); 149 (100.0); 139 (15.9); 113 (25.1); 111 (40.1); 93 (51.6); 71 (32.8); 57 (47.8).

Elemental analysis data. Calculated for C₂₇H₂₁ClN₆O₃S₂ (576.08), %: C, 56.20; H, 3.67; N, 14.56. Found, %: C, 56.32; H, 3.74; N, 14.51.

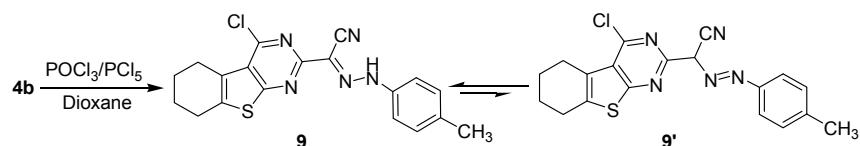


Scheme 2. Synthesis of 4-[arylhydrazone]-5-oxo-3-phenyl-thiazolidin-2-ylidine derivatives 7a–e.

2-(2-(4-(4-Nitrophenyl)hydrazone)-5-oxo-3-phenylthiazolidin-2-ylidene)-2-cyanoacetamido)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxamide (7e). Reddish brown powder; yield 0.6 g (80%); m.p. 230 °C; IR spectrum (KBr), ν , cm⁻¹ = 3378; 3322; 3228; 3172 (NH₂, 2NH); 2191 (CN); 1727; 1643 (2CO); 1492 (N=N); 1400; 1361 (NO₂). ¹H NMR spectrum (200 MHz, DMSO-*d*₆) δ (ppm): 1.70–1.74 (m, 4H, C₅-2H, C₆-2H); 2.63–2.89 (m, 4H, C₄-2H, C₇-2H); 7.02–7.94 (m, 11H, Ar-H, NH₂); 11.35 (br, s, 1H, NHCO); 12.77 (br, 1H, NH, hydrazo).

MS (EI, 70 ev) *m/z* (%) = 465 [M⁺-(*p*-nitrophenylene); 11.8]; 458 (11.5); 439 (14.1); 425 (2.4); 399 (11.8); 386 (14.7); 367 (50.0); 358 (15.0); 350 (20.9); 321 (11.4); 302 (13.3); 294 (18.9); 267 (8.4); 254 (14.4); 245 (15.7); 236 (16.6); 223 (27.2); 206 (36.7); 193 (43.2); 178 (42.3); 151 (33.6); 135 (31.0); 123 (100.0); 109 (36.7); 96 (24.5); 78 (39.6); 69 (25.6); 55 (50.0).

Elemental analysis data. Calculated for $C_{27}H_{21}N_7O_5S_2$ (587.1), %: C, 55.19; H, 3.60; N, 16.69. Found, %: C, 55.27; H, 3.68; N, 16.78.



Scheme 3. Synthesis of benzo[*b*]thieno[2,3-*d*]pyrimidin-2-yl)acetonitrile 9.

Synthesis of 2-(2-*p*-tolylhydrazone)-2-(4-chloro-5,6,7,8-tetrahydrobenzo[*b*]-thieno[2,3-*d*]pyrimidin-2-yl)acetonitrile (9). A solution of compound **4b** (1.5 g, 4 mmol) in dioxane (20 ml) treated with $POCl_3$ (3 ml, mmol) was heated under reflux for 5 h. The reaction mixture was poured on crushed ice, neutralized with sodium bicarbonate and the separated solid was filtered off, dried well and recrystallized from EtOH to give compound **9**. It represents a reddish brown powder; yield 0.6 g (40%); m.p. >320 °C; IR spectrum (KBr), ν , cm^{-1} = 1486 (N=N); 702 (C-Cl). 1H NMR spectrum (200 MHz, $DMSO-d_6$) δ (ppm): 1.72–1.76 (m, 4H, C_5 -2H, C_6 -2H); 2.3 (s, 3H, CH_3); 2.67–2.71 (m, 4H, C_4 -2H, C_7 -2H); 7.21 (d, 2H, Ar-H, J = 7.5 Hz); 7.58 (d, 2H, Ar-H, J = 7.5 Hz); 12.27 (br, 1H, NH, hydrazo).

MS (EI, 70 ev) m/z (%) = 383 ($M^+ + 2$; 5.6); 381 (M^+ ; 15.3); 346 (13.7); 316 (4.0); 293 (100.0); 264 (1.5); 231 (1.7); 203 (1.2); 178 (9.1); 146 (2.6); 119 (3.6); 101 (19.2); 84 (28.9); 76 (2.1); 65 (6.9).

Elemental analysis data. Calculated for $C_{19}H_{16}ClN_5S$ (381.88), %: C, 59.76; H, 4.22; N, 18.34. Found, %: C, 59.83; H, 4.27; N, 18.41%.

Optical properties of compounds **4a–4e** and **7a–7e** are reported in the Table 1.

Table 1. Optical measurements of compounds **4a–4e** and **7a–7e**

Dye	R , %	a^*	b^*	L^*	C^*	H^*	ΔL	ΔC	ΔH	ΔE	K/S
4a	15.5	-2.45	43.43	83.55	43.5	93.23	–	–	–	–	2.30
4b	14.93	1.49	40.48	79.5	40.5	87.89	-4.05	-3	-5.34	7.34	2.42
4c	3.53	22.03	40.83	50.46	46.39	61.65	-33.09	2.89	-31.58	45.8	13.18
4d	3.86	35.3	57.65	58.36	67.6	58.53	-25.19	24.1	-34.7	49.2	11.97
4e	4.33	17.95	36.09	50.97	40.31	63.56	-32.58	-3.19	-29.67	44.2	10.57
7a	4.08	11.75	42.24	60.16	43.85	74.45	–	–	–	–	11.27
7b	7	16.67	50.75	66.52	53.42	71.82	6.36	9.57	-2.63	11.78	6.18
7c	9.85	21.99	39.26	65.93	45	60.74	5.77	1.15	-13.71	14.9	4.12
7d	4.23	23.1	57.32	61.17	61.8	68.05	1.01	17.95	-6.4	19.08	10.84
7e	10.66	5.3	31.93	69.12	32.36	80.58	8.96	-11.49	6.13	15.8	3.74

Dyeing procedures

1) Preparation of dye dispersion

The required amount of the dye (2% shade) was dissolved in the suitable solvent (DMF) and added dropwise with stirring to solution of Dekol-N (2 g/dm³), an anionic dispersion agent of BASF, then the dye was precipitated as a fine dispersion ready for use in dyeing.

2) *Dyeing of polyester at 130 °C under pressure using fescaben as a carrier*

The dye bath (1:20 liquor ratio) containing 5 g·dm³ *Levegal PT* (carrier of *Bayer*) as a carrier, 4% ammonium sulfate and acetic acid (pH = 5.5), was brought to 60 °C. The polyester fabric was entered at this degree and run for 15 minutes. The fine dispersion of dye (2%) was added, temperature was risen to the boiling point within 45 minutes, dyeing was continued at boiling for about 1 hour, then the dyed material was rinsed and soaped with 2% nonionic detergent to improve the rubbing and wet fastness.

Assessment of colour fastness (Table 2)

Fastness to washing, perspiration, light and sublimation was tested according to the reported methods.

Table 2. Fastness properties of compounds 4a–4e and 7a–7e

Dye	Washing, 75 °C	Rubbing		Sublimation		Acid perspi- ration	Light
		Dry	Wet	180 °C	210 °C		
4a	4–5	4–5	4–5	4–5	4–5	4–5	7
4b	4–5	4	4	4–5	4–5	4–5	6–7
4c	3–4	5	4	4–5	4–5	4–5	7–8
4d	4–5	5	5	4–5	4–5	4–5	6–7
4e	4–5	4–5	4	4–5	4–5	4–5	6–7
7a	4–5	4	4	4–5	4–5	4–5	7
7b	4–5	5	5	4–5	4–5	4–5	7
7c	4–5	5	5	4–5	4–5	4–5	6
7d	4–5	4	4	4–5	4–5	4–5	6
7e	4–5	4	4	4–5	4–5	4–5	7

1) *Fastness to washing*

A specimen of dyed polyester fabric was stitched between two pieces of un-dyed cotton fabric, all of equal diameters and then washed at 50 °C for 30 minutes. The staining on the un-dyed adjacent fabric was assessed according to the following grey scale: 1 – poor, 2 – fair, 3 – moderate, 4 – good, 5 – excellent.

2) *Fastness to perspiration*

The samples were prepared by stitching pieces of dyed polyester fabric between two pieces of un-dyed cotton fabric, all of equal diameters and then immersed in the acid medium for 30 minutes. The staining on the un-dyed adjacent fabric was assessed according to the following grey scale: 1 – poor, 2 – fair, 3 – moderate, 4 – good, 5 – excellent. The acid solution (pH = 3.5) contains sodium chloride 10 g/l, lactic acid 1 g/dm³, disodium orthophosphate 1 g/dm³ and histidine monohydrochloride 0.25 g/dm³.

3) *Fastness to rubbing*

The dyed polyester fabric was placed on the base of Crocketeer, so that it rests flat on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloth was allowed to slide on the tested

fabric back and forth twenty times by making ten complete turns of the crank. For wet rubbing test, the testing square was thoroughly wet in distilled water. The rest of the procedure is the same as the dry test. The staining on the white testing closed was assessed according to grey scale: 1 – poor, 2 – fair, 3 – moderate, and 4 – good, 5 – excellent.

4) Fastness to sublimation

Sublimation fastness was measured with an iron tester (Yasuda no. 138). The samples were prepared by stitching pieces of dyed polyester fabric between two pieces of un-dyed polyester, all of equal diameters and then treated at 180 °C and 210 °C for 1 min. Any staining on the un-dyed adjacent fabric or change in tone was assessed according to the following grey scale: 1 – poor, 2 – fair, 3 – moderate, 4 – good, 5 – excellent.

5) Fastness to light

Light fastness was determined by exposing the dyed polyester on a Xenotest 150 (Original Hanau, chamber temperature 25–30 °C, black panel temperature 60 °C, relative humidity 50–60%, and dark glass (UV) filter system) for 40 hours. The changes in colour were assessed according to the following blue scale: 1 – poor, 3 – moderate, 5 – good, and 8 – very good.

Colour assessment

Table (1) report the colour parameters of the dye fabrics assessed by tristimulus colorimetry. The colour parameters of the dyed fabrics were determined on a spectromultichannel photodetector (model MCPD1110A), equipped with a D65 source and barium sulfate as a standard blank. The values of the chromaticity coordinates, luminance factor and the position of the colour in the CIELAB colour solid are reported.

RESULTS AND DISCUSSION

The synthetic procedures adopted to obtain the target compounds are depicted in Schemes 1–3. The starting 2-(2-cyanoacetylamino)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide **3** [9] was obtained *via* cyanoacetylation of 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide (**1**) [10], with 3-(3,4-dimethyl-1*H*-pyrazol-1-yl)-3-oxopropanenitrile (**2**) [11] through modification of the previously reported method for the synthesis of analogues [11, 12].

Also, N-phenylthiazolone derivatives **6** and **8** were prepared according to the methods reported in literature [9]. Coupling of compounds **3** and **6** with various aryl diazonium chlorides in pyridine afforded 2-(arylhydrazone)-3-cyanoacetamides **4a–e** and 2-(4-(arylhydrazone)-5-oxo-3-phenylthiazolidin-2-ylidene)-3-cyanoacetamides **7a–e**, respectively. Treatment of thiocarbamoyl derivative **8** with *p*-methoxyphenyl diazonium chloride in pyridine effected α -phenyl thiocarbamoyl cleavage [13] with the formation of *p*-methoxyphenyl hydrazone derivative **4c**. This may be other type of Japp–Klingemann cyclization of amide **4b** under influence of POCl_3 affording thienopyrimidine derivative **9**.

The structures **4a–e** were confirmed by various spectroscopic techniques, including IR, ^1H NMR and mass spectroscopy. The IR spectra of compounds **4a–e** showed characteristic absorption bands in the region within $\nu = 3411–$

3163 cm^{-1} due to the stretching vibrations of NH and NH_2 groups. The bands in the region within $\nu = 1670$ –1631 cm^{-1} are due to the stretching vibrations of carbonyl group. The absorption bands in the region within $\nu = 1515$ –1464 cm^{-1} are assigned to the symmetric vibrations of azo group. Moreover, the absorption bands appeared in the region within $\nu = 2223$ –2213 cm^{-1} due to cyano function of the coupler moieties. Beside the expected signals in the ^1H NMR spectrum of compound **4a**, it displayed a characteristic broad signal at δ 12.93 ppm assigned to NH or hydrazo group. Also, the ^1H NMR spectrum of compound **4b** showed singlet signal at δ 2.30 due to the methyl group protons and broad signal at δ 12.90 ppm assigned to NH or hydrazo group adsorption. Furthermore, the ^1H NMR spectrum of compound **4c** revealed singlet signal at δ 3.79 ppm due to methoxy protons and broad signal at δ 12.89 ppm due to the NH and hydrazo group protons. Moreover, the ^1H NMR spectra of **4d** and **4e** showed broad signals at δ 12.97 and 13.15 ppm due to NH or hydrazo group protons, respectively.

The mass spectrum of compound **4a** showed the molecular ion peaks at m/z 369 ($\text{M}^{+}+2$), 368 ($\text{M}^{+}+1$), 367 (M^{+}) which is in agreement with molecular formula of the compound $\text{C}_{18}\text{H}_{17}\text{N}_5\text{O}_2\text{S}$ and the main peak at m/z 77 is attributed to the phenyl group. Also, in the mass spectrum of compound **4b** were the molecular ion peaks at m/z 383 ($\text{M}^{+}+2$), 382 ($\text{M}^{+}+1$), 381 (M^{+}), which underwent consecutive and synchronous fragmentation to give the basic fragment ion peak at m/z 91 which could be attributed to the tolyl group. Moreover, the mass spectrum of compound **4c** showed the presence of molecular ion peaks at m/z 399 ($\text{M}^{+}+2$), 398 ($\text{M}^{+}+1$), 397 (M^{+}) and three fragments at m/z 380, 195 and 135 corresponding to (M^{+} -NH₂), 2-imino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide and *p*-methoxyphenyl azo moieties, respectively. Furthermore, in the mass spectrum of compound **4d** showed there are two molecular ion peaks at m/z 403 ($\text{M}^{+}+2$), 402 ($\text{M}^{+}+1$) and 401 (M^{+}), in addition to two fragments at m/z 139 and 111 corresponding to *p*-chlorophenyl azo and chlorophenyl groups, respectively. Also, the mass spectrum of compound **4e** showed the basic peak at m/z 122 due to the nitrophenyl group.

The products **7a**–**7e** were assigned in accordance with their analytical and spectral data. The IR spectra showed the presence of absorption bands in the region of $\nu = 1727$ –1641 cm^{-1} due to the stretching vibrations of carbonyl groups. The absorption bands in the region of $\nu = 1494$ –1483 cm^{-1} can be assigned to the symmetric vibrations of azo groups. Absorption bands in the region with $\nu = 2200$ –2191 cm^{-1} are attributed to cyano groups of the coupler moieties. The ^1H NMR spectra of compounds **7a**–**7e** displayed characteristic signals with $\delta = 11.35$ –11.41 and 12.77–12.35 ppm due to NHCO and NH or hydrazo protons, respectively. Also, the ^1H NMR spectrum of compound **7c** showed the singlet signal at δ 3.73 ppm due to methoxy protons, in addition to the other expected signals. The mass spectra of compounds **7a**–**7e** are in agreement with their molecular formulas.

The structure of the compound **9** was in agreement with the spectral data, its IR spectrum revealed absorption bands at ν 1486 and 702 cm^{-1} due to (N=N) and (C–Cl) group vibrations, respectively. Also, the ^1H NMR spectrum displayed signals at δ 7.21 (d, 2H, Ar–H, $J = 7.5$ Hz); 7.58 (d, 2H, Ar–H, $J = 7.5$ Hz) and 12.27 ppm (br, 1H, NH, hydrazo). Furthermore, its mass spectrum showed the occurrence of the molecular ion peaks at m/z 383 ($\text{M}^{+}+2$) and 381 (M^{+}), in

addition to three fragments at m/z 293, 101 and 76 corresponding to $[M^+-(HCl, HCN, CH_3)]$, *p*-methylphenyl and phenylene moieties, respectively.

Dyeing of polyester fabrics and dyeing properties

Colour measurement

The influence of different substituents on the dyeing behaviour, colour hue, and depth were investigated. This investigation utilized some spectral data for the dyed materials. The most commonly used function $f(R)$ is the one developed theoretically by Kubelka and Munk. In their theory, the optical properties of a sample are described by two values: K is a measure of the light absorption and S is a measure of the light scattering. On textiles, K is determined primarily by the dyestuffs and S only by the substrate. From the wavelength, Kubelka and Munk calculated the following relationship for reflectance R of a thick, opaque sample with constants K and S as follow:

$$K/S = (1 - R)^2/2R. \quad (1)$$

In this equation, R is a fraction (e.g., 0.32 for 32% reflectance). The " K/S " value at " K_{max} " was used as a characteristic of the colour depth. On the other hand, the psychometric coordinates (L^* , a^* , b^* , Table 1) illustrate the colour hues, where " L^* " is the lightness ranging from 0 to 100; [0 for black and 100 for white], " a^* " is the red-green axis [(+) for red, zero for gray, and (-) for green] and " b^* " is the yellow-blue axis [(+) for yellow, zero for gray and (-) for blue] obtained for the each dyed sample.

The parent dyestuff in each group is taken as the standard in the colour difference calculation (ΔL^* , ΔC^* , ΔH^* and ΔE) [14–16]. The results were obtained using CIELAB techniques, and are given in the Table 1, where ΔL^* is the lightness difference, ΔC^* is the chroma difference, ΔH^* is the hue difference and ΔE is the total colour difference. A negative sign of ΔL indicates that the dyed fibre becomes darker than the standard whereas positive sign indicates that the dyed fibre becomes lighter than the standard. Negative sign of ΔC indicates that the dyed fibre becomes duller than the standard; whereas a positive sign indicates that the dyed fibre becomes brighter than the standard. Negative sign of ΔH indicates that the colour is shifted to red colour, while a positive sign indicates that the colour shifted to yellowish one. The K/S values of compounds **4a–4e** vary from 2.3 to 13.18. The introduction of methyl, methoxy, chloro and nitro groups into the dyes **4b**, **4c**, **4d** and **4e**, respectively increases the strength of K/S value of the dyed polyester fabric compared with that of the parent compound **4a**. The K/S values of compounds **7a–7e** vary from 3.74 to 11.72, and the introduction of methyl, methoxy, chloro, bromo and nitro groups into the dye **7b–7e** molecules, respectively, increases the K/S values compared with the parent compound **7a**. The ΔL values for compounds **4a–4e** show that the introduction of methyl, methoxy, chloro and nitro groups into the dye molecules make them darker than those of parent dye **4a**, while dyes **7b–7e** are brighter than the parent dye **7a**. The value of a^* in the compound **4a–4e** group varies from -2.45 to 35.12, where the introduction of an electron donating or withdrawing groups causes the shift of the colour hues of the dye in the reddish direction along the red-green axis. Also, b^* value of this group increases upon introducing of chlorine atom which means that the colour hue of the dye is shifted to the yellowish direction along the yellow-blue axis.

Introduction of methyl, methoxy and nitro groups causes the shifts of the colour hues in the bluish direction along the yellow–blue axis. The positive a^* value of dyes **7a–7e** (red–green axis) indicates that all the members of this group are red. Also, the positive b^* value (yellow–blue axis) of this series indicates that all members of this group are yellow. From ΔC values, these of dyes **4b** and **7e** are duller than the standard whereas the rest are brighter. From the ΔH values, all atoms or groups are shifted in colour to red colour except the dye **7e** which shifted the colour to yellow.

Assessment of colour fastness

Factors that can affect fastness include light, washing, heat, perspiration and atmospheric pollution. The conditions of colour fastness tests are chosen to correspond closely to the treatments employed during manufacture and the conditions associated with the ordinary use [17]. The results are obtained after matching the tested samples against a standard reference sample (the gray scale) [17]. The results obtained for these dyes revealed that they have good fastness properties (Table 2).

In conclusion, two sets of seventeen useful disperse dyes **4a–4e** and **7a–7e** were synthesized by the diazo coupling. The prepared dyes were applied onto polyester fabrics in which, they showed good light, washing, heat and acid perspiration fastness. The remarkable brightness of these dyes after washing is indicative of their good penetrations and excellent fabric affinities due to their accumulation of polar groups.

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NO 2-(2-CIĀNACETAMIDO)-4,5,6,7-TETRAHIDROBENZ[b]TIOFĒN-3-KARBOKSAMĪDA ATVASINĀTU AZODISPERSU KRĀSVIELU SINTĒZE

M.A. Gouda, H.F. Eldien, M.M. Girges, M.A. Berghot

K O P S A V I L K U M S

2-(2-Ciānacetilamino)-4,5,6,7-tetrahidrobenz[b]tiofēn-3-karboksamīda (**3**) vai 2-[2(5-okso-3-feniltiazolidīn-2-ilidēn)]-2-ciānacetamido-4,5,6,7-tetrahidrobenz[b]tiofēn-3-karboksamīda (**6**) reakcijā ar dažādiem diazotētiem arilamīniem piridīnā rodas attiecīgie arilhidrazonopropionitrila atvasinājumi. Dažas no sintezētajām krāsvielām pievienotas poliestera izstrādājumiem (audumiem) kā dispersas krāsvielas, veikti to krāsas mērījumi un izvērtēta krāsas noturība.

Iesniegts 23.08.2011