Short communication

Thieno[2,3-b]thiophenes: Part 7. Some Heterocyclization Reactions with Ethyl 3,4-diamino-5-cyanothieno[2,3-b]thiophene-2-carboxylate

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Abstract

Ethyl 3,4-diamino-5-cyanothieno[2,3-*b*]thiophene-2-carboxylate (**1**) was treated with a mixture of carbon disulfide and halo compounds to give the corresponding bisthiazole and bisthiolane derivatives **2-4**. Treatment of compound **1** with 2,5-dimethoxytetrahydrofuran gave the corresponding 3,4-dipyrrol-1-ylthienothiophene (**5**). Condensation of compound **5** with hydrazine afforded the carbohydrazide derivative **6**, which was treated with CS_2 or PhNCS to afford oxadiazole or triazole derivatives **7a,b.** The cycloaddition reaction of compound **5** with CS_2 or PhNCS under phase transfer conditions gave 1,4-thiazepino- or 1,4-diazepinothieno[2,3-*b*]thiophenes **8** and **9**, respectively. Basic hydrolysis of compound **1** yielded 3,4-diaminothieno[2,3-*b*]thiophene (**10**), which was subjected to react with different reagents to give the corresponding bispyrido- and bispyrrolothieno[2,3-*b*]thiophenes, and bisarylideneaminothieno[2,3-*b*]thiophenes **11**-**15**, respectively.

Keywords: Thieno[2,3-*b*]thiophenes, thiazepinothiophene, pyridothiophene, pyrrylthiophene, pyrrolothiophene, phase transfer catalyst heterocyclization

1. Introduction

Various substituted and fused aminothiophenes have attracted considerable attention as structural motifs in numerous pharmaceuticals and dyes.[1–5] Thieno[2,3-b]thiophenes possess important biological activities, *viz.* antiproliferative activity,[6] inhibition of non-peptide GPIIb/IIIa,[7] and topically active carbonic anhydrase inhibition.[8] Besides, thieno[2,3-b]thiophenes showed useful reactivity as co-polymerization agents[9a] and as semiconductors.[9b] In continuation to our previous work dealing with synthesis of fused and spiro thieno[2,3-*b*]thiophenes,[4,10–18] herein we report for synthesis of new thieno[2,3-*b*]thiophene, fused with different heterocyclic moieties, starting from ethyl 5-cyano-3,4-diaminothieno[2,3-*b*]thiophene-2-carboxylate (**1**).[19]

2. Results and Discussion

The addition reaction of compound **1**[19] with carbon disulfide, followed by treatment with chloroacetonitrile or ethyl chloroacetate under phase transfer catalysis (PTC) conditions (K_2CO_3, tetrabutylammonium bromide (TBAB), dioxane), furnished bisthiazolylthieno[2,3-*b*]thiophene derivatives **2** and **3**, in fair yields (Scheme 1). IR spectra of compounds **2** and **3** showed the absorption bands corresponding to NH_2 group at 3320 and 3103 cm^{-1}, and for C=O group at 1680 cm^{-1}, respectively. Mass spectrum of compound **3** showed the molecular ion peak (M^+) at m/z = 498. The reaction pathway is suggested to proceed *via* the addition of the NH_2 group of compound **1** to the CS_2, forming the corresponding potassium dithiocarbamate derivative, which was alkylated with the halo compound to give the corresponding dithioester. This dithioester underwent intramolecular cyclization through the addition of the NH group either to the cyano group to give compound **2** or to the C=O ester group with elimination of an ethanol molecule to give compound **3.** Moreover, addition followed by cycloalkylation of compound **1** with CS_2 and 1,2-dibromoethane, at 1:1:1 molar ratio under PTC conditions, afforded the corresponding bis-1,3-dithiolan-2-ylidene derivative **4** (Scheme 1). IR spectrum of com-

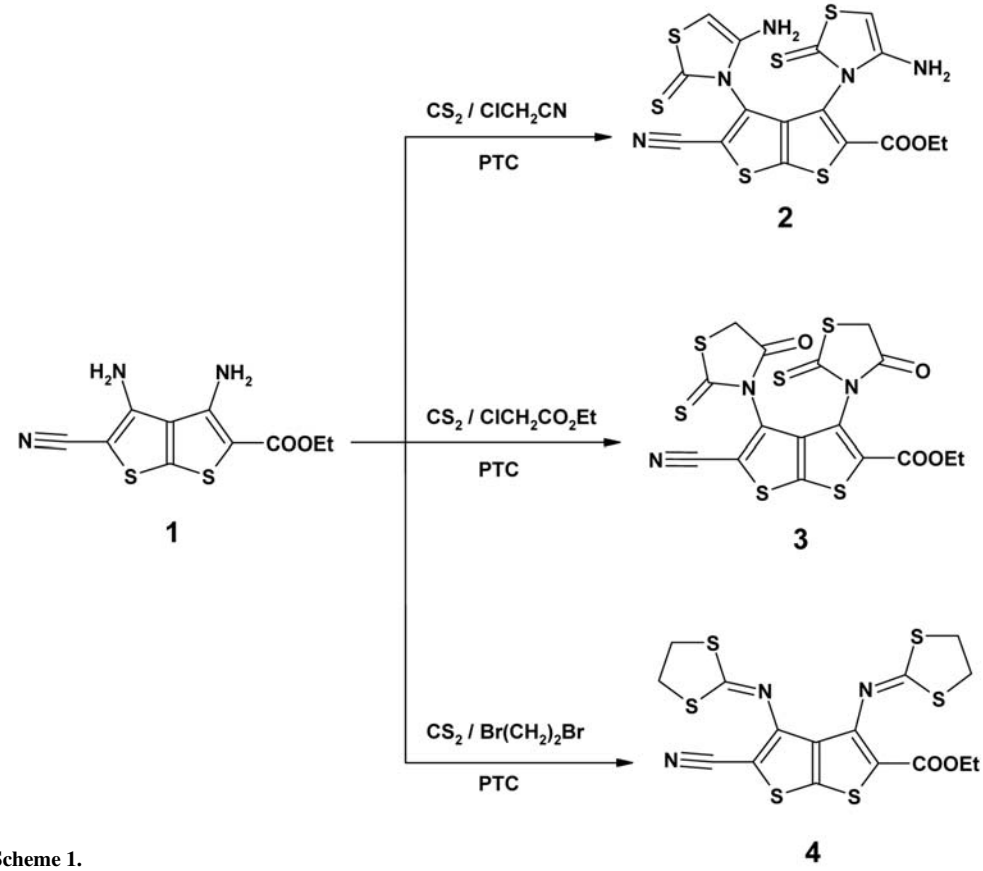
pound **4** showed the disappearance of the absorption bands corresponding to the NH_2 groups, while, its ^1H NMR spectrum showed characteristic signals due to both ethyl ester and $S(CH_2)_2S$ sets of protons at δ 1.10 and 4.00–4.50 ppm.

Condensation of compound **1** with 2,5-dimethoxytetrahydrofuran in acetic acid afforded 3,4-bipyrrol-1-yl derivative **5**. Its IR spectrum showed the disappearance of the absorption bands corresponding to the NH_2 group. Condensation of compound **5** with hydrazine yielded the carbohydrazide derivative **6** (Scheme 2). IR spectrum of compound **6** showed the absorption bands at 3320–3122 (NH-NH_2), 2194 (CN) and 1658 cm^{-1} (CO), respectively.

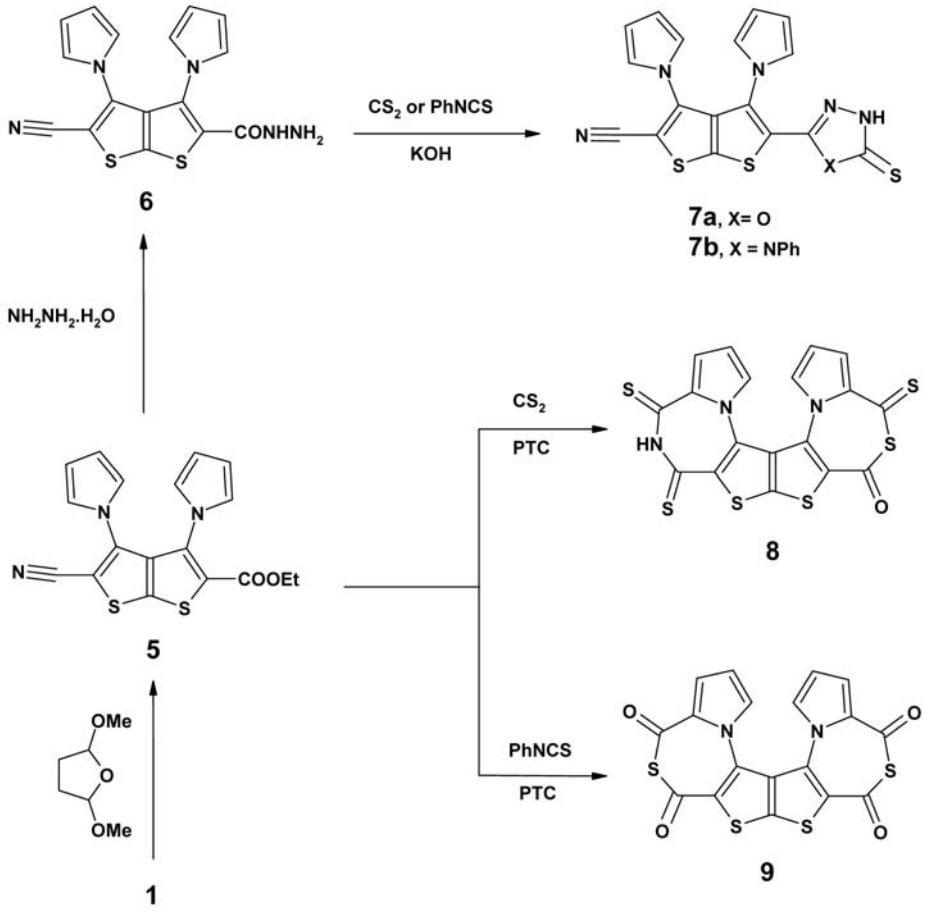
Cycloaddition of carbohydrazide **6** with carbon disulfide or phenylisothiocyanate in presence of KOH gave oxadiazol-2-yl **7a** and 1,3,4-triazol-2-yl **7b** with good yields (Scheme 2). The reaction pathway is suggested to proceed *via* addition of the amino group to CS_2 or PhNCS forming the corresponding dithiocarbamate or thiourea derivative, which undergoes intermolecular cyclization through the attack of enolized OH group to the CS group with elimination of H_2S molecule to give compound **7a** or attack of the NH group to the C=O group with elimination of H_2O molecule to give compound **7b**. IR spectra of compounds **7a,b** showed the disappearance of the absorption bands corresponding to NH and NH_2 groups of compound **6** and appearance of new absorption bands corresponding to NH groups at 3200 and 3100 cm^{-1}, and to C=S group at 1145 cm^{-1}, respectively. MS spectrum of compounds **7a,b** showed molecular ion peaks at *m/z* = 395.97 and 470.52, respectively.

Under PTC conditions, compound **5** was subjected to cycloaddition reaction *via* treatment with carbon disulfide or phenyl isothiocyanate, where thiazepino derivative **8** or diazepino derivative **9** were obtained (Scheme 2). IR spectra of compounds **8** and **9** showed the disappearance of absorption bands corresponding to CN and C=O ester groups of compound **5** and appearance of new absorption bands corresponding to NH (3211 cm^{-1}), C=O (1698–1670 cm^{-1}) and C=S (1145 cm^{-1}) groups, respectively. ^{13}C NMR spectra of compounds **8** and **9** showed the new signals at δ 171, 172 ppm (C=O) and 210, 214 ppm (C=S), respectively. The MS spectrum of compound **9** showed the molecular ion peak at *m/z* = 439.26. The reaction mechanism was illustrated in Figure 1.

Refluxing compound **1** in 20% NaOH solution leads to hydrolysis of cyano and ester groups followed by decarboxylation to give 3,4-diaminothieno[2,3-*b*]thiophene derivative **10**. IR spectrum of compound **10** showed two vibration frequencies for the amino groups at 3320 and 3210 cm^{-1}, respectively. Meanwhile the absorption bands for the cyano and ester groups of com-



Scheme 1.



Scheme 2.

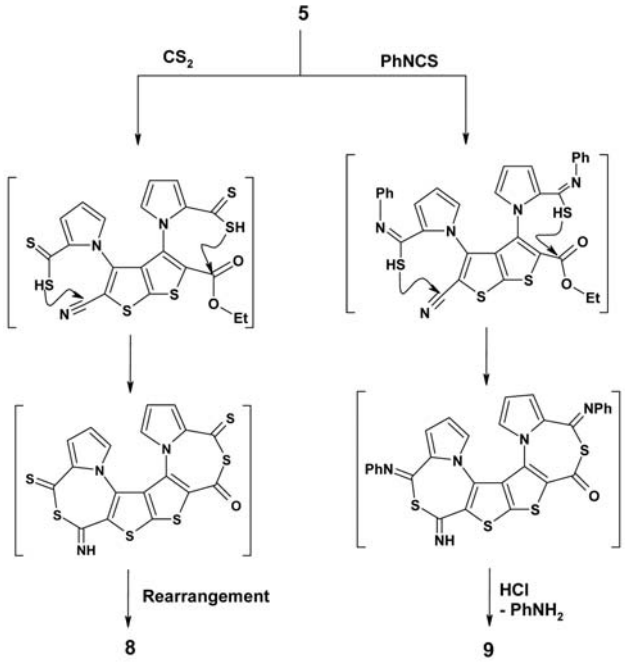
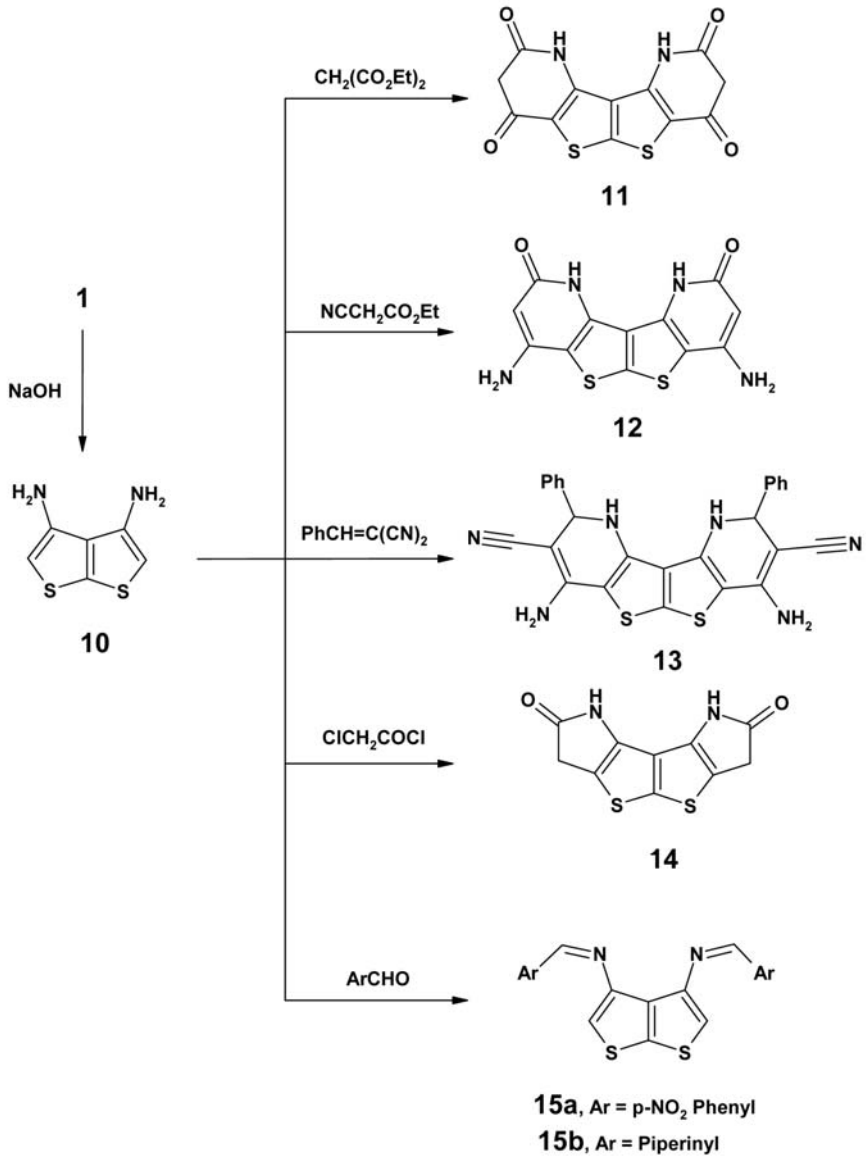


Figure 1.

pound **1** were absent. ^{1}H NMR spectrum of compound **10** showed the absorptions for two protons at positions 2 and 5 as a singlet at 6.7 ppm, and MS spectrum of this compound showed the molecular ion peak at *m/z* = 172. The reaction of compound **10** with diethyl malonate, ethyl cyanoacetate or benzylidenemalononitrile in presence of triethylamine as a catalyst, gave pyridothieno[2,3-*b*]thiophenes **11-13**. (Scheme 3). IR spectra of compounds **11-13** showed the absorption bands at 3340–3211 (NH_2), 3100 (NH), 2100 (NH) and 1690–1670 cm^{-1} (C=O), respectively. Chloroacylation of compound **10** with chloroacetyl chloride was carried out in presence of triethylamine as a catalyst to afford the corresponding pyrrolothieno[2,3-*b*]thiophene **14** (Scheme 3). Its IR spectrum showed new absorption bands corresponding to NH and C=O groups at 3200 and 1670 cm^{-1}, respectively. Finally, condensation of compound **10** with aromatic aldehyde, i.e., *p*-nitrobenzaldehyde or 1,3-benzodioxole-5-carbaldehyde in acetic acid as a solvent, leads to the formation of biarylideneamino derivatives **15a,b** (Scheme 3). IR spectra of compounds **15a,b** showed the disappearance of absorption bands corresponding to the amino groups and MS spectrum showed the molecular ion peak at *m/z* = 436.



Scheme 3.

3. Experimental

All melting points are uncorrected and were recorded on Melt-Tem II melting point apparatus. IR spectra were measured on a Nicolet 710 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in deuterated chloroform or dimethyl sulfoxide at 200 MHz on aVarian Gemini NMR spectrometer using tetramethylsilane as an internal reference. D_2O experiment was carried to check acidic protons. Mass spectra were performed on a Shimadzu GC/MS-QP 1000 mass spectrometer at 70 eV. The elemental analyses were carried on Perkin-Elimer 2400 analyzer.

Synthesis of bithiazolyl- and bidithiolan-2-ylideneaminothieno[2,3-*b*]thiophenes 2-4.

General procedure. A mixture of compound **1** (1.33 g, 0.005 mol), anhydrous potassium carbonate (3 g), dry dioxane (30 mL), carbon disulfide (0.76 mL, 0.01 mol) and TBAB (0.003 g) was initially stirred for 1 hour at 60 °C. After that chloroacetonitrile (0.67 mL, 0.01 mol), ethyl chloroacetate (1.2 mL, 0.01 mol) or 1,3-dibromopropane (1.9 mL, 0.01 mol) was added. The reaction mixture and stirred at 60 °C to the completion of the reaction (followed by TLC). Filtrate was evaporated *in vacuo* and residual solid washed with water and crystallized from the appropriate solvent.

Ethyl 3,4-bis(4-amino-2-thioxothiazol-3(2H)-yl)-5-cyanothieno[2,3-*b*]thiophene-2-carboxylate (2). This compound was crystallized from DMF (60% yield). M.p <300 °C; IR (KBr): ν 3220, 3103 (NH_2), 2222 (CN), 1705 cm^{-1} (C=O). ^{1}H NMR (200 MHz, DMSO-d_6): δ 1.10 (t, 3H, CH_3), 4.40–4.00 (q, 2H, CH_2), 6.00–5.20 (br, 4H, $2NH_2$), 6.70 (s, 2H, =CH). ^{13}C NMR (200 MHz, DMSO-d_6): δ 14

(CH_3), 61 (CH_2), 109 (CN), 106, 115, 123, 139 (thienothiophene), 126 (=CH), 146 (C-NH_2), 167 (C=O), 167 (C=S). Anal. Calcd. for $C_{16}H_{11}N_5O_2S_6$ (M.W. 497.688): C 38.61, H 2.23, N 14.07, S 38.68. Found: C 38.44, H 2.50, N 14.33, S 38.40.

Ethyl 5-cyano-3,4-bis(4-oxo-2-thioxothiazolidin-3-y)] thieno[2,3-*b*]thiophene-2-carboxylate (3). This compound was crystallized from DMF (50 % yield). M.p. 320–2 °C. IR (KBr): ν 2220 (CN), 1704 cm^{-1} (C=O). ^1H NMR (200 MHz, DMSO-d_6): δ 1.10 (t, 3H, CH_3), 4.50–3.90 (m, 6H, 3CH_2). MS *m/z* (I_r/%): 498 (1.00), 498.47 (3.6), 441.60 (2.3), 418.25 (26.6), 416.21(12.4), 386.57(4.9), 350.37(6.5), 339.26(18.6), 315.43(4.7), 313.49 (19.5), 230 (100.0), 192.76 (22.7), 160.80 (14.8), 145.82 (29.7). Anal. Calcd. for $C_{16}H_9N_3O_4S_6$ (M.W. 499.65): C 38.46, H 1.82, N 8.41, S 38.50. Found: C 38.70, H 1.58, N 8.13, S 38.81.

Ethyl 3,4-bis((1,3-dithiolan-2-ylidene)amino)-5-cyanothieno[2,3-*b*]thiophen-2-carboxy-late (4). This compound was crystallized from DMF (52% yield). M.p. <300 °C. IR (KBr): ν 2222 (CN), 1700 cm^{-1} (C=O). ^1H NMR (200 MHz, DMSO-d_6): δ 1.10 (t, 3H, CH_3), 4.50–4.00 (m, 10H, CH_2 ester, 2SCH_2CH_2S). Anal. Calcd. for $C_{16}H_{13}N_3O_2S_6$ (M.W. 471.68): C, 40.74; H, 2.78; N, 8.91; S, 40.79. Found: C, 40.74; H, 2.78; N, 8.91; S, 40.79.

Ethyl 5-cyano-3,4-di(1*H*-pyrrol-1-yl)thieno[2,3-*b*]thiophen-2-carboxylate (5). To a suspension of compound **1** (0.52 g, 0.002 mol) in glacial acetic acid (30 mL) 2,5-dimethoxytetrahydrofuran (0.92 mL, 0.004 mol) was added. The reaction mixture was refluxed for 3 hours, left to cool and poured into cold water (20 mL). The solid product was filtrated, dried and crystallized from DMF (44% yield). M.p. <330 °C. IR (KBr): ν 2200 (CN), 1700 cm^{-1} (C=O). ^1H NMR (200 MHz, DMSO-d_6): δ 1.40–1.00 (t, 3H, CH_3), 4.20–4.00 (q, 2H, CH_2), 7.60–6.70 (m, 8H, aromatic). MS, M_r = 367.44. Anal. Calcd. for $C_{18}H_{13}N_3O_2S_2$ (M.W. 367.44): C 58.84, H 3.57, N 11.44, S 17.45. Found: C 58.66, H 3.72, N 11.20, S 17.67.

5-cyano-3,4-di(1*H*-pyrrol-1-yl)thieno[2,3-*b*]thiophen-2-carbohydrazide (6). To a solution of compound **5** (0.37 g, 0.001 mol) in ethanol (30 mL), hydrazine hydrate (0.05 mL, 0.001 mol) was added. The reaction mixture was refluxed for 2 hr. After cooling the precipitated product was collected by filtration, crystallized from *n*-butanol and isolated with 70% yield. M.p. = 230–2 °C. IR (KBr): ν 3320–3122 (NH-NH_2), 2190 (CN), 1658 cm^{-1} (C=O). ^1H NMR (200 MHz, DMSO-d_6): δ 10.00 (s, 1H, NH), 7.60–6.50 (m, 8H, aromatic), 5.40–5.00 (br, 2H, NH_2). ^{13}C NMR (200 MHz, DMSO-d_6): δ 87 (C-CN), 109 (CN), 106, 117, 127 (pyrrole ring), 87, 122, 138, 145, 146, 159 (thienothiophene ring), 159 (C-pyrrolyl), 161 (C=O). Anal. Calcd. for $C_{16}H_{11}N_5OS_2$ (M.W. 353.21): C 54.37, H 3.14, N 19.82, S 18.15. Found: C 54.66, H 3.30, N 19.60, S 18.44.

3,4-di(1H-pyrrol-1-yl)-5-(5-thioxo-4,5-dihydro-1,3,4-oxadiazol-2-yl)thieno[2,3-*b*]thiophene-2-carbonitrile (7a). To a mixture of compound **6** (0.7 g, 0.002 mol), potassium hydroxide (0.11 g, 0.002 mole) and ethanol (40 mL), carbon disulfide (0.15 mL, 0.002 mol) was added slowly and the reaction mixture refluxed for 4 hrs. After cooling the clear solution was poured onto cold water (200 mL) and neutralized with hydrochloric acid. The precipitated product was filtered off and crystallized from dioxane (70% yield). M.p. <330 °C. IR (KBr): ν 3200 (NH), 2200 (CN), 1142 cm^{-1} (C=S). ^1H NMR (200 MHz, DMSO-d_6): δ 10.0 (s, 1H, NH), 7.70–6.70 (m, 8H, arom.). MS *m/z* (I_r / %): 395.48 (3.00), 352.41 (9.4), 321.41 (3.2), 300.74 (7.4), 283.64 (23.7), 263.73 (9.1), 255.85 (25.7), 230.78 (63.7), 223.03 (66.40), 198.75 (52.3), 177.81 (22.7), 120.84 (83), 74.38 (100). Anal. Calcd. for $C_{17}H_9N_5OS_3$ (M.W. 395.48): C 51.63, H 2.29, N 17.71, S 24.32. Found: C 51.90, H 2.44, N 17.33, S 24.30.

5-(4-phenyl-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl)-3,4-di(1H-pyrrol-1-yl)thieno[2,3-b]thiophene-2-carbonitrile (7b). A solution of compound **6** (0.7 g, 0.002 mol) in benzene (20 mL) was treated with phenyl isothiocyanate (0.27 mL, 0.002 mol) and refluxed for 2 hrs. The precipitated solid was filtered off, dried and refluxed in sodium hydroxide solution (20 mL, 10 %) for 3 hrs. After cooling, the clear solution was neutralized with hydrochloric acid and the precipitated product filtered off and crystallized from DMF (80% yield). M.p. <300 °C. IR (KBr): ν 3100 (NH), 2200 (CN), 1140 cm^{-1} (C=S). ^1H NMR (200 MHz, DMSO-d_6): δ 10.10 (s, 1H, NH), 8.00–6.50 (m, 13H, aromatic). MS *m/z* (I_r / %): 470.51 (8%), 466.41 (9.60), 436.09 (29.1), 404.28 (1.80), 390.77 (25.5), 352.88 (20.8), 337.35 (34.3), 311.62 (61.1), 265.95 (23.9), 209.31 (26.1), 165.70 (20.7), 141.02 (100). Anal. Calcd. for $C_{23}H_{14}N_6S_3$ (M.W. 470.59): C 58.70, H 3.00, N 17.68, S 17.86. Found: C 58.91, H 3.22, N 17.70, S 17.50.

Synthesis of 1,4-thiazepino- and 1,4-diazepinothieno[2,3-b]thiophenes 8 and 9.

General procedure. A mixture of compound **5** (0.7 g, 0.02 mol), anhydrous potassium carbonate (3 g), dry dioxane (30 mL) and TBAB (0.003 g) was stirred at 60 °C for 1 hour. To the abident mixture carbon disulfide (3 mL, 0.04 mol) or phenyl isothiocyanate (4.5 mL, 0.04 mol) was added and the reaction mixture was stirred at 60 °C for 4 hr until the completion of the reaction (TLC). The reaction mixture was filtered off and the filtrate evaporated *in vacuo*. The residual solid was washed with water and crystallized to give compound **8**. The carbonate was

washed with dioxane, dried, dissolved in water (100 mL) and then acidified with HCl. The residual solid product was filtered off and crystallized to give compound **9**.

4,9,11-trithioxo-10,11-dihydro-4*H*-pyrrolo[2,1-*c*]pyrrolo[2''',1''':3'',4'']\[1,4]diazepino[5'',6'':4',5']thieno[3',2':4,5]thieno[3,2-e][1,4]thiazepin-6(9H)-one (8). This compound was crystallized from *n*-butanol (30% yield). M.p. <300 °C. IR (KBr): ν 3211 (NH), 1698 (C=O), 1145 cm^{-1} (C=S). ^{1}H NMR (200 MHz, DMSO-d_6): δ 6.90–6.50 (m, 7H, aromatic NH). ^{13}C NMR (200 MHz, DMSO-d_6): δ 122, 126, 132, 141, 144, 147 (thienothiophene ring), 120, 125, 126, 137, 136 (pyrrole ring), 148 (C=NH), 171 (C=O), 210 (C=S). Anal. Calcd. for $C_{18}H_7N_3OS_6$ (M.W. 473.63): C 45.64, H 1.49, N 8.87, S 40.62. Found: C 45.40, H 1.66, N 8.60, S 40.90.

4*H*-pyrrolo[2,1-*c*]pyrrolo[2''',1''':3'',4'']\[1,4]diazepino[5'',6'':4',5']thieno[3',2':4,5]thieno[3,2-*e*][1,4]thiazepine-4,6,9,11(10*H*)-tetraone (9). This compound was crystallized form DMF (55% yield). M.p. <300 °C. IR (KBr): ν 1680–1670 cm^{-1} (C=O). ^{1}H NMR (200 MHz, DMSO-d_6): δ 7.30–6.50 (m, 6H, arom.). ^{13}C NMR (200 MHz, DMSO-d_6): δ 120, 125, 126, 137, 136 (pyrrole ring), 118, 140, 145, 148 (thienothiophene ring), 172 (C=O), 214 (C=S). MS *m/z* (I_r/%): 439.26 (M-2, 0.5), 418.09 (0.1), 341.97 (1.3), 287.13 (2.30), 214.05 (1.1), 164.08 (1.8), 119.02 (9.60), 85.88 (100). Anal. Calcd. for $C_{18}H_6N_2O_4S_4$ (M.W. 442.51): C 48.86, H 1.37, N 6.33, S 28.98. Found: C 48.60, H 1.50, N 6.57, S 29.80.

Thieno[2,3-*b*]thiophene-3,4-diamine (10). A suspension of compound **1** (0.05 mol, 1.33 g) in sodium hydroxide solution (30 mL, 20%) was refluxed for 3 hours, cooled and poured onto cold water (20 mL) containing few drops of HCl. The solid precipitate was filtered off, dried and crystallized from ethanol to give the product with 80% yield. M.p. 265–7 °C. IR (KBr): ν 3320, 3210 cm^{-1} (NH_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.70 (s, 2H, 2=CH), 5.40–5.00 (br, 4H, $2NH_2$, D_2O exchangeable). MS *m/z* (I_r/%): 172 (59), 149 (100), 129 (32.05), 116 (26.95), 98 (40.44), 85 (55.28), 83 (58.13), 57 (88.64), 55 (79.58). Anal. Calcd. for $C_6H_6N_2S_2$ (M.W. 170.25): C 42.33, H 3.55, N 16.45, S 37.60. Found: C 42.50, H 3.70, N 16.60, S 37.89.

Synthesis of bipyrido[2,3-*b*]thienothiophenes (11-13).

General procedure. To a suspension of compound **10** (0.86 g, 0.005 mol) in dimethylformamide (30 mL), diethyl oxalate (2.02 mL, 0.01 mol), ethyl cyanoacetate (1.13 mL, 0.01 mol) or benzylidenemalononitrile (1.54 g, 0.1 mol) a few drops of triethylamine were added. The mixture was refluxed for 4 hr. After cooling, the reaction mixture was poured onto cold water containing few drops of HC and formed precipitate was collected by filtration, dried and crystallized.

1,2,3,4,7,8,9,10-Octahydrobipyrido(3,2-*b*)thieno[2,3-*b*]thiophen-2,4,7,9-tetraone (11). This compound was crystallized from DMF with 60 % yield. M.p. <330 °C. IR (KBr): ν 3200 (NH), 1690, 1670 cm^{-1} (2C=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.00 (s, 2H, 2NH), 4.1 (s, 4H, $2CH_2$). Anal. Calcd. for $C_{12}H_6N_2O_4S_2$ (M.W. 306.31): C 47.05, H 1.97, N 9.15, S 20.94. Found: C 47.30, H 1.66, N 9.33, S 20.59.

4,7-Diamino-1,2,9,10-tetrahydrobipyrido(3,2-*b*)thieno[2,3-*b*]thiophen-2,9-dione (12). This compound was crystallized from DMF with 50 % yield. M.p <330 °C. IR (KBr): ν 3300, 3211, 3100 (NH, NH_2), 1689 cm^{-1} (C=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.00 (s, 2H, 2NH), 6.00 (br, 2H, 2 =CH), 5.40–5.00 (br, 4H, $2NH_2$). Anal. Calcd. for $C_{12}H_8N_4O_2S_2$ (M.W. 304.34): C 47.36, H 2.65, N 18.41, S 21.07. Found: C 47.50, H 2.80, N 18.60, S 21.19.

4,7-Diamino-1,2,9,10-tetrahydro-2,9-diphenylbipyrido(3,2-*b*)thieno[2,3-*b*]thiophen-3,8-dicarbonitrile (13). This compound was crystallized from *n*-butanol with 70 % yield. M.p 280–3 °C. IR (KBr): ν 3340, 3211, 3100 (NH, NH_2), 2100 cm^{-1} (CN). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.30–9.00 (br, 2H, 2NH), 7.40–6.80 (m, 10H, aromatic), 6.70 (s, 2H, 2CH), 5.60–5.20 (br, 4H, $2NH_2$). Anal. Calcd. for $C_{26}H_{18}N_6S_2$ (M.W. 478.56): C 65.25, H 3.79, N 17.56, S 13.40. Found: C 65.00, H 3.50, N 17.80, S 13.65.

2,3,7,8-Tetrahydrobipyrrolo(3,2-b)thieno[2,3-b]thiophen-2,7-dione (14). To a suspension of compound **10** (0.85 g, 0.005 mol) in dioxane (30 mL) containing a few drops of triethylamine, chloroacetyl chloride (1.12 mL, 0.01 mol) was added and the reaction mixture refluxed for 2 hrs. After cooling the solid product was filtered off, washed with water, dried and crystallized from dioxane (80 % yields). M.p <330 °C. IR (KBr): ν 3310 (NH), 1670 cm^{-1} (C=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.00 (s, 2H, 2NH), 2.50 (s, 4H, $2CH_2$). Anal. Calcd. for $C_{10}H_6N_2O_2S_2$ (M.W. 250.29): C 47.99, H 2.42, N 11.19, S 25.62. Found: C 47.68, H 2.66, N 11.23, S 25.30.

Synthesis of biarylideneaminothieno[2,3-b]thiophenes 15a,b. General procedure. A solution of compound **10** (1.72 g, 0.01 mol) in dioxane (20 mL) containing a catalytic amount of pipreidine (0.05 ml) was treated with *p*-nitrobenzaldehyde (3.0 g, 0.02 mol) or 1,3-benzodioxole-5-carbaldehyde (3 g, 0.02 mol). The reaction mixture was refluxed for 2 hrs. Formed solid product was filtered off and crystallized.

***N*^{3},*N*^{4}-bis(4-nitrobenzylidene)thieno[2,3-*b*]thiophene-3,4-diamine 15a**. This compound was crystallized from ethanol with 80% yield. M.p < 300 °C. IR (KBr): ν 3018 ($CH_{aromatic}$), 1610 (C=N), 1550, 1345 cm^{-1} (NO_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.20 (br, 2H, N=CH),

8.50–7.40 (m, 8H, $H_{aromatic}$), 6.50 (s, 2H, =$CH_{thiophene}$). MS *m/z* (I_r/%): 436.75 (1), 394.73 (0.2), 390.13 (1), 324.85 (0.3), 292.82 (0.2), 287.94 (0.2), 252.77 (20.3), 191.68 (10.20), 148.96 (100), 119.17 (11.70), 73.13 (40.80). Anal. Calcd. for $C_{20}H_{12}N_4O_4S_2$ (M.W. 436.46): C 55.04, H 2.77, N 12.84, S 14.69. Found: C 55.23, H 2.83, N 12.64, S 12.44.

***N*^{3},*N*^{4}-bis(piperidin-1-ylmethylene)thieno[2,3-*b*]thiophene-3,4-diamine 15b** This compound was crystallized from benzene with 66% yield. M.p <300 °C. IR (KBr) ν 3016 ($CH_{aromatic}$), 1613 cm^{-1} (C=N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.40 (s, 2H, N=CH), 8.70–7.70 (m, 6H, aromatic), 6.50 (s, 2H, =CH), 4.00 (s, 4H, $2CH_2$). Anal. Calcd. for $C_{22}H_{14}N_2O_4S_2$ (M.W. 434.48): C 60.82, H 3.25, N 6.45, S 14.76. Found: C 60.64, H 3.46, N 6.56, S 14.90.

4. Conclusions

Ethyl 5-cyano-3,4-diaminothieno[2,3-*b*]thiophene-2-carboxalate **1** was utilized as good synthon for the synthesis of different substituted thieno[2,3-*b*]thiophenes. Also, some fused thieno[2,3-*b*]thiophenes were prepared starting with 3,4-bis(1*H*-pyrrol-1-yl) thieno[2,3-*b*]thiophene derivative **5** under phase transfer conditions. Basic hydrolysis of compound **1** gave 3,4-diaminothieno[2,3-*b*]thiophene **10**, which react with different reagents to give the corresponding bispyridothieno[2,3-*b*]thiophene.

5. References

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Povzetek

V prispevku avtorji opisujejo reakcijo etil 3,4-diamino-5-cianotieno[2,3-*b*]tiofen-2-karboksilata (**1**) z zmesjo ogljikovega disulfida in različnih halogeniranih spojin. Pri tem nastanejo različni bistiazoli in bistiolani **2-4**. Pri reakciji izhodne spojine **1** z 2,5-dimetoksitetrahidrofuranom pa nastane 3,4-dipirol-1-iltienotiofen (**5**). Nadaljnja kondenzacija **5** s hidrazinom vodi do nastanka karbohidrazidnih derivatov **6**. Ti pri reakciji s CS_2 ali PhNCS dajejo oksadiazolne oziroma triazolne derivate **7a,b**. Pri reakciji cikloadicije spojine **5** s CS_2 ali PhNCS pod pogoji katalize s faznim prenosom nastane 1,4-tiazepino- oziroma 1,4-diazepinotieno[2,3-*b*]tiofen (**8**, **9**). Nadalje z bazično hidrolizo izhodne spojine **1** nastane 3,4-diaminotieno[2,3-*b*]tiofen (**10**), iz katerega so z različnimi reagenti pripravili bispirido- in bispirolotieno[2,3-*b*]tiofene ter bisarilidenaminotieno[2,3-*b*]tiofene (**11**-**15**).