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Synthesis of some novel bis-1,2,4-triazole and bis-1,3,4-thiadiazole derivatives from terephthaloyl and isophthaloyl chlorides

Abstract: An efficient synthesis of novel bis-1,2,4-triazole and bis-1,3,4-thiadiazole derivatives starting from terephthaloyl and isophthaloyl chlorides is described. Terephthaloyl or isophthaloyl chloride was allowed to react with hydrazine hydrate in refluxing ethanol to give a corresponding bis-hydrazide derivative. Further reaction of these compounds with isothiocyanates gave bis-thiosemicarbazide derivatives, which then underwent cyclization to bis-1,3,4-thiadiazoles in the presence of sulfuric acid. The cyclization of these compounds in the presence of sodium hydroxide resulted in the formation of bis-1,2,4-triazole-3-thioles. The structure of these compounds was characterized by IR, NMR, and elemental analysis.

Keywords: thiadiazole; thiosemicarbazide; triazole.

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Introduction

Recently, special attention has been focused on the synthesis of heterocyclic compounds which exhibit a wide range of biological activities, including antibacterial, antifungal, and other properties [1–6]. A literature survey has revealed that 1,2,4 triazole derivatives are interesting drug candidates including central nervous system stimulants, sedatives, and anti-inflammatory, antianxiety, antimicrobial [7, 8], antitubercular [9], antihypertensive [10], and antiasthmatic agents [11].

Several potent drug compounds possessing the triazole ring have been used in medicine. These are alprazolam (anxiolytic agent, tranquilizer), estazolam (hypnotic, sedative, tranquilizer), nefazodone (antidepressant, 5-HT2 A-antagonist), and triazolam (sedative and hypnotic) [12]. The 1,2,4-triazole moiety exists in the structure of various natural products [13]. 1,3,4-Thiadiazoles are drug candidates as anti-parkinsonism [14], hypoglycemic [15], and antihypertensive [16] agents. The activity of 1,3,4-thiadiazoles is probably due to the presence of the =N-C-S moiety [17]. Thiosemicarbazides are also associated with many pharmacological activities. The synthesis of bis-heterocyclic compounds, which show various biological activities [18–21], have been the subject of extensive study in recent years.

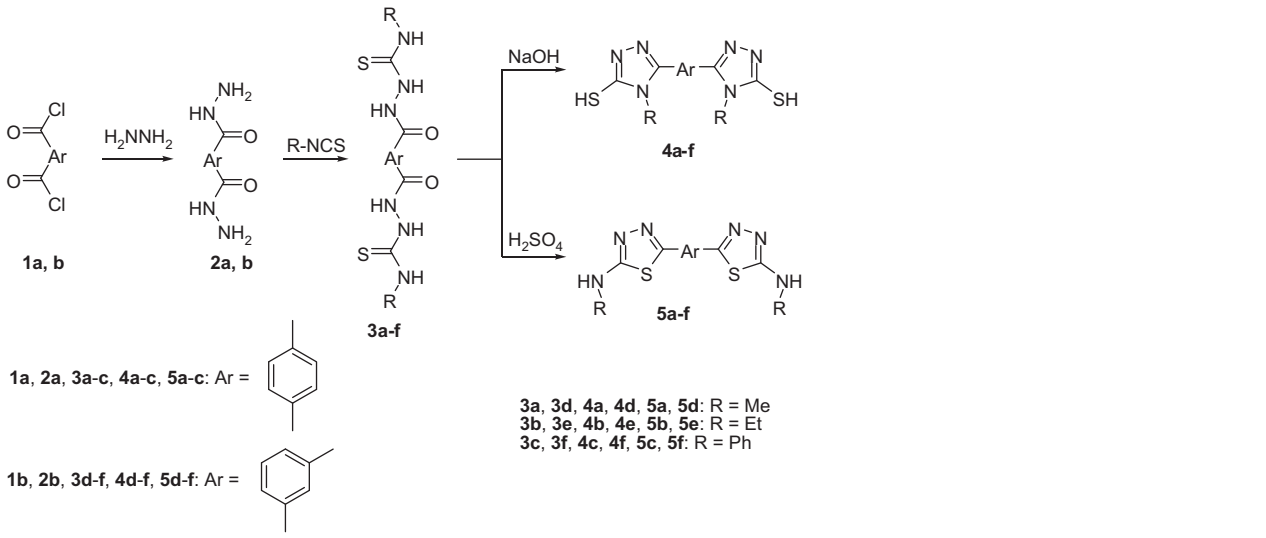
In view of these facts and in continuation of our work on the synthesis of heterocyclic compounds containing nitrogen and sulfur [22–24] and bis-heterocyclic compounds [25–28] with expected biological activity, the aim of the present study was to prepare new bis-1,2,4-triazole and bis-1,3,4-thiadiazole derivatives.

Results and discussion

Phthaloyl and isophthaloyl chlorides **1a,b** are excellent building blocks for the synthesis of new series of bis-heterocyclic compounds **4a–f** and **5a–f** as depicted in Scheme 1. Compounds **1a,b** were converted to bis-(acid hydrazides) **2a,b** by the reaction with hydrazine hydrate in ethanol.

The IR spectrum of compound **2a** shows absorption bands at 3300, 3230, 3030, and 1714 cm^{-1} corresponding to the NH, NH_2, CH-aromatic, and C=O stretching vibration groups, respectively. The ^1H NMR spectrum of this compound contains a broad singlet at δ 4.50 for two NH_2 groups, exchangeable with D_2O, and a doublet for NH group at δ 9.90. The ^{13}C NMR spectrum of **2a** shows signals at δ 127.4, 135.9, and 165.6 due to resonance of aromatic carbons and a carbonyl group. The IR, ^1H NMR, and ^{13}C NMR spectra of other bis-(acid hydrazides) show similar features.

Treatment of compounds **2a,b** with various substituted isothiocyanates gave bis-thiosemicarbazide derivatives **3a,f**. The IR spectrum of **3b** displays absorption bands at 3319, 3240, 2970, 2931, 1680, and 1246 cm^{-1} corresponding to NH, CH-Ar, CH-aliphatic, C=O, and C=S



Scheme 1

groups, respectively. The ^{1}H NMR spectrum of this compound reveals a triplet at δ 1.07 due to the resonance of two CH_3 protons, a quartet for two CH_2 groups, and a singlet for Ar-H protons at δ 8.00. The ^{13}C NMR spectrum of compound **3b** shows peaks at δ 14.9, 39.00, 128.2, 135.8, 165.8, and 181.9 corresponding to aliphatic C-H, aromatic C-H, C=S, and C=O groups. The IR, ^{1}H NMR, and ^{13}C NMR spectra of other bis-thiosemicarbazide derivatives show similar absorption bands.

Bis-thiosemicarbazides **3a–f** on heating with 2 N NaOH in ethanol underwent smooth cyclization through dehydration to afford bis(1,2,4-triazoles-3-thiols) **4a–f**. The IR spectrum of **3e** displays absorption bonds at 1676 cm^{-1} due to C=N and at 2766 cm^{-1} corresponding to an SH group. The formation of bis-triazole moiety is further supported by its ^{1}H NMR spectrum, which shows a triplet for resonance of CH_3 protons at δ 1.15, a multiplet at δ 7.76–7.99 ppm for four aromatic protons and a singlet for an SH proton at δ 14.00, exchangeable with D_2O. The ^{13}C NMR spectrum of compound **4e** shows six different peaks for aromatic and aliphatic carbons in the expected regions and the signals at δ 150.7 and 167.4 assigned to C=S and C=O groups. The IR, ^{1}H NMR, and ^{13}C NMR spectra of other products **4** show similar absorption bands.

5,5′-Phenylene-bis(2-substituted phenyl/alkyl diamino-1,3,4-thiadiazoles) **5a–f** were obtained by cyclization of **3a–f** by treatment with cold concentrated sulfuric acid. The IR spectrum of compound **5d** shows absorption bands at 1539 cm^{-1} due to C=N stretching vibrations. The ^{1}H NMR and ^{13}C NMR spectra of **5a–f** are fully consistent with their structures.

Conclusion

A simple and efficient method for preparation of bis-1,2,4-triazole and bis-1,3,4-thiadiazole derivatives was developed. This procedure offers several advantages such as good yields of cyclization products, short reaction times, and simple purification.

Experimental

General

All chemicals were obtained from Merck or Aldrich Companies. Melting points were determined in open capillary tubes on an electrothermal digital apparatus and are uncorrected. Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel (60 GF_{254}) plates (0.25 mm). All yields refer to isolated products. IR spectra were recorded on a Galaxy FTIR 5000 spectrophotometer using KBr discs. ^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75 MHz) were recorded on a Brucker spectrophotometer in DMSO-d_6 using tetramethylsilane (TMS) as an internal standard. Microanalyses were performed on a Vario EL III instrument at Arak University.

General procedure for the synthesis of hydrazides 2a,b

Terephthaloyl chloride **1a** or isophthaloyl chloride **1b** (1 mmol) and hydrazine hydrate (4 mmol) were dissolved in ethanol (50 mL) and the solution was heated under reflux for 8–10 h. After completion of the reaction, the obtained solid was filtered and crystallized from ethanol.

Terephthalohydrazide (2a) Yield 92%; mp > 300°C; IR: 3300 and 3230 (NH, NH_2), 3030 (CH-aromatic), 1714 cm^{-1} (C=O); ^1H NMR: δ 4.50 (bs, 4H, $2NH_2$, exchangeable with D_2O), 7.87 (s, 4H, Ar-H), 9.90 (s, 2H, 2NH, exchangeable with D_2O); ^{13}C NMR: 127.4 (CH), 135.9 (CH), 165.6 (CO). Anal. Calcd for $C_8H_{10}N_4O_2$: C, 49.48; H, 5.19; N, 28.85. Found: C, 49.68; 5.01; N, 28.59.

Isophthalohydrazide (2b) Yield 91%; mp 232–234°C; IR: 3296 and 3220 (NH, NH_2), 1678 cm^{-1} (C=O); ^1H NMR: δ 4.53 (bs, 4H, $2NH_2$, exchangeable with D_2O), 7.49–7.54 (q, 1H, Ar-H), 7.90, 7.92 (d, 2H, Ar-H), 8.25 (s, 1H, Ar-H), 9.82 (s, 2H, 2NH, exchangeable with D_2O); ^{13}C NMR: δ 126.5 (CH), 128.9 (CH), 129.7 (CH), 134.0 (CH), 165.9 (CO). Anal. Calcd for $C_8H_{10}N_4O_2$: C, 49.48; H, 5.19; N, 28.85. Found: C, 49.27; H, 5.41; N, 28.98.

General procedure for the synthesis of bis-terephthaloyl and isophthaloyl thiosemicarbazides 3a–f

A mixture of **2a** or **2b** (1.95 g, 10 mmol) and methyl, ethyl or phenyl isothiocyanate (20 mmol) in absolute ethanol (50 mL) was heated under reflux for 7 h. The mixture was cooled and filtered. The obtained precipitate was crystallized from DMF-H_2O (2:1) to afford the corresponding bis-thiosemicarbazide derivative **3a–f**.

Terephthaloyl bis(*N*-methylhydrazino-2-thiocarbamide) (3a) Yield 94%; mp 235–237°C; IR: 3252 and 3203 (NH), 2980 (CH-Ar), 2939 (CH_3), 1676 (C=O), 1251 cm^{-1} (C=S); ^1H NMR: 2.88 (s, 6H, $2CH_3$), 8.00 (s, 4H, Ar-H), 8.10 (s, 2H, NH-NH, exchangeable with D_2O), 9.37 (s, 2H, NH, exchangeable with D_2O), 10.47 (s, 2H, NH, exchangeable with D_2O); ^{13}C NMR: δ 31.4, 128.2, 135.7, 165.9, 182.7. Anal. Calcd for $C_{12}H_{16}N_6O_2S_2$: C, 42.34; H, 4.74; N, 24.69; S, 18.84. Found: C, 42.21; H, 4.89; N, 24.50; S, 18.74.

Terephthaloyl bis(*N*-ethylhydrazino-2-thiocarbamide) (3b) Yield 95%; mp 233–234°C; IR: 3319–3240 (NH), 2970 (CH-Ar), 2931 (CH_3), 1680 (C=O), 1246 cm^{-1} (C=S); ^1H NMR: δ 1.07 (t, 6H, $2CH_3$, J = 7 Hz), 3.48 (q, 4H, $2CH_2$, J = 7 Hz), 8.00 (s, 4H, Ar-H), 8.14 (s, 2H, NH, exchangeable with D_2O), 9.26 (s, 2H, NH, exchangeable with D_2O), 10.44 (s, 2H, NH, exchangeable with D_2O); ^{13}C NMR: δ 14.9, 39.0, 128.2, 135.8, 165.8, 181.9. Anal. Calcd for $C_{14}H_{20}N_6O_2S_2$: C, 45.63; H, 5.47; N, 22.81; S, 17.40. Found: C, 45.46; H, 5.53; N, 22.74; S, 17.29.

Terephthaloyl bis(*N*-phenylhydrazino-2-thiocarbamide) (3c) Yield 96%; mp 221–223°C; IR: 3259–3175 (NH), 2928 (CH-Ar), 1672 (C=O), 1253 cm^{-1} (C=S); ^1H NMR: δ 7.14–8.05 (m, 14H, Ar-H), 9.73 (s, 2H, NH, exchangeable with D_2O), 9.86 (s, 2H, NH, exchangeable with D_2O), 10.68 (s, 2H, NH, exchangeable with D_2O); ^{13}C NMR: δ 125.6, 126.6, 128.3, 128.5, 135.8, 139.7, 162.8, 165.9, 181.6. Anal. Calcd for $C_{22}H_{20}N_6O_2S_2$: C, 56.88; H, 4.34; N, 18.09; S, 13.80. Found: C, 56.71; H, 4.39; N, 17.95; S, 13.88.

Isophthaloyl bis(*N*-methylhydrazino-2-thiocarbamide) (3d) Yield 90%; mp 197–199°C; IR: 3302 and 3203 (NH), 3005 (CH-Ar), 2939 (CH_3), 1683 (C=O), 1253 cm^{-1} (C=S); ^1H NMR: δ 2.88 (s, 6H, $2CH_3$), 7.57–8.01(m, 4H, Ar-H), 8.42 (s, 2H, NH, exchangeable with D_2O), 9.35 (s, 2H, NH, exchangeable with D_2O), 10.43 (s, 2H, NH, exchangeable with D_2O); ^{13}C NMR: δ 31.4, 128.2, 130.6, 131.3, 133.2, 166.0, 182.8. Anal. Calcd for $C_{12}H_{16}N_6O_2S_2$: C, 42.34; H, 4.74; N, 24.69; S, 18.84. Found: C, 42.17; H, 4.89; N, 24.51; S, 18.79.

Isophthaloyl bis(*N*-ethylhydrazino-2-thiocarbamide) (3e) Yield 92%; mp 207–209°C; IR: 3311–3180 (NH), 2974 (CH-Ar), 2931 (CH_3), 1676 (C=O), 1242 cm^{-1} (C=S); ^1H NMR: δ 1.06 (t, 6H, $2CH_3$, J = 7 Hz), 3.45–3.50 (q, 4H, $2CH_2$, J = 7 Hz), 8.08–8.43 (m, 4H, Ar-H), 8.11 (s, 2H, NH, exchangeable with D_2O), 9.28 (s, 2H, NH, exchangeable with D_2O), 10.41 (s, 2H, NH, exchangeable with D_2O); ^{13}C NMR: δ 14.9, 39.0, 128.2, 128.6, 131.3, 133.2, 165.9, 181.9. Anal. Calcd for $C_{14}H_{20}N_6O_2S_2$: C, 45.63; H, 5.47; N, 22.81; S, 17.40. Found: C, 45.47; H, 5.58; N, 22.67; S, 17.32.

Isophthaloyl bis(*N*-phenylhydrazino-2-thiocarbamide) (3f) Yield 89%; mp 191–192°C; IR: 3184–3113 (NH), 2939 (CH-Ar), 1676 (C=O), 1207 cm^{-1} (C=S); ^1H NMR: δ 7.15–8.21 (m, 14H, Ar-H), 8.58 (s, 2H, NH, exchangeable with D_2O), 9.94 (s, 2H, NH, exchangeable with D_2O), 10.68 (s, 2H, NH, exchangeable with D_2O); ^{13}C NMR: δ 125.7, 126.5, 128.6, 129.5, 131.5, 133.2, 139.6, 166.1, 181.9. Anal. Calcd for $C_{22}H_{20}N_6O_2S_2$: C, 56.88; H, 4.34; N, 18.09; S, 13.80. Found: C, 56.92; H, 4.47; N, 17.89; S, 13.71.

General method for the synthesis of bis(1,2,4-triazole-3-thiols) 4a–f

A suspension of **3a–f** (2 mmol) in ethanol (25 mL) was dissolved in aqueous sodium hydroxide (2 N, 2 mL) and the solution was heated under reflux for 4 h. Then, the solution was concentrated, cooled, and filtered. The filtrate was adjusted to pH ~4–5 with hydrochloric acid and kept at room temperature for 1 h. The obtained product was filtered, washed with water, dried, and crystallized from DMF-H_2O.

5,5′-(1,4-Phenylene)-bis(4-methyl-4*H*-1,2,4-triazole-3-thiol) (4a) Yield 88%; mp > 300°C; IR: 3111 (NH), 3032 (CH-Ar), 2933 (CH_3), 2756 (S-H), 1564, 1520 (C=N), 1275 cm^{-1} (C=S); ^1H NMR: δ 3.56 (s, 6H, $2CH_3$), 7.93 (s, 4H, Ar-H), 14.04 (s, 2H, SH, exchangeable with D_2O); ^{13}C NMR: δ 32.2, 128.5, 129.5, 151.1, 168.2. Anal. Calcd for $C_{12}H_{12}N_6S_2$: C, 47.35; H, 3.97; N, 27.61; S, 21.07. Found: C, 47.21; H, 3.71; N, 27.51; S, 20.86.

5,5′-(1,4-Phenylene)bis(4-ethyl-4*H*-1,2,4-triazole-3-thiol) (4b) Yield 89%; mp > 300°C; IR: 3111 (NH), 3032 (CH-Ar), 2986, 2933 (CH_3), 2750 (S-H), 1566, 1518 (C=N), 1269 cm^{-1} (C=S); ^1H NMR: δ 1.18 (t, 6H, $2CH_3$, J = 7 Hz), 4.08 (q, 4H, $2CH_2$, J = 7 Hz), 7.88 (s, 4H, Ar-H), 13.95 (s, 2H, SH, exchangeable with D_2O); ^{13}C NMR: δ 13.9, 39.2, 128.6, 128.6, 150.7, 167.7. Anal. Calcd for $C_{14}H_{16}N_6S_2$: C, 50.58; H, 4.85; N, 25.28; S, 19.29. Found: C, 50.41; H, 5.08; N, 25.31; S, 19.43.

5,5′-(1,4-Phenylene)bis(4-phenyl-4*H*-1,2,4-triazole-3-thiol) (4c) Yield 89%; mp > 300°C; IR: 3065 (NH), 2976 (CH-Ar), 2914, 2746 (S-H), 1595, 1498 (C=N), 1273 cm^{-1} (C=S); ^1H NMR: δ 7.03–7.46 (m, 14H, Ar-H), 14.11 (s, 2H, SH, exchangeable with D_2O); ^{13}C NMR: δ 126.7, 128.7, 129.3, 129.8, 130.4, 134.5, 151.3, 169.4. Anal. Calcd for $C_{22}H_{16}N_6S_2$: C, 61.66; H, 3.76; N, 19.61; S, 14.97. Found: C, 61.48; H, 3.89; N, 19.49; S, 15.15.

5,5′-(1,3-Phenylene)bis(4-methyl-4*H*-1,2,4-triazole-3-thiol) (4d) Yield 86%; mp 290–292°C; IR: 3109 (NH), 3047 (CH-Ar), 2914 (CH_3), 2769 (S-H), 1539, 1500 (C=N), 1275 cm^{-1} (C=S); ^1H NMR: δ 3.56 (s, 6H, $2CH_3$), 7.93 (s, 4H, Ar-H), 14.04 (s, 2H, SH, exchangeable with D_2O); ^{13}C NMR: δ 32.2, 128.5, 129.5, 151.1, 168.2. Anal. Calcd for $C_{12}H_{12}N_6S_2$:

C, 47.35; H, 3.97; N, 27.61; S, 21.07. Found: C, 47.23; H, 4.00; N, 27.59; S, 20.85.

5,5′-(1,3-Phenylene)bis(4-ethyl-4*H*-1,2,4-triazole-3-thiol) (4e) Yield 90%; mp 277–279°C; IR: 3101 (NH), 3026 (CH-Ar), 2933 (CH_3), 2766 (S-H), 1541, 1504 (C=N), 1280 cm^{-1} (C=S); ^1H NMR: δ 1.15 (t, 6H, $2CH_3$, J = 7 Hz), 4.07 (q, 4H, $2CH_2$, J = 7 Hz), 7.76–7.99 (m, 4H, Ar-H), 14.00 (s, 2H, SH, exchangeable with D_2O); ^{13}C NMR: δ 13.8, 39.7, 127.4, 129.0, 130.5, 131.3, 150.7, 167.4. Anal. Calcd for $C_{14}H_{16}N_6S_2$: C, 50.58; H, 4.85; N, 25.28; S, 19.29. Found: C, 50.68; H, 4.90; N, 25.17; S, 19.41.

5,5′-(1,3-Phenylene)bis(4-phenyl-4*H*-1,2,4-triazole-3-thiol) (4f) Yield 88%; mp > 300°C; IR: 3192 (NH), 3049 (CH-Ar), 2755 (S-H), 1601, 1550 (C=N), 1226 cm^{-1} (C=S); ^1H NMR: δ 7.03–7.46 (m, 14H, Ar-H), 14.11 (s, 2H, SH, exchangeable with D_2O); ^{13}C NMR: δ 126.7, 128.7, 129.3, 129.8, 130.4, 134.5, 151.3, 169.4. Anal. Calcd for $C_{22}H_{16}N_6S_2$: C, 61.66; H, 3.76; N, 19.61; S, 14.97. Found: C, 61.79; H, 3.84; N, 19.50; S, 15.21.

General procedure for the synthesis of 5,5′-phenylene bis(*N*-alkyl/phenylamino-1,3,4-thiadiazoles) 5a–f

A solution of **3a–f** (3 mmol) in concentrated sulfuric acid (3 mL) was stirred at room temperature for 2 h and then poured into ice-cold water. The mixture was made alkaline to pH ˜8 with aqueous ammonia and the resultant precipitate was filtered, washed with water, and crystallized from DMF-H_2O.

5,5′-(1,4-Phenylene)bis(*N*-methyl-1,3,4-thiadiazol-2-amine) (5a) Yield 90%; mp > 300°C; IR: 3203 (NH), 3095 (CH-Ar), 2991, 2930 (CH_3), 1575, 1523 cm^{-1} (C=N); ^1H NMR: δ 2.94 (s, 6H, $2CH_3$), 7.83(s, 4H, Ar-H), 7.94 (s, 2H, NH, exchangeable with D_2O); ^{13}C NMR: δ 31.8, 127.3, 132.0, 155.5, 169.9. Anal. Calcd for $C_{12}H_{12}N_6S_2$: C, 47.35; H, 3.97; N, 27.61; S, 21.07. Found: C, 47.62; H, 4.21; N, 27.63; S, 20.90.

5,5′-(1,4-Phenylene)bis(*N*-ethyl-1,3,4-thiadiazol-2-amine) (5b) Yield 90%; mp 295–297°C; IR: 3159 (NH), 3059 (CH-Ar), 2966, 2893 (CH_3), 1626, 1562 cm^{-1} (C=N); ^1H NMR: δ 1.21 (t, 6H, $2CH_3$, J = 7 Hz), 3.36 (q, 4H, $2CH_2$, J = 7 Hz), 7.83 (s, 4H, Ar-H), 8.10 (s, 2H, NH, exchangeable with D_2O); ^{13}C NMR: δ 14.7, 40.2, 127.3, 132.1, 155.3, 169.1. Anal. Calcd for $C_{14}H_{16}N_6S_2$: C, 50.58; H, 4.85; N, 25.28; S, 19.29. Found: C, 50.63; H, 4.98; N, 25.33; S, 19.11.

5,5′-(1,4-Phenylene)bis(*N*-phenyl-1,3,4-thiadiazol-2-amine) (5c) Yield 90%; mp > 300°C; IR: 3155 (NH), 3014 (CH-Ar), 1575, 1523 cm^{-1} (C=N); ^1H NMR: δ 6.70 (s, 2H, NH, exchangeable with D_2O) 7.16–7.95 (14H, Ar-H); ^{13}C NMR: δ 118.2, 124.4, 128.0, 129.1, 131.7, 141.6, 156.5, 166.1. Anal. Calcd for $C_{22}H_{16}N_6S_2$: C, 61.66; H, 3.76; N, 19.61; S, 14.97. Found: C, 61.87; H, 3.90; N, 19.58; S, 15.69.

5,5′-(1,3-Phenylene)bis(*N*-methyl-1,3,4-thiadiazol-2-amine) (5d) Yield 90%; mp 238–240°C; IR: 3171 (NH), 3092 (CH-Ar), 2939, 2864(CH_3), 1566 cm^{-1} (C=N); ^1H NMR: δ 2.94 (s, 6H, $2CH_3$), 7.55–8.05 (m, 4H, Ar-H), 8.11 (s, 2H, NH, exchangeable with D_2O); ^{13}C NMR: δ 31.8, 123.4, 127.8, 130.6, 132.1, 155.4, 170.0. Anal. Calcd for $C_{12}H_{12}N_6S_2$: C, 47.35; H, 3.97; N, 27.61; S, 21.07. Found: C, 47.18; H, 3.75; N, 27.65; S, 20.85.

5,5′-(1,3-Phenylene)bis(*N*-ethyl-1,3,4-thiadiazol-2-amine) (5e) Yield 92%; mp 242–244°C; IR: 3188 (NH), 3032 (CH-Ar), 2982 (CH_3), 1631, 1543 (C=N), 1178 cm^{-1} (C=S); ^1H NMR: δ 1.20 (t, 6H, $2CH_3$, J = 7 Hz), 3.37 (q, 4H, $2CH_2$, J = 7 Hz), 6.94–7.75 (m, 4H, Ar-H), 8.15 (s, 2H, NH, exchangeable with D_2O). Anal. Calcd for $C_{14}H_{16}N_6S_2$: C, 50.58; H, 4.85; N, 25.28; S, 19.29. Found: C, 50.81; H, 4.66; N, 25.04; S, 19.02.

5,5′-(1,3-Phenylene)bis(*N*-phenyl-1,3,4-thiadiazol-2-amine) (5f) Yield 88%; mp > 300°C; IR: 3111 (NH), 3032 (CH-Ar), 2933 (CH_3), 2756 (S-H), 1564, 1520 (C=N), 1275 cm^{-1} (C=S); ^1H NMR: δ 6.99–7.87 (m, 14H, Ar-H), 8.27 (s, 2H, NH, exchangeable with D_2O); ^{13}C NMR: δ 117.1, 124.2, 127.0, 129.0, 130.9, 131.5, 141.3, 141.5, 157.6, 164.6. Anal. Calcd for $C_{22}H_{16}N_6S_2$: C, 61.66; H, 3.76; N, 19.61; S, 14.97. Found: C, 61.51; H, 3.83; N, 19.52; S, 15.12.

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