

The Chemistry of 1,2,5-Thiadiazoles. IV.  
Benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]tris[1,2,5]thiadiazole (1)

Andrew P. Komin and Marvin Carmack\*

Contribution No. 2716 from the Department of Chemistry,  
Indiana University, Bloomington, Indiana 47401

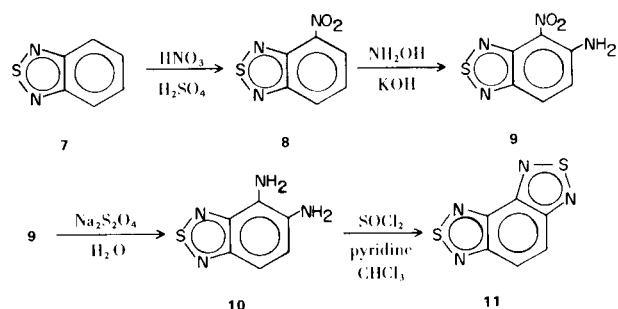
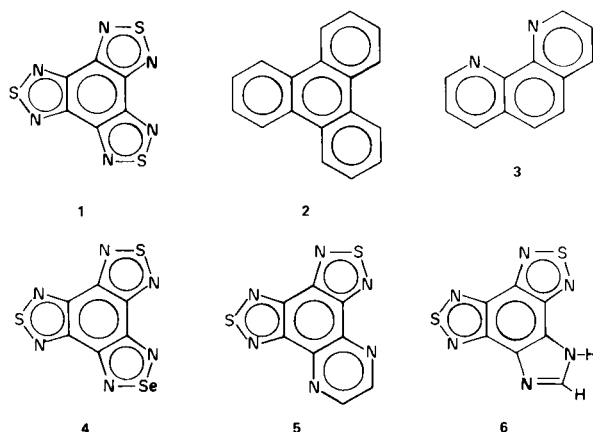
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Benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]tris[1,2,5]thiadiazole (1) was synthesized from benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (11). Nitration of 11 gave compound 15, which on direct amination gave nitroamine 17. Reduction of 17 gave diamine 18, and cyclization of 18 with thionyl chloride gave 1. Diamine 18 was also cyclized with selenium oxychloride, glyoxal, 9,10-phenanthrenequinone, and formic acid to give the compounds 4, 5, 19, and 6, respectively. A new procedure for the preparation of 2,1,3-benzothiadiazole (7) from *o*-phenylenediamine was used.

We have synthesized in good yield the title compound, benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]tris[1,2,5]thiadiazole (1), an analog of triphenylene (2) in which each of the peripheral benzene rings has been replaced with a 1,2,5-thiadiazole ring.

Benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]tris[1,2,5]thiadiazole is a stable, faintly yellow crystalline solid, m.p. 344-346°, which is only slightly soluble in most organic solvents. The strong electron-withdrawing nature of the 1,2,5-thiadiazole ring makes 1 an extremely weak base and, as a consequence, 1 does not form metal complexes as does 1,10-phenanthroline (3). Three more insoluble and high-melting compounds, in which one of the 1,2,5-thiadiazole rings of 1 is replaced with a 1,2,5-selenadiazole (4), pyra-

zine (5), or imidazole (6) ring, were also prepared from the immediate precursor to 1. The syntheses leading to 1, 4, 5 and 6, was prepared by traditional methods of ring closure on *o*-phenylenediamine (2-4), or by a modification of the original Hinsberg method (5) in which 7 was continuously steam distilled from *o*-phenylenediamine in diethylene glycol treated with sulfur dioxide and water at 160-180°. Nitration of 7 in a mixture of nitric and sulfuric acids at 0-10° gave 4-nitro-2,1,3-benzothiadiazole (8) in 95% yield (4). Pesin's procedure (6) for the direct amination of 8 with hydroxylamine in alcoholic potassium hydroxide gave 5-amino-4-nitro-2,1,3-benzothiadiazole (9) which was immediately (7) reduced to 4,5-diamino-2,1,3-benzothiadiazole (10) with sodium hydrosulfite in water (6). Ring closure of 10 with thionyl

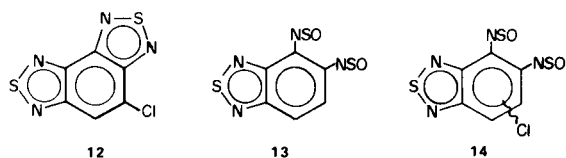


zine (5), or imidazole (6) ring, were also prepared from the immediate precursor to 1.

The starting material, 2,1,3-benzothiadiazole (7), for

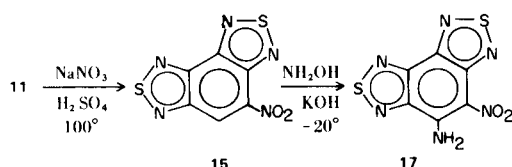
chloride and pyridine in refluxing chloroform (8) gave benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (11) in 89% yield. Sublimed 11 is a white solid, m.p. 179.5-180.5 [lit. (8) 173-175°] showing a singlet at  $\delta$  7.97 in the nmr, and a molecular ion at  $m/e$  193.9722 (100%) in its mass spectrum. An attempt to cyclize 10 in refluxing neat thionyl chloride gave a mixture of products. A mass spectrum of the crude mixture indicated molecular ions for 11 ( $m/e$

194), the monochlorination product **12** (m/e 228, 230), the bis-NSO compound **13** (m/e 258), the chlorinated bis-NSO compound **14** (m/e 292, 294), and a possible dimeric product (m/e 418). Although **7** was readily nitrated in a

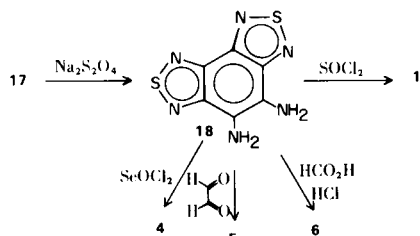


mixture of nitric and sulfuric acids at low temperature, under the same conditions **11** was recovered unchanged due to the additional deactivating 1,2,5-thiadiazole ring. Nitration of **11** with sodium nitrate in sulfuric acid at 100° gave 4-nitro-benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (**15**) in 90% yield. Compound **15** is a faintly yellow solid, m.p. 184.5-185.5°, showing a singlet at  $\delta$  8.91 in the nmr for the strongly deshielded lone proton (**9**), and a molecular ion at m/e 238.9569 (100%) in its mass spectrum. Nitro compound **15** was readily reduced to 4-amino-benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (**16**) with sodium hydrosulfite in warm water. Amine **16** showed a molecular ion at 208.9833 (100%) in its mass spectrum.

Direct amination of a fine suspension (**10**) of **15** with hydroxylamine in methanolic potassium hydroxide at -20° gave a nearly quantitative yield of 4-amino-5-nitro-benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (**17**), a bright



yellow solid, showing a molecular ion at m/e 253.9681 in its mass spectrum. The nitro amine **17** was reduced with sodium hydrosulfite in water at 85° to give 4,5-diamino-benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (**18**), a brown solid. The mass spectrum of **18** gave a molecular ion at m/e 223.9940 (100%). Diamine **18** was cyclized to **1** in refluxing thionyl chloride with a trace of pyridine. Moderation of the closure reaction with chloroform, as in the



preparation of **11**, was unnecessary, since **18** does not have any sites available for chlorination of the benzene ring. Trace amounts of moist pyridine are known to catalyze coupling of two *N*-sulfinyl (R-NSO) groups to give sulfur

dioxide and a sulfodiimide bond (R-N=S=N-R) (**11**), which in the present case is a 1,2,5-thiadiazole ring. Although **1** can be recrystallized from boiling DMF, it is poorly soluble in organic solvents.

The monoselenium analog of **1**, [2,1,3]benzoselenadiazolo[4,5-*c*:6,7-*c'*]bis[1,2,5]thiadiazole (**4**), was prepared by heating diamine **18** in neat selenium oxychloride containing a trace of pyridine at 80°. Compound **4** is a light orange solid, m.p. > 360°, giving a molecular ion at m/e 299.8793 (<sup>80</sup>Se isotope) in its mass spectrum. The fragmentation patterns and the assignments of the ions for **1** and **4** are shown in Table I. The fragment ions produced from **4** preferentially contain selenium, and the selenium ion (m/e 80) predominated over the sulfur ion (m/e 32).

The mono pyrazine analog of **1**, bis[1,2,5]thiadiazolo[3,4-*f*:3',4'-*h*]quinoxaline (**5**), was synthesized by refluxing diamine **18** in aqueous glyoxal for 20 minutes. Sublimed **5** is a white solid, m.p. > 360°. The mass spectrum of **5** shows a molecular ion at m/e 245.9780 and fragments at m/e 219 and 192 corresponding to the loss of two HCN

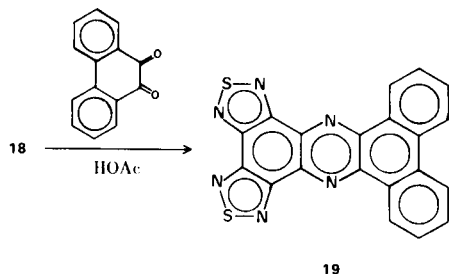
TABLE I

70 eV Mass Spectra of **1** and **4**  
Relative Intensity (b)

m/e (a)	<b>1</b>	<b>4</b>	Assignment
300		100	<b>4</b> M <sup>+</sup> (C <sub>6</sub> N <sub>6</sub> S <sub>2</sub> Se)
268		0.1	C <sub>6</sub> N <sub>6</sub> SSe
252	100		<b>3</b> M <sup>+</sup> (C <sub>6</sub> N <sub>6</sub> S <sub>3</sub> )
220	1.0	1.6	C <sub>6</sub> N <sub>6</sub> S <sub>2</sub>
216		1.1	C <sub>4</sub> N <sub>4</sub> SSe
168	7.8	3.3	C <sub>4</sub> N <sub>4</sub> S <sub>2</sub>
164		2.6	C <sub>2</sub> N <sub>2</sub> SSe
150		1.5	<b>4</b> M <sup>++</sup>
138		0.6	CNSSe
132		0.5	C <sub>2</sub> N <sub>2</sub> Se
126	2.6		<b>1</b> M <sup>++</sup>
118		3.0	C <sub>2</sub> NSe
116	19.1	3.6	C <sub>2</sub> N <sub>2</sub> S <sub>2</sub>
112		30.4	SSe
106		1.6	CNSe
94		1.2	NSe
90	2.2	0.7	CNS <sub>2</sub>
84	9.5	7.1	C <sub>2</sub> N <sub>2</sub> S
80		24.2	Se
70	10.9	2.6	C <sub>2</sub> NS
64	33.9	2.0	S <sub>2</sub>
58	5.3	2.6	CNS
52	1.2	0.8	C <sub>2</sub> N <sub>2</sub>
46	11.2	5.8	NS
32	14.6	7.7	S

(a) Only the <sup>80</sup>Se mass values of selenium containing ions are reported. In all cases the appropriate isotope cluster was observed. (b) The relative intensities of selenium-containing ions were corrected by dividing the <sup>80</sup>Se peak height intensity by 0.49 and normalizing.

molecules. A proton nmr of **5** showed the two strongly deshielded pyrazine protons at  $\delta$  9.15 (12). Diamine **18**



was refluxed in acetic acid with 9,10-phenanthrenequinone to give the heptacyclic compound, dibenzo[*a,c*]bis[1,2,5]-thiadiazolo[3,4-*h*:3',4'-*j*]phenazine (**19**).

Heptacyclic **19** is a light yellow powder, m.p.  $> 360^\circ$ , nearly insoluble in organic solvents, and showing a molecular ion at  $m/e$  396.0249 (100%) in its mass spectrum. The imidazole analog of **1**, bis[1,2,5]thiadiazolo[3,4-*e*:3',4'-*g*]benzimidazole (**6**) was obtained by refluxing diamine **18** overnight with 90% formic acid containing 6 *N* hydrochloric acid. An exact mass measurement gave  $m/e$  233.9785 (100%) for the molecular ion.

#### EXPERIMENTAL

##### General.

Melting points (uncorrected) were determined in a Mel-Temp apparatus in open capillary tubes. Analyses were performed by Midwest Microlab, Indianapolis, Ind. Infrared spectra were recorded on a Perkin-Elmer 137 spectrometer. Low-resolution mass spectra (70 eV) were obtained on a Varian MAT CH-7 instrument using a heated probe. High-resolution mass spectra (70 eV) were obtained on an AEI MS-9 spectrometer. Proton nmr spectra were recorded on a Varian HR-220 instrument with internal TMS as reference.

##### 2,1,3-Benzothiadiazole (**7**).

Practical grade *o*-phenylenediamine (21.6 g., 200 mmoles) was stirred with 50 ml. of diethylene glycol and heated at 160-180 $^\circ$  during the simultaneous slow addition of water (150 ml.) and bubbling of sulfur dioxide over 3 hours. The steam distillate obtained was extracted twice with methylene chloride (25 ml.). The combined methylene chloride extracts were washed with water, dried (magnesium sulfate), and evaporated to give 16.6 g. (61%) of pure white **7**, spectroscopically identical to authentic **7**; mass spectrum  $m/e$  (rel intensity): 136 (100), 135 (8), 109 (21), 90 (10), 77 (8), 76 (8), 64 (8), 52 (10), 51 (16), 50 (10), 46 (17), 45 (34), 39 (8), and 32 (7).

##### 4-Nitro-2,1,3-benzothiadiazole (**8**).

Khaletsky and Pesin's procedure (4) for the nitration of 2,1,3-benzothiadiazole (**7**) was carried out on a 1.0 mole scale with consistent yields of 95%; mass spectrum  $m/e$  (rel intensity): 181 (100), 151 (70), 135 (65), 123 (64), 109 (10), 108 (39), 103 (25), 91 (10), 84 (10), 83 (13), 76 (33), 75 (11), 70 (10), 69 (10), 64 (48), 52 (15), 51 (14), 50 (15), 46 (12), 45 (15), 32 (10), and 30 (70).

##### 5-Amino-4-nitro-2,1,3-benzothiadiazole (**9**).

The procedure of Pesin *et al.* (6) was conducted at lower temperature on a more concentrated mixture. Hydroxylamine hydrochloride (60.0 g., 0.863 mole) was added to a solution of 32.0 g. (0.177 mole) of **8** in 1.4 l. of hot methanol. The mixture was cooled rapidly to  $-15^\circ$  to give a fine suspension. A previously prepared solution of potassium hydroxide (120 g. in 760 ml. of methanol) was added at  $-10$  to  $-15^\circ$  over 20 minutes. The dark mixture was allowed to warm to room temperature and stirred into 10 l. of water. The product was filtered through a 20-cm Buchner funnel and washed with 500 ml. of water; mass spectrum  $m/e$  (rel intensity): 196 (100), 166 (48), 150 (16), 138 (10), 123 (14), 117 (20), 96 (11), 79 (24), 66 (10), 64 (14), 53 (9), 52 (23), 46 (12), 32 (12), 30 (19), and 28 (14).

##### 4,5-Diamino-2,1,3-benzothiadiazole (**10**).

See reference 8 and note 7. The wet filter cake of crude **9** was transferred to a 4 l. stainless steel beaker with 1.5 l. of hot water and heated to boiling with vigorous mechanical stirring. Sodium hydrosulfite (135 g.) was added over 30 seconds (mild foaming), and heating continued for an additional 2 minutes. A few solid particles were removed by hot filtration of the dark red solution through a preheated filter. On cooling to room temperature, **10** crystallized out of the filtrate and was separated.

Recrystallization from boiling water gave 18.3 g. (62.2% from **8**) of **10** as brick red needles; m.p. 168-169 $^\circ$  [lit (6) 168-170 $^\circ$ ]; mass spectrum  $m/e$  (rel intensity): 166 (100), 165 (13), 138 (5), 133 (8), 96 (7), 80 (6), 79 (14), 55 (5), 54 (6), 53 (7), 52 (7), and 28 (9).

*Exact Mass* Calcd. for  $C_6H_6N_4S$ : 166.0313. Found: 166.0315.

##### Benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (**11**).

A solution of 50 ml. of thionyl chloride in 30 ml. of chloroform was added over 15 minutes to a suspension of 10.0 g. (60.2 mmoles) of diamine **10** in 170 ml. of chloroform and 50 ml. of pyridine (8). After the solution had been refluxed for 15 minutes, it was distilled at atmospheric pressure and finally at 0.05 mm to give a dry brown solid. The solid was stirred with 300 ml. of ice water for 1 hour, filtered, washed with 100 ml. of water, and dried. The solid was recrystallized from methylene chloride and acetone with carbon treatment to give slightly yellow **11** (89.1% average yield). Pure white **11** was obtained by sublimation at 95 $^\circ$  (0.02 mm), m.p. 179.5-180.5 $^\circ$  [lit (8) 173-175 $^\circ$ ]; ir (potassium bromide): 6.63, 7.17, 7.37, 8.98, 9.49, 11.40, 12.00, 12.61, 13.90, and 14.78  $\mu$ ; nmr (deuteriochloroform):  $\delta$  7.97 (s); mass spectrum  $m/e$  (rel intensity): 194 (100), 167 (10), 116 (8), 110 (8), 97 (3,  $M^{++}$ ), 84 (5), 83 (3), 70 (13), 64 (21), 59 (3), 58 (4), 52 (4), 51 (3), 46 (12), 45 (5), and 32 (19).

*Exact Mass* Calcd. for  $C_6H_2N_4S_2$ : 193.9721. Found: 193.9722.

*Anal.* Calcd. for  $C_6H_2N_4S_2$ : C, 37.10; H, 1.04. Found: C, 37.41; H, 1.20.

##### 4-Nitro-benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (**15**).

Recrystallized **11** (5.82 g., 30.0 mmoles) was dissolved in 30 ml. of concentrated sulfuric acid and heated to 90 $^\circ$ . Powdered sodium nitrate (6.60 g., 77.6 mmoles) was added in small portions over 10 minutes with stirring so as to maintain the temperature between 95 and 102 $^\circ$ . After being heated an additional 10 minutes at 100 $^\circ$ , the solution was cooled to room temperature and poured onto 90 g. of ice with stirring. The solid was filtered, washed with 500 ml. of water, and dried at 0.05 mm overnight to give 6.40 g. (89.7%) of **15** as a powder. Recrystallization of **15** from acetone gave very pale yellow needles, m.p. 184.5-185.5 $^\circ$ ; nmr (deuteriochloroform):  $\delta$  8.91 (s), ir (potassium bromide): 6.26, 6.52, 6.70,

7.15, 7.41, 7.51, 9.20, 10.36, 10.81, 11.43, 11.89, 12.27, 12.42, 13.14, and 13.79  $\mu$ ; mass spectrum *m/e* (rel intensity): 239 (100), 209 (35), 193 (23), 181 (53), 97 (11), 90 (13), 84 (10), 83 (20), 70 (13), 64 (91), 58 (14), 46 (43), 32 (30), and 30 (77).

*Exact Mass* Calcd. for  $C_6H_5N_5O_2S_2$ : 238.9572. Found: 238.9569.

*Anal.* Calcd. for  $C_6H_5N_5O_2S_2$ : C, 30.12; H, 0.42. Found: C, 29.83; H, 0.51.

#### 4-Amino-benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (**16**).

Nitro compound **15** (239 mg., 1.00 mmole) was stirred vigorously in 7 ml. of water for 1 hour to produce a fine suspension. After heating to 80°, sodium hydrosulfite (800 mg.) was added in one portion (mild foaming) and heating continued for 1 minute. The mixture was cooled to room temperature and filtered. The yellow-tan solid was washed with cold water (4 ml.) and dried under vacuum to give 123 mg. (58.8%) of **16**, m.p. > 195° dec.; mass spectrum *m/e* (rel intensity): 209 (100), 182 (10), 177 (3), 150 (5), 98 (5), 85 (3), 73 (5), 70 (4), 67 (6), 66 (6), 64 (8), 46 (9), 41 (3), 40 (4), 32 (8), and 28 (6).

*Exact Mass* Calcd. for  $C_6H_3N_5S_2$ : 208.9830. Found: 208.9833.

#### 4-Amino-5-nitro-benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (**17**).

Unrecrystallized, powdered **15** (2.39 g., 10.0 mmoles) was stirred overnight with 90 ml. of methanol to produce a fine suspension. Powdered hydroxylamine hydrochloride (4.53 g., 65.2 mmoles) was added and the suspension cooled to -20°. A previously prepared solution of potassium hydroxide (9.05 g., 226 mmoles) in 58 ml. of methanol was cooled to -20° and added dropwise over 15 minutes. The resulting bright yellow suspension was warmed to 25° over 1 hour with stirring. The solid product was isolated in nearly quantitative yield by centrifuging the reaction mixture and washing the crude material twice with methanol. For the reduction of **17** to **18** it was convenient to use the product moist with methanol. However, dried **17** showed mass spectrum *m/e* (rel intensity): 254 (100), 224 (89), 208 (17), 181 (15), 175 (15), 154 (13), 137 (15), 85 (12), 84 (14), 70 (20), 64 (42), 53 (12), 46 (32), 44 (17), 32 (30), 30 (40), and 28 (23).

*Exact Mass* Calcd. for  $C_6H_2N_6O_2S_2$ : 253.9681. Found: 253.9681.

During the work-up of an amination run on 12 g. of **15** (prepared from unrecrystallized **11**), dilute hydrochloric acid was added to pH ~ 7 and the suspension became bright yellow as in the above reaction, and the **17** was isolated by the procedure described above.

#### 4,5-Diamino-benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (**18**).

Nitroamine **17** still moist with methanol from the previous synthesis was transferred to a 600-ml. beaker with 200 ml. of water and heated to 85° with vigorous mechanical stirring. Sodium hydrosulfite (12.5 g., 71.6 mmoles) was added in one portion (mild foaming) and the mixture heated an additional 2 minutes at 85-90°. After cooling to 20°, the brown solid was filtered, washed with water (150 ml.), and dried at 0.05 mm to give 2.20 g. (98.2% based on **15**) of **18**, m.p. > 360°; ir (potassium bromide): 3.00, 6.08, 6.23, 6.61, 6.92, 7.13, 7.79, 11.98, 12.20, 12.69, 13.00, 13.40, and 13.86  $\mu$ ; mass spectrum *m/e* (rel intensity): 224 (100), 223 (16), 191 (8), 138 (7), 137 (21), 85 (9), 60 (7), 55 (12), 53 (10), 46 (6), 32 (7), and 28 (29).

*Exact Mass* Calcd. for  $C_6H_4N_6S_2$ : 223.9939. Found: 223.9940.

#### Benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]tris[1,2,5]thiadiazole (**1**).

Pyridine (50  $\mu$ l.) was added to diamine **18** (2.24 g., 10.0 mmoles) suspended in 20 ml. of thionyl chloride. After heating at reflux for 1.5 hours, the excess thionyl chloride was removed under aspirator vacuum and final traces pumped away at 0.05 mm leaving an orange-yellow solid. The solid was stirred for 1 hour with 50 ml. of ice water, filtered, washed with water, and dried to give 2.34 g. (92.8%) of **1** (shown to be free of **18** by its mass spectrum). The product was dissolved in boiling DMF, treated with carbon, and filtered hot through a preheated filter. After the filtrate had cooled to room temperature, the faint yellow needles of **1** were collected and dried (84% recovery), m.p. 344-346° (sealed tube); ir (potassium bromide): 6.00, 6.48, 7.12, 7.49, 7.68, 9.00, 11.94, and 14.05  $\mu$ ; mass spectrum (see Table 1).

*Exact Mass* Calcd. for  $C_6N_6S_3$ : 251.9347. Found: 251.9345.

*Anal.* Calcd. for  $C_6N_6S_3$ : C, 28.56; H, 0.00; N, 33.31. Found: C, 28.44; H, 0.00; N, 33.46.

#### Bis[1,2,5]thiadiazolo[3,4-*e*:3',4'-*g*]benzimidazole (**6**).

Diamine **18** (224 mg., 1.00 mmole) was refluxed for 4 hours with a mixture of 4 ml. of 90% formic acid and 0.5 ml. of 6 *N* hydrochloric acid. After cooling, the mixture was brought to pH ~ 4 and filtered. The tan solid was washed well with water and dried to give 230 mg. (98.2%) of **6**, which was purified by sublimation at high temperature and showed, m.p. > 360°; ir (potassium bromide): 6.19, 6.35, 7.14, 7.90, 9.22, 10.38, 12.00, and 12.28  $\mu$ ; mass spectrum *m/e* (rel intensity): 234 (100), 207 (7), 150 (7), 123 (3), 117 (4), 84 (3), 71 (4), 70 (9), 64 (16), 46 (7), 32 (6), and 28 (6).

*Exact Mass* Calcd. for  $C_7H_2N_6S_2$ : 233.9782. Found: 233.9785.

#### [2,1,3]Benzoselenadiazolo[4,5-*c*:6,7-*c'*]bis[1,2,5]thiadiazole (**4**).

Diamine **18** (336 mg., 1.50 mmoles) was suspended in 2 ml. of methylene chloride while 1.5 ml. of selenium oxychloride was added dropwise. After the initial exothermic reaction subsided, heating was begun and 20  $\mu$ l. of pyridine added. The methylene chloride was boiled off and the mixture held at 80° for 10 minutes, then cooled to room temperature and poured onto 20 ml. of ice water. The precipitated solid was filtered, washed with water, and vacuum dried to give 402 mg. (89.5%) of light orange **4**, m.p. > 360° (sealed tube); ir (potassium bromide): 6.10, 6.50, 7.15, 7.43, 7.49, 7.76, 7.98, 9.03, 12.00, 13.00, 13.20, 13.90, and 14.45  $\mu$ ; mass spectrum (see Table I).

*Exact Mass* Calcd. for  $C_6N_6S_2^{80}Se$ : 299.8791. Found: 299.8793.

#### Bis[1,2,5]thiadiazolo[3,4-*f*:3',4'-*h*]quinoxaline (**5**).

Glyoxal (1 ml. of a 40% aqueous solution) was added to a suspension of **18** (224 mg., 1.00 mmole) in 4 ml. of boiling water. The mixture was refluxed for 20 minutes and cooled to room temperature. The resulting brown solid was filtered, washed with 50 ml. of water, and dried to give 228 mg. (92.6%) of **5**. Sublimation at high temperature gave white product, m.p. > 360°; ir (potassium bromide): 6.60, 6.99, 7.13, 7.35, 7.41, 7.49, 8.41, 9.01, 9.12, 11.48, 11.95, 12.00, and 14.30  $\mu$ ; mass spectrum *m/e* (rel intensity): 246 (100), 219 (17,  $M^+$ -HCN), 192 (12,  $M^+$ -2HCN), 123 (4), 116 (4), 108 (4), 84 (7), 70 (7), 64 (11), 52 (6), 46 (5), 45 (4), and 32 (7).

*Exact Mass* Calcd. for  $C_8H_2N_6S_2$ : 245.9782. Found: 245.9780.

#### Dibenzo[*a,e*]bis[1,2,5]thiadiazolo[3,4-*h*:3',4'-*j*]phenazine (**19**).

Diamine **18** (224 mg., 1.00 mole) and 9,10-phenanthrenequinone (208 mg., 1.00 mmole) were refluxed with 15 ml. of acetic

acid for 46 hours and then cooled. The resulting solid was filtered and washed with 5 ml. of acetic acid and dried at 0.02 mm overnight to give 332 mg. (83.8%) of yellow **19**, m.p.  $> 360^\circ$ ; ir (potassium bromide): 6.20, 6.94, 7.14, 7.33, 7.48, 8.24, 8.85, 12.00, 12.18, 13.01, 13.64, and 13.83  $\mu$ ; mass spectrum ( $300^\circ$  source) m/e (rel intensity): 396 (100), 395 (6), 363 (11), 280 (7), 198 (6,  $M^{++}$ ), and 176 (10).

*Exact Mass* Calcd. for  $C_{20}H_8N_6S_2$ : 396.0252. Found: 396.0249.

## REFERENCES

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