Sulfur Nitride in Organic Chemistry. Part 19.[1)] Selective Formation of Benzo- and Benzobis[1,2,5]thiadiazole Skeleton in the Reaction of Tetrasulfur Tetranitride with Naphthalenols and Related Compounds

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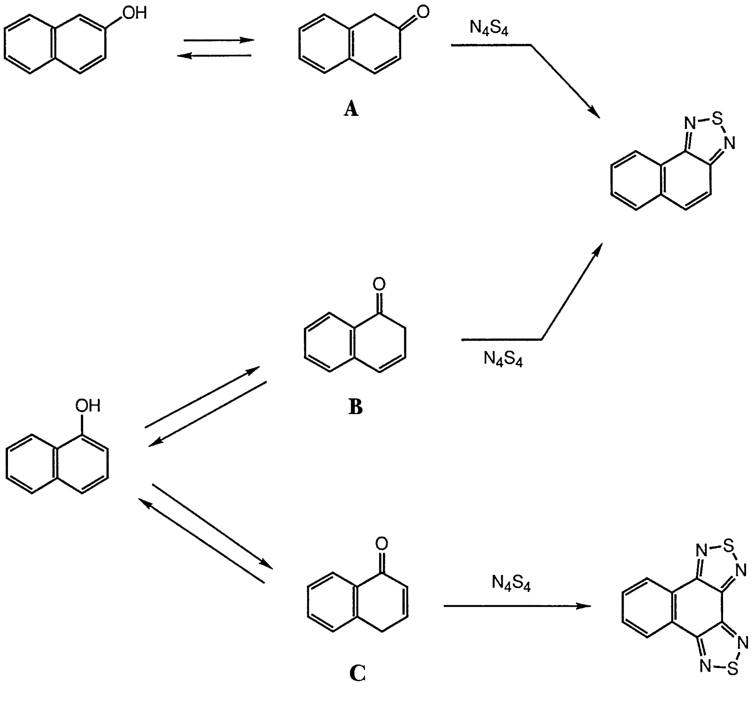
Tetrasulfur tetranitride (N_4S_4) reacted with 2-naphthols to afford naphtho [1,2-*c*][1,2,5] thiadiazoles (**13**) in high yields, while 1-naphthaols gave naphtho[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazoles as a major product, together with a small amount of **13**. In the reactions with naphthalenediols such as 1,5-, 2,6-, 2,7-, 1,6-, and 1,7-diol, naphtho[1,2-*c*:5,6-*c*′]- or naphtho[1,2-*c*:7,8-*c*′]bis[1,2,5]thiadiazoles were obtained in varying yields. In some cases, naphtho[1,2-*c*:3,4-*c*′:5,6-*c*″]tris[1,2,5]thiadiazole was formed as a by-product. In reactions with 5-isoquinolinol, 8-quinolinoles, 9*H*-carbazol-2-ol, and dibenzofuran-2-ol, one and/or two 1,2,5-thiadiazole-ring-fused heteroaromatic compounds were obtained.

Recently, it was reported that the reaction of tetrasulfur tetranitride (N_4S_4) (**1**) with phenols and polyhydroxybenzenes afforded benzo-,[2)] benzobis-,[1)] and benzotris[1,2,5]thiadiazoles.[1)] These 1,2,5-thiadiazoles were converted to polyaminobenzenes[1,2)] such as benzenediamine, -tetramine, and -hexamine.

It was already reported that the reaction of **1** with benzyl ketone derivatives afforded 4-substituted 3-aryl-1,2,5-thiadiazoles in good yields.[3–5)]

As an extention of the above, we investigated the reaction of **1** with naphthalenols from the following viewpoints; in a reaction with 2-naphthol, **1** was expected to attack the benzylic position of tautomer **A**, giving naphtho[1,2-*c*][1,2,5]thiadiazole, while both naphtho[1,2-*c*][1,2,5]thiadiazole and naphtho[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole might be formed in a reaction with 1-naphthol by an attack of **1** on the two tautomers, **B** and **C** (Scheme 1).



Scheme 1.

The present paper describes the reactions of **1** with naphthalenols and some related hydroxy-substituted benzoheterocycles.

Results and Discussion

All reactions of **1** with naphthalenols and hydroxy-substituted benzoheterocycles were carried out in refluxing toluene for 48 h; the results are summarized in Table 1 and Scheme 2.

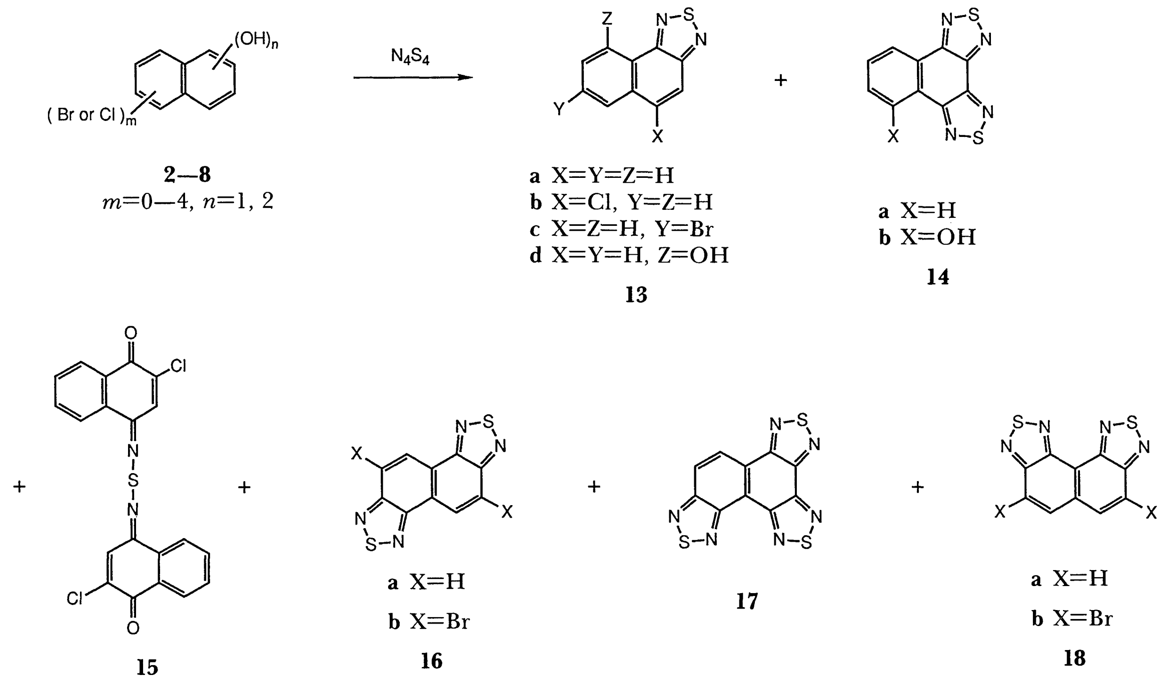
The reaction of **1** with 1-naphthol (**2a**) afforded naphtho[1,2-*c*][1,2,5]thiadiazole (**13a**) and naphtho[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (**14a**) in 9 and 14% yield, respectively. Compound **14a** was obtained from halogenated 1-naphthols, such as 2,4-dichloro-1-naphthol (**2b**) and 2,4-dibromo derivative (**2c**), in better yields than **2a**; the reactions with **2b** and **2c** afforded **14a** in 19 and 27% yield, respectively. In the reaction with **2b**, *N,N'*-thiobis[1,4-naphtoquinone monoimine] (**15**) and 5-chloronaphtho[1,2-*c*][1,2,5]thiadiazole (**13b**) were formed as a side product (3 and 1% yield, respectively).

On the contrary, the reaction with 2-naphthol (**3a**) afforded **13a** as the sole product in fair yield (84%). Similarly, 6-bromo-2-naphthol (**3b**) gave 7-bromo-

Table 1. Reaction of Tetrasulfur Tetranitride (**1**) with Naphthalenols

	Naphthalenols	N_4S_4 (**1**)/substrate[a]	Product/mol %[b]
2a	1-OH	2	**13a** (9), **14a** (14)
2b	1-OH 2,4-Cl_2	2	**13b** (1), **14a** (19), **15** (3)
2c	1-OH 2,4-Br_2	2	**14a** (27)
3a	2-OH	2	**13a** (84)
3b	2-OH 6-Br	2	**13c** (96)
3c	2-OH 1-Br	4	**13a** (51)
4a	1,5-$(OH)_2$	2	**16a** (5), **17** (+)[c]
4b	1,5-$(OH)_2$ 2,6-Br_2	3	**16a** (35), **17** (11)
4c	1,5-$(OH)_2$ 2,4-Br_2	4	**14b** (9), **17** (4)
5a	2,6-$(OH)_2$	2	**16a** (43)
5b	2.6-$(OH)_2$ 1,5-Br_2	3	**16a** (88)
5c	2,6-$(OH)_2$ 1,3,5,7-Br_4	4	**16b** (61)
6a	2,7-$(OH)_2$	2	**18a** (5)
6b	2,7-$(OH)_2$ 1,3,6-Br_3	4	**18b** (61)
7	1,6-$(OH)_2$	2	**16a** (5)
8a	1,7-$(OH)_2$	2	**13d** (+),[c] **18a** (2)
8b	1,7-$(OH)_2$ 2,6,8-Br_3	4	**17** (8)

a) Molar ratio. b) Isolated yield; calculated on the basis of the substrate used. c) Plus sign means that the yield is less than 1%.



2—8
m=0—4, *n*=1, 2

a X=Y=Z=H
b X=Cl, Y=Z=H
c X=Z=H, Y=Br
d X=Y=H, Z=OH

13

a X=H
b X=OH

14

15

a X=H
b X=Br

16

17

a X=H
b X=Br

18

Scheme 2.

[1,2-*c*][1,2,5]thiadiazole (**13c**) in an almost quantitative yield. Also, 1-bromo-2-naphthol (**3c**) gave the expected **13a** in modest yield (51%).

The above-mentioned results demonstrated the selective construction of the naphthobis[1,2,5]thiadiazole and naphtho[1,2,5]thiadiazole skeleton by a reaction of **1** with 1-naphthol (**2**) and 2-naphthol (**3**), respectively.

Next, the reaction of **1** with naphthalenediols and their halogenated derivatives, which have one hydroxyl group in each benzene ring, was investigated. Since 1,5-naphthalenediol (**4a**) has two hydroxyl groups at the *α*-positions in each benzene ring, the formation of naphthotetrakis[1,2,5]thiadiazole was expected. The reaction with **4a** afforded naphtho[1,2-*c*:5,6-*c*′]bis[1,2,5]thiadiazole (**16a**) in only 5% yield, accompanied with a trace amount of naphtho[1,2-*c*:3,4-*c*:5,6-*c*″]tris[1,2,5]thiadiazole (**17**). The yields of **16a** and **17** increased to 35 and 11%, respectively, in the reaction with 2,6-dibromo derivative **4b**. In contrast with this result, the 2,4-dibromo derivative **4c** gave naphtho[1,2-*c*:3,4-*c*]bis[1,2,5]thiadiazol-7-ol (**14b**) (9%) as a main product, accompanied by **17** (4%). Finally, a reaction with the 2,4,6,8-tetrabromo derivative **4d** only gave a complex mixture of unidentified products.

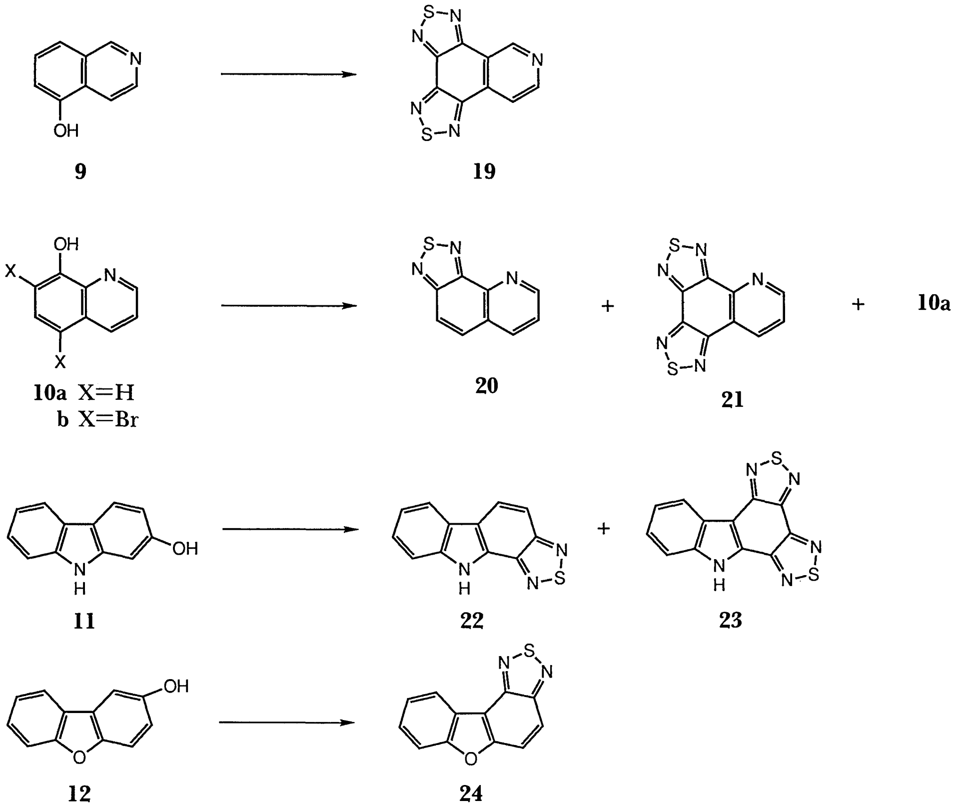
Naphthalenes having two hydroxyl groups on the *β*-positions gave the expected naphthobis[1,2,5]thiadiazoles in a reaction with **1**, generally in good yield. The reaction with 2,6-naphthalenediol (**5a**) afforded naphtho[1,2-*c*;5,6-*c*]bis[1,2,5]thiadiazole (**16a**) in 43% yield. The yield of **16a** was increased up to 88% in a reaction with the 1,5-dibromo derivative **5b**. As expected, the 1,3,5,7-tetrabromo derivative **5c** gave 4,9-dibromo compound **16b** in 61% yield. On the other hand, another *β*,*β*′-dihydroxy type, 2,7-naphthalenediol (**6a**), afforded naphtho[1,2-*c*:7,8-*c*′]bis[1,2,5]thiadiazole (**18a**) in only 5% yield, though the reaction with 1,3,6-tribromo derivative **6b** gave 4,7-dibromo compound **18b** in 61% yield.

Since the unsubstituted compound **18a** was obtained only in poor yield, the hydrodebromination of **18b** was carried out by using $NaBH_4$ in refluxing ethanol, giving **18a** in 58% yield (Scheme 3). Compound **18a** became accessible via **18b** in moderate yield. Compound **16b** was sparingly soluble in any organic solvents and could not be reduced to **16a**.

The reaction of naphthalenediols bearing two hydroxyl groups each on the *α* and *β* positions gave poor results: **16a** and **18a** were obtained from **7** and **8** in 5 and 2% yield, respectively. In the reaction with **8**, a trace amount of naphtho[1,2-*c*][1,2,5]thiadiazol-9-ol (**13d**) was formed. The 2,6,8-tribromo derivative (**8b**)

$$\mathbf{18b} \xrightarrow[(58\%)]{NaBH_4} \mathbf{18a} \xleftarrow[5\%]{N_4S_4} \mathbf{6a}$$

Scheme 3.



Scheme 4.

Table 2. Reaction of Tetrasulfur Tetranitride (**1**) with Hydroxy-Substituted Benzoheterocycles

Hydroxy-substituted benzoheterocycle[a]	Products/mole %[b]
9	**19** (18)
10a	**20** (25), **21** (7), **10a** (4)
10b	**21** (27)
11	**22** (26), **23** (6)
12	**24** (97)

a) Molar ratio of N_4S_4 (**1**): substrate=2:1. b) Isolated yield; calculated on the basis of the substrate used.

afforded **17** in 8% yield.

The selective construction of mono- and bis[1,2,5]-thiadiazole-fused skeleton was also observed in the reaction of **1** with hydroxy-substituted benzoheterocycles (Table 2 and Scheme 4), though not so remarkable as in the case of the naphthalenols. The reaction of **1** with 5-isoquinolinol (**9**) afforded only bis[1,2,5]thiadiazolo[3,4-*f*:3′,4′-*h*]isoquinoline (**19**) in 18% yield. Unexpectedly, 8-quinolinol (**10a**) afforded [1,2,5]thiadiazolo[3,4-*h*]quinoline (**20**) in 25% yield and bis[1,2,5]-thiadiazolo[3,4-*f*:3′,4′-*h*]quinoline (**21**) in 7% yield with a 4% yield of recovered **10a**. Only **21** was obtained in 27% yield in a reaction with 5,7-dibromo derivative **10b**. The reaction with 9*H*-carbazol-2-ol (**11**) afforded predominantly [1,2,5]thiadiazolo[3,4-*a*]carbazole (**22**) in 20% yield, with bis[1,2,5]thiadiazolo[3,4-*a*:3′,4′-*c*]carbazole (**23**) as a by-product.

As previously reported,[6] tetra-*t*-butylated dibenzofuran-1-ol reacted with **1**, gave tri-*t*-butylbenzofuro-[3,2-*e*][2,1,3]benzothiadiazole in 61% yield. The reaction with dibenzofuran-2-ol (**12**) afforded benzofurobenzothiadiazole (**24**) in an almost quantitative yield (97%).

The product selectivity observed in the reaction of **1** with **2**—**12** seems to be correlated with the difference in the mode of keto–enol tautomerism of 1-hydroxy derivatives and 2-hydroxy ones, as stated in the introductory part, though the detailed mechanism of the above-mentioned reactions is not known.

Experimental

General. All melting points were determined on a Mitamurariken MELT THERMO and are uncorrected. The IR spectra were measured as KBr pellets on a Nippon-Bunko A-102. The NMR spectra were recorded at 270 MHz with a JEOL GSX-270 using Me_4Si as an internal standard in $CDCl_3$, unless otherwise stated. Mass spectra were obtained on a JEOL JMS-O1SG-2 mass spectrometer at 75 eV using a direct inlet system. UV and VS spectra were measured on a Hitachi 220A spectrophotometer. Column chromatography was carried out on silica gel (Wako gel, C-300).

Materials. Compounds **2c**,[7] **4b**,[8,9] **4c**,[9] **4d**,[8] and **5b**[10] were prepared by the reported methods.

2,4-Dibromo-1-naphthol (2c): Colorless needles (ethanol); mp 98—101 °C (lit,[7] mp 105 °C). Found: C, 40.09; H, 2.11%.

2,6-Dibromo-1,5-naphthalenediol (4b): Gray needles (AcOH); mp >350 °C (it became colored around 200 °C) [lit,[8] mp >300 °C (darkened at 200 °C) and lit,[9] mp 224 °C (decomp)]. Found: C, 37.89; H, 2.02%.

2,4-Dibromo-1,5-naphthalenediol (4c): Colorless needles (hexane); mp 147—149 °C (lit,[9] mp 147.5 °C); ^{1}H NMR δ=6.00 (1H, s, D_2O-exchanged), 7.11 (1H, dd, J=8 and 1 Hz), 7.45 (1H, dd, J=8 and 8 Hz), 7.65 (1H, s), 7.88 (1H, dd, J=8 and 1 Hz), and 7.95 (1H, s, D_2O-exchanged).

2,4,6,8-Tetrabromo-1,5-naphthalenediol (4d): Yellowish white plates (toluene); mp 220—223 °C (lit,[8] mp >300 °C); IR 3460, 3320 cm^{-1}; MS m/z 480 (M^+), 478 (M^+), 476 (M^+), 474 (M^+), and 472 (M^+). Found: C, 25.55; H, 1.11%.

1,5-Dibromo-2,6-naphthalenediol (5b): Colorless prisms (dioxane), mp 209—213 °C (lit,[10] mp >223 °C); ^{1}H NMR (CD_3OD) δ=7.22 (2H, d, J=9 Hz) and 8.00 (2H, d, J=9 Hz). Found: C, 37.98; H, 1.87%.

1,3,5,7-Tetrabromo-2,6-naphthalenediol (5c). A mixture of **5a** (9.1 g, 57 mmol) and bromine (12 ml, 233 mmol) in AcOH (400 ml) was refluxed for 2 h. After it cooled, the mixture was poured into water and the precipitates were filtered, washed well with acetone, and filtered to give **5c** (0.97 g, 4%): Colorless needles; mp 279—282 °C (decomp); IR 3480 and 3350 cm^{-1}; ^{1}H NMR (CD_3OD) δ=8.32 (s); MS m/z 480 (M^+), 478 (M^+), 476 (M^+), 474 (M^+), and 472 (M^+). Found: C, 25.45; H, 0.92%. Calcd for $C_{10}H_4Br_4O_2$:C, 25.25; H, 0.85%.

1,3,6-Tribromo-2,7-naphthalenediol (6b). To a mixture of **6a** (4.0 g, 25 mmol) in AcOH (100 ml), bromine (5.2 ml, 101 mmol) in AcOH (20 ml) was added dropwise. During the addition, the temperature of the mixture was increased to about 40 °C. The mixture was refluxed for 2 h. After it cooled, precipitated **6b** (7.29 g, 74%) was collected by filtration: Colorless powder; mp 183—197 °C; IR 3490 and 3420 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ=7.57 (1H, s), 8.04 (1H, s), 8.05 (1H, s), 8.69 (1H, s, D_2O-exchanged), 9.57 (1H, s, D_2O-exchanged); MS m/z 400 (M^+), 398 (M^+), 396 (M^+), and 394 (M^+). Found: C, 30.44; H, 1.42%. Calcd for $C_{10}H_5Br_3O_2$:C, 30.26; H, 1.27%.

2,6,8-Tribromo-1,7-naphthalenediol (8b). A mixture of bromine (5 ml, 97 mmol) in AcOH (15 ml) was added dropwise to a mixture of **8a** (5.0 g, 31 mmol) in AcOH (80 ml) at room temperature; the reaction mixture was then stirred for 30 min. The precipitated **8b** (7.56 g, 61%) was collected by filtration and recrystallized from carbon tetrachloride, giving **8b** as grayish blue needles: Mp >300 °C; IR 3500 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ=7.44 (1H, d, J=9 Hz), 7.81 (1H, s), and 8.09 (1H, d, J=9 Hz); MS m/z 400 (M^+), 398 (M^+), 396 (M^+), and 394 (M^+). Found: C, 30.50; H, 1.69%. Calcd for $C_{10}H_5Br_3O_2$: C, 30.27; H, 1.27%.

5,7-Dibromo-8-quinolinol (10b). A mixture of **10a** (5.0 g, 34 mmol) and bromine (1.8 ml, 35 mmol) in AcOH (120 ml) was stirred at room temperature. Compound **10b** gradually precipitated; after one night it was colllected by filtration (2.02 g, 19%): Yellow needles (AcOH); mp 218—220 °C; IR 3300—2400 cm^{-1}; MS m/z 305 (M^+), 303 (M^+), and 301 (M^+). Found : C, 35.52; H, 2.13; N, 4.52%. Calcd for $C_9H_5Br_2NO$: C, 35.68; H, 1.66; N, 4.62%.

General Procedure for the Reaction of 1 with Naphthalenols (2—8) and Hydroxy-Substituted Benzoheterocycles (9—12). After a mixture of **1** and an appropriate amount of naphthalenols or hydroxy-substituted benzoheterocycles in toluene (100 ml) was heated under reflux for 48 h, it was cooled to room temperature. An insoluble material containing unidentified inorganic compounds was filtered off and the filtrate was concentrated to 30 ml; the condensate was then chromatographed. Sulfur was first eluted with hexane and unreacted N_4S_4 with a mixture of hexane and benzene. Then, products **10a**, **13a**[11)]—**13d**, **14a—b**, **16a**, **17**, **18a—b**, **19**, **20**, **21**, **22**, and **24** were obtained from the fraction eluted with benzene. Products **15** and **23** were eluted with chloroform.

Compound **16b** was obtained as precipitates during the reaction and washed successively with benzene, chloroform, and then ethanol. An analytical sample of **16b** was obtained by recrystallization from dioxane. The physical properties of the new compounds obtained in this study are shown below.

5-Chloronaphtho[1,2-*c*][1,2,5]thiadiazole (13b): Colorless needles (ethanol); mp 121—123 °C; MS *m/z* 222 (M$^+$) and 220 (M$^+$). Found: C, 54.54; H, 2.17; N, 12.49%. Calcd for $C_{10}H_5ClN_2S$: C, 54.43; H, 2.28; N, 12.69%.

7-Bromonaphtho[1,2-*c*][1,2,5]thiadiazole (13c): Colorless plates (ethanol); mp 157—160 °C; ^{1}H NMR δ=7.60—7.85 (3H, m), 7.96 (1H, d, J=2 Hz), and 8.51 (1H, d, J=8 Hz); ^{13}C NMR δ=121.1, 123.7, 125.6, 127.0, 131.0, 131.1, 131.6, 134.5, 153.7, and 154.3; MS *m/z* 266 (M$^+$) and 264 (M$^+$). Found: C, 45.39; H, 1.78; N, 10.73%. Calcd for $C_{10}H_5BrN_2S$: C, 45.30; H, 1.90; N, 10.57%.

Naphtho[1,2-*c*][1,2,5]thiadiazol-9-ol (13d): Pale yellow needles (ethanol); mp 113—116 °C; IR 3300 cm^{-1}; ^{1}H NMR δ=7.32 (1H, d, J=8 Hz), 7.44 (1H, d, J=7 Hz), 7.65 (1H, dd, J=7 and 8 Hz), 7.77 (1H, d, J=9 Hz), 7.86 (1H, d, J=9 Hz), and 10.26 (1H, s); MS *m/z* 202 (M$^+$). Found: C, 59.16; H, 2.69; N, 13.63%. Calcd for $C_{10}H_6N_2OS$: C, 59.39; H, 2.99; N, 13.85%.

Naphtho[1,2-*c*:3,4-*c*] bis [1,2,5]thiadiazole (14a): Straw colored needles (ethanol); mp 203—208 °C; UV (MeOH) 331 (ε 17000), 315 (18600), 300 (17400), 263 (16600), and 239 nm (34700); ^{1}H NMR δ=7.78—7.81 (2H, m) and 8.64—8.67 (2H, m); ^{13}C NMR δ=126.4, 127.1, 130.9, 148.2, and 156.4; MS *m/z* 244 (M$^+$). Found: C, 49.33; H, 1.58; N, 22.53%. Calcd for $C_{10}H_4N_4S_2$: C, 49.17; H, 1.65; N, 22.93%.

Naphtho[1,2-*c*;3,4-*c*]bis[1,2,5]thiadiazol-7-ol (14b): Pale pink needles (ethanol); mp 236—239 °C (it changed to prisms around 175 °C); IR 3255 cm^{-1}; ^{1}H NMR δ=7.37 (1H, dd, J=8 and 1 Hz), 7.71 (1H, dd, J=8 and 8 Hz), 8.19 (1H, dd, J=8 and 1 Hz), and 10.38 (1H, s, D_2O-exchanged); MS *m/z* 260 (M$^+$). Found: C, 45.64; H, 1.89; N, 21.17%. Calcd for $C_{10}H_4N_4OS_2$: C, 46.14; H, 1.55; N, 21.52%.

***N,N′*-Thiobis[3-chloro-1,4-naphthoquinone 1-imine] (15):** Red needles (ethanol); mp 260—264 °C (decomp); IR 1660 cm^{-1}; ^{1}H NMR δ=7.65—7.69 (2H, m), 7.75—7.78 (2H, m), 7.98 (2H, s), 8.24 (2H, dd, J=9 and 1 Hz), and 8.35 (2H, dd, J=8 and 2 Hz); MS *m/z* 416 (M$^+$), 414 (M$^+$), and 412 (M$^+$). Found: C, 57.79; H, 2.12; N, 6.86%. Calcd for $C_{20}H_{10}Cl_2N_2O_2S$: C, 58.13; H, 2.44; N, 6.78%.

Naphtho[1,2-*c*:5,6-*c*]bis[1,2,5]thiadiazole (16a): Straw colored needles (ethanol); mp 203—208 °C; UV (MeOH) 331 (ε 16700), 315 (18600), 300 (17400), 263 (16600), and 239 nm (34700); ^{1}H NMR δ=7.78—7.81 (2H, m), 8.64—8.67 (2H, m); ^{13}C NMR δ=126.4, 127.1, 130.9, 148.2, and 156.4; MS *m/z* 244 (M$^+$). Found: C, 49.33; H, 1.58; N, 22.53%. Calcd for $C_{10}H_4N_4S_2$: C, 49.17; H, 1.65; N, 22.93%.

4,9-Dibromonaphtho[1,2-*c*:5,6-*c′*]bis[1,2,5]thiadiazole (16b): Yellow needles (dioxane); mp >350 °C; MS *m/z* 494 (M$^+$), 492 (M$^+$), and 490 (M$^+$). Found: C, 30.13; H, 0.91; N, 13.75%. Calcd for $C_{10}H_2Br_2N_4S_2$: C, 29.87; H, 0.50; N, 13.93%.

Naphtho[1,2-*c*:3,4-*c′*:5,6-*c″*]tris[1,2,5]thiadiazole (17): Pale yellow needles (ethanol); mp 311—313 °C; ^{1}H NMR δ=8.37 (1H, d, J=9 Hz) and 8.97 (1H, d, J=9 Hz); MS *m/z* 302 (M$^+$). Found: C, 39.57; H, 0.53; N, 27.47%. Calcd for $C_{10}H_2N_6S_3$: C, 39.72; H, 0.67; N, 27.79%.

Naphtho[1,2-*c*:7,8-*c′*]bis[1,2,5]thiadiazole (18a): Yellow needles (ethanol); mp 244—248 °C; UV (MeOH) 373 (ε 12300), 356 (14450), 345 (22400), 330 (15850), 255 (46770), and 250 nm (46770); ^{1}H NMR δ=8.14 (2H, J=8 Hz), 8.88 (2H, d, J=8 Hz); ^{13}C NMR δ=121.6 and 127.5; MS *m/z* 244 (M$^+$). Found: C, 49.27; H, 1.52; N, 22.73%. Calcd for $C_{10}H_4N_4S_2$: C, 49.17; H, 1.65; N, 22.93%.

4,7-Dibromonaphtho[1,2-*c*:7,8-*c′*]bis[1,2,5]thiadiazole (18b): Pale yellow plates (benzene); mp 298—316 °C; ^{1}H NMR δ=8.27 (s); MS *m/z* 404 (M$^+$), 402 (M$^+$), and 400 (M$^+$). Found: C, 29.98; H, 0.85; N, 13.69%. Calcd for $C_{10}H_2Br_2N_4S_2$: C, 29.87; H, 0.50; N, 13.93%.

Bis[1,2,5]thiadiazolo[3,4-*f*:3′,4′-*h*]isoquinoline (19): Pink needles (ethanol); mp 220—221 °C; ^{1}H NMR δ=8.48 (1H, d, J=5 Hz), 9.03 (1H, d, J=5 Hz), and 9.99 (1H, s); ^{13}C NMR δ=118.8, 121.2, 131.9, 148.4, 148.8, 149.2, 150.7, 154.2, and 154.3; MS *m/z* 245 (M$^+$). Found: C, 43.87; H, 1.08; N, 28.42%. Calcd for $C_9H_3N_5S_2$: C, 44.07; H, 1.23; N, 28.55%.

[1,2,5]Thiadiazolo[3,4-*h*]quinoline (20): Colorless needles (methanol); mp 139—141 °C; ^{1}H NMR δ=7.65 (1H, dd, J=8 and 4 Hz), 7.83 (1H, d, J=9 Hz), 7.94 (1H, d, J=9 Hz), 8.24 (1H, dd, J=8 and 2 Hz), and 9.09 (1H, dd, J=4 and 2 Hz); ^{13}C NMR δ=121.0, 124.0, 128.7, 130.7, 136.5, 143.1, 150.8, 153.8, and 156.1; MS *m/z* 187 (M$^+$). Found: C, 57.50; H, 2.37; N, 22.81%. Calcd for $C_9H_5N_3S$: C, 57.74; H, 2.69; N, 22.44%.

Bis[1,2,5]thiadiazolo[3,4-*f*:3′4′-*h*]quinoline (21): Pale purple needles (ethanol); mp 257—259 °C; ^{1}H NMR δ=7.72 (1H, dd, J=8 and 4 Hz), 8.96 (1H, dd, J=8 and 1 Hz), and 9.11 (1H, dd, J=4 and 1 Hz); ^{13}C NMR δ=123.5, 125.2, 134.4, 144.0, 148.0, 149.1, 152.7, 154.9, and 155.5; MS *m/z* 244 (M$^+$). Found: C, 44.10; H, 1.11; N, 28.19%. Calcd for $C_{12}H_7N_3S$: C, 44.07; H, 1.23; N, 28.55%.

[1,2,5]Thiadiazolo[3,4-*a*]carbazole (22): Bright yellow needles (purified by sublimation); mp 256—258 °C; IR 3302 cm^{-1}; ^{1}H NMR δ=7.35 (1H, dd, J=7 and 7 Hz), 7.48 (1H, dd, J=7 and 7 Hz), 7.62 (1H, d, J=8 Hz), 7.75 (1H, d, J=9 Hz), 8.10 (1H, d, J=8 Hz), 8.24 (1H, d, J=9 Hz) and 9.33 (1H, br s); MS *m/z* 225 (M$^+$). Found: C, 64.09; H, 2.73; N, 18.65%. Calcd for $C_{12}H_7N_3S$: C, 63.98; H, 3.13; N, 18.65%.

Bis[1,2,5]thiadiazolo[3,4-*a*:3′,4′-*c*]carbazole (23): Green needles (benzene); mp 308—314 °C; IR 3295 cm; ^{1}H NMR (CD_3SOCD_3) δ=7.35—7.51 (2H, m), 7.72 (1H, d, J=9 Hz), 8.41 (1H, d, J=8 Hz), and 12.86 (1H, br s); MS *m/z* 283 (M$^+$). Found: C, 51.08; H, 1.41; N, 24.35%. Calcd for $C_{12}H_5N_5S_2$: C, 50.87; H, 1.78; N, 24.72%.

Benzofuro[3,2-*e*][2,1,3]benzothiadiazole (24): Pale yellow needles (ethanol); mp 115—116 °C; ^{1}H NMR δ=7.46—7.50 (2H, m), 7.59—7.66 (1H, m), 7.84 (1H, d, J=9 Hz), 7.95 (1H, d, J=9 Hz), and 8.34—8.38 (1H, m); ^{13}C NMR δ=112.1, 114.0, 117.7, 119.9, 122.5, 123.7, 124.3, 127.1, 150.0, 153.3, 156.2, and 156.3; MS *m/z* 226 (M$^+$). Found: C, 63.47; H, 2.43; N, 12.25%. Calcd for $C_{12}H_6N_2OS$: C, 63.70; H, 2.67; N, 12.38%.

Hydrodebromination of 18b. A mixture of **18b** (100 mg, 0.25 mmol) and sodium borohydride (500 mg, 13 mmol) in ethanol (50 ml) was refluxed for 5 min, cooled to room temperature, and filtered to give **18a** (35 mg, 58%).

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