NUCLEOPHILIC SUBSTITUTION REACTION OF 4-BROMO-BENZO [1,2-*C*;3,4-*C'*] BIS [1,2,5] THIADIAZOLE AND REDUCTION OF HYDROXY AND METHOXY DERIVATIVE TO THE CORRESPONDING 1,2,3,4-BENZENETETRAAMINE

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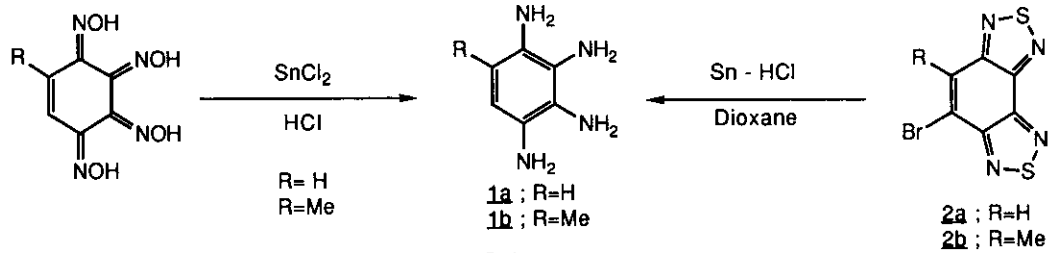
Abstract —— Bromobenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (2a) reacted with a series of nucleophiles to give alkoxy-, propylthio-, and amino-substituted derivatives (3, 8, and 9). Reaction of 2a with allyl alcohol at room temperature gave allyl ether (3e) which, on being heated, rearranged to 4-allyl-5-hydroxy derivative (4). Treatment of methoxy and ethoxy derivatives (3a and 3b) with hydrobromic acid gave hydroxy compound (5). Reduction of 3a and 5 gave the corresponding 1,2,3,4-benzenetetraamine (10•3HCl) and (11•2HCl), respectively. Reduction of piperidino derivative (9b) gave a mixture of hydrochlorides of 1,2,3,4-benzenetetraamine (1a), 11, and 5-piperidino-1,2,3,4-benzenetetraamine (12).

Though 1,2,3,4-benzenetetraamine (1a) and 5-methyl derivative (1b) were prepared by reduction of the corresponding tetraoxime almost a century ago[1] (Scheme 1), they are still the only known member of 1,2,3,4-benzenetetraamine family, to our best knowledge. Recently, we reported on the preparation of 1a and 1b by reduction of 4-bromobenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (2a and 2b), respectively[2] (Scheme 1). Since a bromo atom of

2 is activated by the two 1,2,5-thiadiazole rings having electron-withdrawing nature, nucleophilic substitution reaction of 2 may afford its derivatives having a variety of substituents, which are synthetically equivalent with substituted 1,2,3,4-benzenetetraamines.

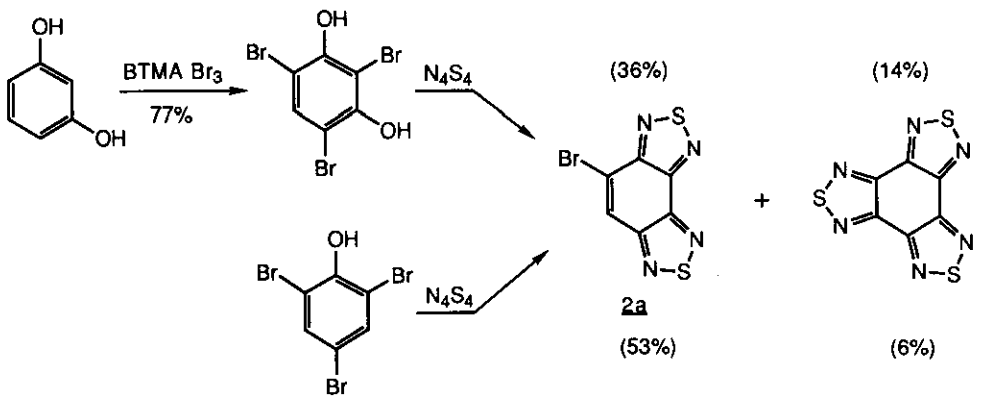


Scheme 1

From these points of view, we undertook the nucleophilic substitution reaction of 2a and the reduction of the produced benzobis[1,2,5]thiadiazoles. The results are described in the present article.

Results and discussions.

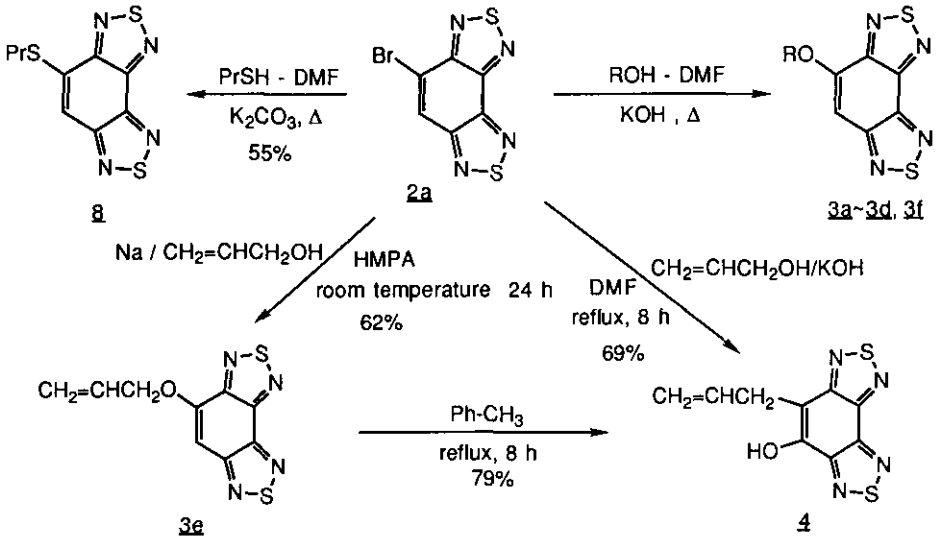
Substitution reaction. Earlier 2a was prepared by the reaction of 2,4,6-tribromo-resorcinol[3] with tetrasulfur tetranitride (N_4S_4)[2] in 36 % yield. Compound (2a) is now more easily obtained *via* the reaction of 2,4,6-tribromophenol with N_4S_4 in 53 % yield (Scheme 2).



Scheme 2

The results of the subsitution of 2a with a series of nucleophiles are summarized in Scheme 3 and Table 1. When 2a was heated in a mixture of methanol and DMF under reflux in the presence of potassium hydroxide for 6 h, the expected 3a[4] was produced in 65 % yield.

Similary ethoxy, isopropoxy, and pentyloxy derivatives (3b, 3c, and 3d) were prepared in the yields shown in Table 1. The similar reaction of 2a with allyl alcohol under reflux afforded the rearranged product (4) in 69 % yield. Ether (3e) was obtained by the reaction



Scheme 3

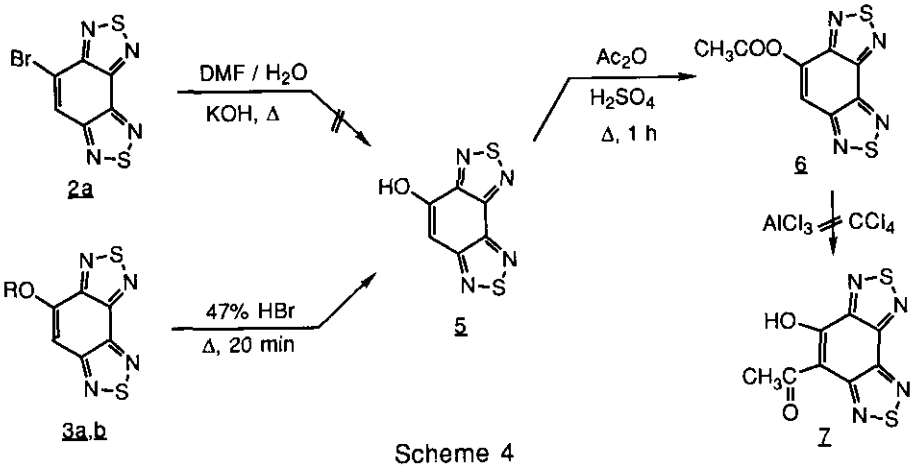
Table 1. Substitution reactions of 2a.

Product	R-	time (h)	Yield (%)
3a	Me-	6	65
3b	Et-	8	94
3c	^{i}Pr-	8	36
3d	C_5H_{11}-	8	53
3f	Ph-	2[a)]	63

a) In the presence of Cu powder.

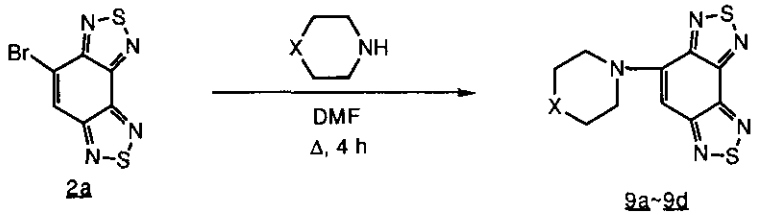
of 2a with sodium allyl oxide in HMPA at room temperature for 24 h. As expected, 3e rearranged to 4 in toluene under reflux in 79 % yield. The reaction of 2a with phenol was carried out in the presence of copper powder, giving 3f in 63% yield. The reaction without copper powder gave a complex mixture of unidentified products. Treatment of 2a with a mixture of propane thiol, DMF, and potassium carbonate gave sulfide (8) (Scheme 3).

None of hydroxy derivative (5) was detected when 2a was heated in a mixture of potassium hydroxide, water, and DMF under reflux and unchanged (2a) was recovered quantitatively. Compound (5) was prepared *via* the cleavage of the ether linkage of 3a and 3b in 78 % and 69 % yields, respectively. Esterification of 5 with acetic anhydride gave 6 in 57 % yield. Fries rearrangement of 6 did not afford the desired 7. Compound (6) was recoverd together with 5 which might be formed during work-up (Scheme 4).



Scheme 4

Cyclic amines reacted with 2a in DMF under reflux, affording 9 in moderate yields (Scheme 5 and Table 2). Addition of a base did not improve the yield ; 9b was obtained in 20% yield in the presence of potassium carbonate.

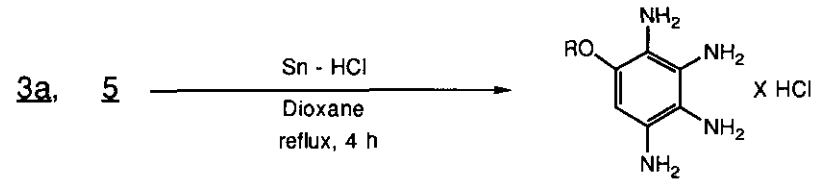


Scheme 5

Table 2. Reactions of 2a with cyclic amines.

Product	X	Yield (%)	Product	X	Yield (%)
9a	none	59	9c	O	31
9b	CH_2	30	9d	NMe	20

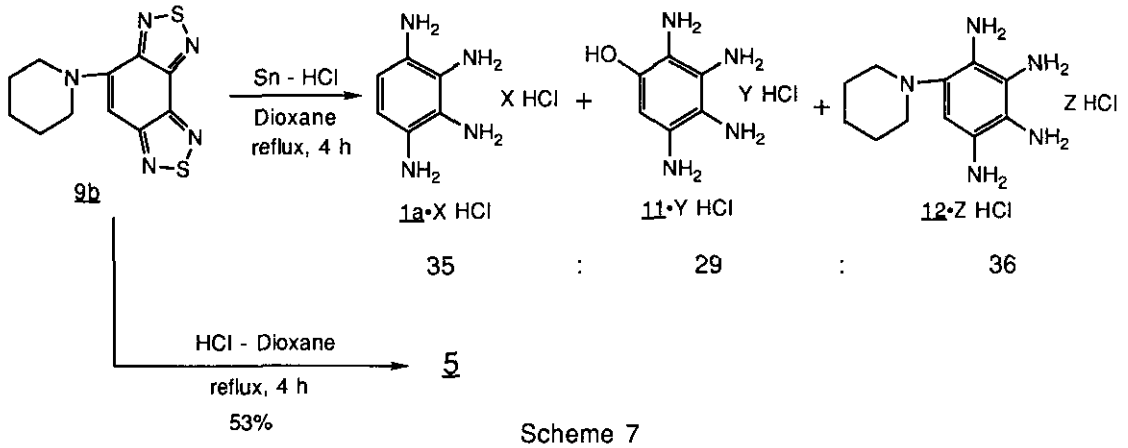
Reduction. Reduction of 3a and 5 according to the reported method[2] afforded the corresponding amine (10) and (11) as tri- and di-hydrochloride, respectively. Both of the hydrochlorides precipitated in the reaction mixture during the reduction and were easily separated by filtration (Scheme 6).



10 ; R=Me, X=3
11 ; R=H, X=2

Scheme 6

Higher homologues (3b, 3c, 3e) and aromatic ether (3f) were also reduced as notified by evolution of hydrogen sulfide during the reduction. Neither isolation of the corresponding tetraamines nor the trapping of them with benzil were successful and only tarry materials were produced.



Scheme 7

The white solid products which precipitated during the reduction of 9b were deduced to be a 35:29:36 mixture of 1,2,3,4-benzenetetraamine hydrochlorides of unsubstituted 1a, hydroxy derivative (11), and piperidino derivative (12) on the basis of its ^{1}H nmr spectrum. Formation of 1a is explained by reductive cleavage of the C-N bond of 9b and/or tetraamine (12). Compound (11) was formed *via* hydrolysis of 9b followed by reduction of the

produced 5. In fact, 9b was hydrolyzed under the above conditions without tin, giving 5 in 53 % yield (Scheme 7).

EXPERIMENTAL

General. All melting points were determined on a Mitamura-riken MELT-THERMO and Yanagimoto micro melting point apparatus and are uncorrected. Ir spectra were measured on a Nippon-Bunko IR-700 and A-102 spectrophotometer as potassium bromide pellets. ^{1}H Nmr spectra were recorded on a Nippon Denshi JEOL FT-100 or GSX-270MHz using TMS (tetramethylsilane) or DSS [sodium 3-(trimethylsilyl)-1-propanesulfonate] as an internal standard. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at 75eV using a direct inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300).

Preparation of 2a : A mixture of tribromophenol (2.00 g, 6.00 mmol) and N_4S_4 (2.20 g, 12.0 mmol) in toluene (100 ml) was heated under reflux for 48 h. After it was cooled to room temperature, insoluble materials were filtered and washed with hot CH_2Cl_2. The filtrate and the washing were combined, condensed *in vacuo*, and chromatographed. After sulfur was eluted with hexane, 2a[2] (874 mg, 53%) was eluted with benzene and benzo[1,2-*c*;3,4-*c'*;5,6-*c''*]tris[1,2,5]-thiadiazole[2] (95 mg, 6%) with ethyl acetate.

4-Methoxybenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (3a) : After a mixture of 2a (297 mg, 1.10 mmol), potassium hydroxide (0.41 g, 7.3 mmol), DMF (5 ml), and methanol (5 ml) was heated under reflux for 5 h, it was cooled to room temperature. The precipitates were collected by filtration and recrystallized to give 3a (160 mg, 65%) as pale yellow needles (benzene - hexane); mp 221~222°C [lit.,[4] pale yellow needles (hexane); mp 200~202°C]. Anal. Calcd for $C_7H_4N_4OS_2$: C, 37.49; H, 1.80; N, 24.98. Found: C, 37.36; H, 1.83; N, 24.94.

4-Ethoxybenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (3b) : After a mixture of 2a (119 mg, 0.436 mmol), potassium hydroxide (72 mg, 13 mmol), DMF (3 ml), and ethanol (3 ml) was heated under reflux for 8 h. The reaction mixture was cooled to room temperature and precipitated 3b was collected by filtration. The filtrate was poured into ice-cold water and acidified (pH=1) with 10% hydrochloric acid, giving an additional crop of 3b which were collected by filtration. The filtrate was extracted with CH_2Cl_2 (20 ml × 2), dried ($MgSO_4$), and evaporated, giving additional 3b. Crude 3b was combined and recrystallized, giving 3b (99 mg, 94%) as colorless needles [benzene - EtOH (1:5)] ; mp 191~193°C; ^{1}H nmr ($CDCl_3$, 100 MHz, δ, ppm) 7.12 (1H, s), 4.36 (2H, q, J=7 Hz), 1.64 (3H, t, J=7 Hz) ; ir (ν, cm^{-1}) 2980, 2940, 1600, 830 ; ms (m/z) 238 (M^+). Anal. Calcd for $C_8H_6N_4OS_2$: C, 40.32; H, 2.53; N, 23.51. Found: C, 40.44; H, 2.41; N, 23.56.

4-Isopropoxybenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (3c) : After a mixture of 2a (119 mg, 0.436 mmol), potassium hydroxide (73 mg, 1.3 mmol), DMF (2 ml), and *i*-propyl alcohol (2 ml) was heated under reflux for 8 h, it was cooled to room temperature, poured into ice-cold water, and acidified (pH=1) with 10% hydrochloric acid. The precipitates were collected by filtration, chromatographed using benzene as an eluent, and recrystallized to give 3c (39 mg, 36%) as pale yellow needles (hexane) ; mp 153~156°C; ^{1}H nmr ($CDCl_3$, 100 MHz, δ, ppm) 7.14 (1H, s), 5.00~4.76 (1H, m), 1.58 (6H, d, J=6Hz) ; ir (ν, cm^{-1}) 3000, 2950, 1590, 830 ; ms (m/z) 252 (M^+). ; Anal. Calcd for $C_9H_8N_4OS_2$: C, 42.84; H, 3.20; N, 22.20. Found: C, 42.52; H, 3.31; N, 22.09.

4-Pentyloxybenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (3d) : A mixture of 2a (212 mg, 0.776 mmol), potassium hydroxide (0.14g, 2.5 mmol), DMF (3 ml), and pentyl alcohol (3 ml) was heated at 80~90°C for 8 h. The mixture was cooled to room temperature, poured into ice-cold water, acidified (pH=1) with 10% hydrochloric acid, and extracted with CH_2Cl_2 (30 ml×3). The extract was washed with brine, dried ($MgSO_4$), and evaporated to leave the residue which, on recrystallization, gave 3d (115 mg, 53%) as colorless plates (EtOH); mp 107~108°C; ^{1}H nmr ($CDCl_3$, 100 MHz, δ, ppm) 7.14 (1H, s), 4.28 (2H, t, J=7 Hz), 2.20~1.84 (2H, m), 1.71~1.26 (4H, m), 0.98 (3H, t, J=7Hz); ir (ν, cm^{-1}) 2960, 1595, 825 ; ms (m/z) 280 (M^+). Anal. Calcd for $C_{11}H_{12}N_4OS_2$: C, 47.12; H, 4.31; N, 19.98. Found: C, 46.91; H, 4.58; N, 19.61.

4-Allyloxybenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (3e) : A mixture of 2a (660 mg, 2.42 mmol) and sodium (0.10 g, 4.3 mmol) in a mixed solvent of dry HMPA (10 ml) and dry allyl alcohol (3.5 ml, 50 mmol) was stirred at room temperature for 24 h under nitrogen atmosphere. The reaction mixture was poured into ice-cold water and acidified (pH=1) with 10% hydrochloric acid. The precipitates were collected by filtration and recrystallized to give 3e (428 mg, 71%) as colorless needles (hexane); mp 160~162°C; ^{1}H nmr ($CDCl_3$, 270 MHz, δ, ppm) 7.20 (1H, s), 6.28~6.13 (1H, m), 5.59 (1H, ddd, J=17, 3, 1 Hz), 5.46 (1H, ddd, J=11, 3, 1 Hz), 4.89 (2H, ddd, J=6, 1, 1 Hz) ; ir (ν, cm^{-1}) 2930, 1520, 830, 810; ms (m/z) 250 (M^+). Anal. Calcd for $C_9H_6N_4OS_2$: C, 43.19; H, 2.42; N, 22.38. Found: C, 43.33; H, 2.57; N, 22.42.

4-Phenoxybenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (3f) : To a warmed mixture of phenol (190 mg, 2.02 mmol) and potassium hydroxide (0.10 g, 1.8 mmol) in DMF (1 ml) at 120°C was added 2a (83 mg, 0.30 mmol) and copper powder (30 mg) and the mixture was heated at 120~140°C for 1 h. Additional 2a (80 mg, 0.30 mmol) was added to the mixture and the whole mixture was heated at 120~140°C for 50 min. After it was cooled to room temperature, 30% aqueous sodium hydroxide solution was added to it in small portions and insoluble solids were collected by filtration. The filtrate was acidified (pH=1) with 10% hydrochloric acid and the precipitates were collected by filtration. The insoluble solids and the precipitates were combined and washed with CH_2Cl_2. The washing was evaporated *in vauo* to leave the resdue which was recrystallized, giving 3f (110 mg, 63%) as colorless needles (cyclohexane); mp 193~194°C ; ^{1}H

nmr ($CDCl_3$, 100 MHz, δ, ppm) 7.60~7.20 (5H, m), 7.02 (1H, s) ; ir (ν, cm^{-1}) 1510, 1250, 830, 800 ; ms (m/z) 286 (M^+). Anal. Calcd for $C_{12}H_6N_4OS_2$: C, 50.34; H, 2.11; N, 19.57. Found: C, 50.21; H, 2.26; N, 19.84.

4-Allyl-5-hydroxybenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (4) : A mixture of 2a (330 mg, 1.21 mmol), potassium hydroxide (0.20 g, 3.6 mmol), allyl alcohol (5 ml, 71 mmol), and DMF (5 ml) was heated under reflux for 8 h. The mixture was cooled to room temperature, poured into ice-cold water, and acidified (pH=1) with 10% hydrochloric acid. Precipitates were collected by filtration and recrystallized to give 4 (209 mg, 69%) as yellow needles (hexane); mp 179~181°C ; ^1H nmr ($CDCl_3$, 270 MHz, δ, ppm) 6.63 (1H, s, D_2O exchageable), 6.21~6.06 (1H, m), 5.24 (1H, ddd, J=17, 3, 1 Hz), 5.12 (1H, ddd, J=10, 3, 1 Hz), 3.92 (2H, ddd, J=6, 1, 1 Hz) ; ir (ν, cm^{-1}) 3200, 1500, 835, 820 ; ms (m/z) 250 (M^+). Anal. Calcd for $C_9H_6N_4OS_2$: C, 43.19; H, 2.42; N, 22.38. Found: C, 43.02; H, 2.56; N, 22.36.

Claisen rearrangement of 3e : After a solution of 3e (138 mg) in toluene (15 ml) was heated under reflux for 8 h, the solvent was evaporated *in vacuo* to leave the residue (122 mg) which, on recrystallization from hexane, afforded 4 (109 mg, 79%).

4-Hydroxybenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (5) : After a mixture of 3a (200 mg) in 47% hydrobromic acid (8 ml) was heated at 60~80°C for 20 min, it was cooled to room temperature. Precipitates were collected by filtration and recrystallized to give 5 (144 mg, 78%) as colorless powder ($CHCl_3$) ; mp 237~244°C (in a sealed tube). Analytical sample was purified by sublimation ; ^1H nmr (DMSO-d_6, 100 MHz, δ, ppm) 7.16 (s) ; ir (ν, cm^{-1}) 3100, 1510, 835 ; ms (m/z) 210 (M^+). Anal. Calcd for $C_6H_2N_4OS_2$: C, 34.28; H, 0.96; N, 26.65. Found: C, 34.70; H, 1.20; N, 26.83.
Similary 3b (108 mg) afforded 5 (70 mg, 69%).

4-Acetoxybenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (6) : To a mixture of 5 (389 mg, 1.85 mmol) and acetic anhydride (20 ml, 210 mmol) was added three drops of concentrated sulfuric acid and the mixture was stirred at room temperature for 1 h, then heated at 125~135°C for 1 h. The mixture was poured into water, neutralized with sodium hydrogencarbonate, and extracted with CH_2Cl_2 (30 ml×4). The extract was washed with water, dried ($MgSO_4$), and evaporated *in vacuo* to leave the residue which was chromatographed using CH_2Cl_2 as an eluent. Crude product was recrystallized to give 6 (264 mg, 57%) as colorless cubics (cyclohexane-benzene) ; mp 146~148 °C ; ^1H nmr ($CDCl_3$, 100 MHz, δ, ppm) 7.78 (1H, s), 2.52 (3H, s) ; ir (ν, cm^{-1}) 1770, 1195, 840 ; ms (m/z) 252 (M^+). Anal. Calcd for $C_8H_4N_4O_2S_2$: C, 38.09; H, 1.60; N, 22.21. Found: C, 37.79; H, 1.83; N, 22.41.

4-Propylthiobenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (8) : After a mixture 2a (193 mg, 0.707 mmol), potassium carbonate (303mg, 2.19 mmol), propanethiol (0.5 ml, 5.4 mmol), and DMF (5 ml) was heated at 90~100°C for 6 h, it was cooled to room temperature, poured into ice-cold water, and acidified (pH=1) with 10 % hydrochloric acid. Precipitates were collected by filtration and recrystallized to give 8 (106 mg, 55%) as yellow needles (cyclohexane) ; mp 147~150°C ; ^{1}H nmr ($CDCl_3$, 100 MHz, δ, ppm) 7.60 (1H, s,), 3.15 (2H, t, J=7 Hz), 2.08~1.72 (2H, m), 1.17 (3H, t, J=7 Hz) ; ir (ν, cm^{-1}) 3000, 1500, 830, 820 ; ms (m/z) 268 (M^+). Anal. Calcd for $C_9H_8N_4S_3$: C, 40.28; H, 3.00; N, 20.88. Found: C, 40.04; H, 3.00; N, 20.82.

Preparation of 9a~c. General procedure : After a mixture of 2a (174~190 mg), DMF (3 ml), and cyclic amine (3 ml) was heated under reflux for 4 h, it was cooled to room temperature, poured into ice-cold water, and acidified (pH=1) with 10% hydrochloric acid. Precipitates were collected by filtration and purified by recrystallization.

4-Pyrrolidinobenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (9a) : orange plates (EtOH); mp 192~194°C ; ^{1}H nmr ($CDCl_3$, 100 MHz, δ, ppm) 6.56 (1H, s), 3.96~3.82 (4H, m), 2.18~2.04 (4H, m) ; ir (ν, cm^{-1}) 2980, 1580, 830, 810 ; ms (m/z) 263 (M^+). Anal. Calcd for $C_{10}H_9N_5S_2$: C, 45.61; H, 3.44; N, 26.59. Found: C, 45.82; H, 3.50; N, 26.45.

4-Piperidinobenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (9b) : yellow needles (MeOH); mp 131~132°C; ^{1}H nmr ($CDCl_3$, 100 MHz, δ, ppm) 7.08 (1H, s), 3.72~3.48 (4H, m), 2.18~2.04 (6H, m) ; ir (ν, cm^{-1}) 2950, 1585, 830, 815 ; ms (m/z) 277 (M^+). Anal. Calcd for $C_{11}H_{11}N_5S_2$: C, 47.63; H, 4.00; N, 25.25. Found: C, 47.73; H, 4.14; N, 25.62.

4-Morphorinobenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (9c) : pale yellow cubics (EtOH with charcoal) ; mp 229~231°C ; ^{1}H nmr ($CDCl_3$, 100 MHz, δ, ppm) 7.10 (1H, s), 4.03~3.96 (4H, m), 3.63~3.54 (4H, m) ; ir (ν, cm^{-1}) 2880, 1585, 1125, 890, 835 ; ms (m/z) 279 (M^+). Anal. Calcd for $C_{10}H_9N_5OS_2$: C, 43.00; H, 3.25; N, 25.07. Found: C, 42.60; H, 3.39; N, 25.05.

4-*N*-Methylpiperazinobenzo[1,2-*c*;3,4-*c'*]bis[1,2,5]thiadiazole (9d) : After a mixture of 2a (190 mg, 0.696 mmol), *N*-methylpiperazine (3 ml, 27 mmol), and DMF (3 ml) was heated at 80~100°C for 4 h, it was cooled to room temperature. Insoluble materials were filtered off and the filtrate was poured into ice-cold water. Insoluble solid was filtered off and the filtrate was adjusted to pH=13 with 10% sodium hydroxide solution and extracted with CH_2Cl_2 (30 ml×4). The extract was washed with brine, dried ($MgSO_4$), and evaporated *in vacuo* to leave the residue which, on recrystallization, gave 9d (45 mg, 21%) as yellow needles (cyclohexane); mp 172~173 °C; ^{1}H nmr ($CDCl_3$, 100 MHz, δ, ppm) 7.13 (1H, s), 3.63 (4H, m), 2.70 (4H, m), 2.42 (3H, s) ; ir (ν, cm^{-1}) 2950, 2820, 1010, 840, 820 ; ms (m/z) 292 (M^+). Anal. Calcd for $C_{11}H_{12}N_6S_2$: C, 45.19; H, 4.14; N, 28.74. Found: C, 45.32; H, 4.40; N, 29.19.

5-Methoxy-1,2,3,4-benzenetetraamine trihydrochloride (10·3HCl) : To a mixture 3a (605 mg, 2.70 mmol) and tin powder (3.22 g, 27.1 mmol) in degassed dioxane (30 ml),

concentrated hydrochloric acid (12 ml) was added dropwise at room temperature under nitrogen atmosphere and the mixture was heated under reflux for 4 h. After it was cooled to room temperature, the precipitated solid was collected by filtration. The crude product was dissolved in hot methanol and to the solution, a 5:1 mixture of hexane and ethanol was added dropwise to give 10•3HCl (277 mg, 30%) as pale gray needles ; mp 207~235°C (decomp.) ; ^{1}H nmr (DMSO-d_6, DSS, 100 MHz, δ, ppm) 6.00 (1H, s), 5.92~4.40 (11H, broad peak), 3.72 (3H, s) ; ir (ν, cm^{-1}) 3375, 3250, 2850, 2550, 1505 ; ms (m/z) 168 (M^+). Anal. Calcd for $C_7H_{15}N_4OCl_3$: C, 30.28; H, 5.45; N, 20.18. Found: C, 30.41; H, 5.40; N, 20.18.

5-Hydroxy-1,2,3,4-benzenetetraamine dihydrochloride (11•2HCl) : A stirred mixture of 5 (531 mg, 2.53 mmol) and tin powder (3.04 g, 25.6 mmol) in degassed dioxane (30 ml) was treated with concentrated hydrochloric acid (12 ml) and worked up as described in the reduction of 3a, giving 11•2HCl (121 mg, 57%) as gray needles ; mp >300°C (decomp.) ; ^{1}H nmr (DMSO-d_6, DSS, 100 MHz, δ, ppm) 5.92 (1H, s), 5.40~2.90 (11H, broad peak) ; ir (ν, cm^{-1}) 3420, 32270, 3020, 2680, 1480 ; ms (m/z) 154 (M^+). Anal. Calcd for $C_6H_{12}N_4OCl_2$: C, 31.72; H, 5.33; N, 24.67. Found: C, 31.68; H, 5.38; N, 24.40.

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