Preparation of 1,2,3-Naphthalenetriamine, 1,2,5,6- and 1,2,7,8-Naphthalenetetramine, and 5,6,7,8-Quinolinetetramine and -Isoquinolinetetramine by Reduction of the Fused 1,2,5-Thiadiazole Ring

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The two fused 1,2,5-thiadiazole-rings of naphthalenes **1a** and **1b**, quinoline **2a**, and isoquinoline **2b** were reduced with tin and concentrated hydrochloric acid in refluxing dioxane, giving the expected 1,2,5,6-naphthalenetetramine (**4a**) and 1,2,7,8-tetramine derivative **4b**, 5,6,7,8-quinolinetetramine (**15a**) and isoquinoline analogue **15b** in moderate yields. Partially reduced diamine **5** was formed as a by-product in the reduction of **1a**. The expected 1,2,3,4-naphthalenetetramine (**4c**) was not obtained in the reduction of **1c** at room temperature and the 1,2,3-triamine **8** was formed in 27% yield. The intermediary formation of **4c** was confirmed by acetylating the crude reduction mixture of **1c**, giving tetraacetyl derivative **11**. The reduction of naphthotris[1,2,5]thiadiazole **3** afforded 4,5-diamine **16** in 44% yield. Polyamines **4a**—**b**, **8**, **15a**—**b**, and **16**, were obtained as their hydrochloride(s).

As shown in the conversion[1—3] of benzo-, benzobis-, and benzotris[1,2,5]thiadiazoles to polyaminobenzenes, such as benzenediamine, -tetramine, and -hexamine, 1,2,5-thiadiazole-ring-fused aromatics are a synthetic equivalent of aromatic polyamines.

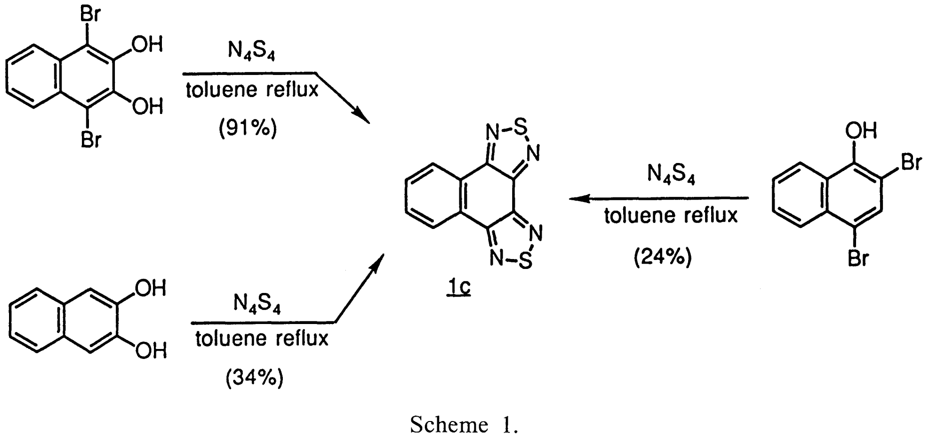
We recently prepared naphthobis[1,2,5]thiadiazoles **1a**—**c**, aza analogues **2a**—**b**, and naphthotris[1,2,5]-thiadiazole **3** by the reaction of tetrasulfur tetranitride (N_4S_4) with naphthol and naphthalenediols.[4] Compounds **1**—**3** seemed to be useful for preparing naphthalenetetramine and -hexamine derivatives, which were unknown until the present time, to the best of our knowledge. This article describes the reduction of **1**—**3**.

Results and Discussion

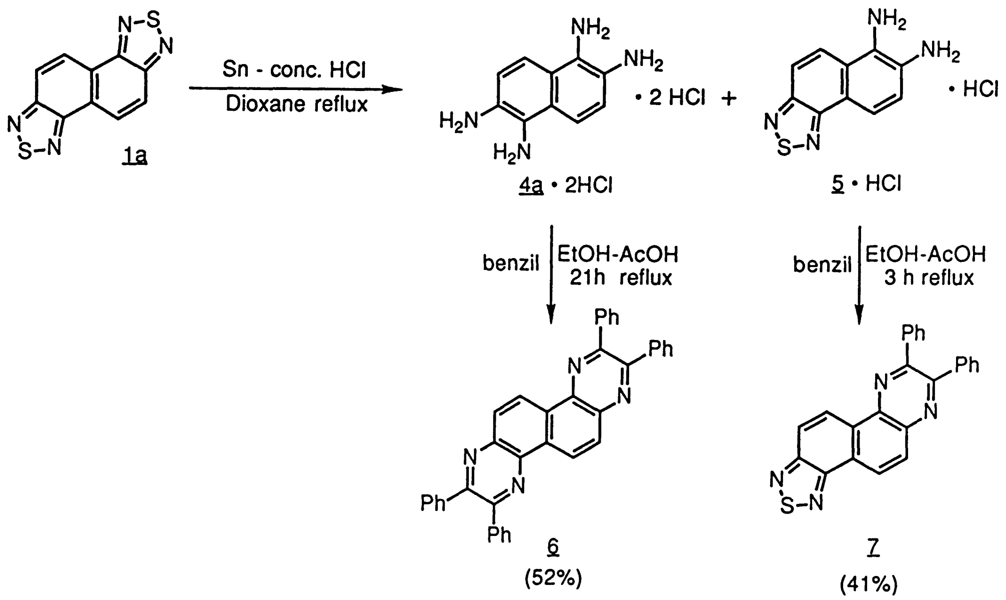
Naphthobis[1,2,5]thiadiazoles **1a** and **1b** were prepared according to a previously reported method.[4] The preparation of **1c** was improved by employing 1,4-dibromonaphthalene-2,3-diol,[4] in place of 2,4-dibromo-1-naphthol, as the starting compound (Scheme 1).

The results of the reduction of **1** are given in Schemes 2—4. Compound **1a** was reduced with 10 equivalents of tin powder in a mixture of concentrated hydrochloric acid and dioxane under reflux for 24 h. The expected 1,2,5,6-naphthalenetetramine (**4a**) precipitated from the reaction mixture as its dihydrochloride, and was easily separated (32% yield) by filtration. Upon standing, the partially reduced product **5** also precipitated from the filtrate as its monohydrochloride in 7% yield. When the reaction time of the reduction was increased to 48 h, **4a·2HCl** was obtained in 37% yield, together with **5·HCl** in less than 1% yield; unchanged **1a** was recovered in 10% yield. The condensation reaction of **4a·2HCl** and **5·HCl** with benzil in acetic acid under reflux afforded the corresponding pyrazine derivatives **6** and **7**, respectively.

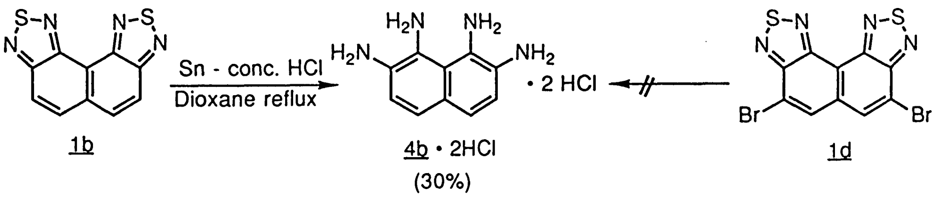
The reduction of **1b** was complete in 4 h, giving the corresponding **4b·2HCl** in 30% yield (Scheme 3). On



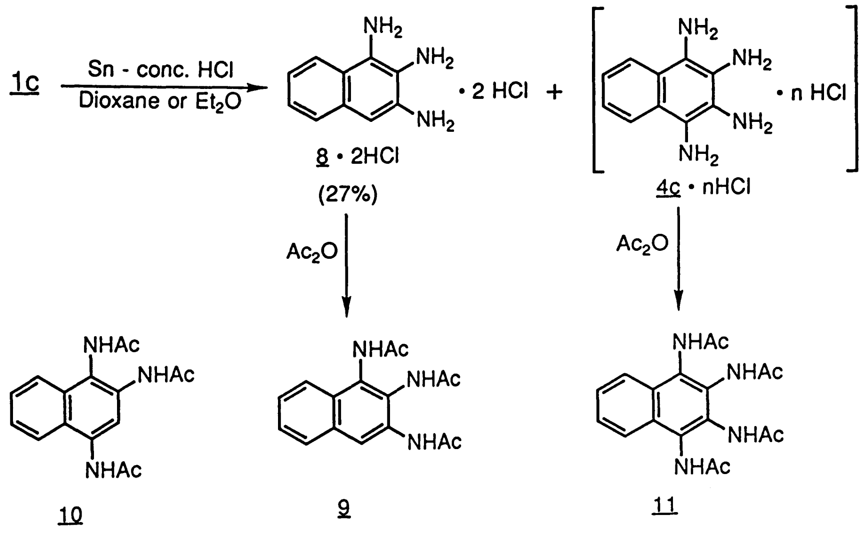
Scheme 1.



Scheme 2.



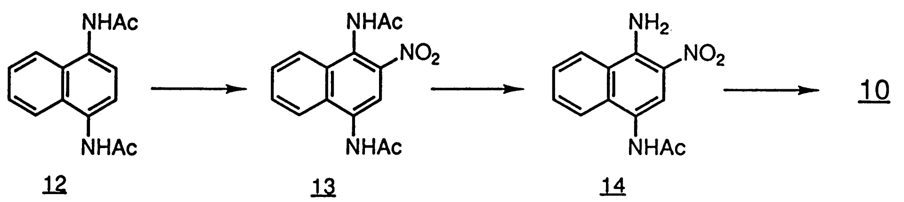
Scheme 3.



Scheme 4.

the other hand, the reduction of the dibromo derivative **1d** resulted in the formation of a complex mixture of unidentified products.

When the reduction of **1c** was carried out under the above-mentioned conditions, the expected 1,2,3,4-tetramine (**4c**) was not produced. Naphthalenetriamine dihydrochloride **8·2HCl**,[5] which might be formed via **4c**, was obtained in 27% yield. Acetylation of the crude reduction product of **1c** afforded **9** in a total yield of 27% from **1c**. The structure **9** was deduced as being *N,N′,N″*-triacetyl derivative of 1,2,3- or 1,2,4-naphthalenetriamine on the basis of spectral data; it was



Scheme 5.

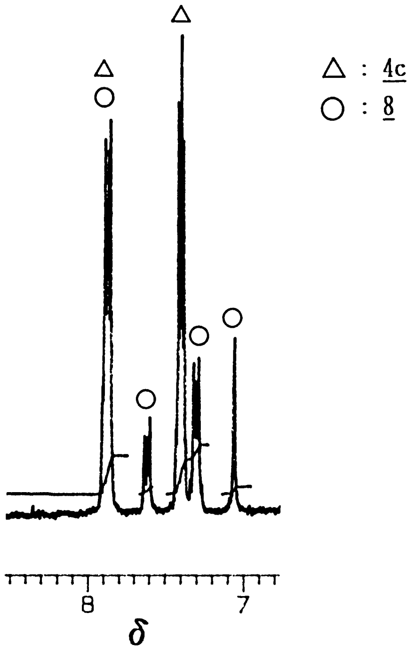
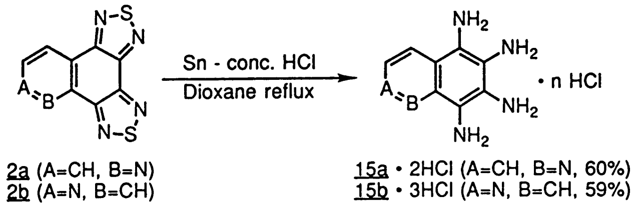
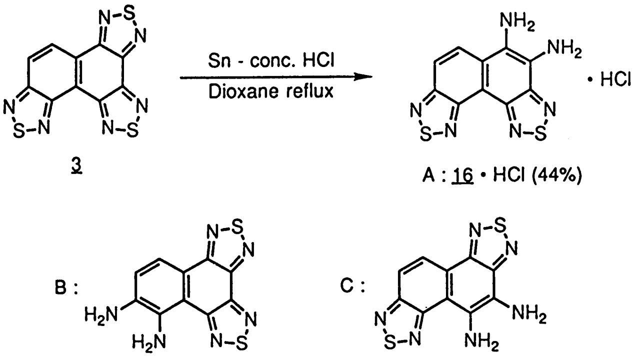


Fig. 1. ^{1}H NMR spectrum of the reduction mixture of **1c** in ether for 25 h.



Scheme 6.



Scheme 7.

unequivocally established as being *N,N′,N″*-triacetyl-1,2,3-naphthalenetriamine by comparing its melting point with the reported one of isomer **10**,[6,7] which was synthesized according to Scheme 5.

During the early stage of the reduction of **1c**, the formation of **8** was detected by ^{1}H NMR spectroscopy. A 1 : 2-mixture of the hydrochloride of **8** and **4c** was produced (Fig. 1) when the reduction was carried out in ether for 25 h. A small amount of the tetraacetyl derivative **11** was isolated from the acetylated mixture of the above-mentioned reduction product. Treatment of **1c** with a milder reducing reagent, tin(II) chloride, under the conditions mentioned above resulted in the recovery of **1c**.

Since dissolving metal reductions in acidic media are considered to proceed via an electron transfer from the metal to the substrate,[8] it seemed curious that **4c**, having an electron-rich tetraminobenzene ring, was reductively deaminated. Since the sterically unfavorable 1,2,7,8-tetramine **4b** was produced as described above, steric factors may not play a role in eliminating the amino group of **4c**. As a possible reason for the overreduction of **4c**, it is presumed that **4c** probably forms a complex with metal chloride(s), and that the complex might be prone to reductive deamination. The reduction of aza analogues **2** of **1c** was carried out since a fused pyridine ring might hinder complexation of **15** by reducing the electron density of the tetraminobenzene ring, as compared to **4c**, and thus make **15** resistant to an overreduction. Indeed, **2** afforded the corresponding tetramines, **15a** and **15b**, as the di- and trihydrochloride, respectively (Scheme 6).

Only one of the three 1,2,5-thiadiazole rings of **3** was reduced by tin under reflux for 3 h in a mixture of concentrated hydrochloric acid and dioxane, giving the diamine **16** as its monohydrochloride in 44% yield. When the reaction time was prolonged (23 h), no further reduction occured, giving **16·HCl** in a similar yield. Compound **16·HCl** showed its peri-proton at 7.85 ppm in the ^{1}H NMR spectrum. Of the two peri-protons of **5·HCl**, the one which is situated close to the 1,2,5-thiadiazole ring showed its ^{1}H NMR signal at a lower magnetic field (8.36 ppm) than the other [8.09 (or 7.90) ppm]. The structure of **16** was therefore deduced to be **A**, not **B** or **C** (Scheme 7).

Experimental

General. All of the melting points were determined on a Mitamura-riken MELT THERMO and are uncorrected. The IR spectra were measured as KBr pellets on a JASCO A-102. The ^{1}H NMR spectra were recorded at 270 MHz with a JEOL GSX-270 in DMSO-d_6 using DSS (sodium 2,2′-dimethyl-2-silapentane-5-sulfonate) as an internal standard, unless otherwise stated. The mass spectra were obtained on a JEOL JMS-O1SG-2 mass spectrometer at 75 eV using a direct inlet system.

The following reactions were carried out using degassed solvents under a nitrogen atmosphere, except for the preparation of **1c**, **14**, and **15**.

Preparation of 1c. A mixture of 1,4-dibromo-2,3-naphthalenediol[9] (1.60 g, 5.03 mmol) and tetrasulfur tetranitride (3.74 g, 20.3 mmol) in toluene (100 cm^3) was heated under reflux for 48 h, and then worked up according to the reported method,[2] giving **1c** (1.116 g, 91%). Similarly **1c** (421 mg, 34%) was prepared in the reaction of 2,3-naphthalenediol (0.81 g, 5.07 mmol) and tetrasulfur tetranitride (3.60 g, 19.5 mmol) under the above-mentioned conditions.

1,2,5,6-Naphtalenetetramine Dihydrochloride (4a·2HCl) and Naphtho[1,2-*c*][1,2,5]thiadiazole-5,6-diamine Hydrochloride (5·HCl). To a warmed mixture of **1a** (252 mg, 1.03 mmol) and tin powder (1.31 g, 11.0 mmol) in dioxane (40 cm^3) at 70 °C, concentrated hydrochloric acid (5 cm^3) was added dropwise for 3 min. The mixture was heated under reflux for 48 h, and then cooled to room temperature. Precipitates (228 mg) were filtered and purified by dissolving in hot methanol and reprecipitating with the addition of a 5:1-mixture of hexane and ethanol, giving **4a·2HCl** as a colorless powder (97 mg, 36%): Mp colored around 185 °C and darkened below 215 °C; IR 3470—2650, 1660, 1635, 1615, 1450, 810, and 780 cm^{-1}; ^{1}H NMR (100 MHz) δ=3.49 (10H, br s), 7.27 (2H, d, J=9 Hz), and 7.54 (2H, d, J=9 Hz); MS m/z 188 (M$^+$).

Found: C, 45.87; H, 5.36; N, 21.30%. Calcd for $C_{10}H_{14}N_4Cl_2$: C, 45.99; H, 5.40; N, 21.45%.

Upon standing the filtrate of the reaction mixture overnight, **5·HCl** appeared as yellow needles, and were filtered (1 mg, 0.4%): Mp colored around 195 °C and darkened below 254 °C (decomp); IR 3500—2700, 1665, 1610, 1550, 1520, 1500, 1470, 1440, 1410, 1370, 1340, 1300, 1190, 1110, 970, 860, 830, 820, and 705 cm^{-1}; ^{1}H NMR δ=3.66 (5H, br s), 7.51 (1H, d, J=8.4 Hz), 7.89 (1H, d, J=9.9 Hz), 8.08 (1H, d, J=8.4 Hz), and 8.35 (1H, d, J=9.9 Hz); MS m/z 216 (M$^+$).

Found: C, 47.27; H, 3.61; N, 21.80%. Calcd for $C_{10}H_9N_4SCl$: C, 47.53; N, 3.59; N, 22.17%.

The filtrate was poured into water, giving a recovery of **1a** (25 mg, 10%).

2,3,8,9-Tetraphenylnaphtho[1,2-*b*; 5,6-*b*′]dipyrazine (6). A mixture of **4a·2HCl** (82 mg, 0.31 mmol), benzil (134 mg, 0.64 mmol), ethanol (10 cm^3), and acetic acid (10 cm^3) was heated under reflux for 21 h, and then cooled to room temperature. The precipitated solid was filtered and recrystallized from toluene, giving **6** (88 mg, 52%) as pale-yellow plates: Mp 385—389 °C; IR 3050, 1440, 1350, 1250, 1155, 1070, 1055, 1020, 960, 845, 800, 760, 710, and 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=7.36—7.44 (12H, m), 7.62—7.67 (4H, m), 7.70—7.74 (4H, m), 8.40 (2H, d, J=9.2 Hz), and 9.65 (2H, d, J=9.2 Hz); MS m/z 536 (M$^+$).

Found: C, 84.70; H, 4.70; N, 10.31%. Calcd for $C_{38}H_{24}N_4$: C, 85.05; H, 4.51; N, 10.44.

7,8-Diphenyl[1,2,5]thiadiazolo[3′,4′-5,6]naphto[1,2-*b*]pyrazine (7). A mixture of **5·HCl** (59 mg, 0.23 mmol), benzil (57 mg, 0.23 mmol), ethanol (9 cm^3), and acetic acid (3 cm^3) was heated under reflux for 3 h, and then worked up as decribed above, giving **7** (37 mg, 39%) as pale-yellow needles: Mp 366—368 °C (toluene); IR 3070, 1510, 1470, 1450, 1355, 1280, 1250, 1170, 1085, 1070, 1030, 970, 850, 840, 825, 800, 770, 755, and 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=7.36—7.43 (6H, m), 7.61—7.65 (2H, m), 7.68—7.72 (2H, m), 8.17 (1H, d, J=9.2 Hz), 8.41 (1H, d, J=8.8 Hz), 9.09 (1H, d, J=9.5 Hz), and 9.50 (1H, d, J=9.5 Hz); MS m/z 390 (M$^+$).

Found: C, 74.11; H, 4.00; N, 13.93%. Calcd for $C_{24}H_{14}N_4S$: C , 73.83; H, 3.61; N, 14.35%.

1,2,7,8-Naphtalenetetramine Dihydrochloride (4b·2HCl). A warmed mixture of **1b** (131 mg, 0.54 mmol) and tin powder (655 mg, 5.50 mmol) in dioxane (10 cm^3) was treated with concentrated hydrochloric acid (5 cm^3), as described in the reduction of **1a**. The mixture was refluxed for 4 h, and then cooled to room temperature, giving the precipitates (134 mg). A part (85 mg) of this solid was dissolved in hot methanol. To the solution, a 5:1-mixture of hexane and ethanol was added dropwise, giving **4b·2HCl** as a colorless crystalline powder (27 mg): Mp darkened around 200 °C and gradually decomposed below 300 °C; IR 3500—2600, 1635, 1560, 1510, 1465, 1360, 1340, 1310, 1270, 1230, 1170, 1140, 1100, 1030, 990, 920, 850, 790, 770, and 710 cm^{-1}; ^{1}H NMR δ=4.95 (10H, s), 7.26 (2H, d, J=8.8 Hz), and 7.61 (2H, d, J=8.8 Hz); MS m/z 188 (M$^+$).

Found: C, 45.84; H, 5.39; N, 20.98%. Calcd for $C_{10}H_{14}N_4Cl_2$: C, 45.99; H, 5.40; N, 21.45%.

1,2,3-Naphthalenetriamine Dihydrochloride (8·2HCl). A mixture of **1d** (135 mg, 0.55 mmol) and tin powder (675 mg, 5.7 mmol) in dioxane (10 cm^3) was treated with concentrated hydrochloric acid (5 cm^3), as described above. This mixture was stirred at room temperature for 3 h; then precipitates were collected by filtration and purified by reprecipitation from hot ethanol with hexane, giving **8·2HCl**:[5] Yellow crystalline powder (36 mg, 26%); mp 180—204 °C (decomp); IR 3460—2600, 1695, 1645, 1560, 1520, 1490, 1470, 1410, 1380, 1310, 1090, 895, 770, and 750 cm^{-1}; ^{1}H NMR δ=4.17 (8H, s) 7.30 (1H, s), 7.33—7.43 (2H, m), 7.71 (1H, d, J=7.7 Hz), and 7.93 (1H, d J=8.1 Hz); MS m/z 173 (M$^+$).

Found: C, 48.85; H, 5.34; N, 17.18%. Calcd for $C_{10}H_{13}N_3Cl_2$: C, 48.80; H, 5.32; N, 17.07%.

***N,N′,N″*-Triacetyl-1,2,3-naphthalenetriamine (9).** The crude reduction product (120 mg) obtained (mentioned above) was treated with acetic anhydride (5 cm^3) in the presence of sodium acetate (85 mg) at room temperature for 1 h. The mixture was poured into ice-water, neutralized with sodium hydrogencarbonate, and extracted with dichloromethane (30 cm^3×3). The aqueous layer was then continuously extracted with chloroform overnight. The extract was combined, dried (magnesium sulfate), and evaporated in vacuo, giving a solid residue (116 mg) which, on recrystallization from methanol, afforded **9** (40 mg, 27% yield from **1c**) as colorless needles: Mp 281—284 °C; IR 3450, 3250, 3025, 1660, 1545, 1450, 1370, 1350, 1290, 880, and 740 cm^{-1}; ^{1}H NMR δ=2.10 (3H, s), 2.11 (3H, s), 2.15 (3H, s), 7.42—7.51 (2H, m), 7.87—7.80 (2H, m) 8.25 (1H, s), 9.18 (1H, s), 9.18 (1H, s, D$_2$O-exchanged), 9.20 (1H, s, D$_2$O-exchanged), and 9.49 (1H, s, D$_2$O-exchanged); MS m/z 299 (M$^+$).

Found: C, 63.87; H, 5.74; N, 14.09%. Calcd for $C_{16}H_{17}O_3N_3$: C, 64.20; H, 5.72; N, 14.04%.

***N,N′,N″,N‴*-Tetraacetyl-1,2,3,4-naphthalenetetramine (11).** To a mixture of tin powder (847 mg, 7.10 mmol) and **1d** (172 mg, 0.70 mol) in ether (20 cm^3) was added dropwise concentrated hydrochloric acid (5 cm^3) for 2 min. The mixture was stirred at room temperature for 25 h. Precipitated solid materials (163 mg) were determined to be the hydrochlorides of a mixture of **4c** and **8** by ^{1}H NMR spectroscopy. A part (79 mg) of this mixture was treated with acetic anhydride (4 cm^3) in the presence of sodium acetate (95 mg) at room temperature for 2 h. The reaction mixture was then poured into ice-water, neutralized with sodium hydrogencarbonate, and extracted with dichloromethane (30 cm^3×3). The aqueous layer was continuously extracted with chloroform overnight. The extracts were combined, dried (magnesium sulfate), and evaporated in vacuo, giving a mixture of **9** and **11** as a white solid (35 mg), which, upon recrystallization from a 1 : 1-mixture of benzene and ethanol, afforded **11** (5 mg, 3% yield from **1c**) as colorless needles: Mp>335 °C; IR 3240, 3025, 1660, 1540, 1390, 1370, 1280, 990, and 750 cm^{-1} MS *m/z* 356 (M$^+$).

Found: C, 60.27; H, 5.57; N, 15.45%. Calcd for $C_{18}H_{20}O_4N_4$: C, 60.66; H, 5.66; N, 15.72%.

Authentic Synthesis of 10. Compound **10** was prepared via a sequence of nitration$^{6)}$ of **12**, hydrolysis$^{6)}$ of **13**, reduction$^{6,7)}$ of **14**, and in-situ acetylation of the reduction product as Scheme 5.

Physical and spectral properties of **12**, **13**, and **14** are as follows.

***N,N′*-Diacetyl-1,4-naphthalenediamine [12-AcOH(4/1)]:** Colorless plates (acetic acid) of mp 344—348 °C (in a sealed tube) (lit,$^{6)}$ mp of the acid-free **12** was reported as 305 °C); IR 3230, 3030, 1655, 1540, 1500, 1360, 1340, 1290, 1270, 1000, 845, and 780 cm^{-1}; ^{1}H NMR δ=2.18 (6H, s), 7.56 (2H, dd, *J*=6.6 and 3.3 Hz), 7.60 (2H, s), 8.06 (2H, dd, *J*=6.6 and 3.3 Hz) , and 9.90 (2H, s, D_2O-exchanged); MS *m/z* 242 (M$^+$).

Found: C, 68.12; H, 5.89; N, 11.00%. Calcd for ($C_{14}H_{14}O_2N_2$+0.25·CH_3CO_2H): C, 67.69; H, 5.88; N, 10.89%.

***N,N′*-Diacetyl-2-nitro-1,4-naphthalenediamine (13):** Orange needles (formic acid) of mp >300 °C (lit,$^{6)}$ mp 295 °C); IR 3260, 3025, 1665, 1600, 1530, 1510, 1390, 1370, 1350, 1330, 1270, 1260, 1010, 980, 870, 790, 760, and 750 cm^{-1}; ^{1}H NMR δ=2.17 (3H, s), 2.23 (3H, s), 7.75—7.84 (2H, m), 8.22—8.36 (2H, m), 8.23 (1H, s), 10.22 (1H, s, D_2O-exchanged), and 10.43 (1H, s, D_2O-exchanged); MS *m/z* 287 (M$^+$); (Found: C, 58.12; H, 4.70; N, 14.60%).

4-Acetoamino-2-nitro-1-napthtylamine (14): Reddish orange needles (ethanol) of mp 291—294 °C (lit,$^{6)}$ mp 273 °C); IR 3525, 3375, 3260, 1655, 1620, 1590, 1560, 1525, 1475, 1420, 1400, 1390, 1305, 1280, 1240, 1210, 1160, 1050, 880, and 760 cm^{-1}; ^{1}H NMR δ=2.14 (3H, s), 7.64 (1H, t, *J*=7 Hz), 7.77 (1H t *J*=7 Hz), 7.94 (1H, d, *J*=8 Hz), 8.04 (1H, s), 8.61 (1H, d, *J*=8 Hz), 8.69 (2H, s, D_2O-exchanged), and 9.71 (1H, s, D_2O-exchanged); MS *m/z* 245 (M$^+$); (Found: C, 58.87; H, 4.71 ; N, 17.03%).

Preparation of 10. Tin(II) chloride (0.48 g, 2.5 mmol) in acetic anhydride (4 cm^3) was stirred at room temperature for 2 h.$^{7)}$ To this mixture, **14** (201 mg, 0.82 mmol) was added. The entire mixture was heated under reflux for 18 min; the acetic acid formed was removed by distillation in vacuo. Water (6 cm^3) was added to the residue, and the mixture was then heated under reflux for 5 min. It was cooled to room temperature and poured into water. A precipitated solid was collected and recrystallized from methanol, giving ***N,N′,N″*-triacetyl-1,2,4-naphthalenetriamine [10-H$_2$O(3/1)]** (14 mg, 6%): Colorless needles; mp 334—337 °C (decomp) (mp of water-free **10**$^{6)}$ was reported as 301 °C); IR 3260, 1665, 1540, 1490, 1425, 1380, 1280, 1260, 1020, 870, 770, and 750 cm^{-1}; ^{1}H NMR δ=2.11 (3H, s), 2.18 (6H, s), 7.48—7.53 (2H, m), 7.81—7.84 (1H, m), 8.00—8.06 (2H, m), 9.37 (1H, s, D_2O-exchanged), 9.45 (1H, s, D_2O-exchanged), and 9.94 (1H, s, D_2O-exchanged); MS *m/z* 299 (M$^+$).

Found: C, 62.96; H, 5.91; N, 13.73%. Calcd for ($C_{16}H_{17}O_3N_3$+1/3·H_2O): C, 63.05; H, 5.84; N, 13.79%.

5,6,7,8-Quinolinetetramine Dihydrochloride (15a·2HCl). A mixture of **2a** (186 mg, 0.76 mmol) and tin powder (967 mg, 8.1 mmol) in dioxane (20 cm^3) was treated with concentrated hydrochloric acid (5 cm^3), as described in the reduction of **1a**; the mixture was heated under reflux for 6 h. After it was cooled to room temperature, the precipitated **15a·2HCl** (119 mg, 60%) was filtered: Dark red powder; mp darkend around 210 °C; IR 3500—2650, 1660, 1600, 1480, 1420, 1325, 1260, 780, and 750 cm^{-1}; ^{1}H NMR δ=4.08 (10H, br s), 7.46 (1H, dd, *J*=5 and 8 Hz), 8.59 (1H, d, *J*=8 Hz), and 8.62 (1H, d, *J*=5 Hz); MS *m/z* 189 (M$^+$).

Found: C, 41.22; H, 4.94; N, 26.30%. Calcd for $C_9H_{13}N_5Cl_2$: C, 41.24.; H, 5.00; N, 26.72%.

5,6,7,8-Isoquinolinetetramine Trihydrochloride (15b·3HCl). A mixture of **2b** (238 mg, 0.97 mmol) and tin powder (1.15 g, 9.70 mmol) in dioxane (10 cm^3) was treated with concentrated hydrochloric acid (5 cm^3), as described above; the mixture was then heated under reflux for 3 h. It was cooled to room temperature and the precipitated yellow powder (263 mg) was filtered, a part (99 mg) of which was heated in concentrated hydrochloric acid (5 cm^3) under reflux for 2 h, giving **15b·3HCl** as yellow crystalline powder (78 mg, 60%): Mp colored around 170° and darkened around 260 °C; IR 3500—2600, 1690, 1670, 1640, 1610, 1570, 1510, 1490, 1470, 1450, 1410, 1390, 1360, 1300, and 805 cm^{-1}; ^{1}H NMR δ=3.73 (11H, s), 7.92 (1H, d, *J*=7 Hz), 8.16 (1H, d, *J*=7 Hz), and 9.33 (1H, s); MS *m/z* 189 (M$^+$).

Found: C, 36.34; H, 4.68; N, 23.35%. Calcd for $C_9H_{14}N_5Cl_3$: C, 36.20; H, 4.73; N, 23.45%.

Naphtho[1,2-*c*; 7,8-*c′*]bis[1,2,5]thiadiazole-4,5-diamine Hydrochloride (16·HCl. A mixture of tin powder (508 mg, 4.28 mmol) and **3** (124 mg, 0.41 mmol) in dioxane (10 ml) was treated with concentrated hydrochloric acid (5 ml), as described above. The mixture was heated under reflux for 3 h, cooled to room temperature, and then filtered, giving **16·HCl** (56 mg, 43%) as a complex with dioxane **[16-HCl-dioxane (1/1/0.1)]**: Yellow crystalline powder; mp 265—273 °C (decomp); IR 3500—2650, 1630, 1605, 1550, 1480, 1400, 1360, 1340, 1320, 1280, 1200, 1080, 830, and 820 cm^{-1}; ^{1}H NMR δ=3.63 (5H, s), 7.32 (1H, d, *J*=8 Hz), and 7.84 (1H, d, *J*=8 Hz); MS *m/z* 274 (M$^+$).

Found: C, 39.43; H, 2.48; N, 26.39%. Calcd for ($C_{10}H_7N_6S_2Cl$+0.1·$C_4H_8O_2$): C, 39.08; H, 2.46; N, 26.30%.

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5) Addition of tin(II) chloride in DMSO-d_6 solution of purified **8·2HCl** caused the up-field shift of ^{1}H NMR signals and reproduced the spectrum of crude **8·2HCl**; δ=7.05 (1H, s), 7.27—7.34 (2H, m), 7.60—7.63 (1H, m), and 7.86—7.90 (1H, m). Crude **8·2HCl** which precipitated down during the reduction might contain some unidentified tin(II) compounds.

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