

Sulfur Nitrides in Organic Chemistry. 18.¹⁾ Preparation and Reduction of Benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]tris- and Benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]-thiadiazole. A Convenient Route to Benzenhexamine and 1,2,3,4-Benzenetetramine

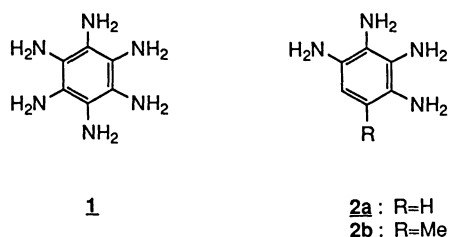
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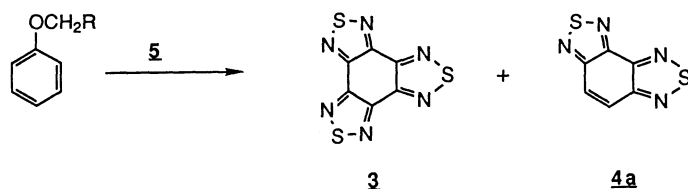
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Benzotris- (**3**) and benzobis[1,2,5]thiadiazole (**4**) were prepared in a moderate yield, respectively, by the reaction of tetrasulfur tetranitride (**5**) with halocatechols (**6**) and -resorcinols (**7**). The reduction of **3** and **4** with Sn powder in a mixture of concentrated hydrochloric acid and dioxane gave benzenhexamine (**1**) and 1,2,3,4-benzenetetramine (**2a**) and its 5-methyl derivative (**2b**) in good yields, as a stable tri- (**1**·3HCl) and dihydrochloride (**2**·2HCl), respectively.

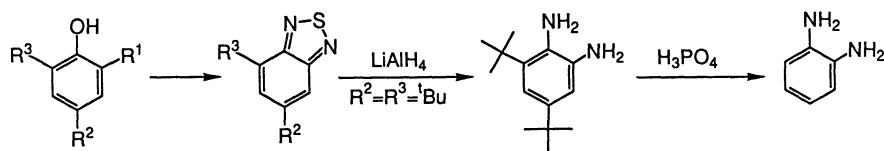
Synthesis of benzenhexamine (**1**) was first reported in 1929²⁾ and some of its derivatives in 1937.³⁾ It attracted little attention until recently when it has been recognized as a building block for materials having interesting physical properties.^{4–8)} As to 1,2,3,4-benzenetetramines (**2**), literature survey revealed that 1,2,3,4-benzenetetramine (**2a**)⁹⁾ and its 5-methyl derivative (**2b**)¹⁰⁾ were already prepared in 1889 and 1890, respectively. To our best knowledge, subsequently, **2** has not been mentioned, except for LCAO-MO calculations on **2a**.¹¹⁾



Previously, it was found¹²⁾ that benzotris- (**3**) and benzobis[1,2,5]thiadiazole (**4a**), which are synthetic equivalents of **1** and **2a**, respectively, were obtained by the reaction of tetrasulfur tetranitride N₄S₄ (**5**) with alkyl phenyl ether but only in poor yield (Scheme 1).



Scheme 1.



Scheme 2.

We recently reported^{13,14)} the reaction of **5** with alkyl- and alkylhalophenols, giving 2,1,3-benzothiadiazoles and the conversion of 4,6-di-*t*-butyl-2,1,3-benzothiadiazole into *o*-phenylenediamine (Scheme 2).

The present paper deals with the convenient preparation of **3** and **4** by the reaction of **5** with benzenediols and benzenetriols such as catechols (**6**), resorcinols (**7**), phloroglucinol (**8a**), and pyrogallol (**8b**) and their reduction to give benzenhexamine (**1**) and 1,2,3,4-benzenetetramine (**2a**) and its 5-methyl derivative (**2b**), respectively.

Results and Discussion

Preparation of 3 and 4. Reactions of **5** with **6**, **7**, and **8** were carried out in refluxing toluene (Schemes 3 and 4). The results are summarized in Tables 1 and 2.

It was found^{14,15)} that, in the reaction of **5** with phenols, *t*-butyl groups and halogen atoms worked well as a leaving group. In the formation of *t*-butylbenzobis[1,2,5]thiadiazole (**4b**), however, the *t*-butyl group was not effective but bromine atom worked well, giving **4b** in 45% yield. The methyl derivative (**4c**) was prepared in 23% yield from 4-

bromo-5-methylcatechol (**6e**). Tribromocatechol (**6f**) gave **4d** in a poor yield (8%). Isopropylcatechol (**6g**) gave the expected **4e** in only 6% yield. In reactions with **6e–6g**, a small amount of benzotris[1,2,5]-thiadiazole (**3**) was obtained as a by-product. Interestingly, **3** was the sole product in 32% yield in the reaction with **6h**. Compound **3** is now easily accessible, starting from catechol in only two steps.

In the reactions of **5** with *t*-butylresorcinols, **7a** and **7b**, **4b** was obtained in low yields. Dibromomethylresorcinol (**7c**) gave the expected **4f** in 11% yield, accompanied with 4-(1,2,5-thiadiazol-3-yl)benzobis[1,2,5]thiadiazole (**4g**). Though **4g** was considered to be formed via **4f**, the reaction of **5** with **4f** did not proceed in refluxing toluene and unchanged **4f** was recovered. The reaction of **5** with polyhaloresorcinols, **7d**, **7e**, **7h**, **7i**, and **7k**, provides a convenient preparative method for halobenzobis[1,2,5]thiadiazoles, **4h** and **4i**. Benzotris[1,2,5]thiadiazole (**3**) was obtained as a by-product in 10–15% yield in these reactions. Only a bromine atom was removed in the reactions with **7h**, **7i**, and **7k**, giving **4i**. Both **4h** and **4i** are inert towards **5** in refluxing toluene. This indicates that **3** was not formed via **4h** and **4i**. The bromo derivative (**4d**) was obtained in a better yield (40%) in the reaction with tribromoresorcinol (**7l**) than with tribromocatechol (**6f**) (8%). The reaction with benzenetriols (**8**) gave unsatisfactory results.

Reduction of 3 and 4. The reduction of benzotris- (**3**) and benzobis[1,2,5]thiadiazole (**4**) to benzenehex-

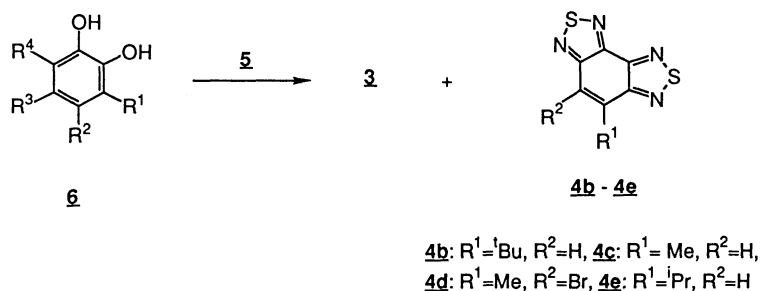
amine (**1**) and 1,2,3,4-benzenetetramine (**2**) were investigated.

LiAlH₄-reduction of **3** and **4** proceeded as evolution of H₂S was observed, but, isolation of unstable **1** and **2** was unsuccessful and tarry materials were formed.

We expected that reduction under acidic conditions might give **1** and **2** as a stable salt. Treatment of **3** with Sn powder in a hot mixture of concentrated hydrochloric acid and dioxane brought about the precipitation of **1-HCl-dioxane** (1/3/0.5) as a white solid during the reaction. This compound gave benzotripyrazine (**9**)⁶ in the reaction with benzil (**10**) in 60% yield from **3** (Scheme 5).

When **4b** was treated under the conditions described above, **4b** was consumed, but precipitation of the expected 5-*t*-butyl-1,2,3,4-benzenetetramine dihydrochloride did not occur. Neutralization of the reaction mixture with NaHCO₃ afforded dark violet resinous materials. On the other hand, the expected **2b·2HCl** was obtained as white solid in the reduction of **4c**. A bromine atom was eliminated in the reduction of **4d**, and **2b·2HCl** was obtained. A halogen atom was also reductively removed in the reduction of **4h** and **4i**, and both of the compounds gave **2a·2HCl**. Reaction of **2a·2HCl** and **2b·2HCl** with **10** in acetic acid afforded the expected benzodipyrzine **11a** and **11b** (Scheme 6).

In conclusion, benzenehexamine (**1**) and 1,2,3,4-benzenetetramines, (**2a**) and (**2b**), are readily accessible, as stable salts, via the reduction of benzotris- (**3**)

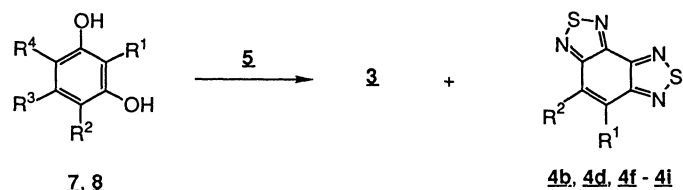


Scheme 3.

Table 1. Reaction^{a)} of **5** with **6**

Entry	Substrate	R ¹	R ²	R ³	R ⁴	5/Substrate ^{b)}	Products (Yield %) ^{c)}
1	6a	H	<i>t</i> Bu	H	H	2/1	4b (17)
2	6b	H	<i>i</i> Bu	H	<i>t</i> Bu	2/1	4b (7)
3	6c	H	<i>t</i> Bu	H	Br	2/1	4b (45)
4	6c	H	<i>t</i> Bu	H	Br	3/1	4b (45)
5	6d	H	Me	H	H	2/1	—
6	6e	H	Me	Br	H	2/1	3 (1), 4c (19)
7	6e	H	Me	Br	H	3/1	3 (2), 4c (23)
8	6e	H	Me	Br	H	4/1	3 (3), 4c (22)
9	6f	Br	Me	Br	Br	3/1	3 (3), 4d (8)
10	6g	<i>i</i> Pr	H	H	H	2/1	3 (2), 4e (6)
11	6h	H	Br	Br	H	3/1	3 (32)
12	6h	H	Br	Br	H	4/1	3 (29)

a) Reaction time; 24 h. b) Molar ratio. c) Yields are calculated upon the substrate.



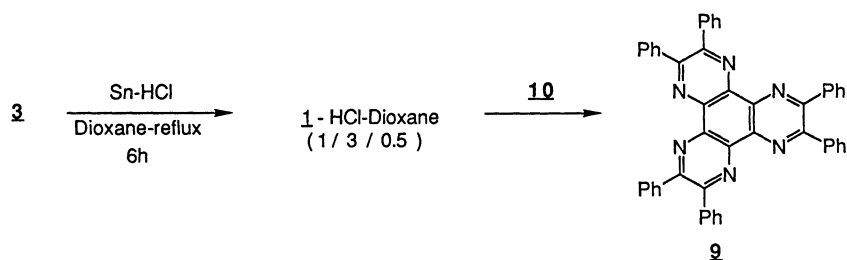
4f: R¹=Et, R²=H, **4g:** R¹=1,2,5-thiadiazol-3-yl, R²=H,
4h: R¹=Br, R²=H, **4i:** R¹=Cl, R²=H

Scheme 4.

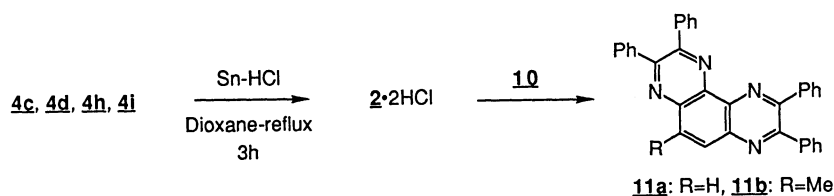
Table 2. Reaction^{a)} of 5 with 7 and 8

Entry	Substrate	R ¹	R ²	R ³	R ⁴	5/Substrate ^{b)}	Products (Yield/%) ^{c)}
1	7a	H	^t Bu	H	^t Bu	2/1	4b (3)
2	7b	Br	^t Bu	H	^t Bu	2/1	4b (15)
3	7c	Br	Et	H	Br	2/1	4f (11), 4g (9)
4	7d	H	Br	H	Br	3/1	3 (7), 4h (30)
5	7e	Br	Br	H	Br	2/1	3 (8), 4h (32)
6	7e	Br	Br	H	Br	3/1	3 (14), 4h (36)
7	7e	Br	Br	H	Br	6/1	3 (13), 4h (37)
8	7f	Me	Br	H	Br	2/1	4h (3)
9	7g	H	Cl	H	H	3/1	4a (+), ^{d)} 4i (3)
10	7h	H	Cl	H	Br	3/1	3 (7), 4i (35)
11	7i	Br	Cl	H	Br	3/1	3 (14), 4i (37)
12	7j	H	Cl	H	Cl	3/1	3 (4), 4i (11)
13	7k	Br	Cl	H	Cl	3/1	3 (15), 4i (48)
14	7l	Br	Br	Me	Br	3/1	3 (1), 4d (40)
15	7m	Br	CHO	H	Br	3/1	3 (7)
16	7n	I	I	H	I	3/1	—
17	8a	Br	Br	OH	Br	3/1	3 (1)
18	8b	OH	H	^t Bu	H	3/1	4b (5)

a) Reaction time; 24 h. b) Molar ratio. c) Yields are calculated upon the substrate. d) Plus sign means less than 1% yield.



Scheme 5.



Scheme 6.

and benzobis[1,2,5]thiadiazole (4), which are obtainable by the reaction of tetrasulfur tetranitride (5) with halobenzenediols, 6 and 7.

Experimental

General. All melting points were determined on a Yana-

gimoto micro melting point apparatus and Mitamura-riken MELT-THERMO and are uncorrected. IR spectra were measured on a Nippon-bunko A-102 spectrophotometer as potassium bromide pellets. NMR spectra were recorded on a Nippon Denshi JEOL FT-100 and GSX-270 using TMS as an internal standard in CDCl₃. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at 75

eV using a direct inlet system.

Materials. Compounds, **6a**, **6b**, **6d**, **6g**, **7a**, **7g**, **7j**, **7n**, and **8b**, are commercially available and **6f**,¹⁵⁾ **6h**,¹⁶⁾ and **8a**¹⁷⁾ were prepared according to the reported methods. Compounds, **6c**, **6e**, **7b**, **7c**,¹⁸⁾ **7d**,¹⁹⁾ **7e**,²⁰⁾ **7f**,²¹⁾ **7h**,²²⁾ **7i**, **7k**,²²⁾ **7l**,²⁰⁾ and **7m**, were prepared by the bromination of the corresponding benzenediols with benzyltrimethylammonium tribromide according to Kajigaeshi-Kakinami's procedure^{23,24)} in the yields as follows. Physical and spectral properties of newly prepared compounds in this study are also given below.

3-Bromo-5-*t*-butylcatechol (6c): Yield 49%; colorless needles (hexane); mp 86–87 °C; IR 3350 cm⁻¹; ¹H NMR δ=1.24 (9H, s), 5.30 (1H, s, D₂O-exchanged), 5.37 (1H, s, D₂O-exchanged), 6.90 (1H, d, *J*=2.0 Hz), and 6.98 (1H, d, *J*=2.0 Hz); MS *m/z* 246 (M⁺) and 244 (M⁺).

Found: C, 49.04; H, 5.41%. Calcd for C₁₀H₁₃BrO₂: C, 49.00; H, 5.35%.

4-Bromo-5-methylcatechol (6e): Yield 68%; colorless needles (cyclohexane); mp 96–98 °C (decomp); IR 3375 cm⁻¹; ¹H NMR δ=2.26 (3H, s), 4.91 (2H, br s, D₂O-exchanged), 6.76 (1H, s), and 7.04 (1H, s); MS *m/z* 204 (M⁺) and 202 (M⁺).

Found: C, 41.33; H, 3.69%. Calcd for C₇H₇BrO₂: C, 41.41; H, 3.47%.

2-Bromo-4,6-di-*t*-butylresorcinol (7b): Yield 71%; pale yellow prisms (light petroleum); mp 109–111 °C; IR 3540 cm⁻¹; ¹H NMR δ=1.36 (18H, s), 5.35 (2H, s, D₂O-exchanged), and 7.14 (1H, s); MS *m/z* 302 (M⁺) and 300 (M⁺).

Found: C, 55.55; H, 7.11%. Calcd for C₁₄H₂₁BrO₂: C, 55.82; H, 7.03%.

2,4-Dibromo-6-ethylresorcinol (7c): Yield 76%; mp 69–70 °C (lit.¹⁸⁾ 74 °C).

4,6-Dibromoresorcinol (7d): Yield 71%; mp 112–114 °C (lit.¹⁹⁾ 110–112 °C).

3,4,6-Tribromoresorcinol (7e): Yield 77%; mp 112.5–113.5 °C (lit.²⁰⁾ 111 °C).

4,6-Dibromo-2-methylresorcinol (7f): Yield 70%; mp 97–99 °C (lit.²¹⁾ 102 °C).

4-Bromo-6-chlororesorcinol (7h): Yield 73%; mp 108.5–111 °C (lit.²²⁾ 108.5 °C).

2,4-Dibromo-6-chlororesorcinol (7i): Yield 75%; pale yellow needles (hexane); mp 104–105 °C; IR 3475 cm⁻¹; ¹H NMR δ=5.88 (1H, s, D₂O-exchanged), 5.92 (1H, s, D₂O-exchanged), and 7.45 (1H, s); MS *m/z* 306 (M⁺), 304 (M⁺), 302 (M⁺), and 300 (M⁺).

Found: C, 23.91; H, 1.01%. Calcd for C₆H₃Br₂ClO₂: C, 23.84; H, 1.00%.

2-Bromo-4,6-dichlororesorcinol (7k): Yield 75%; mp 101.5–102 °C (lit.²²⁾ 101 °C).

5-Methyl-2,4,6-tribromoresorcinol (7l): Yield 74%; mp 97–99 °C (lit.²⁰⁾ 98 °C).

2,4-Dibromo-6-formylresorcinol (7m): Yield 76%; colorless needles (chloroform); mp 185–203 °C (decomp); IR 3275 and 1635 cm⁻¹; MS *m/z* 298 (M⁺), 296 (M⁺), and 294 (M⁺).

Found: C, 28.40; H, 1.50%. Calcd for C₇H₄Br₂O₃: C, 28.41; H, 1.36%.

Reaction of N₄S₄ (5) with Benzenediols, 6 and 7, and Benzenetriol 8. Typical procedure. A mixture of **6**, **7**, or **8** (5 mmol) and an appropriate amount of **5** in toluene (40 cm³) was refluxed for the time shown in Tables 1 and 2. After it was cooled to room temperature, insoluble materials were filtered and extracted with hot CH₂Cl₂. The filtrate

and the extract were combined, condensed in vacuo, and chromatographed on silica gel (Wako gel, C-300). After sulfur was eluted with hexane, **4b**, **4d**, **4e**, and **4h** were eluted with benzene, **4c** with CHCl₃, and **3**, **4f**, **4g**, and **4i** with CH₂Cl₂. Physical and spectral properties of **4** are as follows.

4-*t*-Butylbenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (4b): Colorless needles (hexane); mp 128–129.5 °C; ¹H NMR δ=1.63 (9H, s) and 7.86 (1H, s); ¹³C NMR δ=29.70, 36.57, 118.64, 146.58, 147.58, 148.95, 155.94, and 156.81; MS *m/z* 250 (M⁺).

Found: C, 48.13; H, 4.18; N, 22.14%. Calcd for C₁₀H₁₀N₄S₂: C, 47.93; H, 4.03; N, 22.38%.

4-Methylbenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (4c): Colorless needles (hexane); mp 172–174 °C; ¹H NMR δ=2.78 (3H, d, *J*=1.5 Hz) and 7.78 (1H, d, *J*=1.5 Hz); MS *m/z* 208 (M⁺).

Found: C, 40.13; H, 2.11; N, 27.02%. Calcd for C₇H₄N₄S₂: C, 40.37; H, 1.93; N, 26.90%.

4-Bromo-5-methylbenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (4d): Pale yellow prisms (cyclohexane); mp 203–204.5 °C; ¹H NMR δ=2.90 (s, 3H); ¹³C NMR δ=18.87, 118.71, 134.53, 145.46, 146.80, 154.99, and 157.04; MS *m/z* 288 (M⁺) and 286 (M⁺).

Found: C, 29.31; H, 1.35; N, 19.26%. Calcd for C₇H₃N₄BrS₂: C, 29.28; H, 1.05; N, 19.51%.

4-Isopropylbenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (4e): Pale violet needles (methanol-water); mp 95–97 °C; ¹H NMR δ=1.48 (6H, d, *J*=7.0 Hz), 3.78 (1H, d sept, *J*=7.0 and 0.8 Hz), and 7.80 (1H, d, *J*=0.8 Hz); MS *m/z* 236 (M⁺).

Found: C, 45.51; H, 3.54; N, 23.28%. Calcd for C₉H₈N₄S₂: C, 45.74; H, 3.40; N, 23.66%.

4-Ethylbenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (4f): Colorless prisms (methanol); mp 135–136 °C; ¹H NMR δ=1.48 (3H, t, *J*=7.5 Hz), 3.22 (2H, d, q, *J*=1.3 and 7.5 Hz), and 7.80 (1H, d, *J*=1.3 Hz); ¹³C NMR δ=12.89, 25.42, 119.85, 140.19, 147.54, 148.02, 156.88, and 157.01; MS *m/z* 222 (M⁺).

Found: C, 42.99; H, 2.60; N, 24.98%. Calcd for C₈H₆N₄S₂: C, 43.22; H, 2.72; N, 25.21%.

4-(1,2,5-Thiadiazol-3-yl)benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (4g): Colorless prisms (carbon tetrachloride); mp 206–208 °C; ¹H NMR δ=8.92 (1H, s), and 9.92 (1H, s); MS *m/z* 278 (M⁺).

Found: C, 34.36; H, 0.60; N, 30.07%. Calcd for C₈H₂N₆S₃: C, 34.52; H, 0.72; N, 30.19%.

4-Bromobenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (4h): Pale orange needles (cyclohexane); mp 177–180 °C; ¹H NMR δ=8.32 (1H, s); ¹³C NMR δ=118.91, 126.17, 146.54, 147.55, 154.40, and 156.02; MS *m/z* 274 (M⁺) and 272 (M⁺).

Found: C, 26.39; H, 0.37; N, 20.51%. Calcd for C₆H₂N₄BrS₂: C, 26.59; H, 0.41; N, 20.44%.

4-Chlorobenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazole (4i): Colorless prisms (cyclohexane); mp 167–167.5 °C; ¹H NMR δ=8.15 (1H, s); ¹³C NMR δ=122.54, 130.33, 147.19, 147.26, 153.60, and 155.56; MS *m/z* 230 (M⁺) and 228 (M⁺).

Found: C, 31.61; H, 0.40; N, 24.56%. Calcd for C₆H₂N₄ClS₂: C, 31.51; H, 0.44; N, 24.50%.

Reduction of 3. To a stirred mixture of **3** (252 mg, 1 mmol) and Sn powder (1.54 g, 13 mmol) in degassed dioxane (12 cm³) at reflux, concentrated hydrochloric acid (6 cm³) was added dropwise for 6 h. After it was cooled to room temperature, the precipitated solid was filtered, washed with ethanol, and dried at 90 °C under reduced pressure overnight, giving benzenehexamine trihydrochloride [1-HCl-

dioxane (1/3/0.5)] (230 mg, 70%) as grey powder: mp 140—165 °C (decomp); MS m/z 168 (M^+).

Found: C, 30.22; H, 6.29; N, 26.42%. Calcd for $(C_6H_{15}N_6Cl_3 + C_2H_4O)$: C, 29.87; H, 5.95; N, 26.13%.

Reduction of 4c. To a mixture of **4c** (208 mg, 1 mmol) and Sn powder (1.19 g, 10 mmol) in degassed dioxane (10 cm³) under reflux, concentrated hydrochloric acid (4 cm³) was added dropwise under a nitrogen stream for 3 h. After it was cooled to room temperature, the precipitated solid was filtered. 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 **5-methyl-1,2,3,4-benzenetetramine dihydrochloride (2b·2HCl)** as white powder (134 mg, 60%): mp 160—170 °C (decomp); MS m/z 152 (M^+).

Found: C, 37.05; H, 6.62; N, 24.41%. Calcd for $C_7H_{14}N_4Cl_2$: C, 37.35; H, 6.27; N, 24.89%.

Reduction of 4h. A stirred mixture of **4h** (819 mg, 3 mmol) and Sn powder (3.65 g, 30 mmol) in degassed dioxane (30 cm³) was treated with concentrated hydrochloric acid (12 cm³) and worked up as described in the reduction of **4c**, giving **1,2,3,4-benzenetetramine dihydrochloride (2a·2HCl)** (410 mg, 65%) as white powder: mp 170—195 °C (decomp); MS m/z 138 (M^+).

Found: C, 34.26; H, 5.70; N, 26.38%. Calcd for $C_6H_{12}N_4Cl_2$: C, 34.14; H, 5.73; N, 26.54%.

Preparation of 9. A mixture of **1·3HCl** [prepared from **3** (252 mg, 1 mmol)] and **10** (1.26 g, 6 mmol) in a 3:1-mixture (20 cm³) of degassed ethanol and degassed acetic acid was refluxed for 11 h under a nitrogen atmosphere. After it was cooled to room temperature, the precipitated solid was filtered and washed with ethanol, giving **1,2,5,6,9,10-hexaphenylbenzo[1,2-*b*:3,4-*b'*:5,6-*b''*]tripyrazine (9)** (417 mg, 60% from **3**): mp 360—361.5 °C (lit.⁵) 358 °C).

Preparation of 11a. Crude **2a·2HCl** [obtained from **4h** (550 mg, 2 mmol)] was reacted with **10** (840 mg, 4 mmol) in a mixture of degassed ethanol (15 cm³) and degassed acetic acid (5 cm³) at reflux under nitrogen atmosphere for 3 h. The precipitated solid was filtered and recrystallized from a mixture of hexane and chloroform, giving **2,3,6,7-tetraphenylbenzo[1,2-*b*:3,4-*b'*]dipyrazine (11a)** (395 mg, 41% from **4h**) as colorless needles; mp 260—262 °C; ¹H NMR δ =7.28—7.40 (12H, m), 7.56—7.74 (8H, m), and 8.34 (2H, s); MS m/z 486 (M^+).

Found: C, 84.00; H, 4.53; N, 11.46%. Calcd for $C_{34}H_{22}N_4$: C, 83.93; H, 4.56; N, 11.51%.

From **4i** (460 mg, 2 mmol), **11a** was similarly obtained in 39% overall yield (379 mg).

Preparation of 11b. Crude **2b·2HCl** [obtained by the reduction of **4c** (208 mg, 1 mmol)] was treated with **10** (840 mg, 4 mmol) as described in the preparation of **11a**, giving **5-methyl-1,2,3,8,9-tetraphenylbenzo[1,2-*b*:3,4-*b'*]dipyrazine (11b)** (114 mg, 23% from **4c**) as colorless prisms (cyclohexane); mp 234—237 °C (lit.¹⁰) 222—225 °C; ¹H NMR δ =3.00 (3H, d, J =2.5 Hz), 7.32—7.44 (12H, m), 7.57—7.80 (8H, m),

and 8.20 (1H, d, J =2.5 Hz); MS m/z 500 (M^+); (Found: C, 83.86; H, 4.90; N, 10.94%).

Compound **11b** (253 mg) was obtained from **4d** (574 mg, 2 mmol) in total 25% yield.

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