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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 Benzenehexamine and 1,2,3,4-Benzenetetramine

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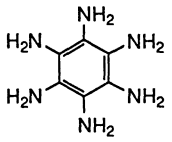
Benzotris- (**3**) and benzobis[1,2,5]thiadiazole (**4**) were prepared in a moderate yield, respectively, by the reaction of tetrasulfur tetranitride (**5**) with halocatechols (**6**) and -resorcinols (**7**). The reduction of **3** and **4** with Sn powder in a mixture of concentrated hydrochloric acid and dioxane gave benzenehexamine (**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 benzenehexamine (**1**) was first reported in 1929[2] 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]



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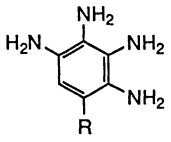


2a: R=H
2b: R=Me

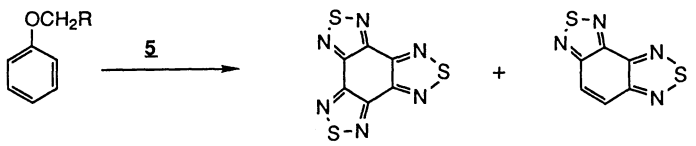
Previously, it was found[12] that benzotris- (**3**) and benzobis[1,2,5]thiadiazole (**4a**), which are synthetic equivalents of **1** and **2a**, respectively, were obtained by the reaction of tetrasulfur tetranitride N_4S_4 (**5**) with alkyl phenyl ether but only in poor yield (Scheme 1). We recently 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 benzenehexamine (**1**) and 1,2,3,4-benzenetetramine (**2a**) and its 5-methyl derivative (**2b**), respectively.

Results and Discussion

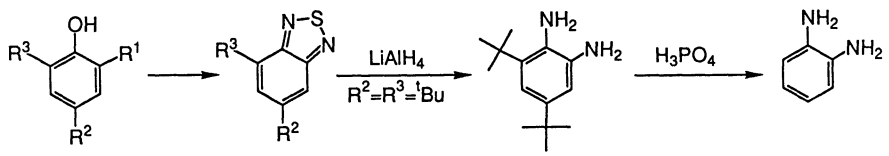
Preparation of 3 and 4. Reactions of **5** with **6**, **7**, and **8** were carried out in refluxing toluene (Schemes 3 and 4). The results are summarized in Tables 1 and 2.

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-



3 **4a**

Scheme 1.



Scheme 2.

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. Dibromoethylresorcinol (**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.

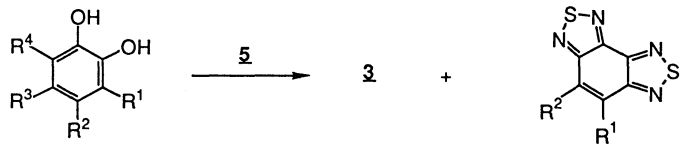
Reduction of 3 and 4. The reduction of benzotris-(**3**) and benzobis[1,2,5]thiadiazole (**4**) to benzenehexamine (**1**) and 1,2,3,4-benzenetetramine (**2**) were investigated.

$LiAlH_4$-reduction of **3** and **4** proceeded as evolution of H_2S 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 $NaHCO_3$ 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 benzodipyrazine **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**)



6 4b - 4e

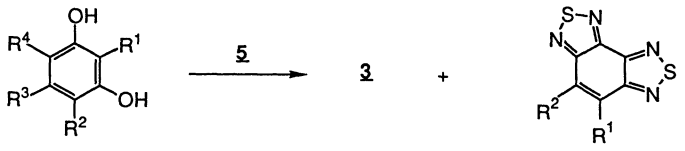
4b: R^1=^{t}Bu, R^2=H, 4c: R^1= Me, R^2=H,
4d: R^1=Me, R^2=Br, 4e: R^1=^{i}Pr, R^2=H

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	^{t}Bu	H	H	2/1	**4b** (17)
2	**6b**	H	$_t$Bu	H	^{t}Bu	2/1	**4b** (7)
3	**6c**	H	^{t}Bu	H	Br	2/1	**4b** (45)
4	**6c**	H	^{t}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}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.



7, 8 — 4b, 4d, 4f - 4i

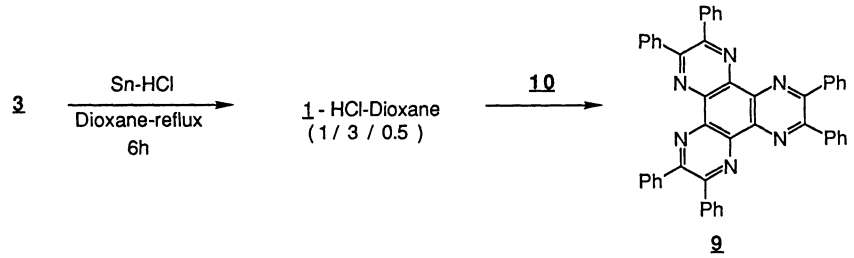
4f: R^1=Et, R^2=H, 4g: R^1= 1,2,5-thiadiazol-3-yl, R^2=H,
4h: R^1=Br, R^2=H, 4i: R^1=Cl, R^2=H

Scheme 4.

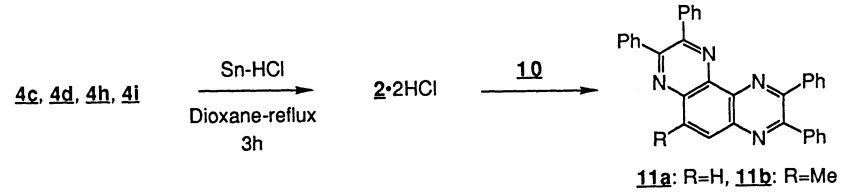
Table 2. Reaction[a] of 5 with 7 and 8

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 Yanagimoto 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 $CDCl_3$. 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, D_2O-exchanged), 5.37 (1H, s, D_2O-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 $C_{10}H_{13}BrO_2$: 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, D_2O-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 $C_7H_7BrO_2$: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, D_2O-exchanged), and 7.14 (1H, s); MS m/z 302 (M^+) and 300 (M^+).

Found: C, 55.55; H, 7.11%. Calcd for $C_{14}H_{21}BrO_2$: 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, D_2O-exchanged), 5.92 (1H, s, D_2O-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 $C_6H_3Br_2ClO_2$: 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 $C_7H_4Br_2O_3$: C, 28.41; H, 1.36%.

Reaction of N_4S_4 (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 cm^3) 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 CH_2Cl_2. 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 $CHCl_3$, and **3**, **4f**, **4g**, and **4i** with CH_2Cl_2. 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): ^{13}C 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 $C_{10}H_{10}N_4S_2$: 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 $C_7H_4N_4S_2$: 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); ^{13}C 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 $C_7H_3N_4BrS_2$: 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 $C_9H_8N_4S_2$: 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): ^{13}C 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 $C_8H_6N_4S_2$: 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 $C_8H_2N_6S_3$: 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); ^{13}C 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 $C_6HN_4BrS_2$: 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); ^{13}C 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 $C_6HN_4ClS_2$: 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 cm^3) at reflux, concentrated hydrochloric acid (6 cm^3) 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 cm^3) under reflux, concentrated hydrochloric acid (4 cm^3) 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 cm^3) was treated with concentrated hydrochloric acid (12 cm^3) 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 cm^3) 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 cm^3) and degassed acetic acid (5 cm^3) 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-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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