Preparation of Benzo-diimidazoles and Benzo-triimidazoles

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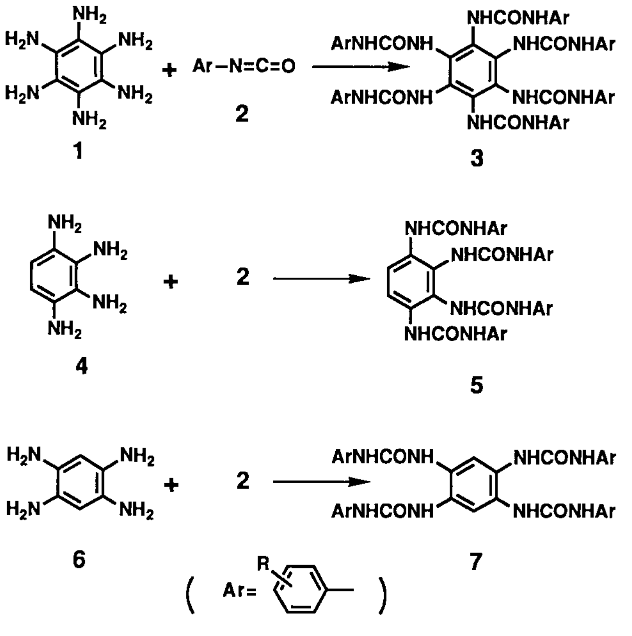
The reaction of benzenehexamine (**1**), benzene-1,2,3,4-tetramine (**4**), and benzene-1,2,4,5-tetramine (**6**) with aryl isocyanate **2** afforded the corresponding hexakis(*N*'-arylureido)benzene **3** and the tetrakis(*N*'-arylureido)benzenes **5** and **7**. Pyrolysis of **3**, **5**, and **7** at 400°C furnished the benzo-triimidazoletrione **8** and benzo-biimidazolediones **10** and **11**.

Some heterocyclic analogs of triphenylene, in which each of the peripheral benzene rings has been replaced by 5- and 6-membered diazaheterocycles[1-10], have attracted considerable attention in recent years because of their interesting physical properties. Since the physical and chemical properties of urea and its derivatives are closely related to their ability to form strong intra- and/or intermolecular hydrogen bonds, we were interested in the benzo-triimidazoletrione **8** and the benzo-biimidazolediones **10** and **11**, all of which have two or three cyclic urea substructures in their peripheral region.

Scheme 1



Benzene-polyamine	Aryl isocyanate (R)	Product	Yield (%)
1	**2a** (H)	**3a**	(76)
1	**2b** (*p*-Me)	**3b**	(80)
1	**2c** (*p*-F)	**3c**	(81)
1	**2d** (*p*-Cl)	**3d**	(91)
1	**2e** (*m*-Cl)	**3e**	(73)
1	**2f** (*p*-Br)	**3f**	(69)
4	**2a** (H)	**5a**	(90)
4	**2b** (*p*-Me)	**5b**	(90)
4	**2c** (*p*-F)	**5c**	(76)
4	**2d** (*p*-Cl)	**5d**	(64)
4	**2e** (*m*-Cl)	**5e**	(82)
4	**2f** (*p*-Br)	**5f**	(78)

This paper deals with the preparation of **8**, **10**, and **11** from benzenepolyamines **1**, **4**, and **6**.

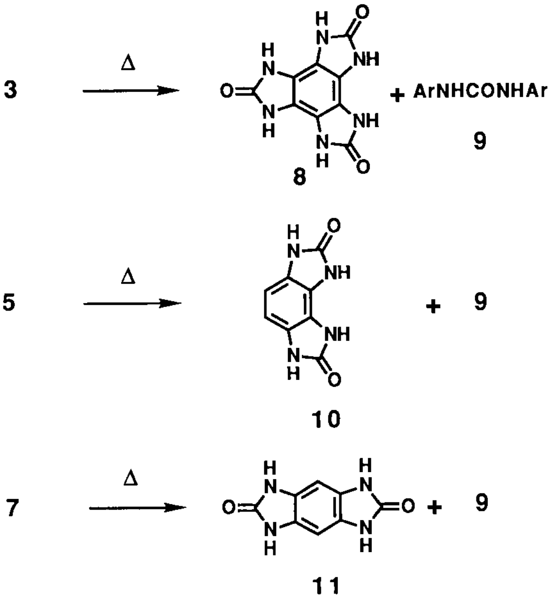
Results and Discussion

In our preceding paper[11], we reported on a convenient preparative method for the synthesis of benzenehexamine (**1**) and benzene-1,2,3,4-tetramine (**4**) via the reduction of benzobi- and benzotri[1,2,5]thiadiazole. A direct preparation of **8**, **10**, and **11** from **1**, **4**, and 1,2,4,5-benzenetetramine (**6**) was first planned, since benzene-1,2-diamine reacts smoothly at room temperature with triphosgene, a synthetic substitute of phosgene[12], giving 1*H*-benzimidazol-2(3*H*)-one. The reaction of tetramine **4** with triphosgene in toluene under reflux conditions did not give the desired **10**. The yellow solids produced in the reaction became dark-colored during work-up and gave tarry materials. Thus, an indirect preparation of **8**, **10**, and **11** via a sequence of the reaction of **1**, **4**, and **6** with isocyanate and the subsequent pyrolysis of the adduct **3**, **5**, and **7** was investigated.

After a detailed survey of the reaction conditions, the desired hexa-adducts **3a**–**f** and 1,2,3,4-tetra-adducts **5a**–**f** with aryl isocyanate **2** were obtained in high yields (Table 1). Under argon and with the exclusion of light, triethylamine was added dropwise to a refluxing suspension of the hydrochloride of the benzenepolyamine and **2** in anhydrous benzene or toluene. The reaction mixture was refluxed for the time given in the experimental section and the white precipitates formed were filtered and washed with hot benzene and hot ethanol in order to remove 1,3-diarylurea **9**.

The 1,2,4,5-tetra-adduct **7** was similary obtained. In contrast to the isomer **5**, compound **7** should not be treated with hot ethanol as it is unstable in ethanol, giving a dark-colored solution; evaporation of the solvent affords tarry materials. Compound **7** was thoroughly washed with a nonpolar solvent such as benzene, though complete removal of **9** is difficult, and then subjected to pyrolysis. Adducts **3**, **5**, and **7** are nearly insoluble in organic solvents.

Scheme 2



Substrate	Product	Yield (%)	Substrate	Product	Yield (%)
3a	**8**	(54)	**5a**	**10**	(19)
3b	**8**	(61)	**5b**	**10**	(27)
3d	**8**	(38)	**5d**	**10**	(46)
7	**11**	(54)			

Alkyl isocyanates such as propyl, hexyl, cyclohexyl, and octadecyl isocyanate and phenyl isothiocyanate are unreactive towards benzenepolyamine.

Chlorosulfonyl isocyanate and tosyl isocyanate are also unreactive under the conditions mentioned above. The reaction with chlorocarbonyl isocyanate gave resinous materials and none of the desired adducts were obtained.

The pyrolyses of **3a**, **3b**, **3d**, **5a**, **5b**, **5d**, and **7** were carried out at 400°C under atmospheric pressure for 20 min. In order to remove **9**, the pyrolysate was thoroughly washed with hot ethanol to give the desired **8**, **10**, and **11** in moderate yields. Compounds **8**, **10**, and **11** were obtained as a white powder and are sparingly soluble in organic solvents. The thermal analysis of **8**, **10**, and **11** shows that these compounds sublime before they undergo decomposition at temperatures above 350°C, i.e. more than 130°C higher than the sublimation point of **12**. These properties may reflect the presence of strong intermolecular hydrogen bonds in **8**, **10** and **11** in the solid phase.

In the ^{1}H-NMR spectra, the signals of the amido protons of **8** and **11** are observed as a single peak, each at $\delta = 9.66$ and 10.28, while **10** shows two singlets (δ = 9.73 and 10.45), assignable to the two different amido groups. In their ^{13}C-NMR spectra, **8**, **10**, and **11** show the signal for the amido carbon around $\delta = 155$. The aromatic carbon signal of **8** appears at $\delta = 107.7$, which is very similar to that of **12** ($\delta = 108.6$). Compound **10** shows the signals of the aromatic carbons at $\delta = 102.0$ and 112.7, respectively. Interestingly, **11** exhibits the corresponding signal at a higher magnetic field ($\delta = 90.8$), while signals of aromatic carbons bearing a hydrogen atom appear in a similar region of **10** and **11** (δ = 124.9 and 123.5, respectively).

Experimental

Melting points: Uncorrected values (sealed tube). – IR (KBr): Jasco IR-700. – ^{1}H NMR Jeol GSX-270, 270 MHz, in [D$_6$]DMSO, TMS as a reference. – MS: Jeol JMS-01SG-2, EI (75 eV). – Elemental analyses: Yanaco MT-5. – Thermal analyses: Seiko TG/DTA 320.

1,2,3,4,5,6-Hexakis(N'-phenylureido)benzene (**3a**): To a refluxing mixture of **1** · 3 HCl (336 mg, 1.21 mmol) and **2a** (1.31 ml, 12.0 mmol) in toluene (20 ml) was added dropwise a solution of triethylamine (0.86 ml, 6.2 mmol) in toluene (10 ml) for 3 min. After the mixture had been heated under reflux for 8 h, it was cooled and the precipitates formed were filtered and washed, in order to remove **9** and triethylammonium chloride, first with hot benzene and then with hot ethanol to afford **3a** (810 mg, 76%) as a white powder, m.p. 262°C (dec.). – IR: $\tilde{\nu}$ [cm^{-1}] = 3316, 1651, 1602, 1556, 1499, 1443, 1313, 1233, 1178, 1073, 1027, 900, 750, 692. – ^{1}H NMR: δ = 6.90–6.96 (6H, m), 7.19–7.25 (12H, m), 7.42–7.45 (12H, m), 7.70 (6H, s, exchange with D$_2$O), 9.38 (6H, s, exchange with D$_2$O). – $C_{48}H_{42}N_{12}O_6$ (882.9): calcd. C 65.30, H 4.79, N 19.07; found C 65.02, H 4.84, N 18.69.

1,2,3,4,5,6-Hexakis[N'-(p-tolyl)ureido]benzene (**3b**): A refluxing mixture of **1** · 3 HCl (168 mg, 0.61 mmol) and **2b** (0.54 ml, 4.8 mmol) in toluene (20 ml) was treated with a solution of triethylamine (0.34 ml, 2.4 mmol) in toluene (10 ml) and worked up as described above to yield **3b** (446 mg, 80%) as a white powder, m.p. 267°C (dec.). – IR: $\tilde{\nu}$ [cm^{-1}] = 3292, 3030, 2918, 1647, 1605, 1555, 1405, 1313, 1294, 1231, 1120, 1019, 814, 753. – ^{1}H NMR: δ = 2.50 (18H, s), 7.02 (12H, d, J = 8.3 Hz), 7.31 (12H, d, J = 8.3 Hz), 7.65 (6H, s, exchange with D$_2$O), 9.25 (6H, s, exchange with D$_2$O). – $C_{54}H_{54}N_{12}O_6$ (967.1): calcd. C 67.07, H 5.63, N 17.38; foundC 66.67, H 5.58, N 17.27.

1,2,3,4,5,6-Hexakis[N'-(p-fluorophenyl)ureido]benzene (**3c**): A refluxing mixture of **1** · 3 HCl (101 mg, 0.36 mmol) and **2c** (0.42 ml, 3.72 mmol) in toluene (20 ml) was treated with a solution of triethylamine (0.26 ml, 1.9 mmol) in toluene (10 ml) and worked up as described above to furnish **3c** (292 mg, 81%) as a white powder, m.p. 281°C (dec.). – IR: $\tilde{\nu}$ [cm^{-1}] = 3294, 1650, 1614, 1562, 1510, 1407, 1304, 1217, 1155, 834. – ^{1}H NMR: δ = 7.03–7.09 (12H, m), 7.43–7.46 (12H, m), 7.69 (6H, s, exchange with D$_2$O), 9.42 (6H, s, exchange with D$_2$O). – $C_{48}H_{36}F_6N_{12}O_6$ (990.9): calcd. C 58.18, H 3.66, N 16.96; found C 57.98, H 3.79, N 16.77.

1,2,3,4,5,6-Hexakis[N'-(p-chlorophenyl)ureido]benzene (**3d**): A refluxing mixture of **1** · 3 HCl (168 mg, 0.60 mmol) and **2d** (0.79 ml, 8.0 mmol) in benzene (20 ml) was treated with a solution of triethylamine (0.91 ml, 6.5 mmol) in benzene (10 ml) and worked up as described above to furnish **3d** (604 mg, 91%) as a white powder, m.p. 303°C (dec.). – IR: $\tilde{\nu}$ [cm^{-1}] = 3324, 1737, 1650, 1600, 1553, 1492, 1399, 1346, 1305, 1284, 1233, 1176, 1094, 1046, 1013, 827, 757. – ^{1}H NMR: δ = 7.29–7.35 (12H, m), 7.43–7.48 (12H, m), 7.72 (6H, s, exchange with D$_2$O), 9.49 (6H, s, exchange with D$_2$O). – $C_{48}H_{36}Cl_6N_{12}O_6$ (1089.6): calcd. C 52.91, H 3.33, N 15.43; found C 52.43, H 3.25, N 15.86.

1,2,3,4,5,6-Hexakis[N'-(m-chlorophenyl)ureido]benzene (**3e**): A refluxing mixture of **1** · 3 HCl (101 mg, 0.36 mmol) and **2e** (0.45 ml, 3.7 mmol) in toluene (20 ml) was treated with a solution of triethylamine (0.26 ml, 1.9 mmol) in toluene (10 ml) and worked up as described above to afford **3e** (289 mg, 73%) as a white powder, m.p. 282°C (dec.). – IR: ṽ [cm^{-1}] = 3320, 1657, 1597, 1556, 1481, 1408, 1229, 773. – ^{1}H NMR: δ = 6.96–7.03 (6H, m), 7.16–7.30 (18H, m), 7.75–7.77 (6H, m), 7.76 (6H, s, exchange with D_2O), 9.57 (6H, s, exchange with D_2O). – $C_{48}H_{36}Cl_6N_{12}O_6$ (1089.6): calcd. C 52.91, H 3.33, N 15.43; found C 52.47, H 3.29, N 15.14.

1,2,3,4,5,6-Hexakis[N'-(p-bromophenyl)ureido]benzene (**3f**): A refluxing mixture of **1** · 3 HCl (101 mg, 0.36 mmol) and **2f** (737 mg, 3.72 mmol) in toluene (20 ml) was treated with a solution of triethylamine (0.26 ml, 1.9 mmol) in toluene (10 ml) and worked up as described above to yield **3f** (338 mg, 69%) as a white powder, m.p. 298°C (dec.). – IR: ṽ [cm^{-1}] = 3286, 1650, 1594, 1548, 1487, 1395, 1305, 1229, 1074, 1010, 822. – ^{1}H NMR: δ = 7.37–7.45 (24H, m), 7.73 (6H, s, exchange with D_2O), 9.50 (6H, s, exchange with D_2O). – $C_{48}H_{36}Br_6N_{12}O_6$ (1356.3): calcd. C 42.51, H 2.68, N 12.39; found C 42.89, H 2.81, N 12.68.

1,2,3,4-Tetrakis(N'-phenylureido)benzene (**5a**): To a mixture of **4** · 2 HCl (138 mg, 0.65 mmol) and **2a** (0.45 ml, 4.1 mmol) in benzene (20 ml) was added dropwise under reflux triethylamine (0.28 ml, 2.0 mmol) in benzene (10 ml) for 3 min and the mixture was further heated under reflux for 8 h. After cooling, the precipitates formed were filtered off and washed with hot benzene and then hot ethanol to furnish **5a** (362 mg, 90%) as a white powder, m.p. 280°C (dec.). – IR: ṽ [cm^{-1}] = 3284, 3038, 1651, 1602, 1556, 1497, 1443, 1314, 1234, 1069, 1028, 897, 834, 749, 692. – ^{1}H NMR: δ = 6.94 (4H, dd, *J* = 7.7 and 1.1 Hz), 7.21–7.49 (8H, m), 7.46 (8H, dd, 8.4 and 1.1 Hz), 7.64 (2H, s, exchange with D_2O), 7.69 (2H, s), 7.99 (2H, s, exchange with D_2O), 9.19 (2H, s, exchange with D_2O), 9.24 (2H, s, exchange with D_2O). – ^{13}C NMR: δ = 117.84, 118.08, 118.27, 120.15, 121.62, 126.33, 128.55, 128.65, 131.36, 152.82, 153.60. – $C_{34}H_{30}N_8O_4$ (614.7): calcd. C 66.44, H 4.92, N 18.23; found C 66.22, H 5.03, N 18.48.

1,2,3,4-Tetrakis[N'-(p-tolyl)ureido]benzene (**5b**): To a mixture of **4** · 2 HCl (276 mg, 1.31 mmol) and **2b** (1.0 ml, 8.0 mmol) in benzene (20 ml) was added dropwise under reflux triethylamine (0.56 ml, 4.0 mmol) in benzene (10 ml) for 3 min and the mixture was further heated under reflux for 8 h. The mixture was worked up as described above to furnish **5b** (786 mg, 90% yield) as a white powder, m.p. 312°C (dec.). – IR: ṽ [cm^{-1}] = 3284, 3028, 2918, 1650, 1605, 1552, 1512, 1405, 1312, 1290, 1235, 1208, 814. – ^{1}H NMR: δ = 2.23 (12H, s), 7.05 (4H, d, *J* = 8.4 Hz), 7.06 (4H, d, *J* = 8.4 Hz), 7.33 (8H, d, *J* = 8.4 Hz), 7.59 (2H, s, exchange with D_2O), 7.66 (2H, s), 7.93 (2H, s, exchange with D_2O), 9.07 (2H, s, exchange with D_2O), 9.13 (2H, s, exchange with D_2O). – ^{13}C NMR: δ = 20.26, 118.21, 118.44, 120.02, 126.29, 128.94, 129.05, 130.38, 131.30, 137.25, 152.87, 153.65. – $C_{38}H_{38}N_8O_4$ (670.8): calcd. C 68.04, H 5.71, N 16.71; found C 67.91, H 5.75, N 16.91.

1,2,3,4-Tetrakis[N'-(p-fluorophenyl)ureido]benzene (**5c**): To a mixture of **4** · 2 HCl (83 mg, 0.39 mmol) and **2c** (0.29 ml, 2.5 mmol) in benzene (20 ml) was added dropwise under reflux triethylamine (0.18 ml, 1.3 mmol) in benzene (10 ml) for 20 min and the mixture was further heated under reflux for 3 h. The solution was worked up as described above, to yield **5c** (204 mg, 76%) as a white powder, m.p. 318°C (dec.). – IR: ṽ [cm^{-1}] = 3296, 3080, 1653, 1616, 1561, 1510, 1407, 1302, 1217, 1155, 1095, 1014, 893, 832, 794, 755. – ^{1}H NMR: δ = 7.04–7.18 (8H, m), 7.42–7.48 (8H, m), 7.61 (2H, s, exchange with D_2O), 7.66 (2H, s), 7.97 (2H, s, exchange with D_2O), 9.23 (2H, s, exchange with D_2O), 9.26 (2H, s, exchange with D_2O). – ^{13}C NMR: δ = 114.93, 115.02, 115.25, 115.34, 119.76, 119.87, 119.94, 120.07, 126.40, 131.37, 136.17, 152.97, 153.71, 155.49, 158.99. – $C_{34}H_{26}F_4N_8O_4$ (686.6): calcd. C 59.48, H 3.82, N 16.32; found C 59.15, H 3.82, N 16.09.

1,2,3,4-Tetrakis[N'-(p-chlorophenyl)ureido]benzene (**5d**): To a mixture of **4** · 2 HCl (83 mg, 0.39 mmol) and **2d** (0.32 ml, 2.50 mmol) in toluene (20 ml) was added dropwise under reflux triethylamine (0.18 ml, 1.30 mmol) in toluene (10 ml) for 20 min and the mixture was further heated under reflux for 3 h. The solution was worked up as described above to give **5d** (190 mg, 64%) as a white powder, m.p. 267°C (dec.). – IR: ṽ [cm^{-1}] = 3294, 1652, 1598, 1547, 1492, 1399, 1094, 1013, 825. – ^{1}H NMR: δ = 7.28–7.32 (8H, m), 7.49–7.52 (8H, m), 7.70 (2H, s, exchange with D_2O), 7.72 (2H, s), 8.05 (2H, s, exchange with D_2O), 9.36 (2H, s, exchange with D_2O), 9.40 (2H, s, exchange with D_2O). – $C_{34}H_{26}Cl_4N_8O_4$ (752.4): calcd. C 54.27, H 3.48, N 14.89; found C 53.98, H 3.50, N 15.10.

1,2,3,4-Tetrakis[N'-(m-chlorophenyl)ureido]benzene (**5e**): To a mixture of **4** · 2 HCl (239 mg, 1.13 mmol) and **2e** (0.98 ml, 8.0 mmol) in toluene (20 ml) was added dropwise under reflux triethylamine (0.59 ml, 4.2 mmol) in toluene (10 ml) for 20 min and the mixture was further heated under reflux for 3 h. The solution was worked up as described above to give **5e** (700 mg, 82%) as a white powder, m.p. 300°C (dec.). – IR: ṽ [cm^{-1}] = 3260, 1655, 1595, 1555, 1480, 1407, 1284, 1227, 773, 681. – ^{1}H NMR: δ = 6.98–7.00 (4H, m), 7.23–7.36 (8H, m), 7.69 (4H, s), 7.74 (4H, s, became 2H, s, treatment with D_2O), 8.07 (2H, s, exchange with D_2O), 9.41 (2H, s, exchange with D_2O), 9.44 (2H, s, exchange with D_2O). – $C_{34}H_{26}Cl_4N_8O_4$ (752.4): calcd. C 54.27, H 3.48, N 14.89; found C 54.20, H 3.50, N 14.69.

1,2,3,4-Tetrakis[N'-(p-bromophenyl)ureido]benzene (**5f**): To a mixture of **4** · 2 HCl (83 mg, 0.39 mmol) and **2f** (499 mg, 2.5 mmol) in benzene (20 ml) was added dropwise under reflux triethylamine (0.18 ml, 1.3 mmol) in benzene (10 ml) for 20 min and the mixture was further heated under reflux for 3 h. The solution was worked up as described above to afford **5f** (284 mg, 78%) as a white powder, m.p. 287°C (dec.). – IR: ṽ [cm^{-1}] = 3298, 1652, 1594, 1541, 1489, 1395, 1306, 1284, 1234, 1074, 1011, 821, 754. – ^{1}H NMR: δ = 7.41–7.44 (16H, m), 7.68 (2H, s, exchange with D_2O), 7.72 (2H, s), 7.97 (2H, s, exchange with D_2O), 9.32 (2H, s, exchange with D_2O), 9.37 (2H, s, exchange with D_2O). – $C_{34}H_{26}Br_4N_8O_4$ (930.2): calcd. C 43.90, H 2.82, N 12.05; found C 43.99, H 2.88, N 12.36.

6,7-Dihydro-1H-benzo[1,2-d:3,4-d':5,6-d'']triimidazole-2,5,8(3H,4H,9H)-trione (**8**): Compound **3a** (200 mg, 0.23 mmol) was pyrolyzed at 400°C under atmospheric pressure for 20 min. In order to remove 1,3-diphenylurea, the pyrolysate was washed, first with hot benzene and then with hot ethanol. Compound **8** was obtained (30 mg, 54%) as a grey powder, m.p. 378–390°C (dec.). – IR: ṽ [cm^{-1}] = 3259, 1697, 1507, 1362, 1314, 989, 766, 689. – ^{1}H NMR: δ = 9.66 (6H, s, exchange with D_2O). – ^{13}C NMR: δ = 107.73, 154.47. – MS: *m/z* = 246 [M$^+$], 202 [M$^+$ – CO]. – $C_9H_6N_6O_3$ (246.2) + 0.25 H_2O: calcd. C 43.12, H 2.60, N 33.52; found C 43.62, H 2.81, N 33.30.

Similarly, **3b** and **3d** were converted to **8** in 61% and 38% yield, respectively.

3,6-Dihydrobenzo[1,2-d:3,4-d']biimidazole-2,5(1H,8H)-dione (**10**): Compound **5d** (411 mg, 0.55 mmol) was pyrolyzed and worked up as described above, to furnish **10** (48 mg, 46%) as a grey powder, m.p. 390–395°C (dec.). – IR: ṽ [cm^{-1}] = 3176, 1675, 1484, 1394, 1248, 1227, 1155, 1051, 1000, 852, 777, 741. – ^{1}H NMR: δ = 6.54 (2H, s), 9.73 (2H, s, exchange with D_2O), 10.45 (2H, s, exchange with D_2O). – ^{13}C NMR: δ = 102.00, 112.74, 124.78, 155.42. – MS:

m/*z* = 190 [M^+], 162 [M^+ – CO]. – $C_8H_6N_4O_2$ (190.2) + 0.3 H_2O: calcd. C 48.98, H 3.42, N 28.56; found C 49.16, H 3.52, N 28.75.

Similarly, **5a** and **5d** were converted to **10** in 19% and 27% yield, respectively.

1,2,4,5-Tetrakis(N'-phenylureido)benzene (**7**): To a mixture of commercial **6** · 4 HCl (276 mg, 0.97 mmol) and **2a** (0.89 ml, 8.2 mmol) in toluene (40 ml) was added dropwise at room temp. triethylamine (1.12 ml, 8.0 mmol) in toluene (10 ml) for 3 min and the mixture was stirred for 20 min at room temp. The precipitates formed were filtered and washed with hot benzene and then hot water to afford **7** (284 mg, 48%) as a pink powder, m.p. 235–260°C (dec.).

3,7-Dihydrobenzo[1,2-d:4,5-d']biimidazole-2,6(1H,5H)-dione (**11**): Crude **7** (310 mg, 0.50 mmol) was pyrolyzed and worked up as described in the pyrolysis of **2a** to yield **11** (52 mg, 54%) as a grey powder, m.p. >400°C. – IR: $\tilde{\nu}$ [cm^{-1}] = 3136, 1691, 1483, 1390, 1317, 1201, 1175, 1030, 899, 819, 783, 741. – ^1H NMR: δ = 6.51 (2H, s), 10.28 (4H, s, exchange with D_2O). – ^{13}C NMR: δ = 90.82, 123.52, 154.95. MS: *m*/*z* = 190 [M^+], 162 [M^+ – CO]. – $C_8H_6N_4O_2$ (190.2) + 0.3 H_2O: calcd. C 48.98, H 3.42, N 28.56; found C 48.72, H 3.44, N 28.82.

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[34/93]