Synthesis and properties of *N*-[2,2-bis(2,4-dihydroxyaryl)ethyl]-*N*-methylamines and their hydrohalides

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Condensation of one molecule of α-methylaminoacetaldehyde dimethyl acetal with two molecules of resorcinol or methylresorcinol in hydrohalogen acid solutions led to substituted *N*-(2,2-diarylethyl)-*N*-methylamine hydrohalides. Reactions of the corresponding amines with acetic anhydride, mono- and diisocyanates, and formaldehyde were studied. Conditions for formation of calixarene from resorcinol and α-methylaminoacetaldehyde dimethyl acetal were invented.

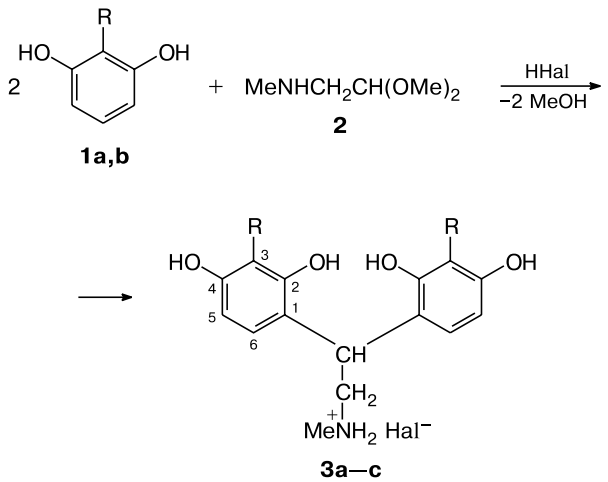
Key words: resorcinols, acetals, α-methylaminoacetaldehyde, amino phenols, amines, calix[4]resorcinarene.

Condensation of resorcinol and its derivatives with aliphatic and aromatic aldehydes is a principal method for the synthesis of calix[4]resorcinarenes.[1—3] Recently, we extended the synthetic potentialities of this method by the use of phosphorylated acetals to obtain calix[4]resorcinarenes bearing phosphorylalkyl substituents at the lower rim of the molecule.[4] Their aminoalkyl analogs are of particular interest, since the presence of amino groups can make them serve as key compounds in the synthesis of new cavitands, carcerands, or nanotubes.

To obtain such structures, we carried out a condensation of resorcinol (**1a**) and 2-methylresorcinol (**1b**) with α-methylaminoacetaldehyde dimethyl acetal (**2**) in hydrohalogen acid solutions (Scheme 1). Unexpectedly, the substituted *N*-(2,2-diarylethyl)-*N*-methylamine hydrohalides **3a—c**, products of the reaction of two molecules of resorcinol with one molecule of α-aminoacetal, were obtained instead of calixarenes. In order to study the influence of the conditions on the outcome of the reaction, we varied the temperature (from 25 to 80 °C) and the duration of the process (from 4 h to 7 days). However, bis-resorcinols **3a—c** were the only products in all the cases. Their structures were confirmed by ^{1}H and ^{13}C NMR spectra, and their molecular weights were determined by MALDI-TOF mass-spectrometry.

It should be noted that there is the only documented[5] example of the condensation of 2-nitroresorcinol with acetaldehyde or 4-methoxybenzaldehyde leading to the compounds of this type, though, the detailed analysis of the product composition has not been done. In all the other known cases, reaction of resorcinol with aldehydes leads to calixarenes. Obviously, the abnormal course of

Scheme 1



1: R = H (**a**), Me (**b**)

3: R = H, Hal = Cl (**a**); R = Me, Hal = Cl (**b**), Br (**c**)

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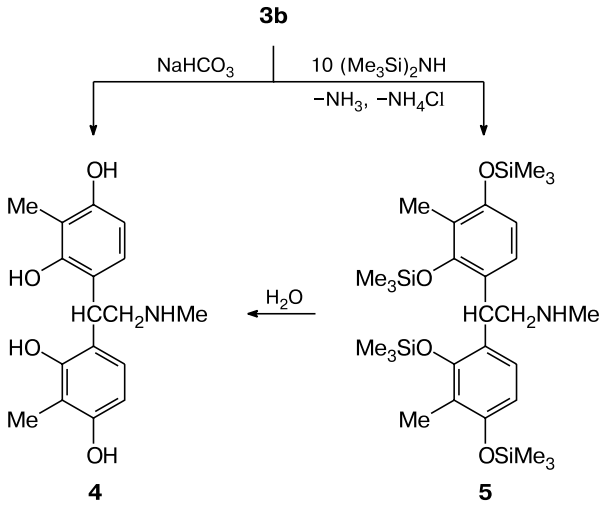
the reaction (see Ref. 5) can be explained by the effect of a strong electron-withdrawing nitro group in position 2 of resorcinol. Thus, the discovered by us aromatic electrophilic substitution with acetal **2** is a unique one. Resulted amines of the type **3** can be considered as promising key intermediates in the synthesis of various organic and organoelement structures, including spatially organized ones.

We also studied the effect of the solvent and acid nature on the synthetic outcome of the reaction and investigated some properties of the products obtained. Reaction of 2-methylresorcinol (**1b**) with acetal **2** was carried out in ethanol, water, and in a mixture of ethanol with water (1 : 1) in the presence of hydrochloric, hydrobromic, sulfuric, and trifluoromethanesulfonic acids. It was shown that the main products of these reactions are polyphenols of the type **3**. The use of the concentrated hydrohalogen acids gives the highest yields of the target amines. The yields of these products are much lower, and the reaction is more complicated in case of sulfuric and trifluoromethanesulfonic acids.

Attempted dehydrochlorination of compounds **3** with aqueous alkali to obtain free amines failed. The use of the less basic sodium bicarbonate gives free amine **4** from hydrochloride **3b** in only 40% yield (Scheme 2). Apparently, the difficulties with the isolation of free aminophenols involve the ionization of the hydroxy groups in alkaline media and formation of soluble phenolates. The tertiary amines also did not yield product **4**.

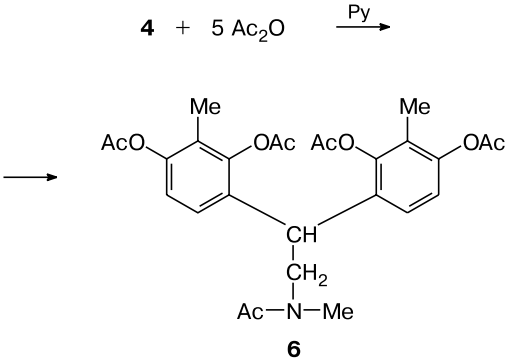
Scheme 2



However, hexamethyldisilazane proved to be a good dehydrohalogenating agent for salts **3.** In fact the prolong heating of salt **3b** in hexamethyldisilazane leads to the *O*-silylated secondary amine **5**. The ^{1}H NMR spectrum of the latter contains two singlets of equal intensity, characterizing the two types of non-equivalent trimethylsilyl groups (δ 0.02 and 0.21). Hydrolysis of compound **5** led to the free amine **4**, spectral characteristics of which were the same as those of the product obtained using sodium bicarbonate.

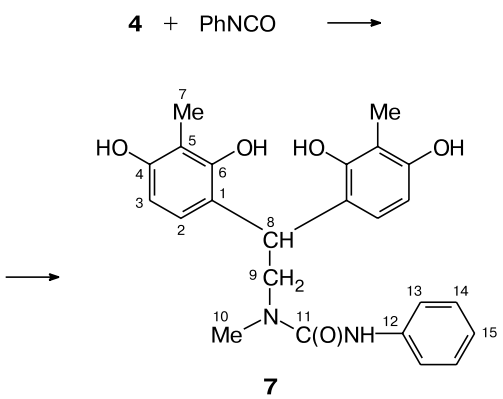
Compounds with amino group of the type **4** and **5** may be of interest as starting reagents in the synthesis of substances with complex-forming and extracting properties, as well as with properties of polymer stabilizers. In this connection, some chemical properties of these compounds were studied. Heating of compound **4** with acetic anhydride (ratio 1 : 5) is accompanied by exhaustive acylation of the amino and hydroxy groups and leads to derivative **6**, readily soluble in organic solvents (Scheme 3).

Scheme 3



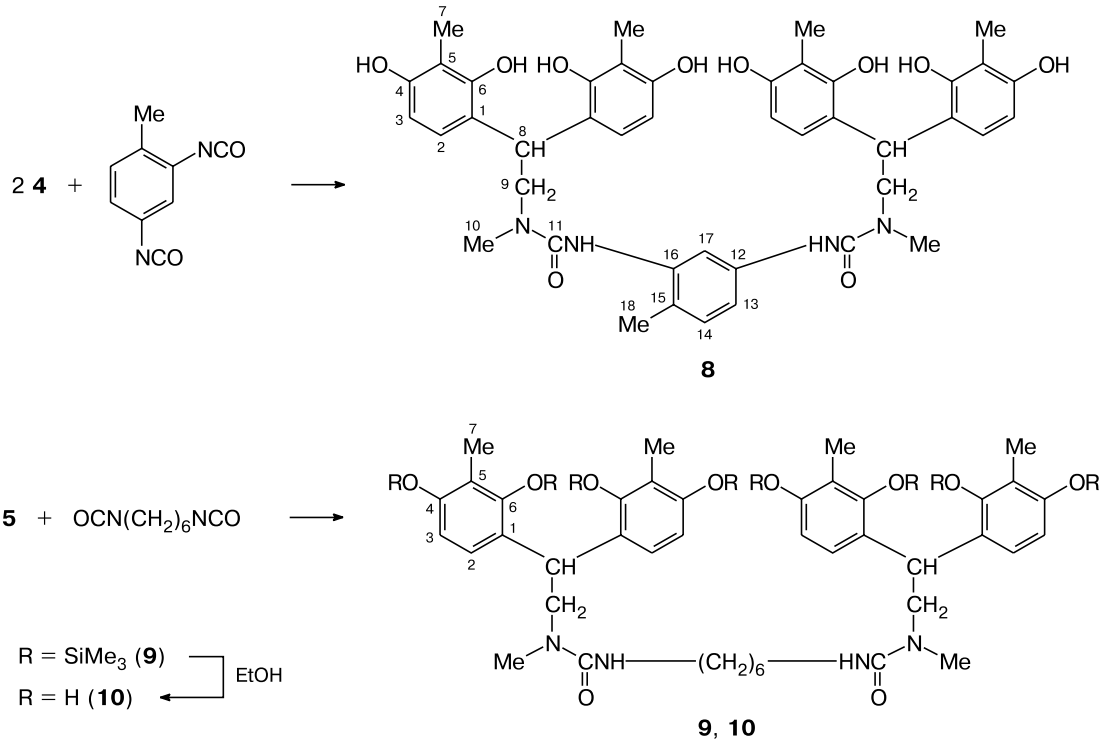
Addition of phenyl isocyanate at compound **4** occurs on the amino group and gives urea derivative **7** (Scheme 4).

Scheme 4



It is known that substances with several ligating centers, able to form chelates, are the most efficient complex-forming reagents. In this connection, tethering of two molecules **4** or **5** by a chain-spacer was of undoubted interest. Hexamethylene and tolylene diisocyanates, easily available and quite active compounds, were chosen as

Scheme 5



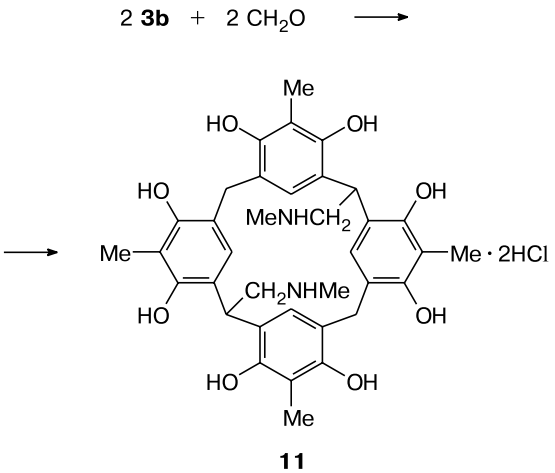
the tethering reagents. As a result, dicarbamates **8—10** with free or silylated phenol groups and linkers between the urea moieties of different flexibility, were obtained (Scheme 5).

Derivatives **4** and **5** are of particular interest for the synthesis of calixarenes with the alternating substituents of various nature at the lower rim of the molecule. The conventional method using reaction of resorcinols with aldehydes or acetals is not suitable for calixarenes of this type. However, they can be accessed by binding of compounds **4** or **5** in reaction with aliphatic and aromatic aldehydes. There is the only documented synthesis[6] of calixarenes by reaction of dimeric polyphenols of similar structure with aldehydes. Moreover, the starting polyphenol was obtained by a complicated way, namely, by condensation of 4-bromoresorcinol with aldehyde and subsequent dehalogenation of the product obtained.

We carried out the reaction of polyphenol **3b** with formaldehyde in aqueous acidic medium to obtain calixarene **11** with two *N*-methylaminomethyl groups at the lower rim of the molecule (Scheme 6).

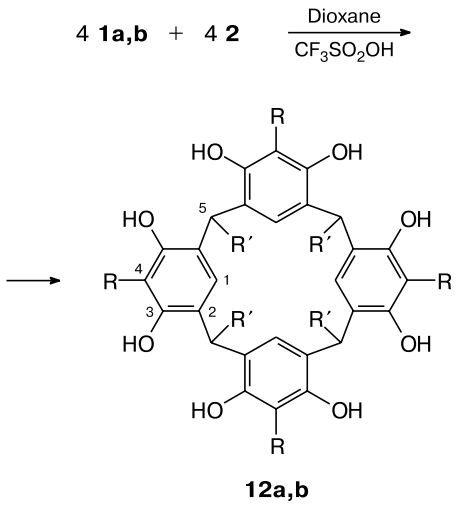
As it was shown above, reaction of resorcinol and methylresorcinol with acetal **2** in ethanol, water or in a mixture of them in the presence of acids of diverse nature leads only to the dimeric products, amines **3**. Further investigation of this reaction, including variations of solvent—acid combination, allowed us to invent conditions (dioxane as the solvent, trifluoromethanesulfonic acid as

Scheme 6



the acidic agent) providing the formation of calixarenes **12a,b** (Scheme 7). Dioxane has been chosen, along with the other factors, for its high enough boiling point (the reaction requires rather drastic conditions), as well as for high solubility of starting compounds in it. The strong trifluoromethanesulfonic acid is also soluble in dioxane and readily forms solvates with it. Unfortunately, the data available now do not allow us to make certain conclusions about the influence of conditions on the course of the reaction of resorcinols with α-amino acetal **2**.

Scheme 7



R = H (**1a**, **12a**), Me (**1b**, **12b**); R′ = $CH_2N^+H_2Me \cdot CF_3SO_3^-$

In the conclusion, changing the experimental conditions in the reaction of resorcinols with α-methylaminoacetaldehyde dimethyl acetal makes it possible to direct it toward formation of either linear dimeric or cyclic tetrameric products. These substances are of interest as key intermediates for synthesis of spatially organized structures of a new type.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-400 spectrometer (250 (^{1}H) and 100.62 MHz (^{13}C)), the chemical shifts were measured relatively to the signals of the deuterated solvent. IR spectra were recorded on a UR-20 spectrophotometer in the range 400—3600 cm^{-1} and on a Vector 22 Fourier spectrometer (Bruker) in the range 400—4000 cm^{-1} (crystal samples were investigated in Nujol mulls or in KBr pellets). The MALDI-TOF mass-spectra were recorded on a Finnigan DYNAMO MALDI-TOF instrument. Acetal **2** was purchased from Lancaster.

***N*-[2,2-Bis(2,4-dihydroxyphenyl)ethyl]-*N*-methylamine hydrochloride (3a).** A mixture of resorcinol (**1a**) (3.88 g, 35.3 mmol), acetal **2** (2.1 g, 17.7 mmol), water (21 mL), ethanol (21 mL), and conc. HCl (4.2 mL) was heated at 70 °C for 10 h. The solvent was removed, the crystalline precipitate formed was filtered off, washed with ether and dried *in vacuo* (2 h, 70 °C, 0.4 Torr). Compound **3a** was obtained in a yield of 3.78 g (68%), m.p. 172—175 °C. Found (%): C, 57.50; H, 5.93; N, 4.27. $C_{15}H_{18}ClNO_4$. Calculated (%): C, 57.79; H, 5.82; N, 4.49. ^{1}H NMR (CD_3OD), δ: 2.74 (s, 3 H, NMe); 3.64 (d, 2 H, NCH_2, ^3J = 7.87 Hz); 4.89 (t, 1 H, CH, ^3J = 7.87 Hz); 6.35 (d, 2 H, H(5) arom., ^3J = 8.53 Hz); 6.45 (s, 2 H, H(3) arom.); 6.99 (d, 2 H, H(6) arom., ^3J = 8.53 Hz). ^{13}C{^{1}H} NMR (CD_3OD), δ: 34.11 (CH); 37.19 (NMe); 53.60 (CH_2); 103.82 (C(6) arom.); 108.51 (C(5) arom.); 118.45 (C(1) arom.); 131.13 (C(3) arom.); 156.22 (C(2) arom.); 158.34 (C(4) arom.). MS, *m/z*: 311.5 $[M]^+$. IR, ν/cm^{-1}: 1600 (arom.), 3100—3500 (OH).

***N*-[2,2-Bis(2,4-dihydroxy-3-methylphenyl)ethyl]-*N*-methylamine hydrochloride (3b). *A*.** The compound was obtained similarly to **3a** from 2-methylresorcinol (**1b**) (4.38 g, 35.3 mmol), acetal **2** (2.1 g, 17.7 mmol), water (21 mL), ethanol (16 mL), and conc. HCl (4.2 mL). The yield was 4.32 g (72%), m.p. 160—163 °C. Found (%): C, 60.37; H, 6.88; Cl, 10.21; N, 4.07. $C_{17}H_{22}ClNO_4$. Calculated (%): C, 60.09; H, 6.53; Cl, 10.43; N, 4.12. ^{1}H NMR (CD_3OD), δ: 2.16 (s, 6 H, Me); 2.75 (s, 3 H, NMe); 3.67 (d, 2 H, NCH_2, ^3J = 7.90 Hz); 5.01 (t, 1 H, CH, ^3J = 7.90 Hz); 6.44 (d, 2 H, H(5) arom., ^3J = 8.40 Hz); 6.89 (d, 2 H, H(6) arom., ^3J = 8.40 Hz). ^{13}C NMR (CD_3OD), δ: 8.99 (MeC(3)); 34.05 (CH); 37.19 (NMe); 53.60 (CH_2); 108.35 (C(6) arom.); 113.51 (C(5) arom.); 119.83 (C(1) arom.); 126.22 (C(3) arom.); 154.43 (C(2) arom.); 156.27 (C(4) arom.). MS, *m/z*: 339.5 $[M]^+$. IR, ν/cm^{-1}: 1600 (arom.), 3100—3500 (OH).

***B*.** The 35% HCl (10 mL) and acetal **2** (1.05 g, 8.82 mmol) were added sequentially to 2-methylresorcinol (**1b**) (2.19 g, 17.6 mmol) under stirring at 5 °C. The reaction mixture was kept at 20 °C for 2 h. The white crystals of the product formed were separated, washed with ether and dried *in vacuo* (2 h, 50 °C, 10 Torr). The yield was 2.51 g (84%), m.p. 160—163 °C.

***N*-[2,2-Bis(2,4-dihydroxy-3-methylphenyl)ethyl]-*N*-methylamine hydrobromide (3c). *A*.** The compound was obtained similarly to **3a** from 2-methylresorcinol (**1b**) (2.19 g, 17.6 mmol), acetal **2** (1.05 g, 8.82 mmol), water (10 mL), ethanol (10 mL), and 40% HBr (8.4 mL). The yield was 1.81 g (54%), m.p. 150—153 °C. Found (%): C, 53.35; H, 5.31; Br, 21.22; N, 3.71. $C_{17}H_{22}BrNO_4$. Calculated (%): C, 53.12; H, 5.73; Br, 20.83; N, 3.64. ^{1}H NMR (D_2O), δ: 2.02 (s, 6 H, Me); 2.67 (s, 3 H, NMe); 3.56 (d, 2 H, CH_2, ^3J = 7.84 Hz); 4.87 (t, 1 H, CH, ^3J = 7.84 Hz); 6.46 (d, 2 H, H(5) arom., ^3J = 8.36 Hz); 6.87 (d, 2 H, H(6) arom., ^3J = 8.36 Hz).

***B*.** The 40% HBr (10 mL) and acetal **2** (1.05 g, 8.82 mmol) were added sequentially to 2-methylresorcinol (**1b**) (2.19 g, 17.66 mmol) at 5 °C. The mixture was kept at 20 °C for 12 h, the crystalline product was separated, washed with diethyl ether and dried *in vacuo* (2 h, 50 °C, 10 Torr). The yield was 2.95 g (87%), m.p. 150—153 °C.

***N*-[2,2-Bis(2,4-dihydroxy-3-methylphenyl)ethyl]-*N*-methylamine (4). *A*.** An aqueous solution of sodium bicarbonate was added to a solution of hydrochloride **3b** (2.30 g, 7.59 mmol) in water (5 mL) until the neutral pH value was achieved (litmus). In 24 h the precipitate formed was filtered off and dried *in vacuo* (12 h, 40 °C, 10 Torr). Compound **4** was obtained (0.90 g, 39%) as amorphous white powder, turning dark upon heating over 250 °C (decomp.). Found (%): C, 67.50; H, 7.93; N, 4.27. $C_{17}H_{21}NO_4$. Calculated (%): C, 67.31; H, 7.38; N, 4.62. ^{1}H NMR (DMSO-d_6, 20 °C), δ: 1.97 (s, 6 H, Me); 2.28 (s, 3 H, NMe); 3.02 (d, 2 H, CH_2, ^3J = 4.92 Hz); 4.41 (t, 1 H, CH, ^3J = 4.92 Hz); 6.16 (d, 2 H, H(5) arom., ^3J = 8.20 Hz); 6.43 (d, 2 H, H(6) arom., ^3J = 8.20 Hz). IR, ν/cm^{-1}: 1600 (arom.), 3100—3500 (OH).

***B*.** A mixture of tetrasilyl ether **5** (0.21 g, 0.35 mmol) and water (10 mL) was refluxed for 1 h, then kept at 20 °C for 5 days. The precipitate was separated, washed with water and dried *in vacuo* (1 h, 60 °C, 0.04 Torr). The yield was 0.08 g (74%), m.p. >250 °C (decomp.). Found (%): C, 67.66; H, 7.69; N, 4.31. $C_{17}H_{21}NO_4$. Calculated (%): C, 67.31; H, 7.38; N; 4.62. ^{1}H NMR spectrum was identical to that of the sample prepared by method *A*.

***N*-{2,2-Bis[2,4-bis(trimethylsilyloxy)-3-methylphenyl]ethyl}-*N*-methylamine (5).** A mixture of hydrochloride **3b** (0.6 g, 1.76 mmol) and hexamethyldisilazane (7.65 g, 47.51 mmol) was kept at 130 °C for 5 h. The excess hexamethyldisilazane was removed *in vacuo* (4 h, 80 °C, 0.8 Torr) to leave compound **5** (0.95 g, 90%) as a viscous liquid. Found (%): C, 58.33; H, 8.92; N, 2.07. $C_{29}H_{53}NO_4Si_4$. Calculated (%): C, 58.83; H, 9.02; N, 2.37. ^{1}H NMR ($(CD_3)_2CO$, 20 °C), δ: 0.02, 0.21 (both s, 18 H each, Me_3Si); 2.32 (s, 6 H, Me); 2.49 (s, 3 H, NMe); 3.08 (m, 2 H, CH_2); 4.48 (m, 1 H, CH); 6.18 (m, 2 H, H(5) arom.); 6.51 (m, 2 H, H(6) arom.).

***N*-[2,2-Bis(2,4-diacetoxy-3-methylphenyl)ethyl]-*N*-methylacetamide (6).** A mixture of amine **4** (0.5 g, 1.47 mmol), acetic anhydride (1.5 g, 14.7 mmol), and pyridine (0.1 mL) was kept at 20 °C for 6 h. The volatile components were removed, the residue was dried *in vacuo* (1 h, 60 °C, 0.4 Torr). Compound **6** (0.61 g, 88%) was obtained, m.p. 200—201 °C. Found (%): C, 63.50; H, 6.83; N, 2.27. $C_{27}H_{31}NO_9$. Calculated (%): C, 63.15; H, 6.08; N, 2.73. ^{1}H NMR ($(CD_3)_2CO$), δ: 2.01 (s, 6 H, Me); 2.35—2.52 (br.s, 15 H, Ac); 2.71 (s, 3 H, NMe); 3.91 (m, 2 H, CH_2); 4.87 (m, 1 H, CH); 6.42 (d, 2 H, H(5) arom., ^3J = 8.29 Hz); 6.61 (d, 2 H, H(6) arom., ^3J = 8.29 Hz).

***N*-[2,2-Bis(2,4-dihydroxy-3-methylphenyl)ethyl]-*N*-methyl-*N*′-phenylurea (7).** Phenyl isocyanate (0.15 g, 12.6 mmol) was added to a solution of amine **4** (0.38 g, 12.6 mmol) in acetone (10 mL) under stirring. The reaction mixture was kept at 20 °C for 18 h, the precipitate formed was filtered off and dried *in vacuo* (2 h, 60 °C, 0.4 Torr). Compound **7** (4.95 g, 93%) was obtained, m.p. 190—192 °C. Found (%): C, 68.20; H, 6.89; N, 6.50. $C_{24}H_{26}N_2O_5$. Calculated (%): C, 68.23; H, 6.20; N, 6.63. ^{1}H NMR ($(CD_3)_2CO$), δ: 2.06 (s, 6 H, Me); 2.84 (s, 3 H, NMe); 3.80 (d, 2 H, CH_2, ^3J = 6.72 Hz); 4.84 (t, 1 H, CH, ^3J = 6.72 Hz); 6.33 (d, 2 H, H(5) arom., ^3J = 8.53 Hz); 6.78 (d, 2 H, H(6) arom., ^3J = 8.53 Hz); 6.90 (m, 1 H, $H(15)_{Ph}$); 7.19 (m, 2 H, $H(14)_{Ph}$); 7.46 (m, 2 H, $H(13)_{Ph}$). ^{13}C NMR (CD_3OD), δ: 9.14, 9.70 (C(7)); 30.61 (C(8)); 38.67 (C(10)); 54.15 (C(9)); 107.16 (C(3) arom.); 112.04 (C(5) arom.); 119.16 (C(13) arom.); 120.03 (C(1) arom.); 123.71 (C(15) arom.); 126.49 (C(2) arom.); 129.41 (C(14) arom.); 140.92 (C(12) arom.); 154.92 (C(4) arom.); 155.50 (C(6) arom.); 157.66 (C(11)=O).

***N*′,*N*′′′-(4-Methyl-1,3-phenylene)bis{*N*-[2,2-bis(2,4-dihydroxy-3-methylphenyl)ethyl]-*N*-methylurea} (8).** A mixture of amine **4** (0.61 g, 20.1 mmol), 2,4-diisocyanato-1-methylbenzene (0.175 g, 10.05 mmol) and acetone (10 mL) was kept at 20 °C for 15 h. The solvent was removed and the product was dried *in vacuo* (6 h, 20 °C, 0.04 Torr). Compound **8** was obtained (0.53 g, 83%) as amorphous white powder, turning dark upon heating over 200 °C (decomp.). Found (%): C, 64.67; H, 9.12; N, 7.01. $C_{43}H_{48}N_4O_{10}$. Calculated (%): C, 65.10; H, 9.02; N, 7.23. ^{1}H NMR ($(CD_3)_2CO$), δ: 2.08 (m, 3 H, Me); 2.11 (m, 12 H, Me); 2.95 (m, 6 H, NMe); 3.89 (m, 4 H, CH_2N); 4.93 (m, 2 H, CH); 6.41 (d, 4 H, H(2) arom., ^3J = 8.53 Hz); 6.88 (d, 4 H, H(3) arom., ^3J = 8.53 Hz); 7.06—7.81 (m, 3 H, H(13), H(14), H(17)). ^{13}C NMR ($(CD_3)_2CO$), δ: 9.18 (C(7)); 13.52 (C(18)); 30.35 (C(8)); 36.77 (C(10)); 54.25 (C(9)); 107.21 (C(3) arom.); 112.13 (C(5) arom.); 117.91 (C(17) arom.); 118.47 (C(13) arom.); 120.27 (C(1) arom.); 126.52 (C(14) arom.); 127.47 (C(2) arom.); 130.57 (C(15) arom.); 138.85, 138.91 (C(12), C(16) arom.); 154.98 (C(4) arom.); 155.36 (C(6) arom.); 158.09 (C(11)=O). IR, ν/cm^{-1}: 1627, 1591 (C=O); 1461, 1580 (arom.); 3100—3600 (OH).

1,1,16,16-Tetrakis(2,4-dihydroxy-3-methylphenyl)-3,14-dimethyl-3,5,12,14-tetraazahexadecan-4,13-dione (10). A mixture of amine **5** (0.8 g, 1.35 mmol), hexamethylene diisocyanate (0.11 g, 0.67 mmol), and benzene (10 mL) was refluxed for 15 h. The solvent was removed to leave the silylated derivative **9** as the viscous oil. This was diluted with ethanol and kept for 14 days. The powder-like product formed was filtered off and dried *in vacuo* (24 h, 20 °C, 8 Torr). Compound **10** was obtained (0.27 g, 55%), m.p. 143—144 °C. Found (%): C, 65.03; H, 7.53; N, 6.81. $C_{42}H_{54}N_4O_{10}$. Calculated (%): C, 65.12; H, 6.98; N, 7.24. ^{1}H NMR (CD_3OD), δ: 1.34, 1.49 (both m, 4 H each, CH_2); 2.08 (s, 12 H, Me); 2.70 (s, 6 H, NMe); 3.14 (m, 4 H, $C\underline{H}_2NH$); 3.80 (d, 4 H, $C\underline{H}_2NMe$, ^3J = 7.31 Hz); 6.32 (d, 4 H, H(2) arom., ^3J = 8.36 Hz); 6.84 (d, 4 H, H(3) arom., ^3J = 8.36 Hz) (the signal of the proton in CH-group overlaps with the signal of the solvent (δ 4.79)). IR, ν/cm^{-1}: 1633, 1596 (C=O); 1601 (arom.); 3100—3600 (OH).

2,14-Di(methylaminomethyl)-5,11,17,23-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-4,6,10,12,16,18,22,24-octaol dihydrochloride (11). A mixture of compound **3b** (0.36 g, 1.06 mmol), formaldehyde (35% aq., 1 mL, 11.66 mmol), water (5 mL), and conc. HCl (0.5 mL) was heated at 100 °C for 8 h. The precipitate formed was filtered off, washed with acetonitrile and dried *in vacuo* (12 h, 20 °C, 8 Torr). Compound **11** (0.28 g, 75%) was obtained, which turns dark on heating over 290 °C (decomp.). Found (%): C, 61.97; H, 6.64; N, 4.31. $C_{36}H_{44}Cl_2N_2O_8$. Calculated (%): C, 61.45; H, 6.26; N, 3.98. ^{1}H NMR (D_2O), δ: 2.06 (s, 12 H, Me); 2.70 (s, 6 H, NMe); 3.58 (d, 4 H, CH_2, ^3J = 7.87 Hz); 4.92 (t, 2 H, CH, ^3J = 7.87 Hz); 6.87 (s, 4 H, H arom.) (the signal of the protons in CH_2 groups overlaps with the signal of the solvent (δ 4.72)). MS, *m/z*: 632 [M − 2 HCl]$^+$.

2,8,14,20-Tetra(methylaminomethyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-4,6,10,12,16,18,22,24-octaol tetra(hydrotrifluoromethanesulfonate) (12a). A mixture of resorcinol (**1a**) (3 g, 27.3 mmol), acetal **2** (3.24 g, 27.3 mmol), trifluoromethanesulfonic acid (8.18 g, 54.6 mmol), and dioxane (25 mL) was refluxed for 9 h. The precipitate was separated, washed with dioxane and dried *in vacuo* (10 h, 20 °C, 8 Torr). Compound **12a** (3.54 g, 41%) was obtained as amorphous white powder, turning dark upon heating over 240 °C (decomp.). Found (%): C, 37.09; H, 3.36; N, 4.08; S, 9.67. $C_{40}H_{48}F_{12}N_4O_{20}S_4$. Calculated (%): C, 38.10; H, 3.84; N, 4.44; S, 10.17. ^{1}H NMR (CD_3OD), δ: 2.47 (s, 12 H, NMe); 3.45 (d, 8 H, CH_2, ^3J = 8.05 Hz); 4.68 (t, 4 H, CH, ^3J = 8.05 Hz); 6.09 (s, 4 H, H(4) arom.); 6.72 (s, 4 H, H(1) arom.). ^{13}C NMR (D_2O), δ: 34.53 (CH); 36.07 (NMe); 53.65 (CH_2); 104.58 (C(4) arom.); 119.06 (C(2) arom.); 122.90 (CF_3S); 127.24 (C(1) arom.); 154.73 (C(3) arom.). IR, ν/cm^{-1}: 1600 (arom.), 3100—3500 (OH). MS, *m/z*: 663 [M − 4 CF_3SO_2OH]$^+$.

2,8,14,20-Tetra(methylaminomethyl)-5,11,17,23-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-4,6,10,12,16,18,22,24-octaol tetra(hydrotrifluoromethanesulfonate) (12b). The compound was obtained similarly to **12a** from 2-methylresorcinol (**1b**) (1.11 g, 8.97 mmol), acetal **2** (1.07 g, 8.97 mmol), trifluoromethanesulfonic acid (1.41 g, 9.40 mmol), and dioxane (10 mL). Compound **12b** (1.27 g, 43%) was obtained as amorphous white powder, turning dark upon heating

over 260 °C (decomp.). Found (%): C, 43.23; H, 5.78; N, 3.79; S, 8.96. $C_{44}H_{56}F_{12}N_4O_{20}S_4$. Calculated (%): C, 43.45; H, 5.61; N, 3.90; S, 8.92. ^{1}H NMR (D_2O), δ: 2.00 (s, 12 H, Me); 2.73 (s, 12 H, NMe); 3.68 (d, 8 H, CH_2, ^3J = 8.20 Hz); 4.90 (t, 4 H, CH, ^3J = 8.20 Hz); 6.62 (s, 4 H, H arom.). ^{13}C NMR (D_2O), δ: 9.72 (Me); 30.43 (CH); 34.05 (NMe); 53.26 (CH_2); 115.83 (C(4) arom.); 118.85 (C(2) arom.); 121.60 (C(1) arom.); 122.48 (CF_3S); 151.28 (C(3) arom.). IR, ν/cm^{-1}: 1600 (arom.), 3100—3500 (OH). MS, *m*/*z*: 719 $[M - 4\ CF_3SO_2OH]^+$.

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