Synthesis of New Resorcinarenes Under Alkaline Conditions

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The preparation of functionalized resorcinarenes is described. Thus, 2-nitroresorcinol (=2-nitrobenzene-1,2-diol), 2-acetylresorcinol (=1-(2,6-dihydroxyphenyl)ethanone), and 2,6-dihydroxybenzoic acid were treated with formaldehyde in alkaline medium to give the corresponding resorcinarenes **1**–**3** (*Scheme 1*). This method is also applicable for resorcinol (=benzene-1,3-diol) itself, but the yields are poorer. In this case, the molecule formed is the simplest resorcinarene **4** on which a number of substituents can be inserted between the two OH groups. Thus, bromation of **4** yields **5** (*Scheme 2*). Some properties and conformations of these new products are discussed, and the X-ray crystal structures of the nitro and bromo compounds **1** and **5**, respectively, are presented.

Introduction. – Resorcinarenes are well known molecules, and a number of reports appear each year on this subject [1–4]. The particular shape of resorcinarenes is suitable for encapsulating small chemical entities such as solvent molecules or metal ions [5]. Such a compound becomes pincer-like at the nanoscale level owing to a change of conformation which is dependent on pH [6]. Cavitands and carcerands, prepared from resorcinarenes, are very interesting synthons for supramolecular chemistry [7–11].

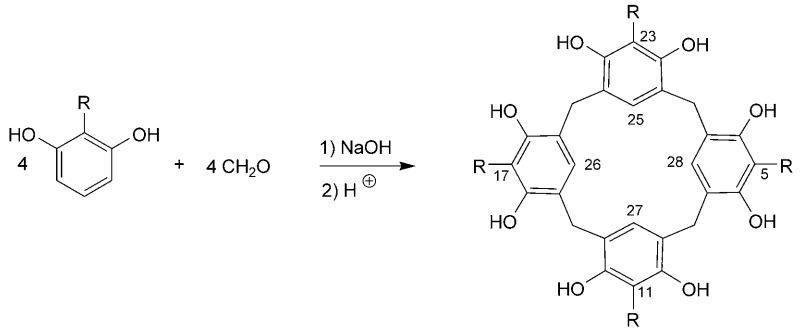
Standard preparation of resorcinarenes is performed in alcoholic acidic medium. An aldehyde (except formaldehyde) and resorcinol (=benzene-1,3-diol) are refluxed together with hydrochloric acid for several hours to permit the formation of the most stable stereoisomer. Therefore, all resorcinarenes have an alkyl group at the C-junction of the aromatic moieties. Under these acidic conditions, formaldehyde will form a copolymer with resorcinol. With 2-methylresorcinol, however, excellent yields of resorcinarene were achieved [12].

All other attempts to synthesize substituted resorcinarenes in acidic medium were unsuccessful. Thus, treatment of 2-nitroresorcinol with formaldehyde gave only dimeric compounds [8]. Reaction of 2,6-dihydroxybenzoic acid with formaldehyde gave polymeric compounds. On changing the reaction conditions, it was quickly realized that basic medium is very convenient for formaldehyde and those resorcinols that bear an electron-attracting group at position 2, such as 2-nitroresorcinol (=2-nitrobenzene-1,2-diol), 2-acetylresorcinol (=1-(2,b-dihydroxyphenyl)ethanone), and 2,6-dihydroxybenzoic acid. The reactions are clean and rapid with yields of *ca.* 50%. The only real problem of this new method is the tedious preparation of the 2-substituted resorcinols.

Results and Discussion. – Surprisingly, attempts to perform the bis(hydoxymethyl)-ation of 2-nitroresorcinol with formaldehyde in basic medium resulted in the isolation

of a reddish polar product, **1**, after neutralization of the medium. The ^{1}H- (3*s*) and ^{13}C-NMR spectra (5*s*) clearly show a symmetry compatible only with a cyclic structure (*Scheme 1*).

Scheme 1. *Synthesis of Resorcinarenes* **1**–**4** *from 2-Substituted Resorcinols and Formaldehyde*



1 R = NO_2
2 R = Ac
3 R = COOH
4 R = H

Usually, isolation and purification of resorcinarenes (this is also true for calixarenes) are very difficult for two reasons: these products have several conformations [13][14], and they form different supermolecular complexes with different solvents, which excludes the use of mixed solvents for crystallization. Fortunately, the new tetranitroresorcinarene **1** was not soluble in either H_2O or in MeOH, and so it was isolated, in good purity, by simply washing with these solvents. The dry red powder was soluble in hot DMF, and a concentrated solution of **1** gave crystals after several days at 0°.

X-Ray crystal-structure analysis of **1** confirmed the resorcinarene structure (*Fig. 1*). The molecule crystallized with five DMF molecules in the lattice. The conformation is 1,3-alternating, and this can be explained by the dipolar nature of the nitroarenes.

On the upper rim of the molecule **1**, the two facing nitro groups are perpendicular to each other indicating an interaction between the N-atom of one group and the O-atom of the other group. On the wider rim of the resorcinarene, both nitro groups are too far from each other for such an interaction.

With 2-acetylresorcinol and formaldehyde in basic medium, the formation of a resorcinarene **2** was also observed (*Scheme 1*) but as expected, the reaction was less clean. This is probably due to a certain extent of aldol condensation taking place at the acetyl groups. Attempts to produce crystals of **2** from pure DMF, suitable for X-ray analysis, were unsuccessful. The ^{1}H-NMR spectrum ((D$_6$)DMSO) of **2** shows the association of one tetracetylresorcinarene with two molecules of DMF.

The 2,6-dihydroxybenzoic acid shows the same reactivity as the two preceding reactants, and compound **3** was prepared without difficulty (*Scheme 1*). However, a new problem appeared in this case: during the neutralization of the reaction medium, a pink precipitate appeared before the stoichiometric quantity of acid was added.

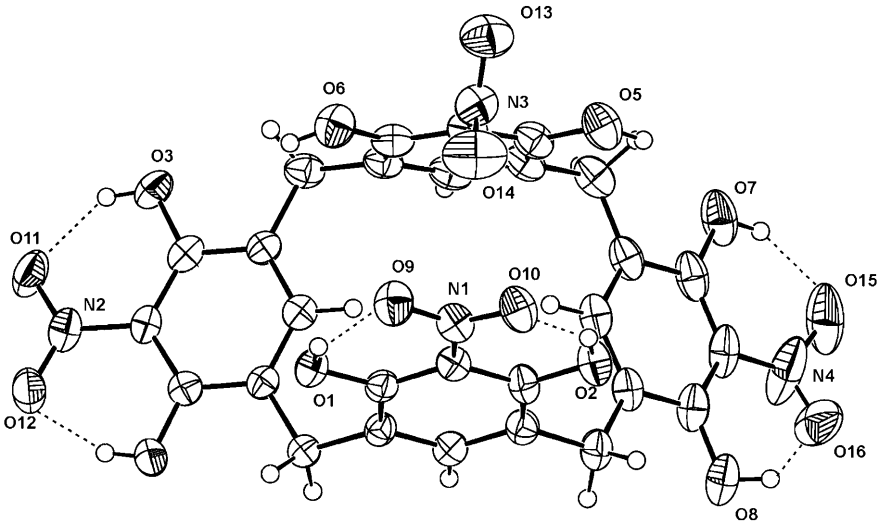


Fig. 1. *Perspective view of the molecular structure of 5,11,17,23-tetranitropentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol* (**1**). Crystallographic numbering scheme; thermal ellipsoids at the 50% probability level. Intramolecular O–H···O H-bonds are shown as dashed lines.

After isolating and drying this pink product **3a**, impurities were washed away with MeOH, in which **3a** is insoluble. On TLC, the spot of **3a** did not migrate at all. Titration of **3a** with NaOH established a lack of protons; hence, it was concluded that **3a** is the monosodium salt of **3**. The ^{1}H-NMR spectrum of **3a** ((D$_6$)DMSO) in the presence of an excess of propan-1-amine (→ product **3b**) shows almost three propylammonium ions. This behavior can be explained by the large difference of the acidity of one of the carboxylic groups as compared to that of the three other carboxylic groups. Even at pH 1–1.5, this very acidic group remains deprotonated. Only treatment with gaseous HCl in MeOH permitted the formation of **3**, totally protonated. The ^{1}H-NMR signal of the phenolic OH groups of **3a** at δ(H) 5.5 is shifted to δ(H) 8.8 in the spectrum of **3**. Considering the conformation of **1**, it can be understood why one carboxylic group is more acidic than the others. Carboxylate and nitro groups are isosteric and an analogues interaction is proposed. As no X-ray crystal structure analysis of **3a** could be performed, this remains a hypothesis.

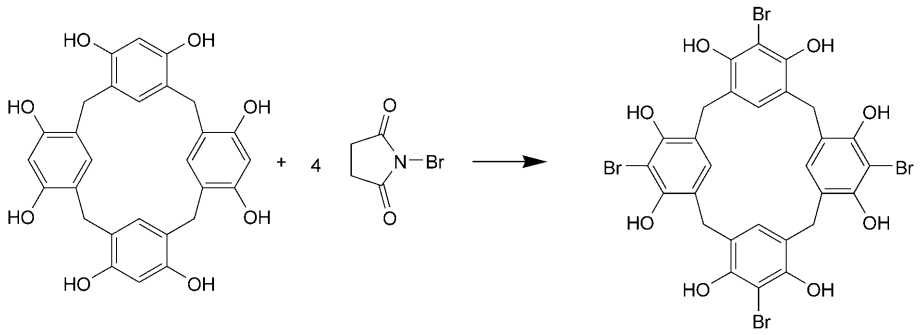
The base-catalyzed condensation of methyl 2,6-dihydroxybenzoate and formaldehyde did not give a good result because this ester is too labile in the presence of OH$^-$ and phenolate ions.

Applied to resorcinol itself, the condensation with formaldehyde in alkaline medium was not a clean reaction. The resorcinarene **4** was formed besides abundant polymeric material that rendered the purification process difficult and reduced substantially the yield (*Scheme 1*). In this case, **4** is soluble in MeOH, and very little solid separated from a concentrated solution after several days at $-18°$. It was recrystallized by evaporation of the solvent from a dimethylformamide (DMF) or MeOH solution. Compound **4** is the simplest possible resorcinarene without any substituents. Certainly,

it has been prepared many times in different laboratories but we have isolated and purified it for the first time. The ^{1}H-NMR spectra of **4** display a surprising chemical shift for H–C(25), H–C(26), H–C(27), and H–C(28): δ(H) 6.29, the same δ as for H–C(5), H–C(11), H–C(17), and H–C(23). We believe that, in this case, the conformational flexibility allows these protons to be under diamagnetic influence of the neighboring aromatic moieties.

Position '2' of the aromatic moieties of **4** remains free for testing various reactions. For example, a Br-atom is easily introduced by reaction with *N*-bromosuccinimide, yielding the tetrabromoresorcinarene **5** (*Scheme 2*).

Scheme 2. *Synthesis of Resorcinarene* **5** *from Resorcinarene* **4**.



4 **5**

For products **2**–**5**, elemental analyses gave poor results; *e.g.*, calculated values for **4** ($C_{28}H_{24}O_8$, 488.492) are C 68.85 and H 4.95%, while the experimental results were C 62.93 and H 6.22%, and even N 4.23% (from associated DMF). Only compound **1** showed a matching elemental analysis. As already stated, a few solvents (DMF, MeOH, H_2O) as well as ions such as Na^+ or Cl^- remain captured in resorcinarenes. To determine the elemental composition of **2**–**5**, high-resolution ESI-MS was used which gave excellent results for the $[M-H]^-$ ion (see *Exper. Part*). The NMR spectra clearly established DMF association in the crystals of **2**, **4** and **5**. The presence of DMF was also observed in the crystal-structure analysis of **5**. Here the compound crystallized with two centrosymmetric molecules per asymmetric unit, each associated with two DMF molecules of crystallization (*Fig. 2*).

Thermogravimetry (TG) and differential scanning calorimetry (DSC) measurements confirmed the presence of associated molecules and ions. Compound **3** showed successive overlapping mass losses. This can be interpreted as follows: Captured solvent molecules are released and carboxylic groups are lost between 100–300°. DSC Experiments established that the consecutive losses are endothermic for products **2**–**5**. However, compound **1** lost DMF under room-temperature conditions. TG and DSC revealed that no solvent loss and no decomposition occurred up to a temperature of 280°; then, the sample **1** lost 25% of its mass, the decomposition being exothermic. This behavior is thought to be due to a self oxido-reduction between the aromatic rings and the nitro groups.

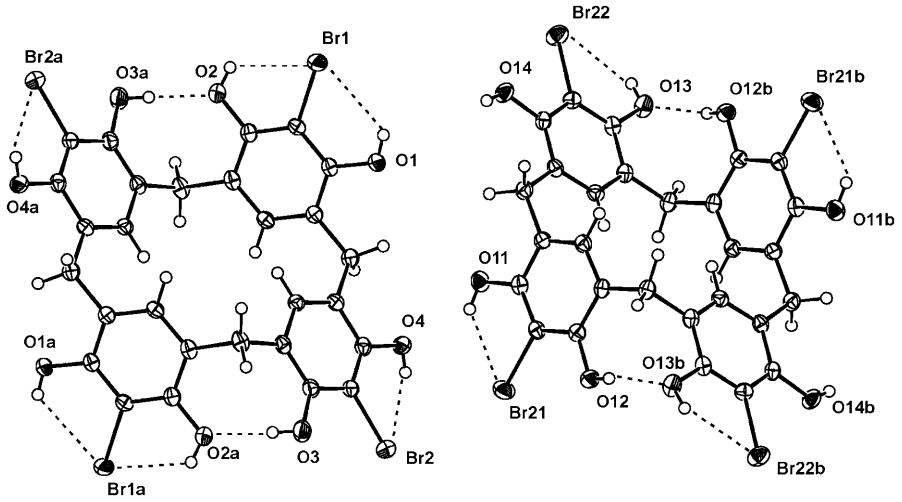


Fig. 2. *Perspective view of the molecular structure of the two independent molecules of 5,11,17,23-tetrabromopentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol* (**5**). Crystallographic numbering scheme, thermal ellipsoids at the 50% probability level. Atoms labeled 'a' (left-hand-side) and 'b' (right-hand-side) are related to the others by the symmetry operations $-x+2$, $-y+1$, $-z+1$ and x, $-y+1$, $-z$, respectively. Intramolecular O–H···O H-bonds are shown as dashed lines.

Reactivity. – Under the chosen condensation conditions, the resorcinarene formation is fast with the disodium salt of 2-nitroresorcinol and paraformaldehyde in H_2O. Yields and purity of **1** are better when all the reactants are mixed together, as compared to the conditions where formaldehyde is added slowly. We think that a maximum concentration of the dimer is reached first at 0°, followed by its association yielding the tetramer, which finally cyclizes as the reaction mixture reaches room temperature. The presence of an electron-attracting group such as NO_2 favors the condensation of the molecules, and the reaction rate follows the order: $NO_2 > COCH_3 > COO^- > H$.

The condensation of resorcinol and acetaldehyde under acidic conditions is reversible [1], so that an equilibrium between numerous stereoisomers is reached after 24 h heating. Resorcinarenes containing five and six aromatic moieties are also observed when the reaction is stopped very early in its evolution. In contrast, the condensation of formaldehyde with 2-nitroresorcinolate and analogues of substituted resorcinolates does not seem to be reversible. It is not known if pentamers or hexamers are formed. In the case of 2-methylresorcinolate, the reaction with formaldehyde produces a black and viscous reaction mixture. Therefore, acidic conditions are better suited when an electron-donating group is present at position 2. With phloroglucinol (=benzene-1,3,5-triol), no resorcinarene was obtained in basic medium. The limiting case for basic conditions is the reaction of formaldehyde with resorcinolate that gives **4**. This simple resorcinarene is easily opened in mineral acids such as hydrochloric or sulfuric acid.

Conclusions. – Basic medium is suitable for the preparation of resorcinarenes which carry electron-withdrawing groups at positions 5, 11, 17, and 23; thus, four 2-substitued resorcinols are linked by CH_2 bridges in a one-pot synthesis. The method also allows the preparation of the completely unsubstituted resorcinarene **4**. This compound can be tetrabrominated at positions 5, 11, 17, and 23 (→ **5**). Currently, we are studying other substitution reactions with **4** such as *Mannich* reactions. X-Ray crystal structure analysis indicates two different conformations for the nitro and the bromo-resorcinarenes (1,3- and 1,2-alternation, respectively).

We hope that the described new products will find applications in catalysis: not only do they entrap small molecules and ions, but they also carry active functional groups in a limited space, with defined geometrical relations and conformational flexibility.

Acknowledgments: We thank *Sophie Gomez-von Allmen* for recording the NMR and IR spectra and for TG and DSC measurements, *Laurence Scheurer* for the elemental analysis, *Fredy Nydegger* for recording mass spectra, and *Jean-Nicolas Aebischer* for help with the manuscript.

Experimental Part

General. All commercially available reagents (*Fluka, Acros Organics*) were used without further purification. TLC (reaction monitoring): *ALUGRAM® SIL G/UV$_{254}$*; detection by UV light, revelation by I_2. Thermogravimetry (TG): *Mettler Toledo TGA-850*. Differential scanning calorimetry (DSC): *Mettler Toledo DSC-820*. IR Spectra: *Bomem MB 155*; in cm^{-1}. NMR Spectra: *Bruker DPX-200* (^1H at 200 MHz, ^{13}C at 50.3 MHz); δ in ppm rel. to $SiMe_4$ as internal reference, *J* in Hz. MS: *Bruker Esquire HCT* and *Bruker FTMS 4.7T BioAPEX II*; ESI, neg. mode; in *m/z*. Elemental analysis: *CE Instrument EA 1110*.

5,11,17,23-Tetranitropentacyclo[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-dodecaene-4,6,10,12,16,18,22,24-octol (=*5,11,17,23-Tetranitroresorcinarene*; **1**). To a soln. of 2-nitroresorcinol (15.5 g, 0.1 mol) in H_2O (500 ml) and NaOH (8 g, 0.2 mol) at 0°, paraformaldehyde (3 g, 0.1 mol) was added at once. The mixture was maintained at 0° for 2 h with good stirring under N_2. After 24 h standing at r.t., the dark mixture was again cooled to 0° before neutralization with HCl (0.2 mol). A red precipitate of **1** separated from the aq. medium, which was filtered, washed with H_2O to eliminate HCl and NaCl, and dried. The reddish solid obtained was covered with MeOH (100 ml) and stirred for 2 h to dissolve any impurities. The insoluble material was filtrated and dried: **1** (60%). Crystals for X-ray structure analysis were obtained from a conc. soln. of **1** in DMF at 4°. Orange powder. M.p. >280° (dec.). IR (KBr): 3220, 1610, 1544, 1438, 1376, 1313, 1260, 1198, 1171, 1126. ^1H-NMR (200 MHz, (D_6)DMSO): 9.84 (*s*, 8 OH); 6.35 (*s*, H–C(25), H–C(26), H–C(27), H–C(28)); 3.69 (*s*, CH_2(2), CH_2(8), CH_2(14), CH_2(20)). ^{13}C-NMR (50.3 MHz, (D_6)DMSO): 146.5 (*s*, C(4), C(6), C(10), C(12), C(16), C(18), C(22), C(24)); 132.27 (*s*, C(25), C(26), C(27), C(28)); 131.35 (*s*, C(1), C(3), C(7), C(9), C(13), C(15), C(19), C(21)); 118.74 (*s*, C(5), C(11), C(17), C(23)); 28.3 (*t*, C(2), C(8), C(14), C(20)). HR-ESI-MS (neg. mode): 667.0806770 ($[M-H]^-$, $C_{28}H_{19}N_4O_{16}^-$; calc. 667.0801542). TG and DSC (heating 10°/min from 25 to 400°): −25.89% from 280 to 310°, −1150.8 J/g. Anal. calc. for $C_{28}H_{20}N_4O_{16}$ (668.480): C 50.31, H 3.02, N 8.38; found: C 50.05, H 3.12, N 8.38.

1,1′,1″,1‴-(4,6,10,12,16,18,22,24-Octahydroxypentacyclo[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-dodecaene-5,11,17,23-tetrayl)tetrakis[ethanone] (=*5,11,17,23-Tetraacetylresorcinol*; **2**). As descirbed as for **1**, with 2-acetylresorcinol (15.2 g, 0.1 mol), NaOH (8 g, 0.2 mol) and formaldehyde (3 g, 0.1 mol). The impure final product was dissolved in DMF, the insoluble material discarded, and the filtrate evaporated: **2** (6 g, 37%). Crystals of **2** were isolated from a DMF soln. at 4°. Red powder. M.p. >300° (dec.). IR (KBr): 3296, 1667, 1618, 1442, 1369, 1331, 1310, 1234, 1098. ^1H-NMR (200 MHz, (D_6)DMSO): 11.26 (*s*, 8 OH); 6.30 (*s*, H–C(25), H–C(26), H–C(27), H–C(28)); 3.62 (*s*, CH_2(2), CH_2(8), CH_2(14), CH_2(20)); 3.33 (*s*, 4 MeCO). ^{13}C-NMR (50.3 MHz, (D_6)DMSO): 205.7 (*s*, 4 MeCO), 157.5 (*s*, C(4), C(6), C(10), C(12), C(16), C(18), C(22), C(24)); 136.5 (*s*, C(25), C(26), C(27), C(28)), 116.8 (*s*, C(1), C(3), C(7), C(9), C(13), C(15), C(19), C(21)); 110.4 (*s*, C(5), C(11), C(17), C(23)); 30.6 (*t*, C(2), C(8), C(14), C(20)); 28.4 (*t*, 4 *Me*CO). HR-ESI-MS (neg. mode): 655.1828980 ($[M-H]^-$, $C_{36}H_{31}O_{12}^-$; calc. 655.1821000). TG and DSC (heating 10°/min from 25 to 400°): −9.33% from 130 to 300°, 8.63 J/g; −15.01% from 300 to 380°, 152.45 J/g.

4,6,10,12,16,18,22,24-Octahydroxypentacyclo[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-dodecaene-5,11,17,23-tetracarboxylic Acid (=*Resorcinarene-5,11,17,23-tetracarboxylic acid*; **3**). As described for **1**, with 2,6-dihydoxybenzoic acid (15.4 g, 0.1 mol), NaOH (12 g, 0.3 mol), and formaldehyde (3 g, 0.1 mol). In a standard procedure, enough HCl was added to reach pH 1. A pink product separated that was a mixture of **3** and the monosodium salt **3a**. With a slow neutralization procedure, the pink precipitate began to separate before the pH reached 4. The total amount of acid added was *ca.* 3/4 mol-equiv. of the required quantity, and the isolated product was the monosodium salt **3a**.

The tris(propylammonium) monosodium salt **3b** was obtained from **3a** by the reaction with an excess of propan-1-amine and MeOH. The salt **3b** was isolated by filtration: beige powder.

To obtain **3** in the tetracarboxylic acid form, the dry monosodium salt **3a** was treated with MeOH sat. with HCl gas. The MeOH and HCl were evaporated to give **3**. Pink powder. M.p. >200° (dec.). IR (KBr): 1676, 1615, 1455, 1391, 1349, 1304, 1223, 1179, 1091, 818. ^{1}H-NMR (200 MHz, (D_6)DMSO): 8.8 (br. *s*, 8 OH, 4 H_2O); 6.40 (*s*, H–C(25), H–C(26), H–C(27), H–C(28)); 3.52 (*s*, CH_2(2), CH_2(8), CH_2(14), CH_2(20)). ^{13}C-NMR (50.3 MHz, (D_6)DMSO): 173.8 (*s*, 4 COOH), 156.9 (*s*, C(4), C(6), C(10), C(12), C(16), C(18), C(22), C(24)); 134.4 (*s*, C(25), C(26), C(27), C(28)); 116.1 (*s*, C(1), C(3), C(7), C(9), C(13), C(15), C(19), C(21)), 100.9 (s, C(5), C(11), C(17), C(23)); 21.2 (*t*, C(2), C(8), C(14), C(20)). HR-ESI-MS (neg. mode) 663.0996470 ([M – H]$^-$, $C_{32}H_{23}O_{16}^-$; calc. 663.0991583). TG and DSC (heating 10°/min from 25 to 400°): –6.07% from 80 to 150°, 49.14 J/g; –13.02% from 150 to 240°, 30.16 J/g; –8.96% from 240 to 280°, 48.24 J/g; –18.22% from 280 to 400°, 75.27 J/g.

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-dodecaene-4,6,10,12,16,18,22,24-octol (=*Resorcinarene*; **4**). As described for **1**, with resorcinol (11 g, 0.1 mol), NaOH (8 g, 0.2 mol) and formaldehyde (3 g, 0.1 mole). From a conc. MeOH soln. of the dark and very impure final product at –18°, a small amount of **4** (2 g, 16%) separated. Beige powder. M.p. >250° (dec.). IR (KBr): 3309, 1655, 1616, 1499, 1439, 1386, 1299, 1158, 1135, 1083. ^{1}H-NMR (200 MHz, (D_6)DMSO): 8.9 (*s*, 8 OH); 6.3 (*s*, H–C(25), H–C(26), H–C(27), H–C(28)); 6.2 (*s*, H–C(5), H–C(11), H–C(17), H–C(23)); 3.4 (*s*, CH_2(2), CH_2(8), CH_2(14), CH_2(20)). ^{13}C-NMR (50.3 MHz, (D_6)DMSO): 152.7 (*s*, C(4), C(6), C(10), C(12), C(16), C(18), C(22), C(24)); 130.7 (*s*, C(25), C(26), C(27), C(28)); 117.9 (*s*, C(1), C(3), C(7), C(9), C(13), C(15), C(19), C(21)); 102.1 (*s*, C(5), C(11), C(17), C(23)); 27.4 (*t*, C(2), C(8), C(14), C(20)). HR-ESI-MS (neg. mode): 487.1398190 ([*M* – H]$^-$, $C_{28}H_{23}O_8^-$; calc. 487.1398413). TG and DSC (heating 10°/min from 25 to 400°): –7.03% from 100 to 150°, 52.12 J/g; –13.21% from 150 to 280°, 116.1 J/g; –20.21% from 280 to 400°, 388.72 J/g.

5,11,17,23-Tetrabromopentacyclo[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-dodecaene-4,6,10,12,16,18,22,24-octol (=*5,11,17,23-Tetrabromoresorcinarene*; **5**). To a soln. of **4** (4 g, 0.0082 mol) in acetone (50 ml), *N*-bromosuccinimide (6.3 g, 0.0354 mol) was progressively added, the temp. being maintained below 25°. The mixture was left at r.t. for 18 h. Then, excess MeOH was added and the acetone evaporated to give precipitated **5**. (3 g, 40%). Crystals for X-ray structure analysis were obtained from of a conc. soln. of **5** in DMF at –10°. Beige powder. M.p. >250° (dec.). IR (KBr): 3379, 1662, 1479, 1448, 1432, 1353, 1261, 1176, 1137, 1097. ^{1}H-NMR (200 MHz, (D_6)DMSO): 8.8 (*s*, 8 OH); 6.4 (*s*, H–C(25), H–C(26), H–C(27), H–C(28)); 3.7 (*s*, CH_2(2), CH_2(8), CH_2(14), CH_2(20)). ^{13}C-NMR (50.3 MHz, (D_6)DMSO): 149.7 (*s*, C(4), C(6), C(10), C(12), C(16), C(18), C(22), C(24)); 132.3 (*s*, C(25), C(26), C(27), C(28)); 120.2 (*s*, C(1), C(3), C(7), C(9), C(13), C(15), C(19), C(21)); 101.8 (*s*, C(5), C(11), C(17), C(23)); 28.3 (*t*, C(2), C(8), C(14), C(20)). HR-ESI-MS (neg. mode): 802.7768030 ([M – H]$^-$, $C_{28}H_{19}{}^{79}Br_2{}^{81}Br_2O_8^-$; calc. 802.7777984). TG and DSC (heating 10°/min from 25 to 400°): –11.73% from 100 to 160°, 58.4 J/g; –36% from 160 to 380°, 174.12 J/g.

X-Ray Crystal-Structure Determination of Compounds **1** *and* **5** (*Table* and *Figs. 1* and *2*)[1]). The intensity data were collected on a *Stoe-Mark-II-Image-Plate* diffraction system [15] equipped with a two-circle goniometer and by using Mo$K\alpha$ graphite monochromated radiation. The structures were solved by direct methods with the programme SHELXS [16]. The refinement and all further calculations were carried out with SHELXL-97 [17]. For both **1** and **5**, the OH H-atoms were located from *Fourier* difference maps and refined isotropically but with the O–H distances restrained to 0.82(2) Å. The remainder of the H-atoms were included in calculated positions and treated as riding atoms by using SHELXL default parameters. The non-H-atoms were refined aniso-

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[1]) CCDC-267519 and -267520 contain the supplementary crystallographic data for this paper (**1** and **5**, resp.). These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre* at http://www.ccdc.cam.ac.uk/data_request/cif.

Table. *Crystallographic Data for* **1** *and* **5**

	1·5DMF	**5**·2DMF
Empirical formula	$C_{43}H_{55}N_9O_{21}$	$C_{34}H_{34}Br_4N_2O_{10}$
M_r	1033.96	950.27
Crystal colour, habit	red rod	orange block
Crystal size [mm]	$0.36\times0.13\times0.08$	$0.50\times0.50\times0.45$
Crystal system	$P\,2_1/n$	P-1
a [Å]	21.1085(16)	9.2759(8)
b [Å]	9.9922(5)	12.5062(11)
c [Å]	23.4575(19)	16.9153(15)
α [°]	90	111.428(6)
β [°]	102.014(6)	94.901(7)
γ [°]	90	103.011(7)
V [Å^3]	4839.3(6)	1749.1(3)
Z	4	2
ρ_{cal} [g cm^{-1}]	1.419	1.804
λ [Å] (MoK_α)	0.71073	0.71073
μ [mm^{-1}]	0.115	4.663
T [K]	153(2)	173(2)
Scan type	ϕ and ω	ϕ and ω
2θ max [°]	52.3	58.7
Transmission (min, max)	–	0.231, 0.693
Reflections measured	29818	19607
Independent reflections	9563	9372
R_{int}	0.084	0.056
Observed reflections ($I>2\sigma(I)$)	4943	7361
Parameters refined	785	487
Number of l.s. restraints	8	1
R (on F; $I>2\sigma(I)$ reflections)	0.0575	0.0467
wR (on F^2; all indepandant reflections)	0.1503	0.1210
Weights: p in $w=[\sigma^2(F_o)+(pF_o)^2]^{-1}$	0.0721	[a])
Goodness-of-fit	0.920	1.030
Final Δ_{max}/σ	0.003	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.257; −0.260	1.180 near atom Br(1); −1.407

[a]) $w^{-1}=\sigma^2(F_o)^2+(0.0663P)^2+1.2255P$, where $P=(F_o^2+2F_c^2)/3$.

tropically, with weighted full-matrix least-squares on F^2. Compound **1** crystallizes with 5 molecules of DMF per molecule of **1**, two of which are disordered over two positions. One of the NO_2 groups in the molecule is also disordered. Compound **5** crystallizes with two independent centrosymmetric molecules per asymmetric unit, each associated with two molecules of DMF. For **5**, an empirical absorption correction was applied by using the DELrefABS routine in PLATON [18]. The crystallographic diagrams were drawn with PLATON [18].

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