Self-Assembly of 2,8,14,20-Tetraisobutyl-5,11,17,23-tetrahydroxyresorc[4]arene

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We report herein the observation of a hexameric structure of a hydroxyresorc[4]arene in the solid state, enclosing a large interior space. This artificial molecular container is stabilized only by hydrogen bonds. The tendency to form aggregates in solution is demonstrated mainly by means of ESI-MS methods.

Self-assembling systems have attracted much attention in recent years[1] and, in particular, modified calixarenes have been prepared with a view to exploring their aggregation behaviour.[2] In many cases, dimer formation has been observed,[3] but large hexameric aggregates have also been found, both in the solid state and in solution.[4] Herein, we report the self-assembling of a hydroxyresorc[4]arene, both in the solid state and in solution.[5] This is a further example of self-organization, in addition to Atwood's hexamer of 2,8,14,20-tetramethylresorc[4]arene.[4]

Hydroxyresorc[4]arenes[6] are easily generated by the acid-catalysed condensation of 2-hydroxyresorcinol with aldehydes in aqueous media. The result is a bowl-shaped cyclic tetramer, which is connected via methine bridges in a specific way (Figure 1).

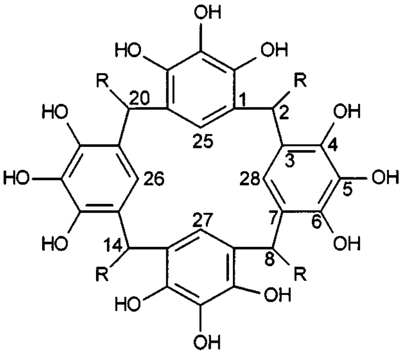

Figure 1. (2*R*,8*R*,14*R*,20*R*)-5,11,17,23-tetrahydroxyresorc[4]arene showing the numbering of substituent positions

Generally, the all-*cis* configured (*rccc*), bowl-shaped cyclic tetramer is precipitated in the course of the reaction because of its low solubility in acidic aqueous media. Under kinetic conditions, the *cis-trans-trans* isomer (*rctt*) can also be isolated. Both configurational isomers lead to the formation of preferred conformations as shown in Figure 2.

Some limitations of the general procedure are known.[6] Use of 5-hydroxyresorcinol or of α-substituted aldehydes or acetals does not result in the expected cyclic tetramers. Aromatic aldehydes tend to form *rctt*-isomers. A number of different hydroxyresorc[4]arenes have been prepared and characterized.[7]

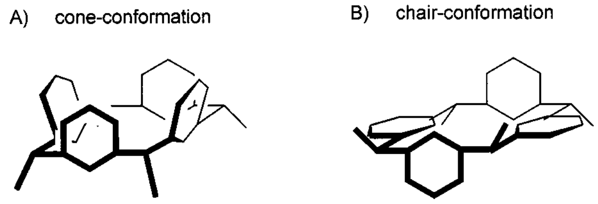

Figure 2. Preferred conformations of (A) the *rccc*- and (B) the *rctt*-hydroxyresorc[4]arene

At room temperature, hydroxyresorc[4]arenes are stable and are frequently obtained as crystalline compounds. Purification and preparation of single crystals suitable for X-ray analysis of the *rccc*-isomers can often be achieved by recrystallization from ethanol.

Results and Discussion

2,8,14,20-Tetraisobutyl-5,11,17,23-tetrahydroxyresorc[4]arene: Tetraisobutyltetrahydroxyresorc[4]arene **1** was prepared both under reflux conditions and at room temperature. The product obtained under reflux conditions exhibited simple ^{1}H- and ^{13}C-NMR spectra, reflecting the C_{4v} symmetry, while mass spectrometric data were consistent with the mass of the expected cyclic tetramer. Crystallization of this compound from both ethanol and acetonitrile led to single crystals, which were subjected to X-ray analysis. The analyses revealed a layer structure as shown in Figure 3.

In the $x-y$ plane, the polar hydroxy groups are arranged in sheets built-up of double layers of hydrogen-bonded ca-

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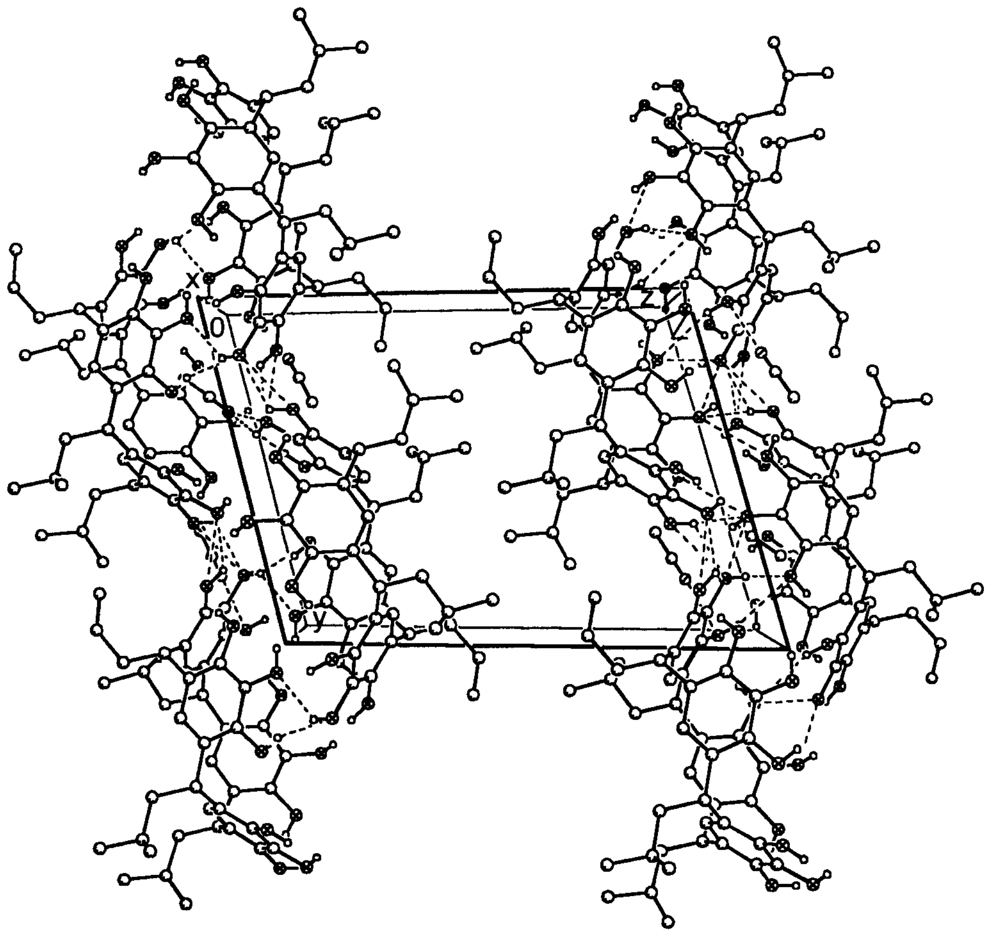

Figure 3. Crystal structure of **1** obtained under reflux conditions; crystal packing along the *x*-axis (hydrogen bonding is shown as dotted lines; for the sake of clarity, all C−H hydrogen atoms and solvent molecules are omitted; ⊕: O, ○: C).

lixarene molecules, with each hydroxyresorcarene orientated face-to-face and tail-to-tail. The polar moieties are separated by the lipophilic alkyl chains. Within one layer, each hydroxyresorcarene is surrounded by eight neighbouring molecules. Hydrogen bonding to the four closest molecules within the same layer and to four molecules in the opposite layer is observed. The acetonitrile molecules are located within the sheets and form O−H···N hydrogen bonds to the hydroxyl groups of the hydroxyresorcarene **1**.

^{1}H-NMR spectroscopy revealed additional interesting properties of **1**. While the expected results were obtained in acetone or ethanol solutions, temperature-dependent spectra in acetonitrile showed strong effects. The splitting and broadening of signals is complicated and therefore the resonances could not be assigned to individual conformers or assemblies.[8] The complex behaviour in acetonitrile suggests that, in spite of the molecular C_{4v}-symmetry, temperature-dependent interaction takes place. This is responsible for the complicated ^{1}H-NMR spectra, although only in sufficiently apolar solvents. We assume that the use of less polar media such as chloroform or toluene would increase the strength of the OH-bonding, but unfortunately tetraisobutylhydroxyresorc[4]arene is poorly soluble in both these solvents.

No major differences were observed in the molecular mass or the dimer regions of the ESI mass spectra of the products prepared under reflux conditions and at room temperature. Compound **1** forms monomeric and dimeric complexes with alkali metal cations.

The product of the room temperature experiment furnished *ccc*-2,8,14,20-tetraisobutyl-5,11,17,23-tetrahydroxyresorc[4]arene as single crystals in relatively low yields after recrystallization from ethanol. Despite recrystallization, the compound gave rather complicated NMR spectra. The ^{1}H-NMR spectrum featured only broad bands, which could not be assigned to specific conformers or impurities, while the ^{13}C-NMR spectra consisted only of undefined patterns of signals.

Adequate single crystals were obtained by recrystallization from acetonitrile. The X-ray structure revealed a complicated self-organized "supermolecule" comprising six hydroxyresorcarenes, which occupy the edges of an octahedron (Figure 4). The polar hydroxy moieties are directed towards the interior of the intermolecular bowl, while the apolar alkyl chains populate the exterior surface. The sphere is of impressive size. The shortest inner diameter between two opposite oxygen atoms is 14.1 Å, while the largest diameter is about 19 Å; the inner volume amounts to at least 1520 Å^3. To the best of our knowledge, this aggregate represents the largest artificial molecular container yet obtained. The stability of the assembly stems from a total of 72 intermolecular O−H···O hydrogen bonds between the hydroxyl groups of adjacent hydroxyresorcarene molecules. The enclosed interior space is populated by ten solvent molecules. In total, 16 CH_3CN molecules are present in the unit cell.

Compared to Atwood's[4] highly stable hexameric superstructure, the hexamer depicted in Figure 4 seems to be much more fragile. However, this structure would seem to be unique. Since its first presentation at the Summer School

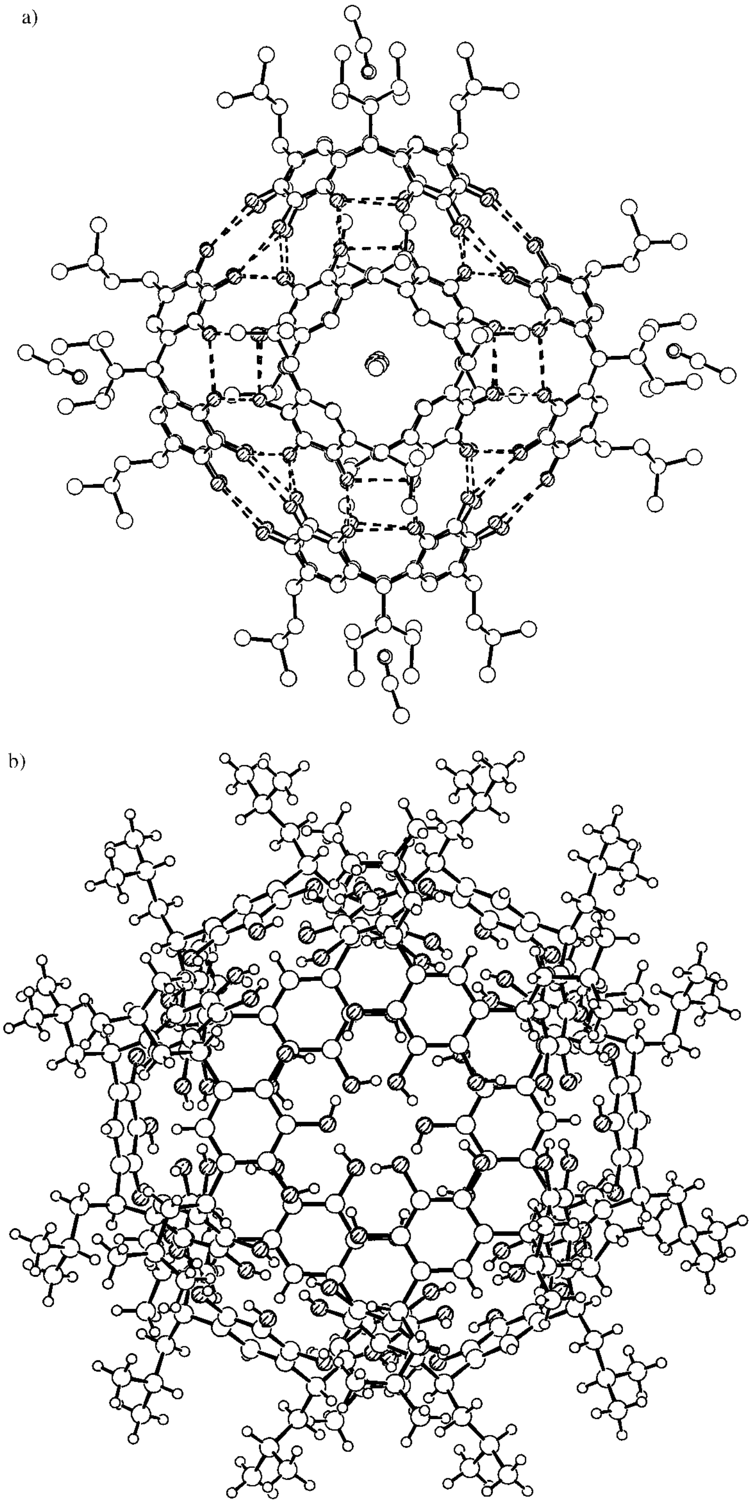

Figure 4. Crystal structure of the tetraisobutylpyrogallo[4]arene **1**-hexamer obtained at room temperature (hydrogen bonding is shown as dotted lines; for the sake of clarity, all C−H hydrogen atoms and the acetonitrile molecules are omitted; ⊘: O, ○: C); (a) top view, (b) side view.

on Supramolecular Chemistry at Ustron in 1996,[5] we have attempted to crystallize other hydroxyresorcarenes with a view to obtaining further hexameric superstructures. Unfortunately, it turned out to be coincidental that a hexamer had been crystallized rather than a layer structure, which was found for the other batch of **1** and for similar compounds.

However, the rather weak hydrogen-bonds might still allow aggregation in solution. Therefore, various analytical tools were employed in order to gain more information about self-assembly in solution.

Chromatographic methods such as GPC in nonpolar solvents did not allow the detection or separation of impurities. Broad bands rather than distinct fractions were obtained. This behaviour was observed for all hydroxyresorcarenes subjected to GPC. We assume that self-assembling processes reversibly and dynamically lead to the formation of a number of different aggregates, which prevent the isolation of any single complex. However, on elution of both batches of **1** in very dilute chloroform solutions, average molar masses of around 2500 g/mol were consistently obtained. The mass of the reference 2,8,14,20-tetraundecylresorc[4]arene was 3600 g/mol. These results encouraged us to apply some other methods in order to find out whether the solid-state coordination phenomenon could be reproduced in solution.

Light scattering was put forward as a possible means of identifying large aggregates in solution, but due to practical limitations of suitable solvents such as ethanol and water, no effects could be detected. A commonly used method for examination of large molecules as well as self-organizing systems is vapor pressure osmometry, VPO. Since polar solvents can be expected to interfere with the aggregation, the most apolar solvents permitted by the solubilities of the hydroxyresorcarene and of the standards were employed. The solvents of choice were *n*-butyl acetate and tetrahydrofuran. 2,8,14,20-Tetraundecylresorc[4]arene was chosen as a reference substance since VPO measurements in benzene and chloroform were reported to give masses around 7100 and 5000 u.[9] In fact, only the molar masses were reproduced for **1** and the reference substance in the polar media.

Mass spectrometric methods have previously been employed by other groups[3d,3h] to examine aggregated calixarene systems in solution. One promising method is electrospray ionization mass spectrometry (ESI-MS). In the case of **1**, FD- and matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF) measurements only showed molecular masses in the monomer region, suggesting that these ionization techniques may be too destructive for the sensitive aggregates. In contrast to the MS methods performed with polar solvents, ESI-MS strongly indicates the existence of self-complexation in solution. Even in ethanol we observed both in the cation and anion detection modes the formation of dimers and even a trimer for the room temperature product. The distribution of the signal intensities of the trimer did not match the calculated trimer pattern well, thus more highly charged aggregates with higher masses cannot be excluded. Intercalated sodium, potassium, or ammonia was also detected in many cases. However, guest-free associates were also observed and hence an exclusively template-driven effect can be ruled out. Singly-charged higher aggregates could not be recorded because of the limited range of the detector.

Conclusions

Based on the analytical data, we deduce that simple hydroxyresorc[4]arenes are capable of self-organization both in solution and as well as in the solid state. Due to the nature of interaction, the stability of the assembly depends on the polarity of the medium, which can interfere as a competing hydrogen bond acceptor/donor. Since GPC failed to separate distinct aggregates, we assume that a dynamic equilibrium of formation and decomposition of aggregates takes place. No specific associate is considered sufficiently stable to be isolated or observed by light scattering.

ESI-MS suggests that defined supramolecular complexes exist in solution, even in polar media. Comparison with tetraundecylresorc[4]arene suggests that **1** should be capable of forming higher aggregates if dissolved in a more apolar solvent. Self-organization effects of hydroxyresorc[4]arenes in the solid state, leading to a hexamer as shown in Figure 4, represent an exception to the rule.[10] No conditions are known under which crystallization of the spatial aggregate occurs rather than that of an ordinary layer structure. However, the sphere can be regarded as an example of a simple artificial molecular container in the solid state. Stabilized only by weak hydrogen bonds, the hexamer is very fragile.

Experimental Section

All solvents used were p.a. quality or were purified by distillation. Chloroform was distilled over $CaCl_2$, acetonitrile over P_2O_5, and THF over $LiAlH_4$. The resorc[4]arene used as a reference compound was prepared following general procedures described in the literature.[11] All melting points were determined on a Büchi B-540 apparatus and are uncorrected. The ^{1}H-NMR spectra were measured on Bruker AC 200 (200.13 MHz) or ARX 300 (300.13 MHz) spectrometers, the ^{13}C-NMR spectra on Bruker AC 200 (50.32 MHz), ARX 300 (75.47 MHz), or DRX 500 (125.77 MHz) instruments. MALDI-TOF spectra were recorded on a Lazarus II spectrometer by Dr. H. Luftmann, University of Münster, ionization by N_2 laser, 337 nm, 3 ns pulse, 16 kV, 1 m flight distance. ESI-MS was performed on a Finnigan TSQ 7000 triple-quadrupole tandem mass spectrometer by electron-spray ionization. X-ray data sets were collected with an Enraf−Nonius MACH3 diffractometer. Programs used: data-reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101190. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure: A solution of 5.00 g (39.8 mmol) of 2-hydroxyresorcinol in 30 mL of ethanol and 6 mL of concentrated hydrochloric acid was combined in a dropwise manner with 1 equiv. of aldehyde under cooling with ice. The mixture was then refluxed for 24 h under argon. After cooling to room temperature, the precipitate was collected, washed with a little cold ethanol, and dried in vacuo.

2,8,14,20-Tetraisobutyl 5,11,17,23-tetrahydroxy-resorc[4]arene (1, Preparation at Reflux Temperature): 4.27 mL (39.8 mol) of isovalerianaldehyde was employed. The product was crystallized from acetonitrile. Yield: 4.09 g (53%); m.p. 306−308°C (dec.). − $C_{44}H_{56}O_{12}\cdot 8CH_3CN$ (776.9 + 328.5): calcd. C 65.2, H 7.29; found C 64.92, H 7.23. − ^1H NMR (200 MHz, [D$_6$]acetone, TMS, 25°C): δ = 0.94 (d, ^3J = 6.6 Hz, 24 H, CH$_3$), 1.48 [m, 4 H, C*H*(CH$_3$)$_2$], 2.15 (t, ^3J = 7.4 Hz, 8 H, CH$_2$), 4.49 [t, ^3J = 7.3 Hz, 4 H, (Ar)$_2$C*H*CH$_2$], 7.11 (s, 4 H, ArH), 7.28 [s, 4 H, OH (C-2)], 8.17 [s, 8 H, OH (C-1, C-3)]. − ^{13}C NMR (125 MHz, [D$_6$]acetone, 25°C): δ = 22.87, 23.01, 23.05, and 23.25 (CH$_3$); 26.91 [*C*H(CH$_3$)$_2$], 32.49 [*C*H(Ar)$_2$], 42.81 and 42.95 (CH$_2$), 114.56 (CH, arom. C-5), 114.65 (CH, arom. C-5), 125.64 [C$_q$ (C-4, C-6)], 133.58 [COH (C-2)], 140.00 [COH (C-1, C-3)]. − MALDI-TOF MS (matrix: 2,6-dihydroxybenzoic acid, ions = positive): *m/z* = 777 [M + H$^+$], 799 [M + Na$^+$]. − ESI MS [$C_{44}H_{56}O_{12}$, 776.9; ethanol, ions = positive, isotope pattern: mass (rel. intensity/intensity scale)]: 777.4 (86%/2.5·10^3), 778.6 (43%/2.5·10^3), 779.5 (9%/2.5·10^3), 794.5 (100%/2.5·10^3), 795.7 (32%/2.5·10^3), 799.5 (64%/2.5·10^3), 800.5 (31%/2.5·10^3), 815.4 (20%/2.5·10^3), 816.4 (12%/2.5·10^3), 1570.3 (8%/6.2·10^3), 1571.2 (32%/6.2·10^3), 1575.0 (75%/6.2·10^3), 1575.8 (78%/6.2·10^3), 1577.3 (100%/6.2·10^3), 1578.1 (44%/6.2·10^3), 1579.0 (28%/6.2·10^3), 1580.0 (7%/6.2·10^3), 1591.7 (12%/6.2·10^3), 1592.6 (14%/6.2·10^3), 1743.4 (56%/8.0·10^2), 1744.4 (96%/8.0·10^2), 1745.4 (100%/8.0·10^2), 1746.3 (44%/8.0·10^2).

X-ray Crystal Structure Analysis of 1: Formula $C_{44}H_{56}O_{12}\cdot 2CH_3CN$, M_r = 859.0, 0.50 × 0.40 × 0.05 mm, a = 10.956(2), b = 13.036(1), c = 17.708(3) Å, α = 73.11(1), β = 75.95(1), γ = 79.61(1)°, V = 2331.1(6) Å^3, ρ_{calcd} = 1.224 g cm^{-3}, μ = 7.16 cm^{-1}, empirical absorption correction on the basis of φ scan data (0.939 ≤ C ≤ 0.998), Z = 2, triclinic, space group *P*1bar (No. 2), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 10010 reflections collected (+h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 9492 independent and 5221 observed reflections [$I \geq 2\,\sigma(I)$], 581 refined parameters, R = 0.083, $wR2$ = 0.230, max. residual electron density 1.43 (−0.53) e Å^{-3}, disorder at C49 (not refined); hydrogens calculated and refined as riding atoms.

2,8,14,20-Tetraisobutyl 5,11,17,23-tetrahydroxyresorc[4]arene (1, Room Temperature Product): 4.27 mL (39.8 mol) of isovalerianaldehyde was employed. The temperature of the reaction mixture was not allowed to exceed 30°C. After 12 h, the reaction was stopped, and the crystals that separated were collected and recrystallized from acetonitrile. The product appeared to be uniform. Selected crystals were subjected to X-ray analysis. Yield: 1.68 g (25%); m.p. 297°C. − ^1H NMR (200 MHz, [D$_6$]acetone, TMS, 25°C): δ = 0.8−1.1 (br. m, 24 H, CH$_3$), 1.4−1.7 [m, 4 H, C*H*(CH$_3$)$_2$], 1.8−2.4 (m, 8 H, CH$_2$), 2.96, 4.13, 4.50 (t, 4 H, C*H*CH$_2$), 7.12 (br. s, 4 H, C*H*$_{ar}$), 7.22, 7.29 (s, 3.5 H, OH), 8.11, 8.18, 8.28 (s, 6 H, OH), 8.55 (br. s, 2.5 H, OH). − ^{13}C NMR (125 MHz, [D$_6$]acetone, 25°C): δ = 206.5 (CO, solvent), 141.1, 140.9, 140.3, 140.2, 140.1, 140.0, 139.3, 134.6, 134.1, 133.8, 133.7, 125.6, 125.4, 125.2, 124.7, 124.5, 120.8, 115.3, 115.2, 62.8, 57.7, 44.0, 43.8, 43.4, 30.6, 30.3, 30.2, 30.0, 29.8, 29.5, 29.3, 29.0, 27.3, 22.8, 22.2, 22.1, 22.0, 18.7. − MALDI-TOF MS (matrix: 2,6-dihydroxybenzoic acid, ions = positive): 777 [M + H$^+$], 799 [M + Na$^+$]. − ESI-MS [$C_{44}H_{56}O_{12}$, 776.9, acetonitrile, ions = negative, isotope pattern: mass (rel. intensity/intensity scale)]: 775.4 (100%/2.0·10^5), 776.5 (48%/2.0·10^5), 777.4 (16%/2.0·10^5), 778.4 (4%/2.0·10^5); ($C_{88}H_{111}O_{24}$, 1552.8): 1552 (97%/2.3·10^3), 1553.1 (100%/2.3·10^3), 1554.2 (35%/2.3·10^3), 1555.1 (23%/2.3·10^3), 1556.3 (8%/2.3·10^3); [acetonitrile, ions = positive, isotope pattern: mass (rel. intensity/intensity scale)]: 777.5 (100%/7.1·10^3), 778.5 (46%/7.1·10^3), 779.6 (14%/7.1·10^3), 794.5 (100%/7.1·10^3), 795.5 (49%/7.1·10^3), 796.5 (16%/7.1·10^3), 799.5 (100%/7.1·10^3), 800.6 (64%/7.1·10^3), 801.6 (18%/7.1·10^3), 815.4 (100%/7.1·10^3), 816.5 (53%/7.1·10^3), 817.6 (24%/7.1·10^3), 818.6 (8%/7.1·10^3), 1570.0 (100%/9.8·10^3), 1574.4 (<5%/9.8·10^3), 1575.6 (71%/9.8·10^3), 1576.6 (100%/9.8·10^3), 1577.5 (34%/9.8·10^3), 1578.5 (32%/9.8·10^3), 1579.7 (12%/9.8·10^3), 1591.8 (100%/9.8·10^3), 1592.7 (97%/9.8·10^3), 1593.7 (44%/9.8·10^3), 1594.5 (20%/9.8·10^3), 1595.5 (15%/9.8·10^3); [ethanol, ions = positive, isotope pattern: mass (rel. intensity/intensity scale)]: 2352.5 (100%/1.4·10^2), 2353.3 (13%/1.4·10^2), 2354.4 (52%/1.4·10^2), 2357.1 (16%/1.4·10^2); [0.002 N HCl in ethanol, ions = positive, isotope pattern: mass (rel. intensity/intensity scale)]: 776.5 (29%/4.5·10^3), 777.5 (100%/4.5·10^3), 778.4 (35%/4.5·10^3), 779.6 (13%/4.5·10^3), 1552 (35%/4.5·10^3), 1553.8 (100%/4.5·10^3), 1555.1 (49%/4.5·10^3), 1556.2 (34%/4.5·10^3), 1557.2 (6%/4.5·10^3), 2329.8 (47%/1.8·10^2), 2330.7 (68%/1.8·10^2), 2331.5 (100%/1.8·10^2), 2332 (42%/1.8·10^2), 2333.3 (30%/1.8·10^2), 2334 (27%/1.8·10^2), 2336.1 (25%/1.8·10^2). − $C_{44}H_{56}O_{12}\cdot 2CH_3CN$: calcd. C 67.11, H 7.27, N 3.26; found C 66.58, H 7.49, N 3.00.

X-ray Crystal Structure Analysis of 1: Formula $[C_{44}H_{56}O_{12}]_6\cdot 11CH_3CN$, M_r = 5112.92, 0.40 × 0.20 × 0.20 mm, a = 21.713(3), b = 21.722(2), c = 21.944(5) Å, α = 63.86(1), β = 85.33(2), γ = 60.93(1)°, V = 8004(2) Å^3, ρ_{calcd} = 1.061 g cm^{-3}, μ = 6.21 cm^{-1}, Z = 1, triclinic, space group *P*1bar (No. 2), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 24979 reflections collected (−h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 24361 independent and 11895 observed reflections [$I \geq 2\,\sigma(I)$], 1609 refined parameters, R = 0.116, $wR2$ = 0.282, max. residual electron density 1.22 (−0.42) e Å^{-3}, five disordered acetonitriles with S.O.F. = 0.5 within the cavity, plus six outside; hydrogens calculated and refined as riding atoms.

Acknowledgments

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