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Ethyl Pyrogall[6]arene and Pyrogall[4]arene: Synthesis, Structural Analysis and Derivatization

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In the acid-catalyzed synthesis of ethyl pyrogall[4]arene, a novel hexamer, ethyl pyrogall[6]arene, is obtained as a readily isolable minor product. Pyrogall[6]arene can be isolated from the reaction mixture in three different ways yielding the hexamer in different forms and stabilities. Crystallization from DMSO and then recrystallization from acetone gives a stable crystalline solid, recrystallization directly from acetone yields an unstable white powder, while direct recrystallization from THF gives a stable white powder. Both pyrogall[4]arene and pyrogall[6]arene crystallize readily with DMSO filling the voids in the crystal lattice. Co-crystallization studies of the hexamer isolated by recrystallization from acetone resulted in a novel directly hydrogen-bonded capsule formed by two pyrogall[4]arenes and an included TMA cation, while the DMSO/acetone isolated product yielded the intact hexamer with clathrate-type TMA inclusion.

Keywords: Resorcinarenes; X-ray crystallography; Encapsulation; Acylation

INTRODUCTION

Pyrogall[4]arenes are synthesized similarly to resorcinarenes in fairly high yields by acid-catalyzed condensation of pyrogallol with aldehydes [1,2]. The result is usually an all-*cis* configured (r-*ccc*), bowl-shaped cyclic tetramer, such as **1** (Scheme 1). Because of their favorable shape and polarity, pyrogall[4]-arenes have been used for liquid-crystal applications [3,4], in complexation studies [5,6] and as starting material for carserand synthesis [7,8]. In the solid state pyrogallarenes have been observed to form directly hydrogen-bonded, highly ordered, hexameric capsules [9]. For resorcinarenes, only a few examples of cyclic hexamers are known [10–12]. Cyclic hexamers show considerable potential as starting compounds for further syntheses and as possible hosts for complexation because of their wider upper rim and larger cavity, if the conformation is suitable, which give them more a elaborate nature than the tetramers. More functional groups at the upper rim give more possibilities for intermolecular interactions and more sites for functionalization. Herein we report the synthesis, characterization and acylation of a previously unknown cyclic hexamer, the r-*trans*–*cis*–*trans*–*cis*–*trans* (r-*tctct*) pyrogall[6]arene **2** with ethyl chains at methine bridges (Scheme 1).

RESULTS AND DISCUSSION

Syntheses and Crystal Structures of Pyrogall[4]arene and Pyrogall[6]arene

Acid-catalyzed condensation of pyrogallol with propionaldehyde gave the known cyclic tetramer **1** [1] and, as a minor product, hexamer **2**. The ^{1}H NMR spectra in DMSO-d_6 indicate high symmetry for both **1** and **2** (Fig. 1). The chemical shift of the protons in the pendant ethyl groups are dissimilar from tetramer to hexamer: $-CH_3$ protons and $-CH_2-$ protons are shifted upfield by 0.15 and 0.41 ppm, respectively, while –CH– protons of the methine bridges experience a downfield shift of 0.24 ppm. Chemical shifts of the protons of the OH groups are also different, giving one broad singlet with hexamer **2**, whereas with tetramer **1** they give two sharp singlets in a 1:2 ratio, indicating the presence of intramolecular hydrogen bonding in **1** but not in **2**. The ESI-TOF mass spectrum showed a major

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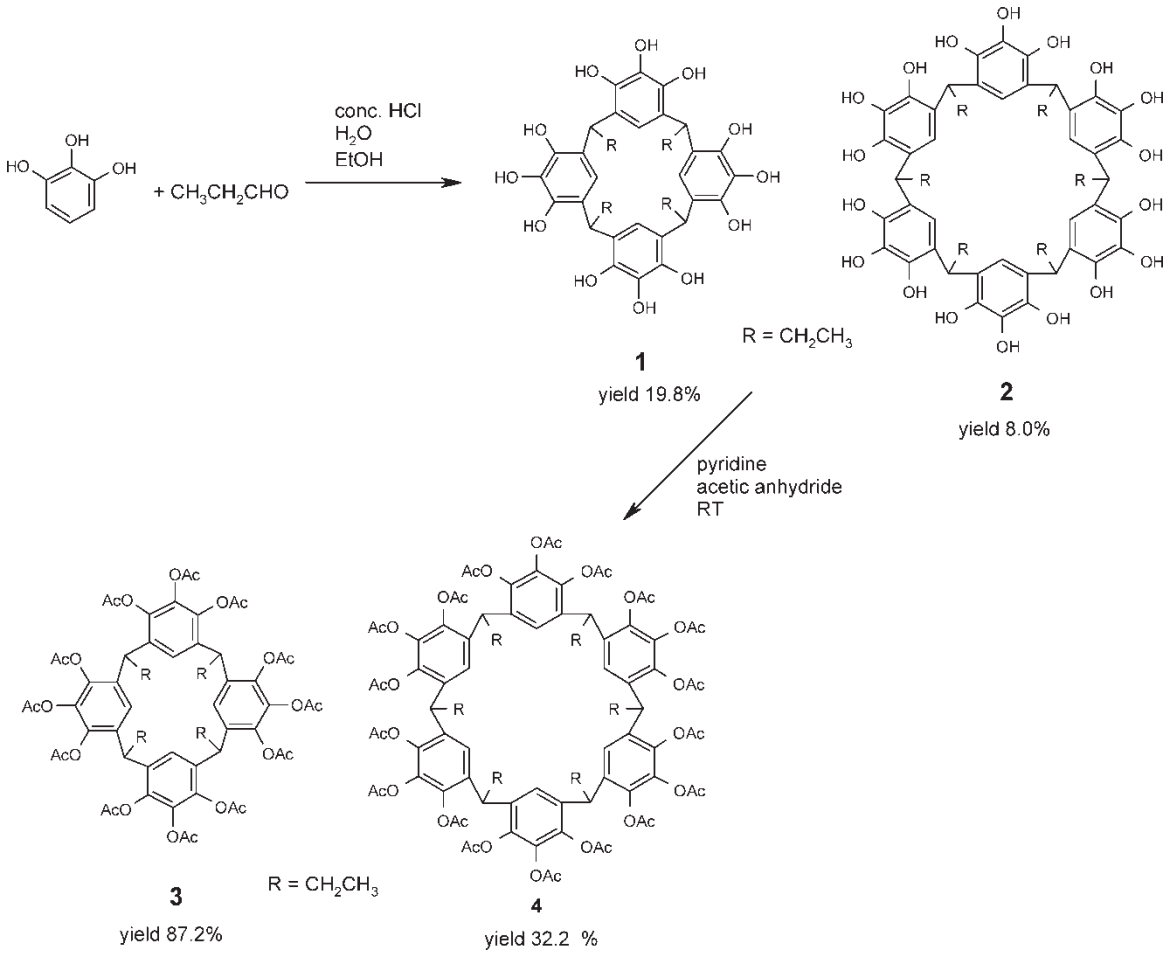

SCHEME 1 Synthesis and acylation of ethyl pyrogall[4]arene and pyrogall[6]arene.

peak at 1019.48 corresponding to the sodium adduct of hexamer **2**.

Condensation of pyrogallol with acetaldehyde and butyrylaldehyde under the same reaction conditions gave only the respective cyclic tetramers, which, together with earlier obtained ethyl resorcin[6]arene [10], indicates that the chain length of an aldehyde has a crucial effect on cyclization.

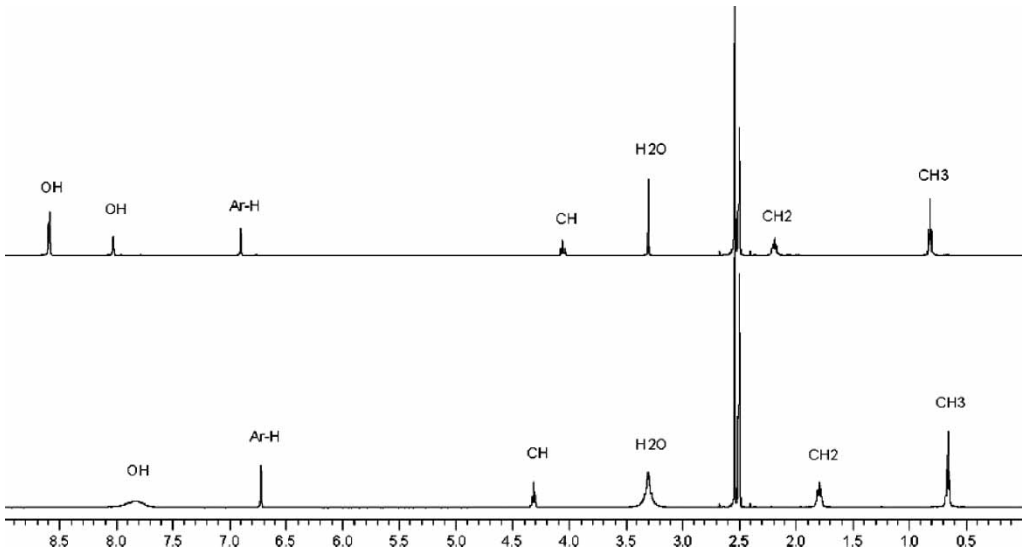

FIGURE 1 ^{1}H NMR spectra of tetramer **1** (above) and hexamer **2** (below) in DMSO-d_6.

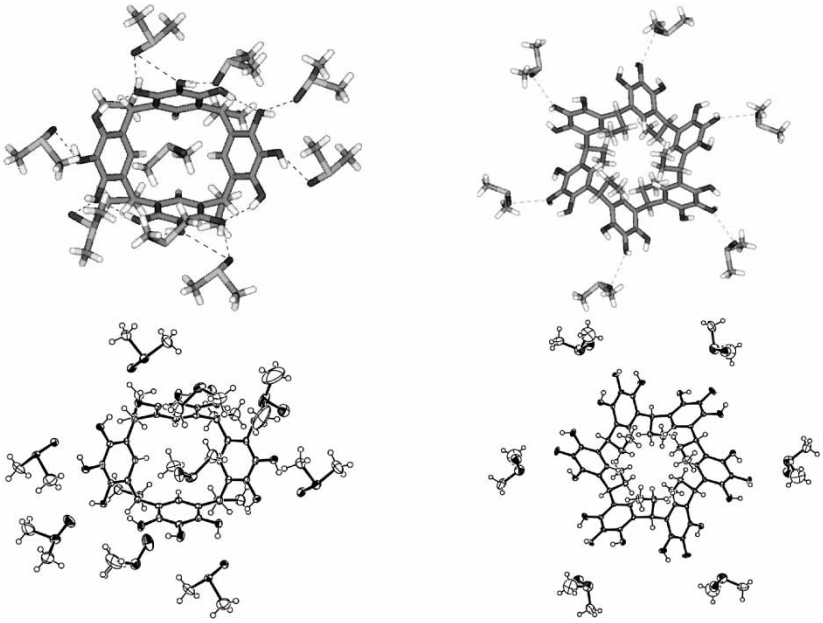

FIGURE 2 Crystal structure of cyclic tetramer r-*ccc* pyrogall[4]arene **1** (left) and cyclic hexamer r-*tctct* pyrogall[6]arene **2** (right). Thermal ellipsoid plots are shown below.

Crystallization of tetramer **1** from DMSO resulted in colorless crystals with the composition **1**·7DMSO (Fig. 2), which corresponds to 45.1% of solvent by weight. Although the number of hydrogen-bonding sites is the same as in quasi-solution forming r-*ctt*-resorcinarenes [13], the intramolecular hydrogen bonding keeping the molecule in the r-*ccc* crown conformation blocks part of the hydrogen-bonding sites from the solvent and the amount of solvent in the crystal is not as high. The cavity of the host is filled by a molecule of DMSO, which is hydrogen bonded to hydroxyl groups of the above host.

The structure of hexamer **2** resembles closely the structure of resorcin[6]arene [10] with a hexagonal crystal system, S_6 symmetry and r-*tctct* configuration (Fig. 2). Although the distance between the neighboring hydroxyl groups is somewhat shorter than in the resorcin[6]arene structure (3.38 vs. 3.57 Å) the distance is still too long for intramolecular hydrogen bonding, which would change the conformation to crown-like. Surprisingly, although there are more hydrogen-bonding sites in pyrogall[6]arene, the crystal contains no acetone and less DMSO than respective resorcin[6]arene crystals (32% of weight vs. 51% in resorcin[6]arene crystals [10]). Instead, intermolecular hydrogen bonds to adjacent pyrogall[6]-arenes are formed, which stabilizes columnar packing to hexagonal arrays efficiently (Fig. 3).

Isolation and Stability of Pyrogall[6]arene

In the first isolation of the hexamer, the crude product was recrystallized from DMSO, filtered, washed and again recrystallized from acetone giving large, slightly reddish crystals. Because DMSO disturbs the subsequent synthesis and the co-crystallization studies of the hexamer, the second method for isolation of the hexamer was just recrystallization from acetone to avoid the presence of interfering DMSO. This procedure gave the pure hexamer as white powder that was, to our surprise,

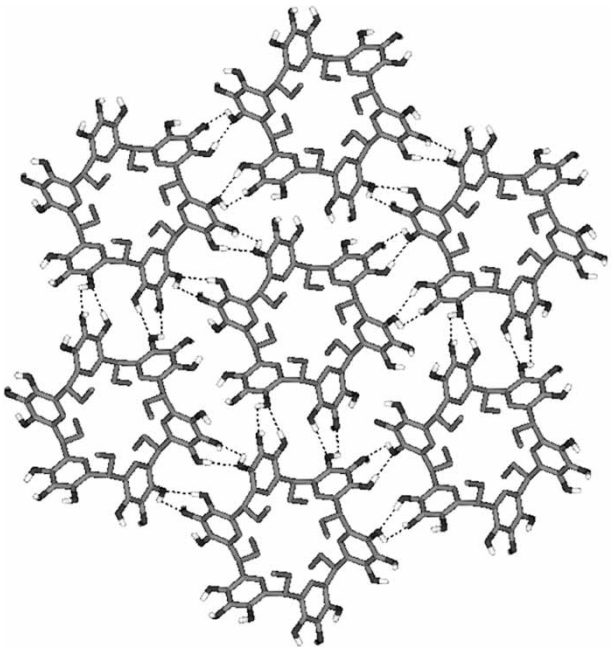

FIGURE 3 Crystal packing of **2**. Adjacent pyrogall[6]arenes are hydrogen bonded to continuous hexagonal clusters. DMSO molecules are omitted for clarity.

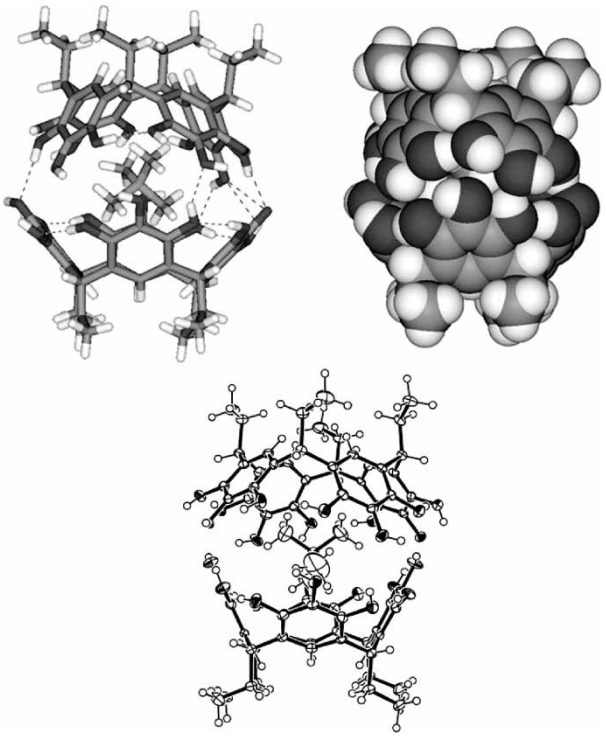

FIGURE 4 Crystallization of hexamer **2** isolated by recrystallization from acetone with TMACl resulted in transformation of hexamer to tetramer **1**, which in the crystalline state packs directly into the hydrogen-bonded dimeric capsules. The thermal ellipsoid plot is shown below.

discovered to be unstable. In our attempts to co-crystallize the pyrogall[6]arene **2** with tetramethylammonium chloride (TMACl) and functionalize the hexamer by acylation, we observed that the hexamer isolated directly from acetone decomposed easily to the tetramer pyrogall[4]arene. Co-crystallization in a 2:1 ratio with TMACl resulted in a dimeric capsule structure of two tetramers encapsulating a TMA cation (Fig. 4). Although the dimeric capsule was an unexpected and, from the hexamer point of view, an unwanted result, it does possess several unique structural features and, as such, is an interesting example of the complexation properties and possibilities of pyrogall[4]arenes.

To the best of our knowledge the capsule formed is the first example of a resorcinarene-type capsule in which the capsule halves are in direct hydrogen-bonding contact. Usually the formation of a dimeric resorcinarene capsule requires the presence of a linking solvent or a spacer [14–18]. In our previous studies with dimeric resorcinarene capsules we assumed that direct hydrogen-bonding contact can only be obtained if the guest is small enough to allow the capsule halves to approach each other close enough for direct contact [17,18]. However, this result with the TMA guest shows that the additional OH group in the 2-position plays a key role by being in perfect spatial position for direct hydrogen bonding to the adjacent host. In addition, the pyrogall[4]arene capsule is not significantly tighter than previous resorcinarene capsules in terms of the diameter of the capsule (defined by the distance between the planes formed by the methine bridges): the diameter is 8.35 Å, while with solvent-mediated capsules the respective distances vary from 8.35 to 8.98 Å [17,18].

Yet another interesting feature is the absence of an anion in the crystal structure. Instead, one of the OH groups is deprotonated, which is easily seen both from shorter hydrogen-bonding distances of the deprotonated oxygen [2.606(4) Å vs. on average 2.981(4) Å] and by the lack of electron density indicating the presence of a proton or chloride.

TMA co-crystallization of hexamer **2** obtained from recrystallization from DMSO and acetone, however, resulted in a hexamer structure surrounded by six TMA cations and chloride anions (Fig. 5).

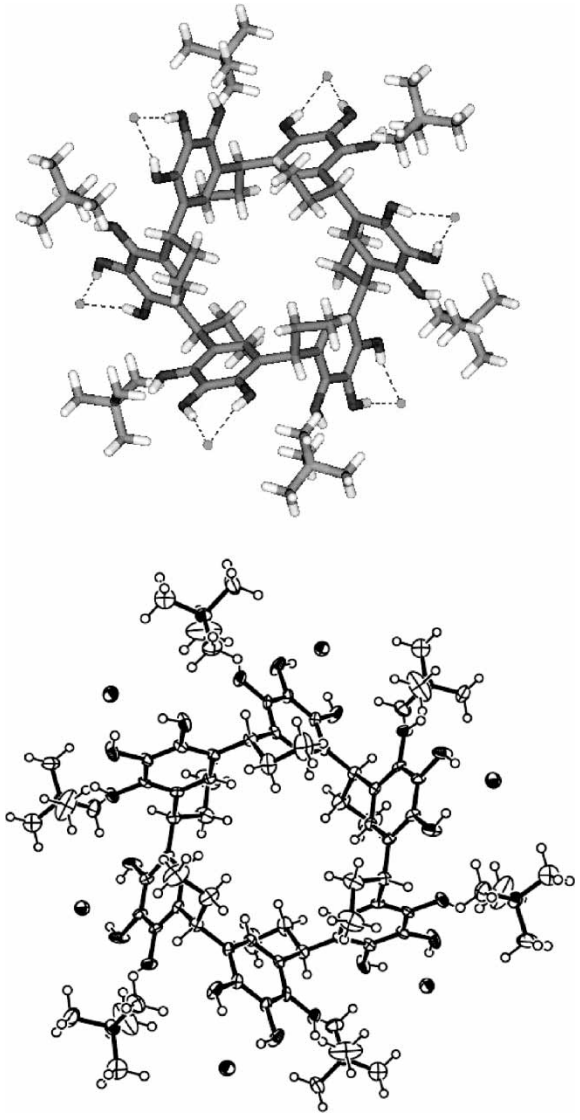

FIGURE 5 Clathrate inclusion complex **2**·6TMACl. Chloride anions are hydrogen bonded to hydroxyl groups. The thermal ellipsoid plot is shown below.

The structure is again strikingly similar to the previous hexamer structures with a hexagonal crystal system, S_6 symmetry and r-*tctct* conformation, which indicates the stability of this conformation regardless of the changes in environment and crystallization conditions. A rather surprising feature of the structure is the fact that the chlorides replace all of the DMSO molecules in the structure, although our earlier experience with pyrogall[4]arenes shows, without exception, that any residual DMSO interferes significantly with the hydrogen bonding and complexation in the solid state and is very difficult to remove from a sample [19]. As hexamer **2** does not have a cavity or any other concave binding site, the TMA cations occupy the space between the hexamers and are also C–H···O hydrogen bonded to three of the surrounding hosts (the shortest C–O hydrogen-bonding distances vary from 3.27 to 3.38 Å).

The crystal packing of the clathrate complex reveals that adjacent hexamers are connected via hydrogen bonds to chloride anions [Cl^-···O distances are 3.042(2), 3.048(2) and 3.289(2) Å] instead of the direct intermolecular connection observed in **2**·6 DMSO (Fig. 6). This type of indirect hydrogen bonding leaves space for the cations, which occupy the interstices between the pyrogall[6]arenes.

Decomposition of the hexamer to the tetramer was also observed when this sample was investigated by NMR spectroscopy. NMR spectra of a dissolved sample directly after synthesis and acetone isolation gave peaks of the hexamer, and after 3 days measurement of the same sample gave spectra of the tetramer, indicating that the decomposition occurs in solution. NMR spectra of our first isolation from DMSO and acetone directly after synthesis, after 3 days and also after 2 weeks gave clear spectra of the hexamer. The only difference in the immediately obtained hexamer spectra of the two samples is the position and appearance of the O*H* peak: in the dissolved powder sample obtained from acetone the O*H* peak was split (main peak and shoulder at 7.77 and 7.92 ppm, respectively), while in the dissolved crystalline sample obtained from DMSO and acetone a single peak at 7.80 ppm was observed. Most probably this indicates the difference in inter- and/or intramolecular hydrogen bonding of two forms of the hexamer product. Another difference is the amount of water left in the sample despite similar drying methods: the acetone-isolated sample contains approximately three times the amount of water compared to the DMSO/acetone-isolated sample, which most probably also affects the hydrogen bonding of the hexamer. Adding water to the crystalline sample did not change the ^{1}H NMR spectra, indicating that the amount of water does not play a role in the stability of the hexamer. Instead, DMSO seems to have a stabilizing effect compared to acetone.

In the third method of isolating hexamer **2**, THF was used in recrystallization of the crude product, giving a stable white powder. The NMR sample isolated directly from THF was also measured several times, directly after the synthesis, after 3 h, 1 day and after 3 days and no decomposition was observed. The NMR spectrum are almost identical to the spectrum of the crystalline hexamer obtained from DMSO and acetone, only the peak for O*H* is slightly broader.

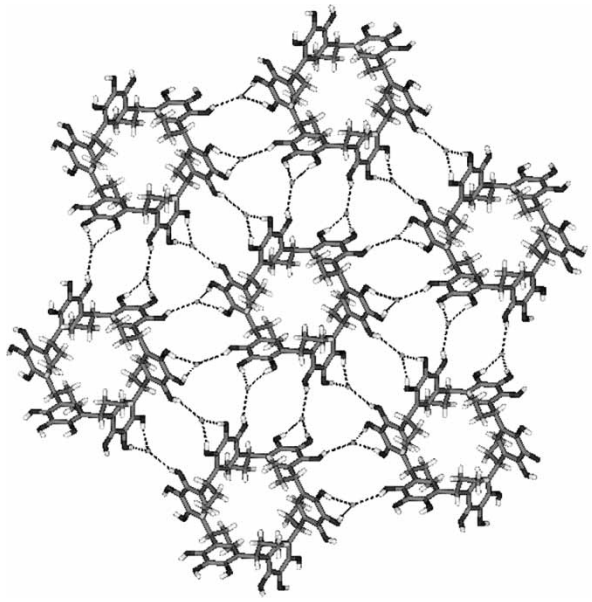

FIGURE 6 Crystal packing of **2**·6TMACl shows remarkable similarity to other hexamer structures. TMA cations are omitted for clarity.

Synthesis and Analysis of Acylated Pyrogall[4]arene and Pyrogall[6]arene

In order to synthesize derivatives of both pyrogall[4]arene and pyrogall[6]arene, acylation was performed. Acylation of **2** with acetic anhydride in pyridine affords the completely acylated derivative **3** in 87.2% yield. The ^{1}H NMR spectrum in $CDCl_3$ contains one triplet for the protons of the methine bridges, one singlet for the protons of the pyrogallol rings, the ethyl groups give one multiplet and one triplet and the acyl groups give two singlets in the ratio 1:2. The ESI-TOF mass spectrum showed only one peak at 1242.49 corresponding to the TMA adduct of *O*-acylated tetramer **3**.

Using acetone-isolated pyrogall[6]arene in the acylation with acetic anhydride in pyridine affords the completely acylated tetramer derivative **3** in 75% yield, which together with crystallization and NMR experiments proves that hexamer **2**, when isolated directly from acetone, is not stable and decomposes

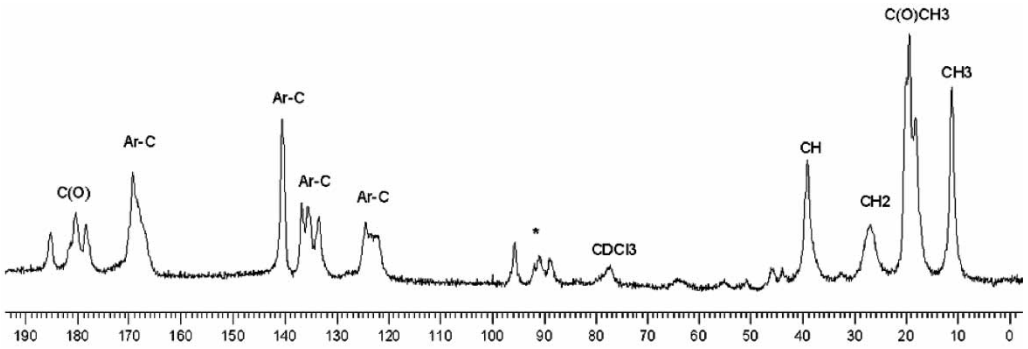

FIGURE 7 ^{13}C CP/MAS NMR spectrum of **4**. The asterisk indicates breakthrough pulses.

to the tetrameric form. However, acylation of hexamer **2** isolated from DMSO and acetone with acetic anhydride in pyridine affords an insoluble white powder. The acylation was also repeated with acetyl chloride and triethylamine as a base in an acetonitrile/THF mixture resulting in the same insoluble product. Both acylation products were identified as acylated pyrogall[6]arenes by ESI-TOF mass spectrometry, which showed a peak at 1791.60 corresponding to the potassium adduct of *O*-acylated hexamer **4**. IR spectra of the compounds were identical and showed characteristic absorptions at 1187 and 1812 cm^{-1} due to C–O and C═O stretching, respectively. Compared to the IR spectrum of hexamer **2**, the extensive absorption of the OH groups at 3406 cm^{-1} disappeared in both cases. Solid-state ^{13}C CP/MAS NMR for these two products gave identical spectra with broad signals. In both cases the spectra indicate complete acylation. A ^{13}C CP/MAS NMR spectrum of acylated compound **4** is shown in Fig. 7. Further studies on the cause of the insolubility of the acylated hexamer are currently under way.

CONCLUSIONS

Pyrogall[6]arene can be synthesized by a simple acid-catalyzed condensation reaction and isolated from the reaction mixture by three different methods. However, only isolation by recrystallization from DMSO followed by another recrystallization from acetone or direct recrystallization from THF results in a stable product, while direct acetone isolation results in a hexamer that decomposes readily to the tetramer.

The decomposition of the hexamer to the tetramer in the acetone-isolated product might be due to the fact that the hexamer is kinetically the most favored product whereas the tetramer is thermodynamically the most favored product. This is supported by the fact that the hexamer is indeed an isolable side product in the normal procedure for synthesizing the pyrogall[4]arenes and resorcin[4]-arenes. Our original explanation for the instability of the acetone-isolated product was the lack of conformation stabilizing intramolecular hydrogen bonds and the difference in inter- and intramolecular hydrogen bonding compared to the DMSO/acetone-isolated product, which indicated to us the significance of DMSO for stability. However, our further studies on co-crystallization with TMACl showed that DMSO can be replaced by chloride anions without any change in conformational properties or stability of the hexamer. Additionally, we discovered that the hexamer can be isolated in a stable form by recrystallization from THF, which indicates that only acetone isolation creates suitable conditions for the hexamer–tetramer conversion. Currently, we are interested in investigating the properties of the THF-isolated product, especially in the solid state, to obtain information on the differences and/or similarities in hydrogen bonding and conformation and thus obtain further knowledge to explain the differences in the stabilities of the hexamer product when obtained by different isolation methods.

In conclusion, pyrogall[6]arene can be synthesized by a simple acid-catalyzed condensation reaction, but the product stability depends on the method of isolation. Derivatization of the crystalline hexamer by acylation affords the completely acylated product, which, however, is almost insoluble and thus challenging to identify and use for further studies. Further co-crystallization and derivatization studies to clarify the relatively unknown chemistry of pyrogall[6]arene are currently under way.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were measured with Bruker Avance DRX 500 (500 MHz for ^{1}H and 126 MHz for ^{13}C) and ^{13}C CP/MAS NMR spectra with Bruker AMX 400 spectrometers. The mass spectrometric studies were performed with a Micromass LCT

ESI-TOF instrument equipped with a *Z* geometry electrospray ion source. Elemental analyses were performed with varioELIII elemental analyzer. IR spectra were recorded on a Mattson Satellite FTIR spectrometer. Melting points were measured with a Mettler Toledo FP62 instrument and are uncorrected.

Pyrogall[6]arene 2

Pyrogallol (37.8 g, 0.3 mol) was dissolved in ethanol (200 mL) under a N_2 atmosphere. Water (100 mL) was added, followed by addition of concentrated hydrochloric acid (50 mL). The solution was stirred at 0°C and propionaldehyde (21.8 mL, 0.3 mol) was added over 45 min. The reaction mixture was allowed to warm to room temperature, then heated to 75°C and stirred at this temperature for 21 h. The precipitate was filtered and washed with cold 1:1 ethanol–water solution.

Work up A: Crude product was recrystallized from DMSO, filtered and washed. The product was then recrystallized from acetone giving slightly reddish or colorless stable crystals. Yield 8.0%.

Work up B: Crude product was recrystallized from acetone, filtered and washed yielding a white unstable powder. Yield 3.0%.

Work up C: Crude product was recrystallized from THF, filtered and washed yielding a white stable solid. Yield 5.0%.

In all cases ^{1}H NMR, ^{13}C NMR and MS ESI-TOF the gave same results. Mp $>$ 300°C. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.64 (t, $J = 7.2$, 18H, CH_2CH_3), 1.77 (m, CH_2CH_3, 12H), 4.29 (t, $J = 7.8$, ArCHRAr, 6H), 6.71 (s, ArH, 6H), 7.82 (s (br), OH, 18H). ^{13}C NMR (DMSO-d_6, 126 MHz) δ 12.46, 28.39, 30.60, 114.67, 123.71, 132.01, 140.76. MS ESI-TOF: $[M + Na]^+$ 1019.48. Anal. Calcd. for $C_{54}H_{60}O_{18}{\cdot}1.5H_2O$(%): C, 63.30; H, 6.14. Found: C, 63.55; H, 6.96.

O-Acylated Pyrogall[4]arene 3

To a solution of **1** (0.3 g, 0.4 mmol) in pyridine (20 mL), acetic anhydride (10 mL, excess) was added with vigorous stirring. The reaction mixture was stirred at ambient temperature for 48 h, after which the solution was evaporated, treated with 2 × 100 mL toluene and 1 × 100 mL diethyl ether and evaporated to dryness giving **3** as a white solid. Yield: 0.3 g (87.2%). Mp $>$ 300°C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, $J = 7.3$, CH_2CH_3, 12H), 1.93 (m, $CHCH_2CH_3$), 2.06 (s (br), $OC(O)CH_3$, 12H), 2.15 (s (br), $OC(O)CH_3$, 24H), 4.02 (t, $J = 7.5$, ArCHRAr), 6.37 (s (br), ArH, 4H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 12.69, 19.98, 22.14, 27.67, 39.07, 122.51, 128.21, 134.03, 140.37, 166.36. MS ESI-TOF: $[M + TMA]^+$ 1242.49. Anal. Calcd. for $C_{60}H_{64}O_{24}{\cdot}1/2H_2O$(%): C, 64.21; H, 6.09. Found: C, 64.28; H, 6.93.

O-Acylated Pyrogall[6]arene 4 (Method A)

To a solution of **2** (DMSO/acetone isolated) (0.3 g, 0.3 mmol) in pyridine (100 mL), acetic anhydride (10 mL, excess) was added with vigorous stirring. The reaction mixture was stirred at ambient temperature for 48 h, after which the solution was evaporated, treated with 2 × 50 mL toluene and 1 × 50 mL diethyl ether and evaporated to dryness giving **4** as a white solid. Yield: 0.15 g (28.4%). Mp $>$ 300°C. ESI-TOF: $[M + K]^+$ 1791.60. ^{13}C CP/MAS 11.21, 18.31, 27.05, 39.17, 124.33, 133.37, 135.50, 136.66, 140.40, 169.21, 178.30, 180.28, 185.11. Anal. Calcd. for $C_{90}H_{96}O_{36}{\cdot}0.5DMSO{\cdot}2H_2O$(%): C, 59.76; H, 5.68. Found: C, 59.83; H, 5.56.

O-Acylated Pyrogall[6]arene 4 (Method B)

To a solution of **2** (DMSO/acetone isolated) (0.3 g, 0.3 mmol) in MeCN:THF (100 mL:50 mL), triethylamine (1.05 mL, 75 mmol) and acetyl chloride (0.53 mL, 75 mmol) were added with vigorous stirring. The reaction mixture was stirred at ambient temperature overnight and evaporated to dryness. After trituration with MeCN, the product was filtered and washed with water and MeCN giving **4** as a white solid. Yield 0.17 g (32.2%). Mp $>$ 300°C. ESI-TOF: $[M + K]^+$ 1791.60. ^{13}C CP/MAS 11.21, 18.35, 26.77, 39.30, 124.39, 133.44, 135.52, 136.76, 140.47, 169.38, 178.39, 180.32. Anal. Calcd. for $C_{90}H_{96}O_{36}{\cdot}0.5Et_3N^+HCl^-{\cdot}3H_2O$(%): C, 59.52; H, 5.91; N, 0.37. Found: C, 59.36; H, 5.57; N, 0.25.

Single-crystal X-ray Diffraction

Tetramer **1** was crystallized from DMSO and hexamer **2** from acetone. DMSO found in the crystal structure of **2** is a residue from the recrystallization of the crude product. The dimeric capsule structure was obtained from the co-crystallization attempt of the hexamer recrystallized from acetone in acetone/MeOH solution to which a minimum amount of water was added to dissolve the TMACl salt. The experiment was also performed in DCM/MeOH solution resulting in the same capsule-type tetramer crystal structure. The structure of **2**·6TMACl was obtained by co-crystallization of the hexamer obtained from DMSO/acetone with TMACl in DCM/MeOH solution.

X-ray crystallographic data were measured on a Nonius Kappa CCD diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 173.0 ± 0.1 K. The data were processed with Denzo-SMN v.0.95.373 [20] and all structures were solved by direct methods using SHELXS-97 [21] and refined on F^2 by full-matrix least-squares techniques using SHELXL-97 [22]. The hydrogen atoms for tetramer **1** and hexamer **2** structures were calculated to their

TABLE I Experimental data for the X-ray diffraction studies on **1**·7DMSO, **2**·6DMSO, **1·1**$^-$·TMA·2.25MeOH·0.75$(CH_3)_2CO$ and **2**·6TMACl

	1·7DMSO	**2**·6DMSO	**1·1**$^-$·TMA·2.25MeOH·0.75$(CH_3)_2CO$	**2**·6TMACl
Formula	$C_{36}H_{40}O_{12}$·7$(CH_3)_2SO$	$C_{54}H_{60}O_{18}$·6$(CH_3)_2SO$	$C_{36}H_{40}O_{12}$·$C_{36}H_{39}O_{12}^-$ $(CH_3)_4N^+$· 2.25CH_3OH·0.75$(CH_3)_2CO$	$C_{54}H_{60}O_{18}$·6$(CH_3)_4N^+Cl^-$
Formula weight	1211.58	1465.79	1518.20	1654.60
Crystal system	Triclinic	Hexagonal	Monoclinic	Hexagonal
Space group	$P\bar{1}$ (No. 2)	*R*-3 (No. 148)	$P2_1/n$ (No. 14)	*R*-3 (No. 148)
a/Å	12.5082(3)	24.755(2)	12.0014(2)	28.604(1)
b/Å	14.1608(3)	24.755	23.4273(3)	28.604
c/Å	17.5365(4)	10.3010(4)	26.8212(5)	9.5608(3)
α/°	79.847(1)	90	90	90
β/°	78.820(1)	90	96.2307(6)	90
γ/°	81.0320(9)	120	90	120
V/Å^3	2975.6(1)	5466.7(7)	7496.5(2)	6774.4(5)
Z	2	3	4	3
μ(Mo Kα)/mm^{-1}	0.334	0.263	0.101	0.255
No. of reflections measured	16269	4892	33928	4602
No. of independent reflections	10462	2293	13190	2472
R_{int}	0.034	0.042	0.078	0.050
R/R_w/% for $I > 2\sigma I$	6.08/11.41	9.21/22.05	6.81/13.42	5.17/9.59
Goodness-of-fit	1.031	1.034	1.032	1.016

idealized positions with isotropic temperature factors (1.2 or 1.5 times the carbon temperature factor) and refined as riding atoms. DMSO in **2**·6DMSO is completely disordered over two positions and sulfurs of five DMSO molecules in **1**·7DMSO are disordered over two positions. The temperature factors of some of the disordered atoms of DMSO in **2**·6DMSO were constrained to a reasonable value by equalizing them with the temperature factors of the better part of the disordered molecule.

One of the MeOHs in the capsule structure **1·1**$^-$·TMA·2.25MeOH·0.75$(CH_3)_2CO$ is disordered over two positions and the other MeOH is disordered with a molecule of acetone. No OH proton was determined to the later disorder. Hydrogens for this structure were located from the difference Fourier but in the final refinement they were refined as riding atoms with isotropic temperature factors. Other X-ray data are presented in Table I.

X-ray Data Deposition

X-ray data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos CCDC 204643, 204644, 233978 and 239890.

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