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Serendipity in the Crystallization of a Series of C-Alkylcalix[4]resorcinarenes from Alcoholic Solvents

Aaron Alexander Momose and Eric Bosch*

Chemistry Department, Missouri State University, 901 South National Avenue, Springfield, Missouri 65897.

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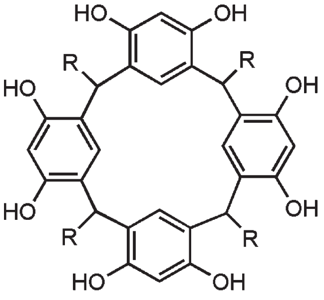
ABSTRACT: The crystal structures of a series of C-alkylcalix[4]resorcinarenes (alkyl = methyl, propyl, butyl, pentyl, hexyl, heptyl, and undecyl), each crystallized from *tert*-butanol, are reported. In all seven of these structures, eight *tert*-butanol molecules link two resorcinarenes with 16 hydrogen bonds, thereby facilitating the formation of simple dimeric hydrogen-bonded capsules, each of which encapsulates one (disordered) *tert*-butanol molecule as guest. These structures are compared with, and contrasted to, those obtained from the same series of resorcinarenes recrystallized both from mixed solvents containing *tert*-butanol and from methanol alone.

Introduction

The versatility of C-alkylcalix[4]resorcinarenes and their derivatives in the formation of hydrogen-bonded capsules, in which multiple resorcinarenes adopt a bowl-like conformation, is well established.[1] The formation of capsules from resorcinarenes should not, however, be considered routine, as the resorcinarenes may adopt one of several nonbowl-like conformations, as amply demonstrated by a series of elegant and extensive studies.[2] Our early studies with resorcinarenes concentrated on the formation of chain-link hydrogen bonded capsules based on the self-assembly of C-methylcalix[4]resorcinarene with bipyrimidines.[3] During the preparation of a series of resorcinarenes for an extension of that study, we encountered some difficulty in obtaining analytically pure products and found that the organic chemists standby, chromatography, was both tedious and largely ineffective. Furthermore, repeated attempts at recrystallization from a host of single and mixed solvents were time-consuming and of limited success until we happened upon *tert*-butanol. Surprisingly, recrystallization from *tert*-butanol, or mixtures of *tert*-butanol with methanol, ethanol, or isopropanol, yielded clear colorless crystals even from highly colored solutions of the crude resorcinarenes for each of the resorcinarenes we prepared (see Scheme 1).

Intrigued by this observation, we subjected a series of crystals to X-ray crystallographic analysis and present evidence herein that *tert*-butanol is particularly successful for crystallization/purification of C-alkylresorcinarenes, since it not only serves as hydrogen-bond acceptor and donor linking the resorcinarenes into dimeric capsules but is itself also included as a guest within the capsules. While other alcohols are clearly equally efficient as hydrogen bond acceptors and donors, it is the size and shape of *tert*-butanol that is crucial for its inclusion as guest within the dimeric capsules. These observations will be compared and contrasted to other studies of the aggregation of resorcinarenes both in the solid state and in solution.

Scheme 1



R = propyl, butyl, pentyl, hexyl, heptyl, undecyl

Experimental Section

General Procedure for the Synthesis of Calix[4]resorcinarenes.[4] Resorcinol (8.81 g, 80 mmol), aldehyde (80 mmol), and 95% ethanol (80 mL) were added to a 200 mL round-bottom flask equipped with a magnetic stir bar. The solution was sparged with argon for 15 min, and concentrated HCl (13 mL) was then added. The solution was refluxed under an argon atmosphere for 18 h and then cooled to room temperature and poured into a separatory funnel containing 80 mL of diethyl ether. 360 mL of brine was added, and the organic layer was separated, dried over magnesium sulfate, and evaporated under vacuum to produce the crude product as a yellow/brown solid. The crude product was recrystallized twice from 4:1 *tert*-butanol/methanol and dried at 100 °C under vacuum for 30 min to afford the calix[4]resorcinarene in more than 80% yield.

Preparation of Crystals. Approximately 20 mg of the resorcinarene was placed in a screw cap vial and dissolved in the minimum volume of hot *tert*-butanol. Crystals generally began to form after several days and were harvested for X-ray analysis directly from the mother liquor. Commercially available C-methylresorcinarene (Aldrich) was also recrystallized from *tert*-butanol with a small amount of methanol as cosolvent. The resultant complexes of *tert*-butanol with methyl-, propyl-, butyl-, pentyl-, hexyl-, heptyl-, and undecylresorcinarene respectively, are numbered **1**−**7**, respectively. Similar procedures were used for recrystallization from mixed solvents or from methanol alone. The C-butylcalix[4]resorcinarene complex was recrystallized from methanol/*tert*-butanol, and the crystalline complex **8** included both *tert*-butanol and methanol in a *tert*-butanol/methanol/C-butylresorcinarene ratio of 5:4:2. Recrystallization of purified C-propylresorcinarene and

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*To whom correspondence should be addressed. Telephone: 417-823-8735. Fax: 417-836-5507. E-mail: ericbosch@missouristate.edu. Web: http://chemistry.missouristate.edu/31072.htm.

Table 1. Crystal Data for C-Alkylresorcinarene Complexes with *tert*-Butanol

complex	**1**, C-methyl	**2**, C-propyl	**3**, C-butyl	**4**, C-pentyl	**5**, C-hexyl	**6**, C-heptyl	**7**, C-undecyl
formula	$C_{50}H_{77}O_{12.5}$	$C_{58}H_{93}O_{12.5}$	$C_{62}H_{101}O_{12.5}$	$C_{66}H_{109}O_{12.5}$	$C_{70}H_{117}O_{12.5}$	$C_{76}H_{130}O_{13}$	$C_{91}H_{157}O_{13}$
M/(g mol^{-1})	878.12	990.32	1046.43	1102.53	1158.64	1251.80	1467.17
crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P21/n$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a/Å	15.2339(8)	15.1886(8)	15.352(2)	15.2253(13)	15.1627(18)	15.2662(12)	15.2237(12)
b/Å	18.7155(10)	15.5624(8)	15.722(2)	15.5029(13)	15.7027(18)	15.6752(12)	15.7919(13)
c/Å	18.5473(10)	15.97878(14)	16.276(2)	17.3279(14)	17.246(2)	18.6790(15)	22.0893(18)
α/deg	90	104.897(1)	113.402(2)	104.9870(10)	111.205(2)	113.1150(10)	106.962(1)
β/deg	98.166(1)	113.095(1)	106.967(2)	113.9090(10)	101.202(2)	100.7750(10)	92.499(1)
γ/deg	90	105.025(1)	103.345(2)	100.9750(10)	102.036(2)	101.8430(10)	101.835(1)
V/Å^3	5234.4(5)	3069.5(4)	3167.84(7)	3404.1(5)	3597.6(7)	3841.7(5)	4941.1(7)
Z	2	2	2	2	2	2	2
$\rho_{calcd.}$/(g cm^{-3})	1.115	1.071	1.097	1.076	1.070	1.082	0.986
μ/mm^{-1}	0.079	0.074	0.075	0.072	0.071	0.072	0.064
F(0,0,0)	1908	1082	1146	1210.0	1274	1380	1622
crystal size, mm^3	0.32 × 0.28 × 0.22	0.63 × 0.42 × 0.39	0.32 × 0.18 × 0.09	0.22 × 0.19 × 0.15	0.61 × 0.27 × 0.18	0.38 × 0.12 × 0.12	0.20 × 0.30 × 0.40
temp/K	100(2)	135(2)	100(2)	100(2)	100(2)	100(2)	140(2)
θ range/deg	1.6−27.1	1.5−25.0	1.5−26.4	1.4−26.0	1.3−27.3	1.2−25.0	1.0−25.0
reflections collected	62832	33061	34383	36176	45359	40308	53133
independent reflections	11557	10789	12894	13358	15963	13519	17409
data/restraints/parameters	11557/2/712	10789/2/846	12894/2/747	13358/1/781	15963/0/785	13519/15/850	17409/53/939
GOF	1.022	1.023	0.963	1.014	1.012	1.027	1.119
R(int)	0.079	0.040	0.097	0.057	0.070	0.091	0.084
final R indices [$I > 2\sigma(I)$], $R1/wR2$	0.057/0.152	0.053/0.155	0.062/0.141	0.057/0.144	0.065/0.183	0.099/0.196	0.111/0.4000
largest diff peak/hole/(e Å^3)	0.50/−0.39	0.62/−0.41	0.39/−0.53	0.76/−0.44	0.43/−0.43	0.76/−0.48	0.59/−0.35

C-pentylresorcinarenes from methanol alone yielded single crystals, suitable for X-ray analysis, of complexes **9** and **10** respectively.

X-ray Structure Determination. Crystals were mounted on fine glass fibers using viscous hydrocarbon oil. Data were collected using a Bruker Apex2 CCD diffractometer equipped with Mo Kα radiation with $\lambda = 0.71073$ Å. Data collection at low temperatures was facilitated by use of a Kryoflex system with an accuracy of ±1 K. Initial data processing was carried out using the Apex II software suite.[5] Structures were solved by direct methods using SHELXS-97 and refined using standard alternating least-squares cycles against F2 using SHELXL-97.[6] The program X-Seed was used as a graphical interface.[7] Methine and methylene hydrogen atoms attached to carbon were placed in idealized positions and refined with a riding model. Methyl hydrogen atoms attached to carbon were positioned according to maximum electron density. Hydrogen atoms attached to oxygen were generally placed based on electron density peaks in the difference maps. Crystallographic details for complexes **1**−**7** and **8**−**10** are summarized in Tables 1 and 2, respectively.

Special Refinement Details. Since most structure solutions followed the same general sequence, the structure determination for complex **1** will be presented and differences then discussed for each individual structure. Thus, for complex **1**, the asymmetric unit consists of one C-methylresorcinarene with four *tert*-butanol molecules hydrogen-bonded to the resorcinarene hydroxyl groups as well as one-half of a *tert*-butanol molecule inside the bowl-shaped cavity of the resorcinarene. Solution/refinement of the resorcinarene and three of the four hydrogen bonded *tert*-butanol molecules was routine. In each of these molecules the acidic hydroxyl hydrogen atoms were placed based on peaks in the difference maps. Two of the hydrogen bonded *tert*-butanol molecules were disordered over two positions. One was disordered only with respect to the methyl groups, while all the carbons were disordered over two positions for the other *tert*-butanol. Both were therefore refined over these two positions with free variables which converged to 0.44 and 0.5, respectively. The central *tert*-butanol was refined as a disordered molecule over two major positions. The central carbon atom (C49) was assumed to be at an average position between the two true positions of the disordered central carbon. The oxygen atom (O13) was assigned based on the shortest bond to the central carbon atom. The hydrogen on the oxygen was positioned using a riding model. The central carbon and the oxygen atom were then set at 50% occupancy while the other two carbon atoms (C50 and C51) were set at 75% occupancy. With this assignment this portion of the asymmetric unit represents half of a *tert*-butanol molecule ($C_2H_5O_{0.5}$). Thermal ellipsoid parameters and bond lengths were understandably large for this central disordered molecule. Thus, the bond lengths for C49−O13, C49−C50, and C49−C51 were longer than those expected at 1.487, 1.676, and 1.659 Å. The six highest Q peaks (0.3 to 0.5) were, not surprisingly, all located around the central disordered *tert*-butanol. These latter results were fairly typical.

Table 2. Crystal Data for Complexes Formed in the Presence of Methanol

complex	**8**, C-butyl	**9**, C-pentyl	**10**, C-propyl
formula	$C_{56}H_{89}O_{12.5}$	$C_{25}H_{36}O_5$	$C_{45}H_{68}O_{13}$
M/(g mol^{-1})	962.27	417.54	816.99
crystal system	triclinic	monoclinic	triclinic
space group	$P\overline{1}$	$C2/c$	$P\overline{1}$
a/Å	14.6157(11)	13.9179(14)	11.3939(14)
b/Å	15.0200(132)	23.2095(14)	12.9275(16)
c/Å	15.481(2)	14.575(1)	15.898(2)
α/deg	106.670(2)	90	81.150(2)
β/deg	107.365(2)	90.126(2)	79.891(2)
γ/deg	104.3930(10)	90	79.710(2)
V/Å^3	2892.4(5)	4708.1(6)	2247.8(5)
Z	2	4	2
$\rho_{calcd.}$/(g cm^{-3})	1.105	1.175	1.206
μ/mm^{-1}	0.076	0.080	0.087
F(0,0,0)	1050	1808	884.0
crystal size, mm^3	0.54 × 0.28 × 0.26	0.53 × 0.34 × 0.15	0.34 × 0.14 × 0.14
temp/K	173(2)	173(2)	100(2)
θ range/deg	1.5−25.0	1.7−25.0	1.31−25.0
reflections collected	31441	25186	12068
independent reflections	10192	4158	7636
data/restraints/parameters	10192/6/680	4158/16/341	7636/0/584
GOF	1.017	1.030	1.014
R(int)	0.071	0.056	0.036
final R indices [$I > 2\sigma(I)$], $R1/wR2$	0.060/0.2046	0.047/0.128	0.053/0.132
largest diff peak/hole/(e Å^3)	0.35/−0.33	0.33/−0.23	0.44/−0.27

For complex **4** the central *tert*-butanol was somewhat better defined. Thus, the central carbon atom (C66) was not disordered over two positions—rather it shared a location with the third methyl group of the second disordered position. C66 was therefore modeled with an occupancy of 100% while the other two carbon atoms

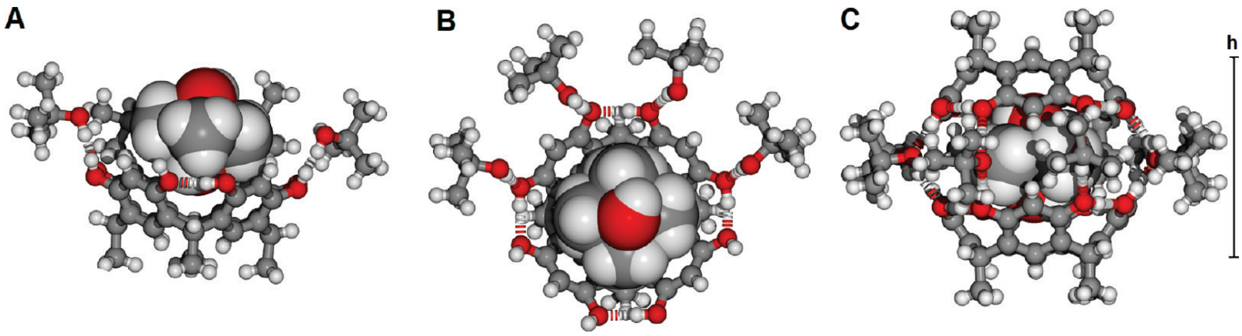

Figure 1. (A) Side view of the asymmetric unit of the C-methylresorcinarene complex, **1**, containing one C-methylresorcinarene and four hydrogen-bonded peripheral *tert*-butanols and one-half of an encapsulated *tert*-butanol. The inner *tert*-butanol is shown as a space filling model disordered over two positions: (B) top view of the asymmetric unit; (C) side view of the capsule comprising two hydrogen bonded resorcinarenes.

(C65, C67) were modeled with occupancies of 50%. The oxygen atom (O13) was assigned based on the shortest bond to the central carbon atom. The hydrogen on the oxygen was positioned using a riding model. The thermal ellipsoid for C66 is, as expected, unusually large. Also, the two highest Q peaks (0.7 and 0.42) appear close to the end of one pentyl chain (C32 and C33 specifically). This was modeled as disorder with a free variable; however, this minor component of the terminus of the chain only corresponded to about 10% occupancy for the side chain. Furthermore, the atoms could not be refined anisotropically. Consequently, this minor disorder model was not included.

For complex **6** an extra *tert*-butanol was included in the asymmetric unit close to one of the resorcinarene O-atoms. The aromatic portion of the resorcinarene and the *tert*-butanols and two legs of the resorcinarene were well-defined; however, the ends of the other two legs were disordered and restraints were used to solve the structure. The same general comments apply to the undecyl derivative, complex **7**. Two of the legs of the resorcinarene were modeled as disordered over two major positions. Restraints were also used extensively during refinement. The remaining disordered center of electron density was modeled as a disordered methanol.

For complex **8** the asymmetric unit consists of one resorcinarene with two *tert*-butanol molecules and two methanol molecules bonded to the resorcinarene hydroxyl groups as well as one-half of a *tert*-butanol molecule inside the bowl-shaped cavity of the resorcinarene. The refinement of the resorcinarene and the two hydrogen bonded *tert*-butanols and two hydrogen bonded methanols was routine. In each of these molecules the acidic hydroxyl hydrogen atoms were placed based on peaks in the difference maps.

For complex **9**, the asymmetric unit contained half of one C-pentylresorcinarene molecule and two methanol molecules, each of which is positioned along an axis of symmetry. Hydrogen atoms on the resorcinol oxygen atoms were located based on difference maps and were found to occupy two major positions, each with approximately 50% occupancy. One pentyl chain, C20−C21−C22−C23−C24, was disordered and refined over two positions, with the major component having 80% occupancy. Anisotropic refinement of the terminal methyl group of the minor conformation resulted in it going nonpositive definite, and therefore, the ISOR command was used with this atom.

For complex **10** the asymmetric unit contained one C-propylresorcinarene molecule and five methanol molecules. The refinement of the resorcinarene and the methanols was routine. In each of these molecules, the acidic hydroxyl hydrogen atoms were placed based on peaks in the difference maps.

Results and Discussion

The formation and crystallographic characterization of dimeric capsules by crystallization of C-alkylresorcinarenes from *tert*-butanol solutions will first be described. These structures will then be compared and contrasted with the crystal structures of some of the same resorcinarenes crystallized either from mixed solvents including *tert*-butanol or from methanol alone.

The series of C-alkyl resorcinarenes shown in Scheme 1 was prepared by hydrochloric acid catalyzed reaction of the corresponding aldehyde with resorcinol at reflux in deaerated ethanol under an argon atmosphere.[4] The crude products were recrystallized from *tert*-butanol or mixtures of *tert*-butanol with one of the alcohols methanol, ethanol, or isopropanol as cosolvent. Gentle heating under high vacuum then afforded the C-alkyl calix[4]resorcinarenes as colorless solids, free of the alcohols, in more than 80% yield.

Crystallization from *tert*-Butanol. Crystals suitable for X-ray analysis were prepared in small screw-capped vials or test tubes by crystallization of the resorcinarene from warm *tert*-butanol. Commercially available C-methylresorcinarene (Aldrich) was also recrystallized from *tert*-butanol with a small amount of methanol as cosolvent.

X-ray Crystallographic Analysis. The crystallographic data for this series of compounds was collected at 100 K (see Tables 1 and 2) with the exception of those crystals which cracked when cooled to 100 K. For complex **1**, the asymmetric unit was found to consist of a C-methylresorcinarene in the bowl conformation along with four *tert*-butanol molecules hydrogen-bonded to four resorcinarene hydroxyl groups and one-half of a *tert*-butanol molecule nestled inside the bowl-shaped cavity of the resorcinarene. The C-methylresorcinarene is held in the bowl conformation by four phenol−phenol hydrogen bonds with O···O bond distances ranging from 2.628 to 2.676 Å. The phenol−*tert*-butanol hydrogen bonds had O···O bond distances ranging from 2.573 to 2.801 Å. Two of the hydrogen bonded *tert*-butanol molecules were disordered over two positions with relative occupancies of 50:50 and 44:56, respectively. One of these was disordered only with respect to the methyl groups while all the carbons were disordered over two positions for the other *tert*-butanol. The inner *tert*-butanol was disordered over two major positions with the central carbon atom at an average position between the two true positions of the disordered central carbon. The asymmetric unit is shown in Figure 1A and B, showing one conformation of each of the disordered peripheral *tert*-butanol molecules. The encapsulated *tert*-butanol is shown as a space filling model disordered over both positions. Two of these asymmetric units then combine to form a dimeric capsule, with each of the eight *tert*-butanol molecules acting as both hydrogen bond donor and hydrogen bond acceptor, thereby stitching the rim of the two resorcinarene molecules together with a total of 16 hydrogen bonds (Figure 1C).

The X-ray structures of the series of C-alkylresorcinarenes **1**−**7** are very similar. In each case a hydrogen-bonded capsule is formed with two bowl-conformation resorcinarenes stitched together by 16 hydrogen bonds with eight *tert*-butanol molecules.

Table 3. Structural Characteristics of the *tert*-Butanol Complexes

complex	**1**, C-methyl	**2**, C-propyl	**3**, C-butyl	**4**, C-pentyl	**5**, C-hexyl	**6**, C-heptyl	**7**, C-undecyl
arene−arene distance[a]	6.834, 6.837	6.658, 6.871	6.798, 6.870	6.816, 6.866	6.809, 6.849	6.797, 6.893	6.788, 6.885
complex height[b]	9.127	9.014	9.095	9.109	9.061	9.046	9.097
intramolecular H-bond O···O	2.628−2.676	2.659−2.691	2.634−2.689	2.651−2.677	2.642−2.688	2.650−2.703	2.677−2.682
distance[c] (range, avg)/Å	2.658	2.679	2.665	2.669	2.677	2.682	2.680
tert-butanol H-bond O···O	2.573−2.801	2.615−2.782	2.592−2.766	2.613−2.743	2.606−2.715	2.659−2.746	2.592−2.765
distance[d] (range, avg)/Å	2.706	2.678	2.692	2.656	2.648	2.710	2.691

[a] Arene centroid−arene centroid across the resorcinarene. [b] Distance between planes defined by methine C's on the resorcinarenes. [c] Phenol OH hydrogen bonds. [d] *tert*-Butanol−phenol hydrogen bonds.

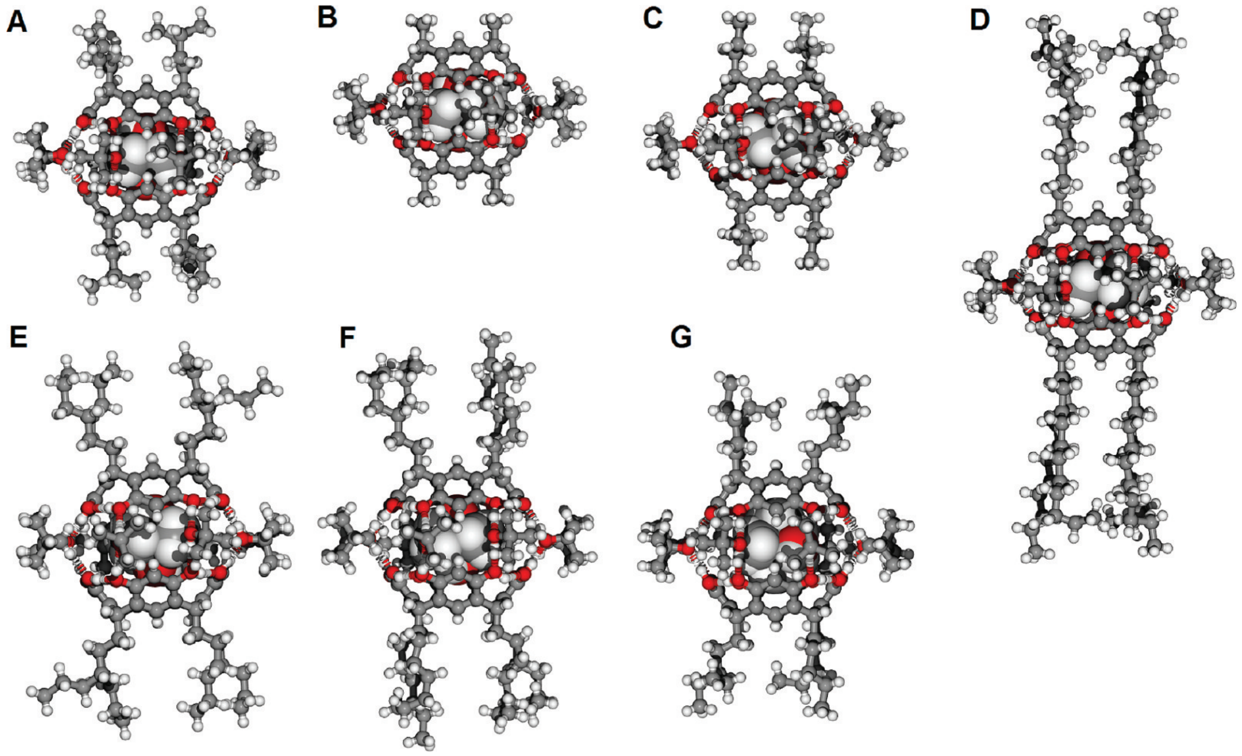

Figure 2. View of individual capsules formed between each of the C-alkylresorcinarenes and *tert*-butanol taken from the corresponding X-ray structures: (A) C-butylcalix[4]resorcinarene, **3**; (B) C-methylcalix[4]resorcinarene, **1**; (C) C-propylcalix[4]resorcinarene, **2**; (D) C-undecylcalix[4]resorcinarene, **7**; (E) C-hexylcalix[4]resorcinarene, **5**; (F) C-heptylcalix[4]resorcinarene, **6**; (G) C-pentylcalix[4]resorcinarene, **4**.

Within each resorcinarene there are four intramolecular hydrogen bonds between adjacent resorcinol units that ensure the bowl-like resorcinarene conformation is adopted. The O···O distances in these phenol−phenol H-bonds range from 2.63 to 2.70 Å for all structures (see Table 3). The *arene centroid−arene centroid* distance measured diagonally across the bowl-shaped resorcinarene is consistent—varying from 6.66 to 6.87 Å for all the structures. Furthermore, the hydrogen-bonding O···O distances for the intermolecular H-bonds between the resorcinarene and the *tert*-butanol molecules vary between 2.57 and 2.80 Å for all structures. Not unexpectedly then, the "height"'of each capsule, *h*, measured between the planes defined by the methine hydrogens on each resorcinarene, is almost the same in all the capsules, varying between 9.014 and 9.127 Å ("*h*" is shown in Figure 1C). In all the structures, the encapsulated *tert*-butanol molecule is disordered over two positions within the dimeric assembly. This similarity is demonstrated in Figure 2, which shows the dimeric capsules **1**−**7**. The inner *tert*-butanol molecule is shown as a space filling model disordered over both positions.

We were interested in the packing between adjacent capsules and show partial packing diagrams for complexes **3**−**7** in Figure 3. This figure clearly demonstrates the role of van der Waals forces. The polar portion of the capsule, the hydrogen bonded central seam, is effectively hidden by the bulk of the tertiary butyl group, which effectively renders the complete exterior of the capsule hydrophobic. The *tert*-butyl groups have close contact with the methyl groups on the alkyl chains in all five structures. While there is initially little interaction between alkyl chains of adjacent capsules, this increases with the hexyl derivative, where there is significant interdigitation of the alkyl chains of adjacent resorcinarenes that increases with increasing chain length.

Mixed Alcohol Structures. We occasionally noted that the solubility of the resorcinarenes was relatively low in pure *tert*-butanol, so a cosolvent such as methanol or ethanol was used. Indeed, on a practical level, crystallization of the crude resorcinarenes from a mixture of methanol and *tert*-butanol was often the method of choice. We selected a crystal of the C-butylcalix[4]resorcinarene complex recrystallized from methanol/*tert*-butanol for X-ray analysis. The structure of this complex, **8**, shown in Figure 4 clearly shows the same general structure observed in complexes **1**−**7** with the exception that two methanol molecules replace two of the peripheral *tert*-butanols as the linking hydrogen bond donor−acceptor. The dimensions of the capsule are very similar to those reported in Table 2. For example, the diagonal intramolecular arene−arene distances

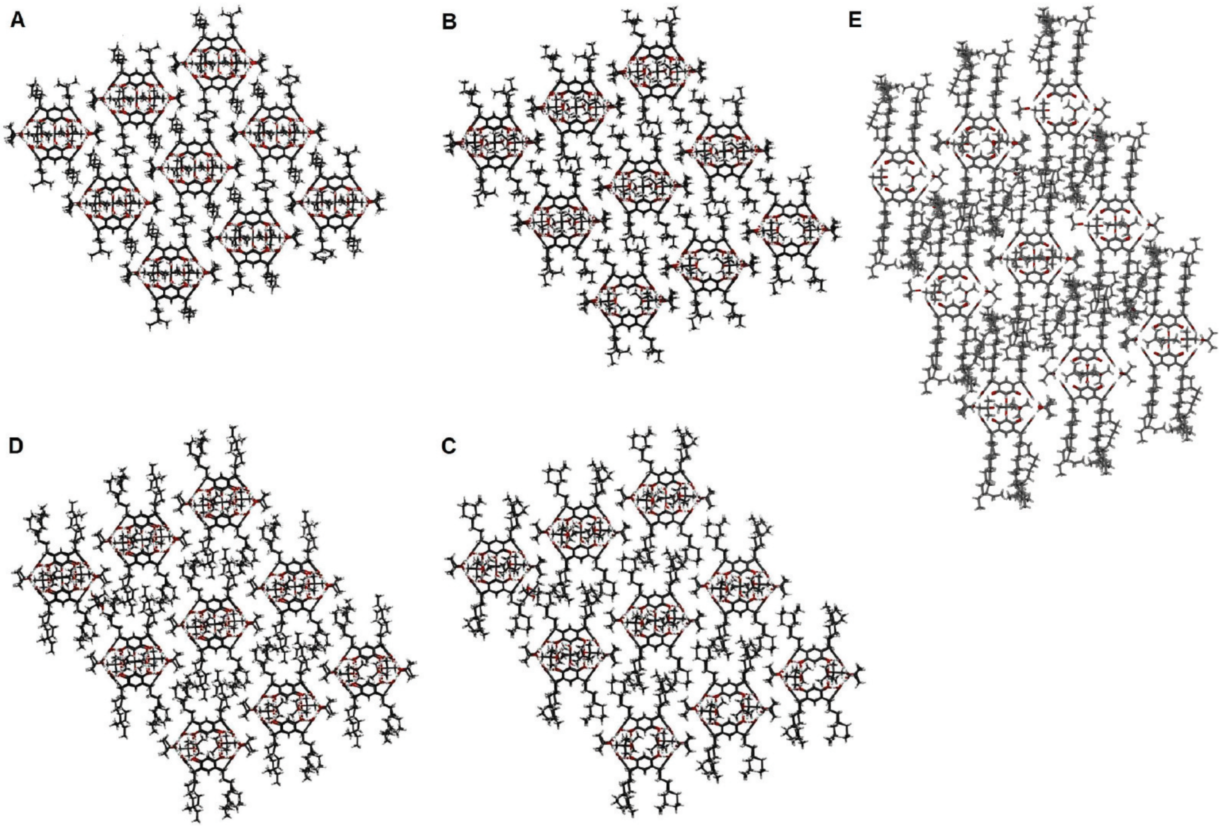

Figure 3. Packing of the complexes formed between C-alkylresorcinarenes and *tert*-butanol, showing the interaction between the alkyl chains: (A) C-butylresorcinarene; (B) C-pentylresorcinarene; (C) C-hexylresorcinarene; (D) C-heptylresorcinarene; (E) C-undecylresorcinarene.

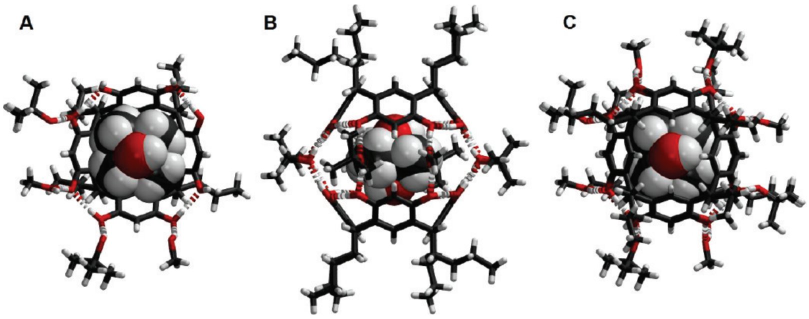

Figure 4. (A) View of the asymmetric unit of complex **8** formed between C-butylresorcinarene and *tert*-butanol and methanol. (B) Side view of the capsule and (C) top view of the capsule.

are 6.758 and 6.917 Å while the "height" of the capsule is 9.196 Å.

Methanol Structures. Recrystallization of the crude resorcinarenes from methanol alone was generally unsuccessful in terms of growing crystals and, in contrast to the use of *tert*-butanol, generally required several successive recrystallizations to generate colorless material. Nevertheless, we prepared X-ray quality crystals by crystallization of purified C-propylresorcinarene and C-pentylresorcinarenes from methanol alone (structures **9** and **10**, respectively). While the resorcinarene adopts the bowl conformation in both structures, hydrogen bonded network type structures are formed in lieu of capsule formation in the absence of a suitable guest. In structure **10** the asymmetric unit consists of a C-propylcalix[4]resorcinarene and five methanol molecules, as shown in Figure 5A. These components form one-dimensional bilayered hydrogen-bonded ribbons with the resorcinarenes arranged in an off-center head-to-head arrangement. The ribbons stack on top of each other with interdigitation of the propyl chains as shown in Figure 5B. The one-dimensional ribbons are held together by bifurcated hydrogen bonds as shown in Figure 5C. Thus, O1H is hydrogen bonded to both O4 of an adjacent resorcinarene as well as O8 in the neighboring resorcinol moiety. The hydrogen bonds are characterized by O−O distances of 3.006 and 2.836 Å for O1−O8 and O1−O4, respectively, and O−H−O angles of 137.71 and 137.86° for O1−H1O−O8 and O1−H1O−O4, respectively.

Comparison to Previously Published Crystal Structures of Hydrogen Bonded Dimeric Resorcinarene Capsules. Not surprisingly, many of the resorcinarene structures in the Cambridge database contain alcohol molecules. For example, when this manuscript was in preparation, there were 114 structures containing C-methylcalix[4]resorcinarene collected in the Cambridge database and 21 of those structures contained alcohols. Many of these alcohols combine via hydrogen-bonding either to the resorcinarene or, in some instances, to the amines that were cocrystallized with the resorcinarene. In a few isolated cases, the

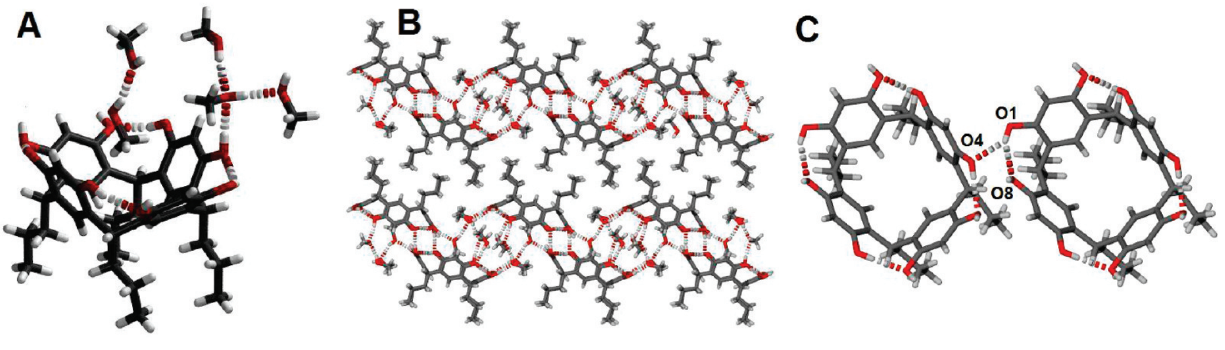

Figure 5. (A) Asymmetric unit of the complex formed between C-propylresorcinarene and methanol showing the bowl-conformation. (B) Packing of the complex showing the hydrogen bonded network in one dimension and the interdigitation of the propyl chains. (C) Cross-linking bifurcated hydrogen bonds between adjacent ribbons of the hydrogen bonded complexes shown in part B.

alcohol facilitates the formation of discrete capsules containing two resorcinarenes. An early example of the formation of a discrete dimeric capsule containing two C-phenethylresorcinarenes linked by isopropanol molecules was reported by Atwood and Barbour in 1998.[8] In that structure, the authors were unable to definitively locate solvent molecules within the capsule and speculated that a mixture of isopropanol and 1,2-dichlorobenzene may have been included. It is, however, noteworthy that Rissanen and co-workers reported the encapsulation of small ammonium cations of similar size to *tert*-butanol, like diethyldimethylammonium cation, in alcohol bridged dimeric capsules.[1b,9,10] In this series of structures, ethanol or methanol molecules, occasionally in combination with water molecules, hydrogen bonded the two resorcinarenes together. Also, Aoki had earlier shown that water can bridge two resorcinarenes in the encapsulation of the similarly sized tetramethylammonium cation by two C-ethylresorcinarenes.[11] In another report, the encapsulation of triethylammonium cation was also facilitated by water molecules bridging between two resorcinarenes.[12] In other structures reported,[13,9] chloride and bromide were also shown to bridge two resorcinarenes to encapsulate an ammonium cation and mixed bridging ligands were observed (i.e., water and halide or alcohol and halide). Furthermore, Rissanen and co-workers noted that crystallization of C-ethyl resorcinarene from ethanol[14] resulted in a hydrogen bonded complex in which the resorcinarene adopted the cone- or bowl-like conformation and the ethanol molecules were involved in multiple hydrogen bonds without capsule formation. A similar observation can be made of the structure of the C-benzylresorcinarene crystallized from methanol reported by Rebek and co-workers.[15] These related studies serve to confirm that dimeric alcohol-bridged resorcinarene capsules may be formed provided that an appropriately sized guest is available. Consequently, while crystallization from alcohols alone is rare and seldom results in the formation of dimeric capsules, the formation of dimeric capsules occurs in our case because *tert*-butanol is an appropriately sized guest.

Comparison to Studies of Resorcinarene Aggregation in Solution. In addition to the reports of dimeric capsule formation described in the previous section, there is considerable interest in the significantly larger hexameric capsules reported by MacGillivray and Atwood in 1997.[16] The hexamer included eight water molecules in the framework, and the superstructure was held together by a total of 60 hydrogen bonds. Mattay and co-workers reported the crystal structure of a similar hexameric superstructure based on pyrogalloarene.[17] More recently, Ogano and Holman reported that six of the water molecules in the superstructure could be replaced by alcohols provided that the correct alcohol was chosen.[18] Thus, they noted that crystallization in the presence of 2-ethylbutanol or 2-butanol yielded dimeric capsules while crystallization in the presence of 2-ethylhexanol yielded the hexameric capsule with six alcohol and two water molecules included in the framework. These authors also noted that crystallization of resorcinarenes in the presence of other alcohols did not yield capsules. These observations are nicely complimented by Mattay and co-workers' elegant study of the nature of resorcinarene assembly with alcohols in apolar solvents.[19] In that study, diffusion NMR spectroscopy was used to determine the nature of the resorcinarene assemblies. The authors concluded that dimeric capsules were formed in dry $CDCl_3$ containing 2-butanol while hexameric capsules were formed in 2-ethylhexanol. Given the results here, it is reasonable to propose that dimeric capsules would also be formed in dry $CDCl_3$ solution if *tert*-butanol were added as cosolvent.

Conclusions

We have clearly demonstrated that use of *tert*-butanol in the crystallization of crude C-alkylresorcinarenes provides good yields of colorless, crystalline products that comprise dimeric capsules, formed between two resorinarenes and eight *tert*-butanol molecules, that encapsulate a single disordered *tert*-butanol molecule. These results are consistent with previously reported solution and solid state studies of dimeric and hexameric resorcinarene capsule formation. Furthermore, it is apparent that dimer capsule formation is favored provided that an appropriate guest molecule is available—in this case *tert*-butanol.

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Supporting Information Available: X-ray crystallographic information files (CIF) are available for complexes **1**−**10**. This information is available free of charge via the Internet at http://pubs.acs.org/.

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