

Symmetry induced supramolecular assembly of a resorcinarene trimeric molecular box

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A novel trimeric resorcinarene molecular box is induced during hydrothermal synthesis by use of the 3-fold symmetric tripyridyl triazine linker molecule.

Molecular containers such as cages, capsules and carcerands can find application in molecular recognition, materials, drug delivery and separation science.^{1,2} Calixarenes, calixresorcinarenes, pyrogalloarenes and their related derivatives are important families for assembling such materials, as they can form capsules through hydrogen-bonding with short bridges such as water,³ halides⁴ or alcohol⁵ molecules and longer spacers like bipy and bpe.⁶ Such capsules are capable of including a variety of charged as well as neutral guest species.

The capsule formation is not limited to dimeric resorcinarene assemblies. Notably, resorcinarenes can self-arrange into an Archimedean snub cube structure, with six resorcinarenes forming the sides and eight water molecules located at the truncated corners of the cube,⁷ an assembly that exists in both solid and solution. Other similar assemblies are clearly possible. We have pointed out that symmetry mismatching between linker and node molecules may lead to multiple-cavity solids, or induce an assembly of node molecules with the symmetry of the linker,⁸ and describe here an example of the second possibility, resulting in a solid containing pillbox-like trigonal prismatic resorcinarene trimers, capped on each side by a water molecule. Different solvent molecules have been included to give three isomorphous structures: [3CECR·2H₂O·G]·2tpt·3G (CECR = C-ethylcalix[4]resorcinarene; tpt = 1,3,5-tri(4-pyridyl)-2,4,6-triazine (Scheme 1); G = benzene **1a**; *o*-xylene **1b**; cyclohexane **1c**). The trigonal prisms are connected into novel 2D sheets by the tpt linker molecules.

Good quality crystals of **1** were prepared under hydrothermal conditions.[†] They are poorly soluble in methanol, ethanol, acetonitrile, CHCl₃ and CH₂Cl₂ etc. and decompose in DMSO.

Low temperature X-ray diffraction analysis shows the compounds to be isostructural⁹ and to contain a disk-like molecular box formed by three resorcinarenes and two water molecules linked by O–H···O hydrogen bonding, with crystallographic C_{3h} symmetry, as illustrated in Fig. 1a. The molecular box has the shape of a trigonal prism,¹⁰ in which the rectangular faces correspond to CECRs and the triangular faces correspond to water molecules (Fig. 1b). The oxygens of two water molecules are located on the 3-fold axis, while the mirror planes bisect the two opposing phenyl rings of each CECR. The angle between these two phenyl rings is relatively large at 115.2–117.7°, while the second opposing set of phenyl rings are almost parallel to the mirror plane with an interplanar angle of 14.4–20.1°, allowing simultaneous hydrogen bonding with two hydroxyl groups from the same phenolic ring of an adjacent resorcinarene. This is a bowl-shaped structure, distorted towards the boat conformation (Fig. 1c). The box has an approximate diameter of 10 Å. Two water molecules serve as

bottom and cap of its cavity to give a box height (the distance between the two water molecules) of approximate 6.8 Å (Figs. 1a and 1d). In **1a** one benzene guest molecule with C_{3h} symmetry, is encapsulated within box. The encapsulated *o*-xylene in **1b** and cyclohexane guests in **1c** are disordered because of the 3-fold axis being imposed on the non-axially symmetric guest molecules.

In **1a** and **1b** all hydrogen atoms were located directly, thus allowing complete analysis of hydrogen bonding. The hydrogen bond patterns of the O1–H, O2–H and O4–H hydroxyl groups can be unambiguously established given their chemical environment. The hydrogen bond arrangement of the water molecule and the connected O3 hydroxyl groups from the resorcinarenes is complex because of the symmetry-imposed disorder of the water molecule. The two hydrogen atoms of the water molecule must be distributed over three positions.¹¹ They form hydrogen bonds to the phenolic oxygen atoms from two different CECR molecules, O3 of a third CECR is a hydrogen bond donor in a bond with the water's oxygen atom. This results in the breaking of a pair of intramolecular hydrogen bonds in one CECR, while the other two CECR's retain their four intramolecular hydrogen bonds.

Thus, two of the resorcinarenes are fully hydrogen bonded while in the third the typical bowl-type H-bonding scheme which includes an H-bond between O3 and O4 is interrupted. As a result O4 in the crystal is disordered over two positions as indicated by the anisotropic atomic displacement parameters of O4 in **1a** and in **1b**, which are larger by a factor of about three parallel to the mirror plane compared to the other directions. The O3–O4_{average} separa-

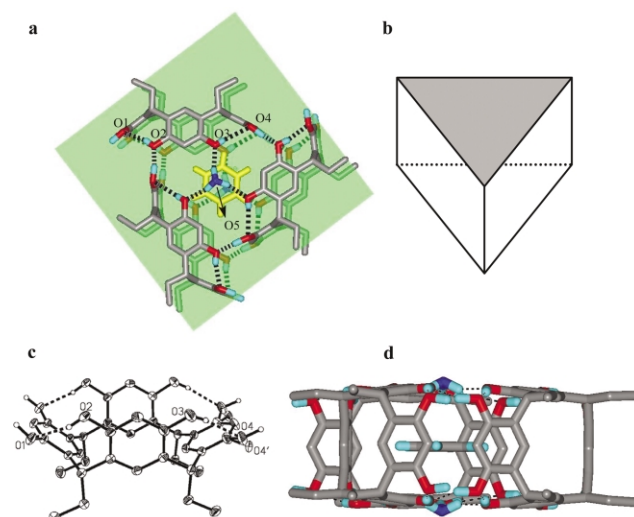
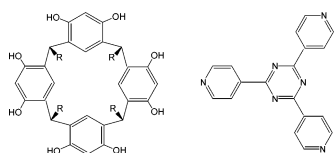


Fig. 1 (a) Top view of trimeric molecular box 3CECR·2H₂O in **1a**. Intra- and inter-molecular hydrogen bonds in **1a**: O2···O1 = 2.794(2) Å, O2–H2···O1 = 165(2)°; O3···O4 = 3.065(2) Å, O3–H3···O4 = 174(2)°; O4···O2a = 2.676(2) Å, O4–H4···O2a = 161(2)°; O5···O3b = 2.8048(7) Å, O5–H5···O3b = 155(2)°; [a –y + 1, x – y, z; b y, –x + y + 1, –z + 1]. (b) The trigonal prism polyhedron. The rectangular faces correspond to the CECRs and triangular faces correspond to the water molecules. (c) Bowl shaped resorcinarene conformation in **1a**. The mirror plane is vertical in the picture and the H-bond scheme shown is that of two of the three CECR molecules. (d) Side view of trimeric molecular box in **1a**, with the mirror plane horizontal and perpendicular to the plane of the paper.



Scheme 1

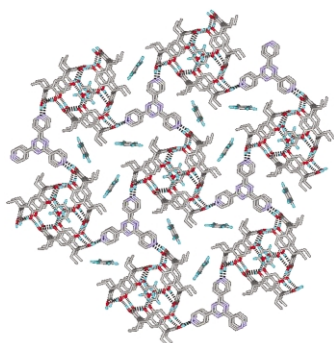


Fig. 2 Two-dimensional architecture formed by tpt dimers connecting resorcinarene trimeric molecular boxes through hydrogen bonding [$O1 \cdots N1 = 2.684(2)$ Å, $O1-H1 \cdots N1 = 173(2)^\circ$] in **1a**.

tions (3.065 and 3.184 Å for **1a** and **1b**, respectively) are significantly longer than other hydrogen bond donor–acceptor distances, which is consistent with the disordered 2-position model. In **1c**, the separation is larger, allowing refinement of two O4 positions with an occupancy ratio of 0.68/0.32 (essentially 2 : 1) and corresponding O3–O4/O4' distances of 2.927/3.473 Å, giving further support to the hybrid resorcinarene conformation.

In contrast to the 36 intermolecular hydrogen bonds for six resorcinarenes and eight water molecules in the *C*-methylcalix[4]resorcinarene hexamer capsule,⁷ the trimeric molecular box is held together by 12 intermolecular hydrogen bonds distributed on three resorcinarenes and two water molecules.

Pairs of tpt dimers stabilized by π – π interactions (interplanar distance 3.56 Å) are located on the three-fold axis and, through O–H \cdots N hydrogen bonding with the remaining two hydroxyl groups of each resorcinarene, connect the molecular boxes into two-dimensional sheets, as shown in Fig. 2. Exterior cavities exist between the ethyl tails of the resorcinarenes and tpt, in which guest molecules are trapped across a mirror plane.

Replacement of the guest with chlorobenzene or toluene under similar preparative conditions gave essentially the same framework,¹² providing further evidence that the formation of the trigonal prism is induced by the C_3 -symmetric tpt linker molecule.

We note that the C_3 -symmetric tpt linker does not fit the resorcinarene node molecule in terms of symmetry, no matter what kind of conformation resorcinarene adopts. This results in the resorcinarenes combining with the water molecules to form a new molecular moiety with the 3-fold symmetry of the other structural component. While resorcinarene dimers and hexamers have been reported in both solid and solution, the trimeric structure described here has not been observed before.

Though there is evidence that the snub cube capsule also exists in solution,⁷ in the present case formation of the molecular box in the crystal is induced by the external linker, so its occurrence in solution may be less likely. We conclude that new supramolecular structures can be synthesized by careful selection of the symmetry of the reactants.

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Notes and references

† [3CECR·2H₂O·G]·2tpt·3G **1**: CECR (0.05 mmol, 30 mg), tpt (0.1 mmol, 31.2 mg), the corresponding guest (benzene **1a**; *o*-xylene **1b**; cyclohexane **1c**) (0.2 mL) and 4 mL of water were sealed in a 6 mL Pyrex glass tube. The

was allowed to stay at 140 °C for 24 hours, followed by cooling to room temperature within 4 days. Yellow prismatic crystals were collected. They are very stable in air.

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- Crystal data: Compound **1a**: C₁₆₈H₁₇₂N₁₂O₂₆; $M_r = 2775.18$, hexagonal, space group $P6_3/m$ (no. 176), $a = b = 22.9483(11)$, $c = 16.1980(12)$ Å, $U = 7387.4(7)$ Å³, $Z = 2$, $D_c = 1.248$ Mg m⁻³, crystal size $0.28 \times 0.12 \times 0.10$ mm³, $\mu(\text{Mo-K}\alpha) = 0.084$ mm⁻¹, $F(000) = 2944$, GoF = 1.070. Among 54639 reflections, 4195 reflections are unique ($R_{\text{int}} = 0.1198$). The final $R1$ and $wR2$ are 0.0656 and 0.1676, respectively, for 447 parameters and 2620 reflections [$I > 2\sigma(I)$]. Compound **1b**: C₁₇₆H₁₈₈N₁₂O₂₆; $M_r = 2887.38$, hexagonal, space group $P6_3/m$, $a = b = 22.9898(10)$, $c = 16.4458(10)$ Å, $U = 7527.6(7)$ Å³, $Z = 2$, $D_c = 1.274$ Mg m⁻³, crystal size $0.24 \times 0.14 \times 0.08$ mm³, $\mu(\text{Mo-K}\alpha) = 0.086$ mm⁻¹, $F(000) = 3072$, GoF = 1.022. Among 89657 reflections, 7915 reflections are unique ($R_{\text{int}} = 0.1729$). The final $R1$ and $wR2$ are 0.0914 and 0.2247, respectively, for 477 parameters and 3146 reflections [$I > 2\sigma(I)$]. Compound **1c**: C₁₆₈H₁₉₆N₁₂O₂₆; $M_r = 2799.37$, hexagonal, space group $P6_3/m$, $a = b = 23.0604(11)$, $c = 16.2247(13)$ Å, $U = 7472.1(8)$ Å³, $Z = 2$, $D_c = 1.244$ Mg m⁻³, crystal size $0.26 \times 0.18 \times 0.12$ mm³, $\mu(\text{Mo-K}\alpha) = 0.084$ mm⁻¹, $F(000) = 2992$, GoF = 1.029. Among 86480 reflections, 5634 reflections are unique ($R_{\text{int}} = 0.1088$). The final $R1$ and $wR2$ are 0.0547 and 0.1400, respectively, for 461 parameters and 3830 reflections [$I > 2\sigma(I)$]. The data were collected on a Bruker SMART1000 CCD with MoK α radiation ($\lambda = 0.71073$ Å) at 90 (1) K. Reflections were reduced by the SAINT program. The structures were solved by direct methods and refined by a full matrix least squares technique based on F^2 using the SHELXL 97 program. CCDC 230024–230026. See <http://www.rsc.org/suppdata/cc/b3/b315091g/> for crystallographic data in CIF or other electronic format.
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- The absence of a hydrogen atom peak along the 3-fold axis in difference electron density maps supports the hydrogen bonding scheme described in which the water molecule is the acceptor in one and the donor in two hydrogen bonds.
- Unit cell dimensions: for the toluene inclusion complex: $a = b = 22.9717(15)$, $c = 16.3385(16)$ Å, $U = 7466.7(7)$ Å³; for the chlorobenzene inclusion complex: $a = b = 22.9720(11)$, $c = 16.3861(11)$ Å, $U = 7488.7(7)$ Å³.