

Self-assembly of carcerand-like dimers of calix[4]resorcinarene facilitated by hydrogen bonded solvent bridges

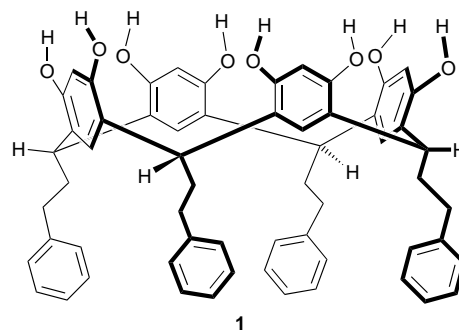
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In the presence of solvent molecules which can act simultaneously as hydrogen bond donors and acceptors, the calix[4]resorcinarene **1** can self-assemble into a dimeric carcerand-like complex utilizing an intricate array of hydrogen bonds with the solvent such that pairs of concave molecules associate indirectly in a rim-to-rim fashion to form a relatively large supramolecular cavity.

One of the main goals of supramolecular chemistry¹ is to use cleft-containing molecules to 'recognize' a substrate on the basis of size, shape, functionality and electrostatic profile. This concept was borrowed from Nature where the process of molecular recognition is central to the chemistry of life.² Although bowl-shaped molecules such as the calixarenes³ and cyclodextrins⁴ have been studied extensively over the last two decades, their molecular cavities are relatively small. An increasing trend towards the design of systems with larger voids has resulted in the development of systems which utilize multiple bowl-shaped molecules as building blocks. In this context, the pioneering work of Cram⁵ and Collet⁶ introduced the carcerands and cryptophanes—covalent cavities with the ability to confine guest molecules. Although these systems are of great conceptual importance, the guest cannot usually be removed without the rupture of at least one covalent bond of the host. Consequently, there has been much interest in the utilization of hydrogen bonded interactions to assemble concave building blocks in order to produce large cavities. In general, such cage systems are attractive because the molecular association is reversible under relatively mild conditions. Rebek and co-workers⁷ have elegantly demonstrated these principles using self-complementary molecules that contain hydrogen bond donor and acceptor moieties positioned about the rims of their cavities. Moreover, one of us recently reported⁸ a solid-state supramolecular assembly composed of six calix[4]resorcinarene molecules which are linked by solvent water molecules, thus forming a large cavity approximately 1375 Å³ in volume. We are keenly interested in the supramolecular complexation of fullerenes,⁹ and have been investigating the possibility of encapsulating C₆₀ within a calix[4]resorcinarene hexamer. Since a solitary C₆₀ molecule is too small to fill the void efficiently, the complex would also require encapsulation of a significant amount of solvent in order to stabilize the structure. During the course of our attempts at assembling such a system, we have instead produced a dimeric carcerand-like complex in which two concave calix[4]resorcinarene molecules are linked indirectly by hydrogen bond bridges involving eight propan-2-ol solvent molecules. Crystallographic characterization of a dimeric system of this nature is unprecedented and is an important extension of the work initiated by Rebek.

Single crystals suitable for X-ray diffraction analysis[‡] were grown by slow diffusion of propan-2-ol into a solution of **1**¹⁰ and C₆₀ (5:1 molar ratio) in *o*-dichlorobenzene. The most striking feature of the structure is that pairs of concave calix[4]resorcinarene molecules are arranged in a rim-to-rim fashion to form dimers, as shown in Fig. 1. The eight hydroxy groups of one calix[4]resorcinarene form hydrogen bonds with eight oxygen atoms belonging to propan-2-ol solvent molecules. The latter, in turn, form hydrogen bonds to a second



calix[4]resorcinarene molecule, thus completing the dimer. No hydroxy group hydrogen atoms were located and hydrogen bonds are inferred from short O...O contacts. The proximate hydroxy O...O contacts within each calixresorcinarene are 2.771(7) Å, implying that these oxygen atoms are also hydrogen bonded to one another. The unique calix[4]resorcinarene-to-solvent O...O distances are 2.660(9) and 2.743(9) Å. The two calix[4]resorcinarene molecules each have C_{4v} symmetry and are related to one another by a mirror plane at *x,y,0* which passes through all of the propan-2-ol oxygen atoms. The assembly of the dimer is thus facilitated by the formation of sixteen intermolecular hydrogen bonds, while a further eight intramolecular hydrogen bonds impart structural rigidity of the calix[4]resorcinarene molecules. The symmetry relationship between the constituents of the dimer requires all of the hydrogen atoms involved in hydrogen bonding to be disordered.

The effective van der Waals volume of the cavity was calculated¹¹ to be 230 Å³ and its cross section, measured at *x,y,0*, is approximately equal in dimensions to a molecule of *o*-dichlorobenzene. In order to maintain structural stability, it is probable that the cavity contains several solvent molecules, perhaps of both *o*-dichlorobenzene and propan-2-ol. Relatively

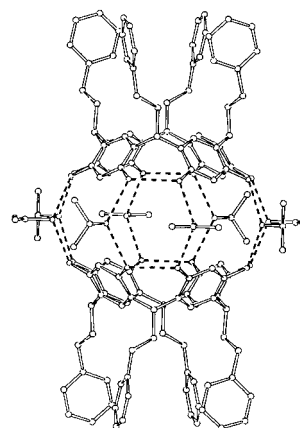


Fig. 1 Projection showing the calix[4]resorcinarene dimer. Hydrogen atoms are omitted for clarity and hydrogen bonded interactions are shown as broken bars.

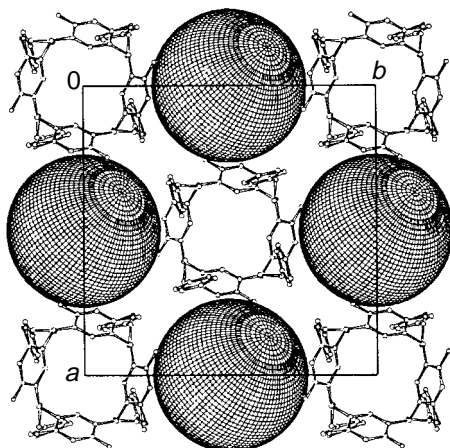


Fig. 2 Packing diagram (only calix[4]resorcinarene and C_{60} molecules are shown) viewed along [001], parallel to the molecular columns

large peaks of electron density within the cavity appear to indicate the presence of chlorine atoms, but crystallographically imposed symmetry precludes the use of a cogent model for included solvent molecules. As shown in Fig. 2, the calix[4]resorcinarene dimers are stacked in columns along $0,0,z$ and $\frac{1}{2},\frac{1}{2},z$ while the C_{60} molecules are similarly arranged along $0,\frac{1}{2},z$ and $\frac{1}{2},0,z$. The calix[4]resorcinarene columns involve alternating head-to-head and tail-to-tail associations of the molecules. The latter result in the formation of lattice voids bounded by phenethyl moieties belonging to the host and also appear to contain disordered *o*-dichlorobenzene solvent.

We have shown that the solvent-assisted hexameric assembly of calix[4]resorcinarenes to form carcerand-like complexes has a dimeric analogue. Characterization of such systems is a significant step towards understanding the principles involved in the design of supramolecular cavities of diverse shapes and sizes, and assemblies of this nature are important because, like their biological counterparts, the contents of large molecular voids are often considered¹² to represent an additional phase of matter.

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Notes and References

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‡ Crystal data for $C_{60}H_{56}O_8 \cdot 4(C_3H_8O) \cdot C_{60}$: $M = 1866.14$; dark red orthorhomboid, $0.30 \times 0.25 \times 0.20$ mm, tetragonal, $I4/m$; $a = b = 18.9296(7)$, $c = 27.2702(13)$ Å; $Z = 4$; $V = 9771.7(7)$ Å³, $D_c = 1.216$ g cm⁻³, Siemens SMART CCD diffractometer, Mo-K α radiation, $\lambda = 0.7107$ Å; $T = -100$ °C; $2\theta_{max} = 54.4^\circ$, 27652 reflections

collected, 5531 unique ($R_{int} = 0.0388$). final GoF = 1.045, $R1 = 0.1193$, $wR2 = 0.3393$, R indices based on 5531 reflections with $F > 4\sigma(F)$, Lp and absorption corrections applied, $\mu = 0.077$ mm⁻¹, min transition factor = 0.743. All calculations were performed using the Siemens SHELX-TL software suite. All non-hydrogen atoms of the calix[4]resorcinarene molecule were refined anisotropically and, with the exception of the hydroxy group hydrogen atoms which are disordered, hydrogens were placed in calculated positions. The C_{60} molecule is disordered over two orientations and was modeled accordingly. The final model also included propan-2-ol and disordered *o*-dichlorobenzene solvent molecules. CCDC 182/731.

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