Odd-membered higher heterocalixarene architecture featuring cage conformation. Synthesis and X-ray structure analysis of a 1 : 2 : 2 inclusion cascade complex with acetone and dichloromethane

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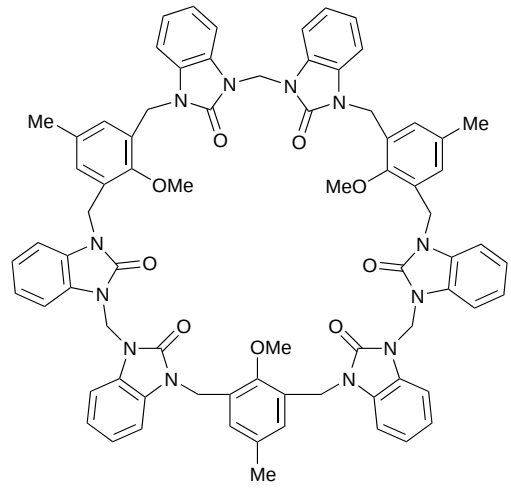
The first crystal structure of a heterocalix[9]arene host molecule created from six benzimidazol-2-one and three *p*-methylanisole units displays guest binding *via* a cascade of interactions of the two acetone and two dichloromethane guest molecules with the host and with each other as well.

Calixarenes and their analogues have emerged as an important topic of supramolecular chemistry.[1] In the past decade a great many structural modifications involving ring sizes and functionalization of the calixarenes have been performed and studied in terms of conformational flexibility, hollow space effects and inclusion behaviour.[2] Current directions focus on the use of calixarene frameworks as modular building blocks in order to construct higher molecular architectures.[3] Notwithstanding the great structural variety in calixarene chemistry, odd-membered higher calixarene homologues having more than eight arene subunits are very rare, to say nothing of derivatives containing heterocycles[4] instead of the conventional phenol subunits. The following study considers both items. Compared with hydrogen-bond stabilized conformations of conventional calixarene systems of the same ring size the alternate arrangement of the subunits in the new metacyclophane causes the formation of a cavity. We report the versatile synthesis of a novel heterocalix[9]arene **1** and the remarkable crystal structure of its supramolecular complex with acetone and dichloromethane, **1**·Me_2CO·CH_2Cl_2 (1 : 2 : 2). The heterocalix[9]arene host molecule **1**, in which benzimidazol-2-one moieties as heterocyclic units are involved, was obtained *via* two-step fragment condensation[4] from 2,6-bis(bromomethyl)-6-methylanisole and methylene-1,1′-bis(benzimidazol-2-one) building elements using blocking/deblocking, high dilution and template (3 equiv. Cs_2CO_3) techniques in dry DMF to yield 26% of **1** (mp 249–250 °C). On recrystallization from a solvent mixture of acetone and dichloromethane (1 : 1), **1** readily forms a crystalline complex composed of **1** and the two solvents in a 1 : 2 : 2 stoichiometric ratio.

An X-ray structure model‡ of the present complex in the crystal (Fig. 1) reveals typical calix-inclusion formation as one of the acetone guest molecules sits in the cavity and is visibly held fixed by a C–H··O interaction from a benzimidazolone entity.§ Steric and electrostatic matching with other neighbouring residues is also important. The second acetone molecule is bound on the perimeter *via* another C–H··O interaction, again from a benzimidazolone residue. The enhanced activity of the benzimidazolones is also shown by the cascade-like binding of the two further dichloromethane guests. These are located on the host molecular surface, kept by C–H··Cl interactions to each other and to the host in a consecutive manner. The cascade ends on a Cl··π interaction[5] with a chlorine atom to anisole ring centre distance of 3.55 Å. This anisole moiety is the only one that plays a role in the active fixing of guest molecules. As reported recently for other smaller-ring hetero-calixarene cases,[4] the side-on-side stacking of symmetry centre-related host molecules with reference to the benzimidazolone plane (interplanar distances 3.4–3.6 Å) appears repeatedly. This is also visible in the crystal packing (Fig. 2). Thus stacking of the hetero-units is an important motif, apparently contributing to crystal formation for this type of host molecule.



1

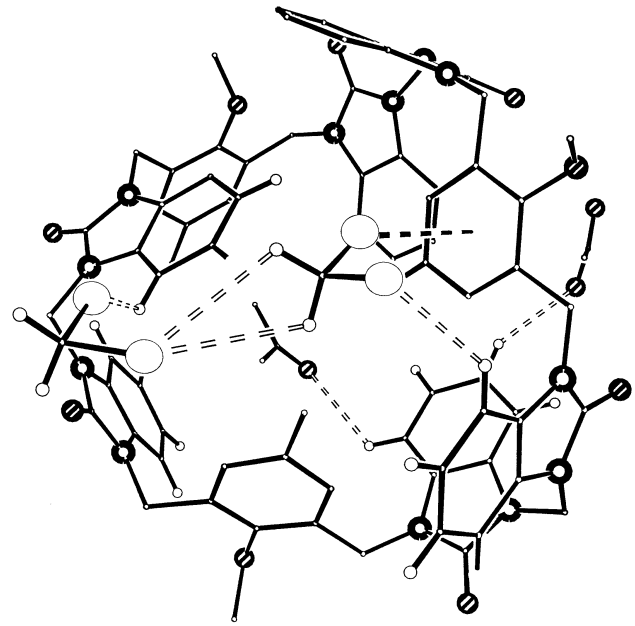


Fig. 1 View of the **1**·acetone·dichloromethane (1 : 2 : 2) inclusion complex, with the principal cooperative interactions shown in broken lines. Only relevant hydrogen atoms are retained in the picture.

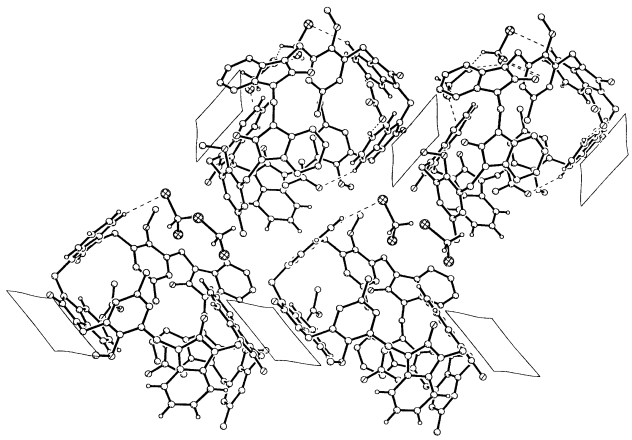


Fig. 2 Packing in the **1**·acetone·dichloromethane (1 : 2 : 2) crystal illustrating stacking on the benzimidazolone sides (highlighted by irregular rectangles) and C–H··Cl interactions (broken lines)

We thus conclude that the unusual activity of the benzimidazol-2 one moiety renders it a particularly interesting building block for new calix frameworks, not only due to its ability to exaggerate ring dimensions and make such large rings somewhat stiffer than anisole units usually do alone, but also for its enhanced cooperativity in interactions with guest molecules.

E. W. and M. C. are indebted to an INTAS Grant (No. 94-972) for financial support. M. C. and E. W. also thank the Hungarian Research Fund (Grant OTKA 015181) and the Fonds der Chemischen Indüstrie, respectively for support-in-part. The authors in Dresden greatly acknowledge financial support by the Deutsche Forschungsgemeinschaft (GK 155).

Footnotes

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‡ *X-Ray structure analysis* of **1**·acetone·dichloromethane (1 : 2 : 2): monoclinic, $P2_1/c$ space group, a = 13.127(3), b = 23.977(5), c = 25.526(5) Å, β = 96.75(3)°, Z = 4, total data collected (refs. 6,7) = 16 388, independent reflections = 16 098 $R_{(int)}$ = 0.179. Crystals were of poor quality, soft, air-sensitive, and could only be exposed to moderate cooling (T = 203 K, they became brittle below −80 °C). The initial structure model, obtained by direct methods [SHELXS-86 (ref. 8)], was refined against 11 943 non-negative observations (using alternating conjugate gradient and full-matrix least-squares refinement on F^2 data) to convergence at relative poor R values [final R indices $I > 2\sigma(I)$: R_1 = 0.151, wR_2 = 0.395, R (all data): R_1 = 0.289, wR_2 = 0.548, program SHELXL-93 (ref. 9)]. Atomic assignments in the critical regions were checked by scrutinizing U_{iso} values. All non-hydrogen atoms were treated with anisotropic displacement parameters. Hydrogen atom positions were generated from geometric evidence and were kept riding on their mother atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/500.

§ The hydrogen-bonding cascade in this crystal structure is maintained in part by weak C–H··Cl interactions [C(78)–H(78)··Cl(1) = 0.94(2), 2.94(1) Å, 136(1)°; C(1e)–H(1ec)··Cl(2) = 0.98(2), 3.12(2) Å, 106(2)°; C(1e)–H(1ed)··Cl(2) = 0.98(2), 3.05(2) Å, 111(2)°] and by C(1e)–Cl(2)··X(1a) = 3.537(7) Å, 152(1)°, where X(1a) denotes a benzimidazolone ring centre. The C(49)–O(1a) = 3.07(2) Å distance is indicative of the electrostaic attraction between a benzimidazole carbon and the acetone oxygen. The long H··O distance of 2.8 Å [C(49)–H(49)··O(1a) 0.94 (2), 2.8(2) Å, 122(1)°] indicates that this is not a C–H··O interaction (ref. 10). The acetone binding also occurs *via* the benzimidazolone C–H and guest O interactions [C(69)–H(69)··O(1n) 0.96(2), 2.497 Å, 152(1)°].

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Received in Cambridge, UK, 28th April 1997; 7/02861J