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THE SOLID-STATE INCLUSION COMPLEX BETWEEN THE MONO-ANION OF CALIX[4]ARENE AND PROTONATED DIAMINO-BICYCLOUNDECANE

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Abstract: Diamino-bicycloundecane mono-deprotonates H-calix[4]arene and the solid-structure of the resulting salt has been determined by X-ray crystallography. Two different complexes are present in the structure with the Diamino-bicycloundecane cation held in the calix[4]arene cavity by CH-p interactions. In the packing there is a hydrogen-bonded polymeric chain. Both the complexes formed layered structures with differing inter-layer distances.

Keywords: Calix[n]arenes, X-ray Crystallography, Structure, Mono-anionic, Diamino-Bicycloundecane, inclusion polymer.

Introduction

The calix[n]arenes are a class of macrocycle organic host compounds widely studied for their complexation properties [1], they have been shown to complex molecules at sizes varying from metallic cations [2], anions [3], small organic molecules [4] through peptides [5] to proteins [6] and DNA [7]. As they possess two different chemistries: at the *para*-aromatic position and at the phenolic hydroxyl position, their selective chemical modifycation may be achieved [8], and hence groups with divergent chemical and physical properties may be readily introduced at either face.

A wide range of amphiphilic calix[n]arene derivatives have been developed by modification at one or two faces. We have some time been interested in the synthesis of amphiphilic calix[n]arenes having a geometry tuned to the formation of micellar structures, such molecules are based mono-functionalisation at the phenolic face followed by use of quinine-methide substitution at the three remaining phenolic groups [9]. Obviously the key step is the initial mono-substitution.

The synthesis of such molecules has been studied by Casnati *et al.* [10] *via* the 1-3 dialkoxy or tetraalkoxycalix[4]arenes followed by hydrolysis with respectively 1 or 3 equivalents of trimethylsilyl iodide. We have previously demonstrated mono-substitution of calix[4]arene using potassium carbonate as a base, however yields are very low, ca 10%. Kalchenko has used sodium hydroxide as a base with DMSO as a solvent for mono-substitution [11]. Work by Groenen *et al.* [12] showed that cesium fluoride or potassium fluoride could be used as suitable mono-alkylating agents. An interesting article by Cunningham *et al.* showed that certain organic bases such as diamino-bicycloundecane (DBU) could be used, with total selectivity to mono-deprotonate all the calix[n]arenes [13].

Experimental

Suitable crystals for X-ray diffraction, were grown from an acetonitrile solution of a 1:1 mixture of calix[4]arene and diamino-bicycloundecane by slow evaporation.

The crystal collection and refinement data for 1 are given in Table 1.

H atoms were treated as riding atoms in geometrically idealized positions, with C–H distances of 0.95 (aromatic ring), 0.99 (CH_2), 0.98 (CH_3), 0.88 (NH) and 0.84 Å (OH), and with $U_{iso}(H) = kU_{eq}(C, O)$, where k = 1.5 for the methyl and hydroxyl groups and k = 1.2 otherwise.

Data collection: COLLECT [14]; cell refinement and data reduction: DENZO and SCALEPACK [15]; programs used to solve structure and refine structure: SHELXS97 and SHELXL97 [16]; molecular graphics: Diamond 3.1f [17].

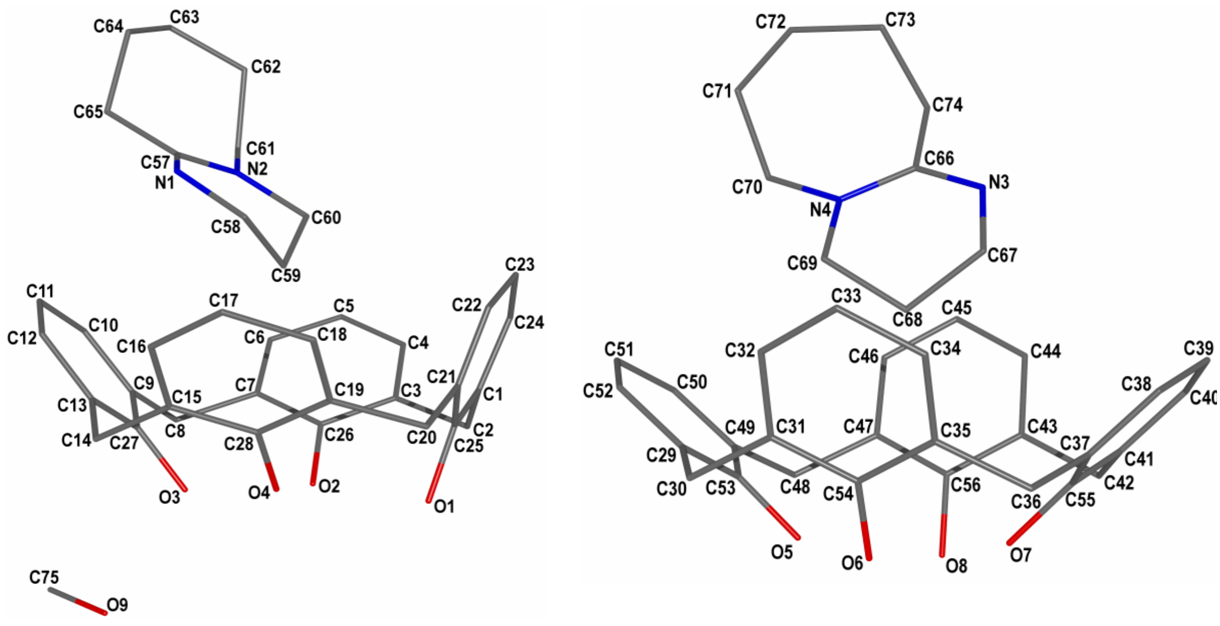
Results and Discussion

While the yields obtained from the use of DBU as a selective mono-deprotonation agent for calix[4]arene are too low to allow its use in the production of mono-O-alkylated calix[4]arene derivatives, during the course of the study suitable crystals for crystallographic study were obtained by slow evaporation from a chloroform-methanol solvent mixture.

Table 1

Crystal data and structure refinement details of 1.DBU

	1.DBU
Empirical formula	$C_{28}H_{23}O_4^-\cdot C_9H_{17}N_2^+\cdot 0.5CH_3OH$
Formula weight	592.73
Temperature (K)	100(2)
Diffractometer	Nonius KappaCCD
Wavelength (Å)	0.71073
Crystal	colourless
Crystal size (mm^3)	0.45 × 0.40 × 0.30
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimension	
a (Å)	16.9981(2)
b (Å)	19.1230(2)
c (Å)	19.7663(2)
α (°)	90
β (°)	107.8250(4)
γ (°)	90
Volume (Å^3)	6116.7(1)
Z	8
Calculated density (g·cm^{-3})	1.287
F(000)	2536
Absorption coefficient (mm^{-1})	0.084
θ Range for data collection (°)	2.97–27.46
hkl Ranges	$-22 \leq h \leq 22$, $-24 \leq k \leq 24$, $-25 \leq l \leq 25$
Reflections collected/unique	90818 / 13966
Completeness (%) to θ	99.9 / 27.46
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints / parameters	13966 / 0 / 802
Goodness-of-fit on F^2	1.06
Final R indices [$I > 2\sigma(I)$]	$R = 0.041$, $wR = 0.090$
R indices (all data)	$R = 0.049$, $wR = 0.094$



a **b**

Figure 1. The molecular structures of Complexes I and II along with the atom labelling.

The solid-state structure shows a 2:2 complex of two mono-anions of calix[4]arene **1** with two protonated DBU cations and a single molecule of methanol present as a solvate in the structure.

The two different complexes are given, along with atom labelling in Figure **1a** and **b**.

Bond Lengths are given in Table 1 and Bond Angles in Table 2 (for non-hydrogen atoms), atomic coordinates are given in the Supplementary data.

Table 2

Bond length (Å)

Bond	*d*, Å	Bond	*d*, Å
O1—C25	1.373(2)	C35—C54	1.408(2)
O2—C26	1.362(2)	C35—C36	1.517(2)
O3—C27	1.356(2)	C36—C37	1.518(2)
O4—C28	1.372(1)	C37—C38	1.399(2)
C1—C24	1.399(2)	C37—C55	1.401(2)
C1—C25	1.405(2)	C38—C39	1.387(2)
C1—C2	1.522(2)	C39—C40	1.386(2)
C2—C3	1.521(2)	C40—C41	1.395(2)
C3—C4	1.397(2)	C41—C55	1.409(2)
C3—C26	1.402(2)	C41—C42	1.517(2)
C4—C5	1.390(2)	C42—C43	1.518(2)
C5—C6	1.387(2)	C43—C44	1.398(2)
C6—C7	1.394(2)	C43—C56	1.400(2)
C7—C26	1.406(2)	C44—C45	1.389(2)
C7—C8	1.518(2)	C45—C46	1.385(2)

C8—C9	1.521(2)	C46—C47	1.399(2)
C9—C10	1.395(2)	C47—C56	1.401(2)
C9—C27	1.409(2)	C47—C48	1.523(2)
C10—C11	1.390(2)	C48—C49	1.514(2)
C11—C12	1.387(2)	C49—C50	1.398(2)
C12—C13	1.395(2)	C49—C53	1.404(2)
C13—C27	1.410(2)	C50—C51	1.387(2)
C13—C14	1.518(2)	C51—C52	1.387(2)
C14—C15	1.519(2)	N1—C57	1.320(2)
C15—C16	1.397(2)	N1—C58	1.464(2)
C15—C28	1.404(2)	N2—C57	1.325(2)
C16—C17	1.389(2)	N2—C60	1.480(2)
C17—C18	1.387(2)	N2—C61	1.480(2)
C18—C19	1.391(2)	C57—C65	1.498(2)
C19—C28	1.400(2)	C58—C59	1.517(2)
C19—C20	1.519(2)	C59—C60	1.515(2)
C20—C21	1.522(2)	C61—C62	1.525(2)
C21—C22	1.393(2)	C62—C63	1.527(2)
C21—C25	1.405(2)	C63—C64	1.526(2)
C22—C23	1.389(2)	C64—C65	1.539(2)
C23—C24	1.391(2)	N3—C66	1.316(2)
O5—C53	1.355(2)	N3—C67	1.469(2)
O6—C54	1.350(1)	N4—C66	1.324(2)
O7—C55	1.371(2)	N4—C70	1.475(2)
O8—C56	1.381(2)	N4—C69	1.478(2)
C29—C52	1.397(2)	C66—C74	1.498(2)
C29—C53	1.406(2)	C67—C68	1.512(2)
C29—C30	1.515(2)	C68—C69	1.516(2)
C30—C31	1.517(2)	C70—C71	1.526(2)
C31—C32	1.393(2)	C71—C72	1.527(2)
C31—C54	1.410(2)	C72—C73	1.525(2)
C32—C33	1.387(2)	C73—C74	1.540(2)
C33—C34	1.391(2)	C75—O9	1.404(2)
C34—C35	1.392(2)		

An expected the cone conformations of the calix[4]arene mono-anions are stabilized by hydrogen bonds at the phenolic face, distances 2.703(1), 2.524(1), and 2.521(1) Å for anion **I** and 2.559(1), 2.587(1), and 2.788(1) Å for anion **II**. In both cases the two shorter hydrogen bond lengths are associated with the deprotonated phenolic groups.

Table 3

Angles between bonds (Å)

Angle	∠, °	Angle	∠, °
C24—C1—C25	118.1(1)	C38—C37—C36	119.5(1)
C24—C1—C2	120.0(1)	C55—C37—C36	122.0(1)
C25—C1—C2	121.8(1)	C39—C38—C37	121.4(1)
C3—C2—C1	111.1(1)	C40—C39—C38	119.3(1)
C4—C3—C26	118.5(1)	C39—C40—C41	121.4(1)
C4—C3—C2	120.3(1)	C40—C41—C55	118.5(1)
C26—C3—C2	121.2(1)	C40—C41—C42	120.6(1)
C5—C4—C3	121.0(1)	C55—C41—C42	120.8(1)
C6—C5—C4	119.6(1)	C41—C42—C43	111.8(1)
C5—C6—C7	121.3(1)	C44—C43—C56	118.5(1)
C6—C7—C26	118.3(1)	C44—C43—C42	120.0(1)
C6—C7—C8	120.3(1)	C56—C43—C42	121.5(1)
C26—C7—C8	121.3(1)	C45—C44—C43	120.8(1)
C7—C8—C9	115.6(1)	C46—C45—C44	119.5(1)
C10—C9—C27	119.1(1)	C45—C46—C47	121.6(1)
C10—C9—C8	119.9(1)	C46—C47—C56	117.9(1)
C27—C9—C8	121.0(1)	C46—C47—C48	120.0(1)
C11—C10—C9	121.1(1)	C56—C47—C48	122.1(1)
C12—C11—C10	119.5(1)	C49—C48—C47	112.5(1)
C11—C12—C13	121.2(1)	C50—C49—C53	118.5(1)
C12—C13—C27	119.1(1)	C50—C49—C48	122.0(1)
C12—C13—C14	119.9(1)	C53—C49—C48	119.6(1)
C27—C13—C14	121.1(1)	C51—C50—C49	121.0(1)
C13—C14—C15	114.1(1)	C50—C51—C52	119.7(1)
C16—C15—C28	118.6(1)	C51—C52—C29	121.3(1)
C16—C15—C14	120.3(1)	O5—C53—C49	116.5(1)
C28—C15—C14	121.1(1)	O5—C53—C29	122.2(1)
C17—C16—C15	120.9(1)	C49—C53—C29	121.3(1)
C18—C17—C16	119.4(1)	O6—C54—C35	120.2(1)
C17—C18—C19	121.6(1)	O6—C54—C31	120.7(1)
C18—C19—C28	118.4(1)	C35—C54—C31	119.2(1)
C18—C19—C20	120.2(1)	O7—C55—C37	122.0(1)
C28—C19—C20	121.4(1)	O7—C55—C41	117.2(1)
C19—C20—C21	112.6(1)	C37—C55—C41	120.9(1)
C22—C21—C25	118.7(1)	O8—C56—C43	119.7(1)
C22—C21—C20	120.4(1)	O8—C56—C47	118.8(1)
C25—C21—C20	120.9(1)	C43—C56—C47	121.6(1)
C23—C22—C21	121.2(1)	C57—N1—C58	123.4(1)
C22—C23—C24	119.4(1)	C57—N2—C60	120.6(1)
C23—C24—C1	121.4(1)	C57—N2—C61	121.6(1)
O1—C25—C21	120.3(1)	C60—N2—C61	117.7(1)
O1—C25—C1	118.5(1)	N1—C57—N2	122.1(1)
C21—C25—C1	121.2(1)	N1—C57—C65	117.5(1)
O2—C26—C3	117.9(1)	N2—C57—C65	120.3(1)
O2—C26—C7	120.9(1)	N1—C58—C59	108.7(1)
C3—C26—C7	121.1(1)	C60—C59—C58	109.5(1)
O3—C27—C9	120.3(1)	N2—C60—C59	110.2(1)
O3—C27—C13	119.6(1)	N2—C61—C62	114.2(1)
C9—C27—C13	120.1(1)	C61—C62—C63	115.2(1)
O4—C28—C19	117.5(1)	C64—C63—C62	115.3(1)
O4—C28—C15	121.4(1)	C63—C64—C65	113.5(1)

C19—C28—C15	121.1(1)	C57—C65—C64	112.9(1)
C52—C29—C53	118.2(1)	C66—N3—C67	124.3(1)
C52—C29—C30	120.9(1)	C66—N4—C70	121.8(1)
C53—C29—C30	120.9(1)	C66—N4—C69	120.3(1)
C29—C30—C31	114.3(1)	C70—N4—C69	117.9(1)
C32—C31—C54	119.3(1)	N3—C66—N4	122.1(1)
C32—C31—C30	119.7(1)	N3—C66—C74	117.5(1)
C54—C31—C30	121.1(1)	N4—C66—C74	120.4(1)
C33—C32—C31	121.8(1)	N3—C67—C68	109.5(1)
C32—C33—C34	118.8(1)	C67—C68—C69	110.2(1)
C33—C34—C35	121.1(1)	N4—C69—C68	110.3(1)
C34—C35—C54	119.9(1)	N4—C70—C71	113.4(1)
C34—C35—C36	120.0(1)	C70—C71—C72	113.7(1)
C54—C35—C36	120.0(1)	C73—C72—C71	114.6(1)
C35—C36—C37	113.0(1)	C72—C73—C74	114.0(1)
C38—C37—C55	118.5(1)	C66—C74—C73	112.2(1)

The DBU cation **I** is included within the calix[4]arene **I** cavity. There are $CH\cdots\pi$ interactions between the two hydrogen atoms of the most deeply inserted methylene group, distances of 3.691(2) and 3.572(2) Å and two further interactions between one hydrogen of the other two methylene groups and the other two aromatic rings, distance of 3.604(2) and 3.666(2) Å. The protonated nitrogen of this DBU cation is hydrogen bonded to the deprotonated phenolic hydroxyl group of anion **II**, $N–H\cdots O$ distance 2.791(1) Å.

In the case of the second DBU cation (**II**) $CH\cdots\pi$ interactions are stronger (3.459(2), 3.345(2), 3.572(2), 3.546(2) Å) which correlates with more flattened conformation for **II** (cone angles of 55.34(3), 86.34(3)° for **I** and 43.27, 86.67° for **II).** The methanol molecule forms hydrogen bond with deprotonated hydroxyl group of **I**, so DBU cation connects with other hydroxyl group *via* hydrogen bond of 2.916(1) Å.

As a result of $N–H\cdots O$ bonding and $CH\cdots\pi$ interactions (Table 3) each DBU cation binds two neighbouring calixarenes (Fig. 2). DBU cations present in the crystal structure as racemic mixture, so both complexes **I** and **II** are assembled by pairs into syndiotactic H-bond polymer in [201] direction: …-$\mathbf{I}_L$–$\mathbf{II}_L$–$\mathbf{I}_D$–$\mathbf{II}_D$-…

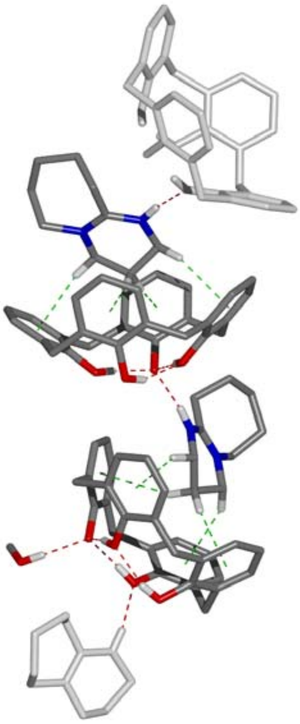
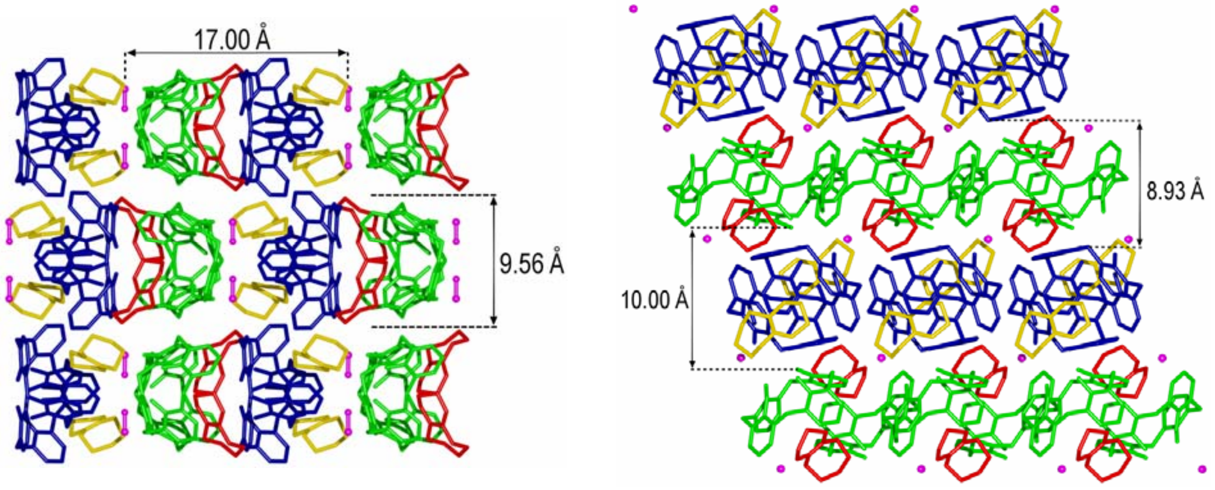


Figure 2. Hydrogen-bonded polymeric chain of 1. Protons not involved in intermolecular interactions or hydrogen bonding have been removed for clarity.

The distance between methanol molecules corresponds to the polymer link length (17.00 Å). All polymeric chains which lie in *xz* plane are parallel, so folded layers consisted of complexes **I** and **II** are anti-parallel (Figure 3a). Hydrogen bonds and contacts, as listed in Table 3, link the units in the chain, and then the inter-chains cohesion is via held electrostatic and van der Waals interactions. The layer formed by calixarenes **I** is thinner than that formed by calixarenes **II** due to the presence of a methanol molecule (Figure 3b).



a **b**

Figure 3. The packing diagrams of the complexes 1. Hydrogen atoms have been removed for clarity.

Table 3

Hydrogen-bond and C−H···π contact geometry

D—H···A	D—H, Å	H···A, Å	D···A, Å	D—H···A, °
O1—H1···O4	0.84	1.89	2.703(1)	163
O2—H2···O3	0.84	1.70	2.524(1)	168
O4—H4···O3	0.84	1.70	2.521(1)	167
O5—H5A···O6	0.84	1.74	2.559(1)	163
O7—H7···O6	0.84	1.76	2.587(1)	167
O8—H8···O7	0.84	1.99	2.787(1)	158
N1—H1···O6^{i}	0.88	1.92	2.791(1)	173
N3—H3···O2^{ii}	0.88	2.07	2.916(1)	162
O9—H9···O3	0.84	1.90	2.741(1)	179
C2—H2A···O9^{iii}	0.99	2.66	3.631(1)	166
C16—H16···O5^{iv}	0.95	2.65	3.542(1)	157
C74—H74B···O3^{ii}	0.99	2.60	3.533(1)	158
C58—H58A···π4	0.99	2.72	3.691(1)	168
C59—H59A···π1	0.99	2.74	3.707(1)	165
C59—H59B···π3	0.99	2.73	3.722(1)	176
C60—H60B···π2	0.99	2.80	3.774(1)	167
C65—H65A···π6^{iv}	0.99	2.66	3.594(1)	157
C67—H67B···π7	0.99	2.78	3.765(1)	173
C68—H68A···π6	0.99	2.40	3.380(1)	172
C68—H68B···π8	0.99	2.49	3.438(1)	160
C69—H69A···π5	0.99	2.74	3.646(1)	152

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x, y+1/2, −z+1/2; (iii) x, 1/2−y, −1/2+z; (iv) 1−x, 1−y, 1−z.

Phenolic ring name in table above is defined by oxygen atom label, for example π1 means phenolic ring with O1 atom.

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