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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1190). Services for accessing these data are described at the back of the journal.

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Calix[4]arene Piperidinium Salt

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Abstract

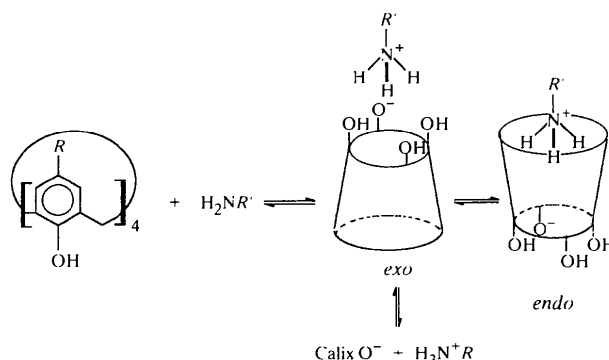
In the crystal structure of piperidinium 26,27,28-trihydroxypentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosal(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-25-olate hemiacetonitrile solvate sesquihydrate, 2(C₅H₁₂N⁺·C₂₈H₂₃O₄⁻)·CH₃CN·3H₂O, two monoanions of calix[4]arene, two piperidinium ions, three molecules of water and one molecule of acetonitrile are observed in the asymmetric unit. They form an intricate network of intra- and intermolecular hydrogen bonds. Each calix-

arene molecule has a cone conformation. The H atoms of the piperidinium N⁺ atom are not directed towards the phenyl rings, indicating that no (N⁺—H)··π interaction occurs.

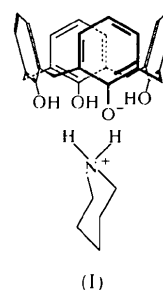
Comment

Calixarenes are a class of synthetic macrocycles having phenolic residues in a cyclic array. They are able to form inclusion compounds with a wide variety of organic guest species, such as toluene (Andreotti *et al.*, 1979), ammonium cations (Harrowfield *et al.*, 1993) and fullerenes (Raston *et al.*, 1996). The simplest representation of these compounds is calix[4]arene (*R* = H in scheme below), which forms clathrates with several solvents, such as acetone (Ungaro *et al.*, 1984) and acetonitrile (Harrowfield *et al.*, 1993), the crystal structures of which have been determined, revealing 1:3 calixarene–solvent clathrate structures.

The *pK_a* values of calixarenes are 5–7 *pK_a* units below those of the corresponding phenols (Shinkai *et al.*, 1991), allowing the formation of salts with amines. The nature of these salts in CH₃CN was studied by Gutsche *et al.* (1987), who proposed the *endo*–*exo* equilibrium to *p*-alil-calix[4]arene and *tert*-butylamine, based on chemical shifts and relaxation times (*T*₁) of *tert*-butyl H atoms of the amine. The scheme below shows the equilibria of calix[4]arene and primary amines.



During our attempts to understand the compounds formed by calix[4]arenes and amines, we have determined the structure of the salt formed by calix[4]arene and piperidine, (I).



The structure determined by X-ray analysis has two monoanions of calix[4]arene, two piperidinium ions, three molecules of water and one molecule of acetonitrile in the asymmetric unit.

The most commonly cited geometric parameters for calix[4]arenes are the dihedral angles formed by each of the aromatic ring planes and the plane defined by the four methylenes. For the unprimed calix[4]arene (Fig. 1), these angles are $119.0(1)$ (phenyl ring C11–C16), $128.3(1)$ (C21–C26), $127.0(1)$ (C31–C36) and $122.5(1)^\circ$ (C41–C46); for the primed calix[4]arene, these angles are $133.7(1)$, $127.4(1)$, $122.1(1)$ and $120.0(1)^\circ$, respectively. These values show that both calixarenes are in slightly distorted cone conformations. A least-squares plane of the four phenolic O atoms shows that they are coplanar within $0.006(1)$ and $0.04(1)$ Å for the unprimed and primed molecules, respectively.

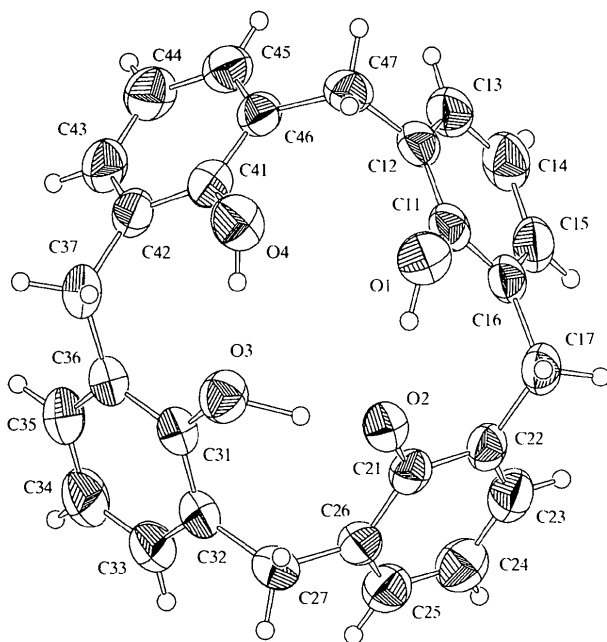


Fig. 1. ORTEP (Zsolnai, 1996) drawing of the unprimed molecule of calix[4]arene. Displacement ellipsoids are shown at the 50% probability level.

As the H atoms of the phenolic O atoms and water molecules were found by difference Fourier maps, an assignment of donor–receptor character was possible. One O atom of each calixarene molecule (O2 and O2') is deprotonated and acts as a receptor of two hydrogen bonds from the vicinal phenolic O atoms (O1 and O3; O1' and O3'). This can be seen in the C—O bonds in which they are involved (C21—O2 and C21'—O2'), which have lengths slightly shorter the other C—O

bonds. These hydrogen bonds are very strong, as can be seen by the short O···O distances $\text{O3}\cdots\text{O2} = 2.527(3)$ and $\text{O1}'\cdots\text{O2}' = 2.494(3)$ Å, characteristic of strong hydrogen bonds (Gilli *et al.*, 1994).

The piperidinium ions are located at the rim of the calix and are not oriented in relation to the cavity, which means that there is no kind of interaction to direct the piperidinium to the inner of the cavity to form the *endo* complex. The significant interactions of the piperidinium ions are the hydrogen bonds with the vicinal calix[4]arenes and water molecules.

One piperidinium ion (N1, C51–C55), with puckering coordinates (Cremer & Pople, 1975) $Q = 0.294(8)$ Å, $\theta = 5.5(16)$ and $\varphi = 2(22)^\circ$, adopts a flattened chair conformation, while the other (N2, C61–C65), with $Q = 0.477(5)$ Å, $\theta = 2.7(6)$ and $\varphi = 333(12)^\circ$, has a chair conformation.

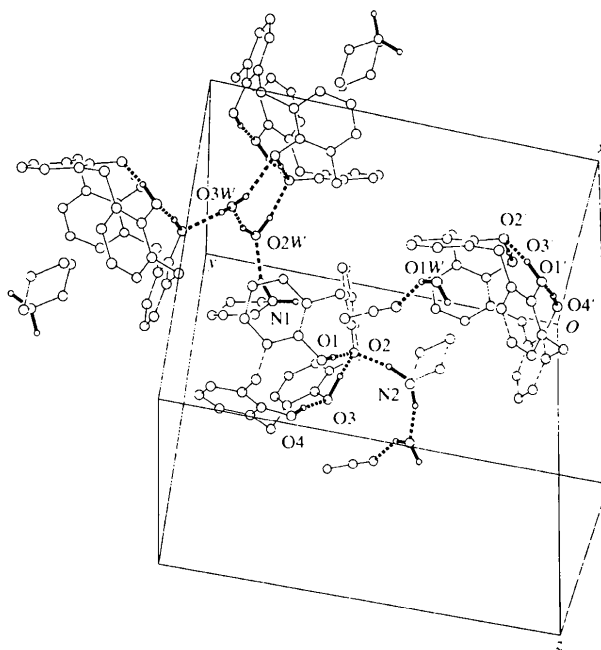
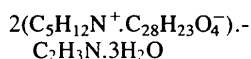


Fig. 2. Packing diagram with dashed lines representing hydrogen bonds. Peripheral H atoms have been omitted for clarity.

Experimental

Calix[4]arene was obtained by debutylation of *p*-*tert*-butyl-calix[4]arene in AlCl_3 /toluene as described by Gutsche *et al.* (1985). Piperidine was distilled before use. The colourless crystals were obtained from a 1:1 solution of calix[4]arene and piperidine in acetonitrile, by slow evaporation of the solvent. The CHN analysis reveals that the crystal structure loses one H_2O and acetonitrile in the determination process. Elemental analysis based on 2 calix[4]arene + 2 piperidine + $3\text{H}_2\text{O}$ + CH_3CN : calculated C 73.23, H 7.27, N 3.77% ($\text{C}_{68}\text{H}_{79}\text{O}_{11}\text{N}_2$); found C 72.91, H 7.37, N 3.77%.

Crystal data $M_r = 1114.34$

Triclinic

 $P\bar{1}$ $a = 11.159(2) \text{ \AA}$ $b = 16.210(3) \text{ \AA}$ $c = 16.807(3) \text{ \AA}$ $\alpha = 87.58(3)^\circ$ $\beta = 81.48(3)^\circ$ $\gamma = 80.65(3)^\circ$ $V = 2966.2(9) \text{ \AA}^3$ $Z = 2$ $D_x = 1.248 \text{ Mg m}^{-3}$ D_m not measured*Data collection*

Nonius CAD-4 diffractometer

 $\omega/2\theta$ scans

Absorption correction: none

10 815 measured reflections

10 413 independent reflections

6695 reflections with

 $I > 2\sigma(I)$ *Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.057$ $wR(F^2) = 0.192$ $S = 1.024$

10413 reflections

783 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0767P)^2 + 2.3860P]$ where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.045$ Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

 $\theta = 9.76\text{--}15.43^\circ$ $\mu = 0.084 \text{ mm}^{-1}$ $T = 295(2) \text{ K}$

Irregular

 $0.47 \times 0.45 \times 0.35 \text{ mm}$

Colourless

 $R_{\text{int}} = 0.020$ $\theta_{\text{max}} = 25.0^\circ$ $h = -13 \rightarrow 13$ $k = 0 \rightarrow 19$ $l = -19 \rightarrow 19$

3 standard reflections

frequency: 60 min

intensity decay: -1.4% $\Delta\rho_{\text{max}} = 0.491 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.349 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL97 (Sheldrick, 1997)

Extinction coefficient:

0.0214 (13)

Scattering factors from

International Tables for Crystallography (Vol. C)

N2—H2A···O1W'	1.05 (6)	1.77 (6)	2.775 (4)	159 (5)
N2—H2B···O2	1.20 (6)	1.64 (6)	2.805 (4)	162 (5)
O1W—H1W1···N1A	0.98 (5)	2.08 (6)	2.901 (6)	140 (5)
O1W—H2W1···O1''	0.88 (5)	2.06 (6)	2.919 (4)	163 (6)
O2W—H1W2···O3W	0.99 (2)	1.76 (3)	2.727 (6)	163 (6)
O2W—H2W2···O2'''	1.00 (2)	1.83 (3)	2.781 (4)	158 (5)
O3W—H1W3···O3'''	0.87 (7)	2.30 (7)	2.790 (4)	115 (6)
O3W—H2W3···O4'''	0.91 (6)	1.99 (6)	2.778 (5)	144 (6)

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, 1-y, -z$; (iv) $x, 1+y, z$.

There are two independent molecules of calix[4]arene in the asymmetric unit, which are not significantly different from each other. The relatively large displacement parameters of the piperidinium, acetonitrile and water molecules can be attributed to slight disorder in these groups. The hydroxy and water H atoms were found from $\Delta\rho$ maps and refined isotropically with a common displacement parameter. The H atoms on the piperidinium N atoms were found in $\Delta\rho$ maps, but only those on N2 were refined; those on N1 were placed in calculated positions. The acetonitrile methyl H atoms were found from $\Delta\rho$ maps and were not refined. The other H atoms were placed geometrically with fixed individual displacement parameters [$U(\text{H}) = 1.5(C_{\text{methyl}})$ or $1.2(C_{\text{phenyl}})$] using a riding model with aromatic C—H = 0.93 and methyl C—H = 0.97 Å.

Data collection: CAD-4 EXPRESS (Enraf-Nonius, 1992). Cell refinement: SET4 in CAD-4 EXPRESS. Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: ZORTEP (Zsolnai, 1996). Software used to prepare material for publication: SHELXL97. Computing system: DEC 3000 AXP and PC/486.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1004). Services for accessing these data are described at the back of the journal.

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C11	1.367 (4)	O1'—C11'	1.358 (4)
O2—C21	1.355 (3)	O2'—C21'	1.349 (4)
O3—C31	1.379 (4)	O3'—C31'	1.366 (4)
O4—C41	1.372 (4)	O4'—C41'	1.375 (4)
O1—C11—C16	119.5 (3)	O1'—C11'—C16'	120.4 (3)
O1—C11—C12	119.3 (3)	O1'—C11'—C12'	118.6 (3)
O2—C21—C22	120.0 (3)	O2'—C21'—C22'	119.8 (3)
O2—C21—C26	120.0 (3)	O2'—C21'—C26'	119.7 (3)
O3—C31—C36	118.6 (3)	O3'—C31'—C32'	120.3 (3)
O3—C31—C32	120.1 (3)	O3'—C31'—C36'	118.4 (3)
O4—C41—C46	117.8 (3)	O4'—C41'—C42'	118.9 (3)
O4—C41—C42	120.3 (3)	O4'—C41'—C46'	119.7 (3)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O2	0.97 (6)	1.64 (6)	2.605 (3)	178 (5)
O3—H3O···O2	1.22 (6)	1.32 (6)	2.527 (3)	171 (5)
O4—H4O···O3	0.89 (6)	1.74 (6)	2.623 (3)	171 (6)
O1'—H1O'···O2'	1.02 (2)	1.49 (2)	2.494 (3)	165 (6)
O3'—H3O'···O2'	1.03 (6)	1.60 (6)	2.635 (3)	179 (5)
O4'—H4O'···O1'	1.07 (6)	1.52 (6)	2.579 (3)	172 (5)
N1—H1B···O2W	0.90	2.11	2.922 (9)	149

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Tris(phenylseleno)methane

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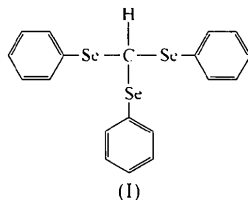
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Abstract

Tris(phenylselenanyl)methane, $\text{C}_{19}\text{H}_{16}\text{Se}_3$, crystallizes in the rhombohedral space group $R\bar{3}$, with the CH group situated on a threefold axis. The selenium–carbon bond to the aromatic ring is slightly shorter than that to the aliphatic C atom. The tetrahedral angles at the methane C atom range between $107.4(1)$ and $111.5(1)^\circ$.

Comment

As part of our systematic work on selenium and tellurium compounds with the potential to coordinate to metal ions, we studied the structure of tris(phenylseleno)methane, (I), which may act as a tridentate bridging selenoether ligand. The title compound is the first representative of tris(alkylseleno) or tris(arylseleno) compounds to have been studied crystallographically.



The molecular structure of tris(phenylseleno)methane is illustrated in Fig. 1. Atoms C1 and H1 are situated on a threefold axis, producing three symmetry-related phenylseleno units. C—Se bond lengths of $1.928(3)$ and $1.958(1)$ Å have been found. The shorter one belongs to the bond to the aromatic C11 atom. This is in agreement with the bonding situation in other asymmetric selenoethers which have both an aliphatic and an aromatic substituent (Dupont *et al.*, 1990; Fong

et al., 1996). The C—Se—C angles of $101.4(1)^\circ$ have the expected magnitude, due to the repulsion of the electron pairs. The torsion angle H1—C1—Se—C11 is $-47.67(8)^\circ$, and the angle between the phenyl ring and the plane which is formed by H1, C1 and Se has been found to be $80.53(7)^\circ$. This obviously results in slight sterical hindrance, and has consequences for the tetrahedral angles at C1. The Se—C—Se angles are slightly smaller than, and the H—C—Se angles slightly greater than, 109.5° . This is in contrast to the situation in the comparable sulfur compounds tris(ethylsulfonyl)methane (McGregor & Speakman, 1969) and methylidynetrisioacetic acid (Cannone *et al.*, 1980), where the S—C—S angles almost fit the ideal tetrahedral angle. S—C—S angles greater than 109.5° have been found for tripotassium methanetrissulfonate hydrate (Hall *et al.*, 1980).

At 3.73 Å, the Se···Se distances are too long to suggest bonding interactions.

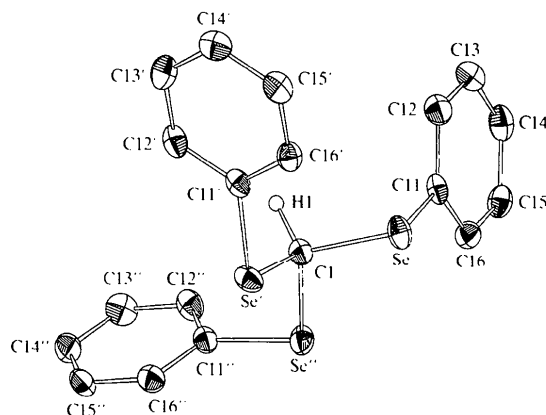


Fig. 1. ZORTEP (Zsolnai, 1997) diagram of $(\text{PhSe})_3\text{CH}$ showing 30% probability displacement ellipsoids. Phenyl H atoms have been omitted for clarity.

Experimental

Tris(phenylseleno)methane was prepared according to the literature procedure of Syper & Młochowski (1984) and was characterized by elemental analysis (found: C 48.12, H 3.28%; $\text{C}_{19}\text{H}_{16}\text{Se}_3$ requires: C 47.38, H 3.33%), IR, ^1H and ^{13}C NMR spectroscopy, and FAB mass spectrometry. The spectroscopic data obtained are in agreement with values published previously.

Crystal data

$\text{C}_{19}\text{H}_{16}\text{Se}_3$
 $M_r = 481.20$
 Trigonal
 $R\bar{3}$
 $a = 12.5841(8)$ Å
 $c = 18.993(2)$ Å
 $V = 2604.7(4)$ Å³
 $Z = 6$
 $D_x = 1.841$ Mg m⁻³
 D_m , not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 6.47$ – 15.20°
 $\mu = 6.348$ mm⁻¹
 $T = 203(2)$ K
 Block
 $0.20 \times 0.20 \times 0.15$ mm
 Colourless