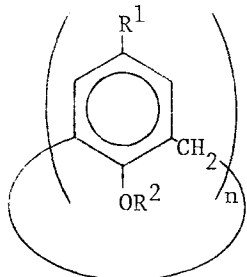


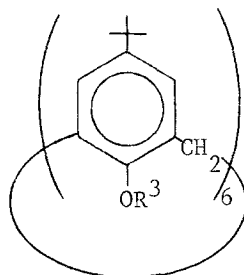
SOLID STATE STUDIES ON p.t-BUTYL-CALIX[6]ARENE DERIVATIVES

G.D. Andreotti, G. Calestani*, F. Ugozzoli
Institute of Structural Chemistry, University of Parma
A. Arduini, E. Ghidini, A. Pochini, R. Ungaro*
Institute of Organic Chemistry, University of Parma
Viale delle Scienze
I-43100 Parma, Italy

Calix[n]arenes¹ (1) are a class of phenol-formaldehyde macrocyclic oligomers which exhibit different sizes and shapes depending on the number of phenolic units in the cyclic array and on the nature of substituents on the aromatic nucleus (R^1) and on the phenolic oxygen (R^2).



(1)



(2) $R^3 = H$

(3) $R^3 = CH_2CON(C_2H_5)_2$

They are particularly attractive in Host-Guest Complex Chemistry because of their ability to form inclusion complexes with ions or/and neutral molecules², so they can function as ion and neutral molecule receptors in which the shape and the dimension of the cavity determine the selectivity toward the guest.

In calix[4] and calix[5]arenes^{3,4} the macrocycle is blocked in a "cone" conformation, both in solution and in solid state, through the formation of strong intramolecular hydrogen bonds.

Calix[6] and calix[8]arenes are more mobile in solution⁵ and these macrocyclic hosts have shown little ability to form inclusion complexes.

Recently an X-ray crystal structure of the cyclic octamer derived from p.t-butyl-calix[8]arene has been reported⁶ but no data are available on the correspondent calix[6]arene (2) which has been used as starting materials for the synthesis of various host compounds⁷.

The crystal structure of compound (2) has been obtained by X-ray diffraction, following the same experimental conditions reported previously⁸ on a colourless transparent single crystal obtained from chloroform.

The following crystal data have been obtained: $a=18.344$; $b=19.945$; $c=17.079$ Å; $V=6248$ Å³; $Z=4$. Laue Group D_2^h , Space Group $Pna2_1$ or $Pnma$. Although the structure is characterized by high disorder mainly in the *t*-butyl groups, which makes it difficult to obtain a completely satisfactory R value, the resolution is sufficient to establish the conformation of the molecule (Fig. 1).

No guest molecule has been evidenced inside the macrocycle which shows a distorted cone structure with the *t*.butyl groups pointing outside the macroring and the six phenolic oxygens pointing toward the interior.

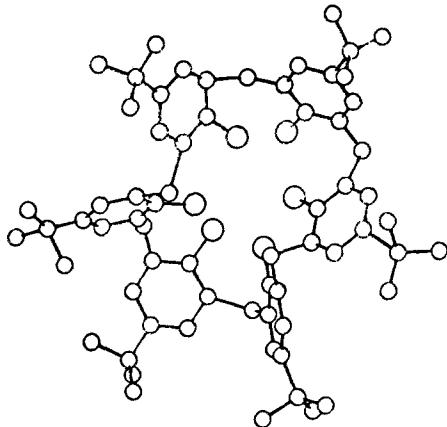


Fig. 1.
Perspective view of
p.t-butylcalix[6]arene

By treating *p.t*-butylcalix[6]arene (2) with α -chloro-*N,N*-diaethylacetamide (NaH, THF/DMF=5 v/v) the ligand (3), m.p. 238-240°C was obtained in 90% yield.

The ¹H and ¹³C NMR spectra show a complex pattern indicating a mixture of conformational isomers to be present in solution and a reduced mobility of the macrocycle at room temperature.

The X-ray crystal structure of compound (3) has been solved following improved techniques.

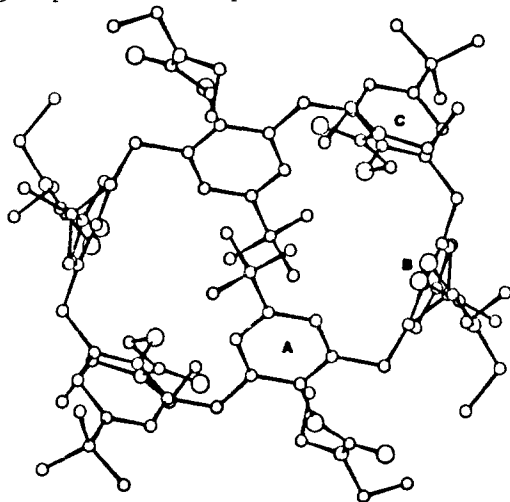


Fig. 2.
The X-Ray crystal
structure of *p.t*-butyl-
calix[6]arene amide:
view perpendicular to the
mean molecular plane.

Crystal data are as follows: $a = 24.564(4)$; $b = 14.509(3)$; $c = 14.380(5)$ Å; $\beta = 91.3(1)^\circ$ Monoclinic, Space Group $P 2_1/n$, $V = 5111.9$ Å³; $Z = 4$; $D_{\text{calc}} = 1.09$ g.cm⁻³.

The structure has been refined up to $R = 0.10$ using 1987 independent observed reflections from 8740 collected reflections.

The molecule, shown in Fig. 2, possesses a center of symmetry which coincides with a crystallographic center of symmetry.

The conformation can be referred to the mean molecular plane through the CH₂ bridging groups, that can be taken as a reference plane.

The dihedral angles formed by the three adjacent phenolic units A, B, C, with respect to the reference plane are = 35.09, 82.03, 40.36° respectively.

The amide chains and the *t*-butyl groups of the units B and C do not point toward the interior of the macroring. The phenolic unit A points its amide chains outside the macroring below the reference plane, while its *t*-butyl group points inside the macroring above the reference plane (and its centrosymmetrically related *t*-butyl group lies below) partially filling the intramolecular cavity.

Two methanol molecules for each macrocycle are guested in the intermolecular holes of the crystal lattice.

The situation is quite different if compared to that observed in the *p,t*-butylcalix[6]arene hexapodand⁹, where the intramolecular cavity was partially filled by two centrosymmetrically related ethereal chains and no guest molecules were observed.

With the aim of blocking the conformational mobility of the parent *p,t*-butylcalix[6]arene (2) creating a species able to perform molecular inclusion and to be active in catalysis, the *p,t*-butylcalix[6]arene-titanium(IV) complex has been synthesized, by treating (2) with Ti(OiPr)₄ in boiling toluene. A compound of molecular formula C₆₆H₇₈O₇Ti₂ · 3C₇H₈ crystallizes from toluene in the form of orange prisms suitable for X-ray analysis⁸.

Crystal data are: $a = 26.334(7)$; $b = 17.052(7)$; $c = 21.462(7)$ Å, $\beta = 94.89^\circ$. Monoclinic, Space Group $P 2_1/n$, $V = 9600(1)$ Å³, $Z = 2$.

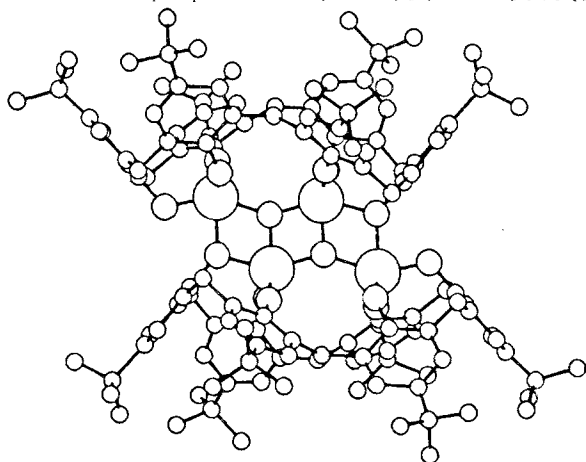


Fig. 3. X-Ray crystal structure of *p,t*-butylcalix[6]arene Ti(IV) complex.

The refinement is now performed up to $R = 0.199$. The molecule (Fig. 3) is dimeric and consists of two p.t-butylcalix[6]arene molecules in a "cone" structure, created by two Ti(IV) atoms which are bonded to six phenolic oxygen atoms and share a Ti-O-Ti bond.

The Ti atom is penta-coordinated in the form of a slightly distorted trigonal bi-pyramid as already observed in some Titanium(IV) oxygenated complexes¹⁰, although their preferred geometry is generally octahedral¹¹. The Ti-O bond distances in the rather unusual Ti-O-Ti bridge (it has not been observed in the other two calixarene - Ti(IV) complexes previously reported^{12,13}) range from 1.922(5) to 1.944(7) Å and the bond angle is 110.8° . A toluene molecule is guested in the intramolecular apolar cavity of each macrocycle, whereas two other molecules occupy intermolecular voids of the crystal lattice. These two molecules are rather disordered and this causes probably problems in the final refinement of the crystal structure.

Interestingly the rigid structure shown in the solid state is also retained in solution as inferred from the ^1H NMR spectrum which shows three doublets for the equatorial protons of the bridging methylenes centered at 3.25, 3.35, 3.53 δ and three doublets 4.66, 4.75, 5.14 δ for the axial ones.

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