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Calixarenes 11. Crystal and Molecular Structure of *p-tert*-Butylcalix[8]arene

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Abstract. Monoclinic prisms were obtained by slow evaporation of a pyridine solution of *p-tert*-butylcalix[8]arene: space group $P2_1/c$, $a = 20.312(3)$, $b = 23.020(2)$, $c = 20.006(6)$ Å; $\beta = 113.05(2)°$; $V = 8707.6$ Å^3; $Z = 4$. Refinement led to an R value of 0.166 for 4231 reflections which, although high, is sufficient to establish the conformation of the molecule as a pleated loop in which the eight hydroxyl groups are arranged in a slightly undulating, almost planar, intramolecularly hydrogen bonded cyclic array. The possible inferences for the conformation of *p-tert*-butylcalix[8]arene in solution are discussed.

Key words: X-ray crystal structure analysis; cyclic oligomer of *p-tert*-butylphenol and formaldehyde, calixarene conformation.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82019.

1. Introduction

The calixarenes have been the subject of a variety of investigations during the past several years [1,2], and the structures of a number of these macrocyclic compounds have been established by single crystal X-ray methods. For example, Andreetti and coworkers [3–5] have shown that *p-tert*-butylcalix[4]arene, *p*-(1,1,3,3-tetramethylbutyl)calix[4]arene, and calix[5]arene exist in a 'cone' conformation with a molecule of solvent inside the cone (i.e., an *endo*-calix complex). Comparable information for the calix[8]arene, however, has not been available, although Andreetti and coworkers [6] have reported an X-ray determination of the octaacetate of *p-tert*-butylcalix[8]arene. While their study served the critical function of definitively establishing the gross structure of the cyclic octamer, it sheds no light on the conformation of the parent compound in which intramolecular hydrogen bonding plays a critical role. The present study reports a single crystal X-ray crystallographic determination of *p-tert*-butylcalix[8]arene itself which reveals the conformation of this compound.

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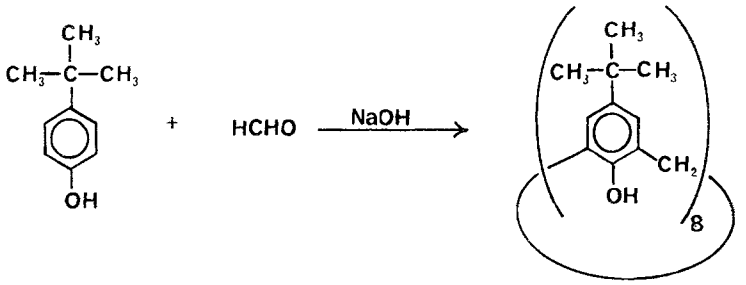
2. Experimental

2.1. SYNTHESIS

p-tert-Butylcalix[8]arene (**1**) was synthesized by refluxing a mixture of *p-tert*-butylphenol, paraformadehyde, and a trace of base in xylene for several hours [7] and was isolated in 70% yield as small, glistening needles after recrystallization from chloroform; mp 410–412°. Upon standing in air for a few minutes, however, the needles changed to an amorphous powder,



presumably the result of the loss of solvent of crystallization. To minimize this problem, crystallization from a higher boiling solvent was employed. A single crystal suitable for X-ray analysis was grown in pyridine by the process of slow evaporation. A boiling solution of 150 mg of noncrystalline **1** in 25 ml of pyridine was concentrated to *ca.* 10 ml and then allowed to slowly evaporate over a period of one month to *ca.* 2 ml, yielding diamond-shaped plates which were stable in this solution. To avoid loss of crystal integrity through evaporation of solvent of crytallization the moist crystals were mounted in a glass capillary tube.

2.2. CRYSTAL DATA

$C_{88}H_{112}O_8$: Formula weight = 1297.87. Monoclinic prisms, a = 20.312(3), b = 23.020(2), c = 20.006(6) Å; β = 113.05(2)°; V = 8707.6 Å^3; Z = 4. Space group $P2_1/c$.

2.3. STRUCTURE DETERMINATION

The experimental X-ray data, consisting of 8837 independent reflections, were collected from a crystal 0.3 × 0.2 × 0.4 mm on an Enraf–Nonius CAD 4 diffractometer using Ni-filtered Cu$K\alpha$ radiation (λ = 1.54178 Å) and $\omega/2\theta$ scan up to θ = 50°. Lattice parameters were refined using 25 reflections. Two standard reflections were measured after every 100 reflections, showing no decay in the crystals during the data collection. An Lp and a semi-empirical absorption correction were applied, the minimal and maximal transmission values (63% and 99%, respectively) indicating severe absorption (crystal plus capillary). The structure was solved using the RANTAN direct method developed at York [8], a best E-map (combined FOM = 2.999) revealing nearly all of the 96 nonhydrogen basis atoms. A least-squares refinement with isotropic thermal parameters and unit weights using 4231 reflections with $I > 2\sigma(I)$ converged at R = 0.166 with an average e.s.d. of the coordinates less than 0.015 Å. Although this R value is considerably higher than is desirable, the resolution is sufficient to establish the conformational details of the molecule, which is the point of primary interest in the present investigation.

3. Discussion of Results

The present data show that *p-tert*-butylcalix[8]arene (**1**), obtained from pyridine solution, exists in a conformation that has the architecture of a circular pleated ribbon in which the eight hydroxyl groups are arranged in a slightly undulating, almost planar, intramolecularly hydrogen bonded cyclic array as shown in Figure 1. This will be referred to as the 'pleated

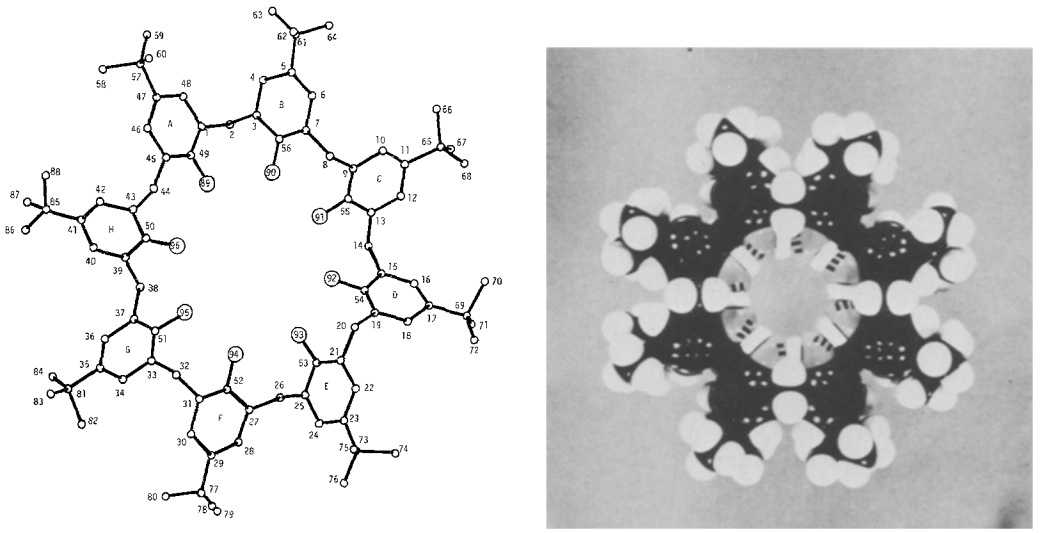


Fig. 1. 'Pleated loop' conformation of *p-tert*-butylcalix[8]arene.

loop' conformation. The molecule has two mutually perpendicular pseudo-mirror planes passing through the pairs of methylene groups at C(2) to C(26) and C(14) to C(38), normal to the mean plane of the molecule. In contrast, the octaacetate of *p-tert*-butylcalix[8]arene has a center of symmetry [4]. The arrangement of the aryl rings with respect to the average plane of the molecule is also different in **1** and its octaacetate. In the free calixarene **1** the dihedral angles between the benzene rings and the average plane are 40.6, 146.3, 40.3, 48.8, 138.7, 33.5, 41.0, and 140.4°, respectively, starting with benzene ring *A* and proceeding around the macrocycle in counterclockwise fashion. The corresponding values for the octaacetate of **1** [4] are 49.7, 60.2, 59.6, 40.0, 49.7, 60.2, 59.6, and d 40.0°. Whereas, the methylene groups of the octaacetate lie approximately in a plane (the minimum deviation is 0.13 Å), the parent calixarene **1** shows greater deviation, viz. 1.48 Å for C(2), − 1.15 Å for C(8), 2.16 Å for C(14), − 1.75 Å for C(20), 1.16 Å for C(26), − 1.57 Å for C(32), 1.68 Å for C(38), and − 1.66 Å for C(44). The hole formed by the circular array of hydroxyl groups is empty, and the distances between the transannular oxygen centers are 7.18 Å for O(89) to O(93), 7.55 Å for O(90) to O(94), 6.89 Å for O(91) to O(95), and 6.56 Å for O(92) to O(96).

The conformation of *p-tert*-butylcalix[8]arene in solution has been studied by Gutsche and Bauer [9]. They observed that in nonpolar solvents such as chloroform and bromobenzene there is a remarkable similarity in the temperature-dependent ^{1}H NMR spectral behavior between the calix[8]arene and the calix[4]arene. Since the latter exists in a 'cone' conformation the majority of the time (although it is conformationally mobile), a 'pinched' conformation having the appearance and, presumably, the conformational characteristics of a pair of cyclic tetramers 'stuck' together was postulated for the calix[8]arene, as illustrated in

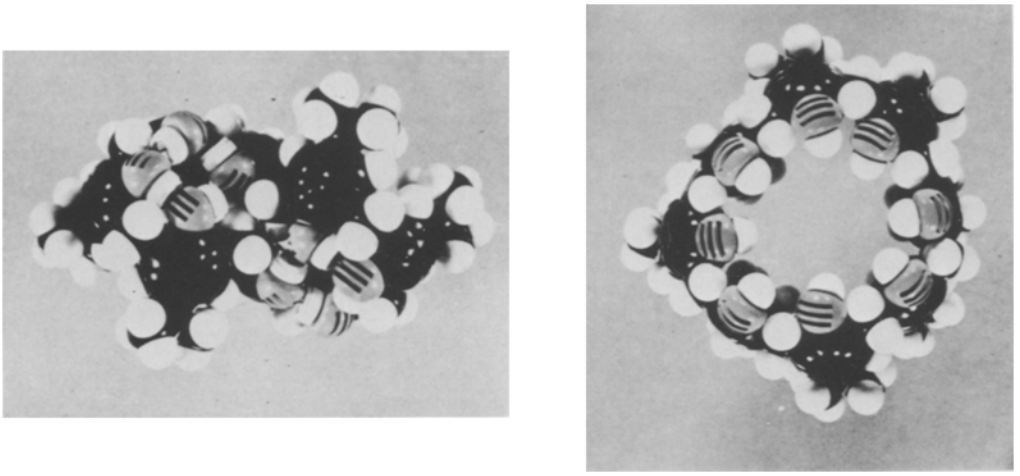


Fig. 2. 'Pinched' and 'expanded' conformations of *p-tert*-butylcalix[8]arene.

Figure 2. The similarity in the temperature-dependent ^{1}H NMR behavior of the calix[8]arene and calix[4]arene disappears in the more polar and more basic solvent pyridine, and it was postulated that the 'pinched' conformation gives way to an 'expanded' conformation. With the revelation that the solid state conformation is neither 'pinched' nor 'expanded' but is a 'pleated loop', an alternative explanation for the temperature-dependent ^{1}H NMR behavior of the calix[8]arene must be considered.

The disappearance of the near identity of temperature-dependent ^{1}H NMR behavior in pyridine can be ascribed to competition between intramolecular —O—H···O bonding and intermolecular —O—H···N bonding, resulting in reduction of the intramolecular hydrogen bond stabilization of the calixarene. In the inherently more rigid cyclic tetramer the reduction in conformational stability is relatively small, the coalescence temperature falling from *ca.* 45 °C to *ca.* 15 °C. In the inherently more flexible cyclic octamer, however, the reduction is much greater, the coalescence temperature falling from *ca.* 45 °C to well below − 90 °C. Although the conformation of a molecule in solution cannot necessarily be inferred from its conformation in the solid state and although the hydrogen bonding solvent pyridine was used to obtain the crystal for X-ray study, the 'pleated loop' hypothesis seems to us to provide at least as plausible a basis for explaining the temperature-dependent ^{1}H NMR behavior of the cyclic octamer as does the 'pinched-expanded' hypothesis. And, by not requiring the corollary hypothesis of a pseudo rotation it is in better accord with the principle of Occam's razor [10]. Possible pathways for the conformational interconversion of these compounds are discussed in another paper in this series [11].

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