

# Crystal and Molecular Structures of 5-Allyl-25-methoxy-26,27,28-tribenzoylcalix[4]arene

ALICE VRIELINK and PENELOPE W. CODDING★

*Departments of Chemistry and Pharmacology and Therapeutics, University of Calgary, Calgary, Alberta, Canada T2N 1N4*

C. DAVID GUTSCHE and LEE-GIN LIN

*Department of Chemistry, Washington University, St. Louis, MO 63130, U.S.A.*

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**Abstract.** The crystal and molecular structures of 5-allyl-25-methoxy-26,27,28-tribenzoylcalix[4]arene, an unsymmetrically substituted macrocycle, are reported. The space group is orthorhombic,  $P2_12_12_1$ , with  $a = 13.4181(6)$ ,  $b = 16.6652(10)$  and  $c = 18.9936(14)$  Å and  $Z = 4$ . Refinement by least-squares calculations converged with a  $R = 0.060$  for 4018 observed reflections. The molecule assumes a 1,3 alternate conformation with 2 benzoate rings and the disordered allyl side chain on one side and the third benzoate ring and the methoxy group on the opposite side of the mean plane of the methylene bridging groups. The four phenyl rings that comprise the macrocycle are approximately parallel in pairs; the members of a pair are 5.6 Å apart. The carbonyl oxygen atoms of the 3 benzoate groups are oriented away from the center of the cavity while the ester oxygen atoms and the methoxy oxygen atom are oriented toward the cavity center.

**Key words:** calix[4]arene, X-ray crystal structure analysis, enzyme mimic.

**Supplementary Data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82033 (26 pages).

## 1. Introduction

Calixarenes are cyclic compounds that are of interest due to their potential use as enzyme mimics [1,2]. They are formed by the base-induced condensation of formaldehyde and *p*-alkylphenols to give macrocycles of 4, 5, 6, and 8 aryl rings. The calixarenes form complexes with a variety of small molecules that bind in the cavity of the calix in much the same way as observed in cyclodextrin host-guest complexes. They differ from the cyclodextrins, however, in that they are synthetic molecules and thus have greater possibility for controlled design and functionality.

The calixarenes exist in a number of different isomeric conformations, some of which are not useful as hosts as they lack a definable cavity. The four isomeric forms are the cone, partial cone, 1,2 alternate and 1,3 alternate [1]. For enzyme mimics, the most useful isomeric forms are the cone and partial cone conformers. To assure these conformers, the molecule can be modified to decrease conformational flexibility and to enforce a cavity large enough to trap other molecules. The tribenzoate, 5-allyl-25-methoxy-26,27,28-tribenzoyloxycalix[4]arene [3], shown in Figure 1 is unsymmetrically substituted. Such a substitution pattern allows the selective functionalization of the calixarene to direct the molecular conformation, the type of

★ Author for correspondence.

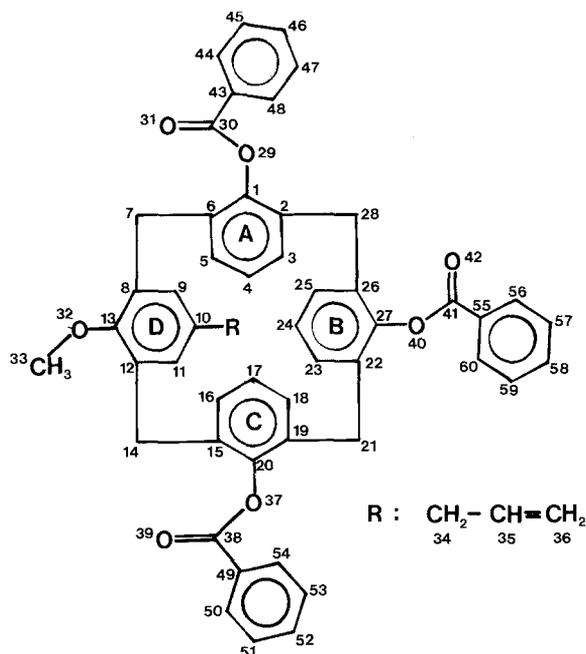


Fig. 1. The structure and atomic labelling scheme for allyl benzoyloxy calixarene.

inclusion complexes formed, and the reaction specificity achieved. The crystal structure of this synthetic compound was determined to elucidate the effect the asymmetry has on the conformation and to provide insight into further modifications that might be useful in the design of enforced-cavity calixarenes.

## 2. Experimental

### 2.1. CRYSTAL DATA

Formula weight = 790.92, hexagonal plates,  $a = 13.4181(6)$ ,  $b = 16.665(1)$ ,  $c = 18.994(1)$  Å;  $V = 4247.3(2)$  Å<sup>3</sup>,  $Z = 4$ , space group  $P2_12_12_1$ ,  $D_c = 1.24$  g cm<sup>-3</sup>,  $D_0 = 1.24$  g cm<sup>-3</sup>,  $\mu = 6.64$  cm<sup>-1</sup>,  $\lambda(\text{CuK}\alpha) = 1.5418$  Å.

### 2.2. STRUCTURE DETERMINATION

The reflection data were collected from a  $0.24 \times 0.45 \times 0.26$  mm colorless crystal on an Enraf Nonius CAD4 automated diffractometer using  $\omega/2\theta$  scans up to  $\theta_{\text{max}} = 70^\circ$ . Lattice parameters were defined by 50 reflections. Three reflections were remeasured every 1800 seconds of exposure and showed less than 2% variation in intensity. Two octants of data (11465 reflections) were collected and averaged to give 4457 unique data of which 4018 had  $I > 2.0\sigma(I)$ . The structure was solved by MULTAN78 [4]. The allyl side chain is disordered in the crystal. The terminal two atoms of the allyl side chain are found in two sites of equal occupancy. These positions were included in the model with population parameters set to 0.50. The positions and anisotropic thermal parameters of the nonhydrogen atoms were refined by a restrained least squares procedure [5]. The hydrogen atoms were included in

calculated ideal positions and were not refined separately but were allowed to ride on the atoms to which they were bonded. The thermal parameters of the hydrogen atoms were defined as 1.2 times those of the bonded atoms and were not refined. In the final cycles of refinement of the nonhydrogen atoms, there were no constraints on the positional parameters and, to achieve convergence, there were 30% constraints on the anisotropic thermal parameters so that the final geometry reflects the true molecular dimensions. The thermal parameters of the disordered atoms were fixed in the final cycles. The refinement gave a final  $R$  value of 0.060 and  $R_w$  of 0.072 with weights defined as  $w^{-1} = [\sigma^2(F_o) + 0.0005 F_o^2]$ . In the final cycle of refinement, the maximum shift/error for the coordinates was 0.734 Å for C(35a): the maximum shift/error for the thermal parameters was 0.814 Å for C(34). The magnitudes of both of these values were due to the disorder in the allyl side chain. The goodness of fit was 0.50. The atomic coordinates for the nonhydrogen atoms are given in Table I with the atoms labeled as in Figure 1. The bond distances and angles for the nonhydrogen atoms are given in Table II. Tables of hydrogen atom parameters, non-hydrogen atom anisotropic thermal parameters, and structure factors may be found with the supplementary material.

Table I. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\times 10$ ) for allyl benzyloxy calixarene (Beq is defined as 1/3 the trace of the Bij matrix)

Atom	$x/a$	$y/b$	$z/c$	Beq(Å <sup>2</sup> )
C(1)	391(2)	1559(2)	8133(2)	38(4)
C(2)	1054(3)	1557(2)	7572(2)	42(4)
C(3)	1659(3)	2233(2)	7495(2)	52(5)
C(4)	1600(3)	2865(2)	7972(2)	56(6)
C(5)	964(3)	2826(2)	8534(2)	51(5)
C(6)	342(3)	2166(2)	8631(2)	42(5)
C(7)	-349(3)	2114(2)	9262(2)	48(5)
C(8)	-167(3)	1408(2)	9746(2)	42(4)
C(9)	-933(3)	880(2)	9908(2)	48(5)
C(10)	-789(3)	240(3)	10363(2)	54(6)
C(11)	146(3)	123(2)	10657(2)	50(5)
C(12)	939(3)	637(2)	10504(1)	41(4)
C(13)	768(3)	1283(2)	10053(2)	39(4)
C(14)	1959(3)	481(2)	10818(2)	44(5)
C(15)	2792(3)	367(2)	10294(1)	37(4)
C(16)	3652(3)	831(2)	10342(2)	44(5)
C(17)	4409(3)	752(2)	9855(2)	47(4)
C(18)	4325(3)	213(2)	9300(2)	42(5)
C(19)	3479(2)	-264(2)	9237(2)	35(4)
C(20)	2739(2)	-187(2)	9749(2)	35(4)
C(21)	3389(3)	-866(2)	8641(2)	40(4)
C(22)	2504(3)	-770(2)	8156(2)	39(4)
C(23)	1922(3)	-1436(2)	7987(2)	47(5)
C(24)	1098(3)	-1365(2)	7552(2)	52(5)
C(25)	840(3)	-627(2)	7277(2)	48(5)
C(26)	1408(3)	55(2)	7414(1)	39(4)
C(27)	2236(2)	-39(2)	7846(1)	35(4)
C(28)	1139(3)	847(2)	7075(2)	47(5)
O(29)	-279(2)	909(1)	8203(1)	39(3)
C(30)	-1181(3)	1007(2)	7887(2)	50(5)
O(31)	-1377(2)	1588(2)	7548(2)	90(6)

Table I (continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Beq(Å <sup>2</sup> )
O(32)	1545(2)	1801(1)	9894(1)	49(4)
C(33)	1678(4)	2460(3)	10375(3)	70(8)
C(34)	-1655(4)	-335(4)	10527(3)	86(9)
C(35)	-2577(9)	71(9)	10881(8)	93(20)
C(36)	-3369(9)	-152(10)	10725(10)	106(27)
O(37)	1918(2)	-703(1)	9682(1)	38(3)
C(38)	1851(3)	-1307(2)	10157(2)	40(4)
O(39)	2390(2)	-1371(1)	10656(1)	56(4)
O(40)	2798(1)	656(1)	7989(1)	37(3)
C(41)	3688(2)	739(2)	7663(2)	39(4)
O(42)	4041(2)	228(1)	7295(1)	53(4)
C(43)	-1865(3)	327(2)	8024(2)	45(5)
C(44)	-2802(3)	369(3)	7716(3)	67(7)
C(45)	-3483(3)	-243(3)	7817(3)	72(8)
C(46)	-3237(4)	-892(3)	8225(3)	65(7)
C(47)	-2312(4)	-932(3)	8533(2)	62(7)
C(48)	-1613(3)	-330(2)	8433(2)	51(6)
C(49)	1050(3)	-1888(2)	9978(2)	45(4)
C(50)	455(3)	-1801(3)	9395(2)	60(6)
C(51)	-235(4)	-2409(4)	9236(3)	79(8)
C(52)	-306(4)	-3073(3)	9661(3)	84(8)
C(53)	283(5)	-3147(3)	10239(4)	90(9)
C(54)	960(4)	-2557(3)	10409(3)	68(7)
C(55)	4160(3)	1533(2)	7818(2)	44(5)
C(56)	3819(3)	2029(2)	8347(2)	52(5)
C(57)	4293(4)	2771(3)	8445(3)	68(7)
C(58)	5089(4)	2997(3)	8019(3)	77(8)
C(59)	5430(4)	2483(3)	7499(3)	78(8)
C(60)	4964(4)	1749(3)	7392(3)	61(7)
C(35a)	-1522(14)	-1216(10)	10564(13)	137(36)
C(36a)	-2159(19)	-1647(13)	10926(14)	173(43)

### 3. Results

The molecule adopts a 1,3 conformation, as shown in Figures 2 and 3, with the distances between the two sets of phenyl rings, *A-C* and *B-D* of 5.6(4) and 5.7(5) Å, respectively. The diagonal dimensions of the torus are 7.155(6) Å (C(7)⋯C(21)) and 7.220(6) Å (C(14)⋯C(28)). The phenyl rings are slightly tilted so that the ester and methoxy oxygen atoms point inward towards each other and the center of the torus. The angle between the planes of rings *A* and *C* is 21.5(2)° and between the planes of rings *B* and *D* is 28.7(2)°. The distance between ester oxygen atoms is 4.878(4) Å and between the ester and methoxy oxygen atoms is 4.423(4) Å. This tilting of the phenyl rings brings these oxygen atoms closer and enhances the hydrophilicity of the torus. The angles that the rings (*A,B,C,D*) make with the least squares plane defined by the bridging methylene groups are 81.49(2)°, 78.76(2)°, 77.05(2)° and 72.58(2)°; these values indicate the tilting of the rings.

In contrast to the phenyl rings, the two benzoyloxy rings lying on the same side of the plane defined by the bridging methylene groups are parallel to each other. The closest intramolecular distances between the rings are between C(47)⋯C(51) = 3.95(1) Å and

Table II. Bond distances (Å) and angles (°) for allyl benzoyloxy calixarene

Atoms	Distance (Å)	Atoms	Angles (°)
C(1)–C(2)	1.388(6)	C(2)–C(1)–C(6)	123.8(4)
C(1)–C(6)	1.386(6)	C(2)–C(1)–O(29)	118.5(3)
C(1)–O(29)	1.414(5)	C(6)–C(1)–O(29)	117.7(3)
C(2)–C(3)	1.396(6)	C(1)–C(2)–C(3)	116.8(4)
C(2)–C(28)	1.518(6)	C(1)–C(2)–C(28)	121.8(4)
C(3)–C(4)	1.392(7)	C(3)–C(2)–C(28)	121.3(4)
C(4)–C(5)	1.368(7)	C(2)–C(3)–C(4)	120.6(4)
C(5)–C(6)	1.393(6)	C(3)–C(4)–C(5)	120.5(4)
C(6)–C(7)	1.518(6)	C(4)–C(5)–C(6)	121.0(4)
C(7)–C(8)	1.513(6)	C(1)–C(6)–C(5)	117.2(4)
C(8)–C(9)	1.387(6)	C(1)–C(6)–C(7)	121.7(4)
C(8)–C(13)	1.399(6)	C(5)–C(6)–C(7)	121.0(4)
C(9)–C(10)	1.386(6)	C(6)–C(7)–C(8)	115.2(4)
C(10)–C(11)	1.387(7)	C(7)–C(8)–C(9)	120.6(4)
C(10)–C(34)	1.538(8)	C(7)–C(8)–C(13)	120.9(4)
C(11)–C(12)	1.396(7)	C(9)–C(8)–C(13)	118.5(4)
C(12)–C(13)	1.395(6)	C(8)–C(9)–C(10)	121.5(4)
C(12)–C(14)	1.515(6)	C(9)–C(10)–C(11)	119.0(4)
C(13)–O(32)	1.387(5)	C(9)–C(10)–C(34)	120.0(5)
C(14)–C(15)	1.508(6)	C(11)–C(10)–C(34)	120.9(5)
C(15)–C(16)	1.392(6)	C(10)–C(11)–C(12)	121.3(4)
C(15)–C(20)	1.389(5)	C(11)–C(12)–C(13)	118.4(4)
C(16)–C(17)	1.380(6)	C(11)–C(12)–C(14)	120.1(4)
C(17)–C(18)	1.390(6)	C(13)–C(12)–C(14)	121.5(4)
C(18)–C(19)	1.391(6)	C(8)–C(13)–C(12)	121.2(4)
C(19)–C(20)	1.396(5)	C(8)–C(13)–O(32)	119.4(4)
C(19)–C(21)	1.517(6)	C(12)–C(13)–O(32)	119.4(4)
C(20)–O(37)	1.403(5)	C(12)–C(14)–C(15)	115.5(3)
C(21)–C(22)	1.511(6)	C(14)–C(15)–C(16)	120.1(4)
C(22)–C(23)	1.394(6)	C(14)–C(15)–C(20)	122.5(4)
C(22)–C(27)	1.400(6)	C(16)–C(15)–C(20)	117.4(4)
C(23)–C(24)	1.385(7)	C(15)–C(16)–C(17)	120.9(4)
C(24)–C(25)	1.380(7)	C(16)–C(17)–C(18)	120.7(4)
C(25)–C(26)	1.393(6)	C(17)–C(18)–C(19)	120.1(4)
C(26)–C(27)	1.390(5)	C(18)–C(19)–C(20)	117.9(4)
C(26)–C(28)	1.512(6)	C(18)–C(19)–C(21)	120.5(4)
C(27)–C(40)	1.408(5)	C(20)–C(19)–C(21)	121.6(3)
C(29)–C(30)	1.360(5)	C(15)–C(20)–C(19)	123.0(4)
C(30)–O(31)	1.192(6)	C(15)–C(20)–O(37)	121.0(3)
C(30)–C(43)	1.481(6)	C(19)–C(20)–O(37)	116.0(3)
C(32)–C(33)	1.440(7)	C(19)–C(21)–C(22)	116.6(3)
C(34)–C(35)	1.562(16)	C(21)–C(22)–C(23)	119.7(4)
C(34)–C(35a)	1.481(19)	C(21)–C(22)–C(27)	123.4(4)
C(35)–C(36)	1.164(20)	C(23)–C(22)–C(27)	116.9(4)
C(37)–C(38)	1.355(5)	C(22)–C(23)–C(24)	121.1(4)
C(38)–O(39)	1.197(5)	C(23)–C(24)–C(25)	120.1(4)
C(38)–C(49)	1.486(6)	C(24)–C(25)–C(26)	121.3(4)
C(40)–C(41)	1.352(5)	C(25)–C(26)–C(27)	117.1(4)
C(41)–O(42)	1.199(5)	C(25)–C(26)–C(28)	120.1(4)
C(41)–C(55)	1.496(6)	C(27)–C(26)–C(28)	122.7(4)
C(43)–C(44)	1.388(7)	C(22)–C(27)–C(26)	123.5(4)
C(43)–C(48)	1.384(7)	C(22)–C(27)–O(40)	119.8(3)
C(44)–C(45)	1.383(8)	C(26)–C(27)–O(40)	116.7(3)

Table II (continued)

Atoms	Distance (Å)	Atoms	Angles (°)
C(45)–C(46)	1.371(9)	C(2)–C(28)–C(26)	115.7(3)
		C(1)–O(29)–C(30)	115.6(3)
		O(29)–C(30)–O(31)	122.1(4)
C(46)–C(47)	1.373(8)	O(29)–C(30)–C(43)	112.4(4)
C(47)–C(48)	1.386(7)	O(31)–C(30)–C(43)	125.4(4)
C(49)–C(50)	1.373(7)	C(13)–O(32)–C(33)	115.5(4)
C(49)–C(54)	1.388(7)	C(10)–C(34)–C(35)	114.5(4)
C(50)–C(51)	1.405(9)	C(10)–C(34)–C(35a)	122.4(9)
C(51)–C(52)	1.373(10)	C(35)–C(34)–C(35a)	120.3(11)
C(52)–C(53)	1.358(10)	C(34)–C(35)–C(36)	118.4(15)
C(53)–C(54)	1.377(9)	C(20)–C(37)–C(38)	116.6(3)
C(55)–C(56)	1.379(6)	O(37)–C(38)–O(39)	123.6(4)
C(55)–C(60)	1.395(7)	O(37)–C(38)–C(49)	112.3(3)
C(56)–C(57)	1.403(7)	O(39)–C(38)–C(49)	124.1(4)
C(57)–C(58)	1.392(9)	C(27)–C(40)–C(41)	117.9(3)
C(58)–C(59)	1.385(9)	O(40)–C(41)–O(42)	122.9(4)
C(59)–C(60)	1.389(8)	O(40)–C(41)–C(55)	112.0(3)
C(35a)–C(36a)	1.311(33)	O(42)–C(41)–C(55)	125.1(4)
		C(30)–C(43)–C(44)	116.6(4)
		C(30)–C(43)–C(48)	123.5(4)
		C(44)–C(43)–C(48)	119.8(4)
		C(43)–C(44)–C(45)	120.2(5)
		C(44)–C(45)–C(46)	120.1(5)
		C(45)–C(46)–C(47)	119.8(5)
		C(46)–C(47)–C(48)	121.2(5)
		C(43)–C(48)–C(47)	119.0(5)
		C(38)–C(49)–C(50)	122.4(4)
		C(38)–C(49)–C(54)	116.8(4)
		C(50)–C(49)–C(54)	120.7(5)
		C(49)–C(50)–C(51)	118.7(5)
		C(50)–C(51)–C(52)	120.0(6)
		C(51)–C(52)–C(53)	120.5(6)
		C(52)–C(53)–C(54)	120.6(6)
		C(49)–C(54)–C(53)	119.5(5)
		C(41)–C(55)–C(56)	122.2(4)
		C(41)–C(55)–C(60)	116.2(4)
		C(56)–C(55)–C(60)	121.6(4)
		C(55)–C(56)–C(57)	118.3(5)
		C(56)–C(57)–C(58)	120.6(5)
		C(57)–C(58)–C(59)	120.0(5)
		C(58)–C(59)–C(60)	120.0(6)
		C(55)–C(60)–C(59)	119.4(5)
		C(34)–C(35a)–C(36a)	119.3(18)

C(48)···C(50) = 4.130(9) Å. This parallel arrangement of the rings causes a narrowing of the channel on this side of the torus. The torus would be more accessible from the opposite side where there is only one benzoyloxy ring. The two positions of the allyl side chain are shown in Figure 2. The torsion angles: C(9)–C(10)–C(34)–C(35) =  $-60.9(9)^\circ$  and C(9)–C(10)–C(34)–C(35a) =  $138(1)^\circ$  indicate that the side chain either points away from or towards the two parallel benzoate rings. The crystalline environment has a large unoccupied volume in the region of the side chain which can accommodate the disorder. The closest

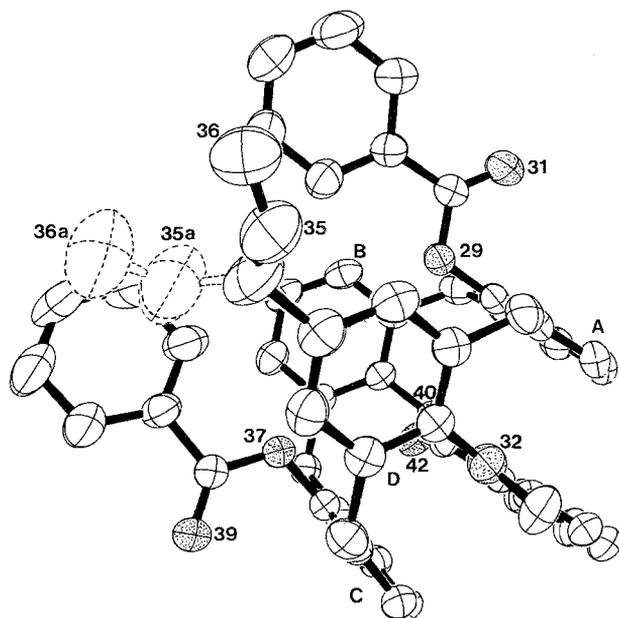


Fig. 2. The molecular conformation of allyl benzoxy calixarene showing the two positions of the disordered side chain (one conformer is shown in dashed lines). This drawing was made with the computer program ORTEP [11].

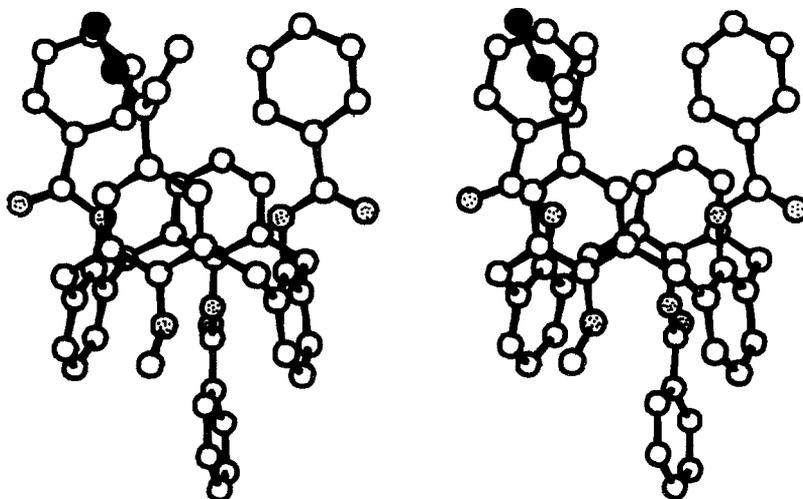


Fig. 3. Stereoscopic drawing of the molecular conformation showing the disordered allyl side chain (one position of the side chain is shown with darkened atoms). This drawing was made with the computer program PLUTO [12].

intermolecular contacts to either disordered side chain are greater than 4.0 Å. The large space occupied by the disordered side chain is surrounded by benzoxy rings making a hydrophobic environment for the allyl side chains. Neither position of the side chain is well-ordered, as is evident from the large thermal parameters shown in Table I; this arises either from atomic motion or from the existence of alternative unmodeled positions.

The 1,3 conformation adopted by this unsymmetrically-substituted calixarene is different from that observed for phenolic calixarenes [6–9]. In these cases, the phenolic hydroxyl group stabilized the cone conformation by the formation of a ring of intramolecular hydrogen bonds around the cavity. Replacement of the hydroxyl groups by acetoxy groups gives a tetraacetoxy calixarene with a partial cone conformation [10]. The acetoxy derivative cannot form the intramolecular hydrogen bonds that stabilize the cone conformation over other conformations. The tribenzoyloxy calixarene reported here, like the acetoxy calixarene, cannot form hydrogen bonds to stabilize the cone conformation and so is observed in an alternative conformer.

The 1,3 conformation observed in this structure is due to intramolecular effects rather than to the crystalline environment. The crystal packing shows no close intermolecular contacts between the aromatic ring systems and thus no ring stacking. Also, there are no close intermolecular or intramolecular interactions of the carbonyl or ester oxygen atoms. Crystal packing forces are not the prime determinant of the molecular conformation, instead either the large substituents on the calixarene ring system force it into the 1,3 alternate conformation or the conformation is a function of the reaction conditions employed in the benzylation reaction. Experiments are underway at the University of Washington to explore this second possibility.

The bulk of the substituents on the macrocycle influences the conformer observed. The partial cone conformer observed for the tetraacetoxy calixarene [10] mentioned above may be due in part to the increase in size of the substituent from the hydroxyl to acetoxy. Recently, the X-ray structure of a *p-t*-butylcalix[4]arene with ethyl acetate substituents has been reported; the molecule adopts a distorted cone conformation [13]. Such a conformation supports the assumption that bulky groups dictate the isomer formed since the bulky carbonyl group is positioned one carbon atom further along the chain than for the acetoxy substituent. The resulting reduction in the size of the substituent attached to the phenyl rings allows the molecule to adopt the cone conformation. The benzyloxy groups are bulkier than the acetoxy groups so the unfavorable steric interactions disfavor the cone conformation. Computer graphics modelling of the cone conformation of the tribenzoyloxy calixarene shows that the cone is sterically unfavorable due to the close contacts between the benzyloxy rings.

Although the cone conformation is not accessible to the molecule the partial cone conformer is. The asymmetry of the molecule allows two possible partial cone conformations. Rings *A*, *B* and *C* could make up the partial cone, however unfavorable steric interactions of the three benzyloxy groups would be expected. The second possible partial cone isomer could be made with rings *A*, *C* and *D*. In this case the methoxy group would lie on the same side of the molecule as the benzyloxy substituents on rings *A* and *D*. A guest molecule could provide the stabilizing force for the molecule to adopt a conformation more useful as an enzyme model. Work is in progress at the University of Calgary to crystallize this calixarene complexed with a guest molecule. Comparisons of the crystal structures of different substituted calixarenes both with and without guest molecules as well as potential energy calculations of these conformations will provide more insight in the further design of conformationally restricted isomers.

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