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Monique Perrin[a]; Sylvain Lecocq[a]; Paula M. Marcos[b]; J. L. C. Pereira[b]
[a] Laboratoire de Cristallographie-ESA5078 43, Villeurbanne cedex, France [b] Departamento de Quimica, Faculdade de Ciěncias de Lisboa, R: Escola Politécnica, Lisboa, Portugal

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Substituent Effects in Dihomooxacalix [4] arenes: Conformations and Crystal Structures of Dihomooxacalix [4] arenes Tetrasubstituted at the OH Groups

MONIQUE PERRIN[a,*], SYLVAIN LECOCQ[a], PAULA M. MARCOS[b] and J. L. C. PEREIRA[b]

[a] *Laboratoire de Cristallographie-ESA5078 43, boulevard du 11 November 1918, 69622 Villeurbanne cedex - France;*
[b] *Departamento de Quimica, Faculdade de Ciências de Lisboa, R: Escola Politécnica, 58, 1200 Lisboa, Portugal*

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The crystal structures of four derivatives of the *p*-tert-butyldihomooxacalix [4] arenes are reported. These four compounds are obtained by substitution of the four phenolic hydrogens by CH_3 or CH_2CH_3 or $CH_2 — CH{=}CH_2$ or  $-\underset{CH_3}{\overset{O}{\overset{\|}{C}}}$ groups. The four calixarenes exhibit a 1,2 alternate conformation; the geometry of the dimethyleneoxa group is studied for the different compounds.

Keywords: Dihomooxacalix [4] arenes, crystal structures, conformations

INTRODUCTION

We recently published [1] a comparison of the conformations of dihomooxacalix [4] arenes when different neutral molecules have been complexed. These calixarenes are all in the cone conformation, some of them with a symmetry plane. Some changes occurs at the $CH_2—O—CH_2$ bridge, particularly when the comparison is made with the empty form. The hydrogen bonds at the OH groups are also different sometimes with a bifurcated H-bond with the guest.

Another approach to the variations of the conformations of calixarenes were studied by Grootenhuis *et al.* [2] both by computational and structural methods on calix [4] arenes substituted at the OH groups by methyl groups. These authors have shown that the substitutions by two methyls give a cone conformation with an approximative C_{2v} symmetry; with three methyl groups they obtained an irregular cone; then the cone conformation is destroyed and a partial cone conformation is obtained when the compound is tetrasubstituted.

In this paper we study the dihomooxacalix [4] arenes with a *tert-butyl* group at para position of the hydroxyl groups and the hydrogen of the hydroxyl groups substituted by: CH_3 (compound **1**), $CH_2—CH_3$ (compound **2**),

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[*] Corresponding author.

$CH_2—CH{=}CH_2$ (compound **3**) and  (compound **4**). These compounds were prepared and their conformation studied by NMR [3]. This paper concerns the conformation in the solid state determined by X-ray diffraction.

EXPERIMENTAL

Synthesis

For compounds **1**, **2** and **4**, the preparations have been described [3]. Compounds **3** was prepared in the same way as compounds **1** and **2** [4].

X-ray Data

For all four compounds, a crystal, obtained from DMF solution, was sealed in a Lindeman glass capillary for X-ray analysis. Accurate unit cell dimensions were obtained by a least-squares fit of 25 reflections measured on an Enraf-Nonius CAD-4 diffractometer. Intensity data were collected up to $\theta = 73°$ by using to ω-2θ scan mode with monochromated CuKα radiation. Three standard reflections were measured every hour to control intensity variation. Lorentz and polarisation corrections were applied and absorption was corrected with the program PSI and EAC of SDP [5]. The number of reflections measured and used in the refinement is given with crystal data in Table I.

Structure Analysis and Refinement

The structures were solved by MULTAN [6] and refined by SHELX76 [7]. The parameters of non H-atoms were refined by several cycles of full-matrix least-squares calculations, first with isotropic and then with anisotropic temperature factors. H positions were calculated at theoretical positions and included in the refinement with fixed contributions with B factors values equal to the Beq of the corresponding carbon atom. In the case of compound **1**, the refinement shows peaks near the atoms of the $CH_2—O—CH_2$ bridge. In fact, there is a

TABLE I Crystal data

	1	2	3	4
Fomula	$C_{49}O_5H_{66}$	$C_{53}O_5H_{74}$	$C_{57}O_5H_{74}$	$C_{53}O_9H_{66}$
For.wt	735.06	791.17	839.21	847.10
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Temp, °C	20	20	20	20
Cell constants:				
a	10.126 (3)	16.338 (8)	17.892 (3)	11.961 (4)
b	31.571 (6)	12.009 (8)	10.019 (1)	14.978 (3)
c	14.378 (7)	24.687 (8)	28.367 (4)	15.338 (3)
α				67.94(2)
β	99.43(4)	91.14(4)	99.05(1)	76.72(2)
γ				87.40(2)
Range of θ for cell constants, °	$19<\theta<48$	$6<\theta<48$	$10<\theta<34$	$8<\theta<50$
Volume, $Å^3$	4534(3)	4843(4)	5021(1)	2476(1)
Z	4	4	4	2
D_{calc}, $g \cdot cm^{-3}$	1.077	1.085	1.110	1.136
μ calc, cm^{-1}	4.97	4.93	5.03	5.77
$F(000)$	1600	1728	1824	912
Radiation CuKα	1.54056	1.54056	1.54056	1.54056
R	0.11	0.08	0.09	0.09
Residual peak: e $Å^{-3}$	0.31	0.26	0.31	0.30
N refl. measured	9561	10458	10977	10269
N refl. refinement	6164	8584	4999	9088

disorder giving two positions for this bridge as well as for the carbon atom of the methyl group substituted on the hydroxyl group. However, the refinement of the non-H atoms: O(2)A, C(2)A, C(02)A, C(25)A and O(2)B, C(2)B, C(02)B and C(25)B was anisotropic. For this compound H atoms were placed in calculated positions and allowed to ride on the bonded carbon atom. The *R* values as well as the residual electron density are given in Table I. Figure 1 gives the numbering scheme used for the macrocycle without substituents at OH groups.

The atomic coordinates, bond lengths and bond angles are given as supplementary data.

RESULTS AND DISCUSSION

From the RMN studies [3], three conformations were first suggested, two 1,2- and one 1,3-alternate conformation. These conformations show for one of them a symmetry plane, for the two others a two-fold axis. Additional studies reject the possibility of a symmetry plane in the 1,2 alternate conformation giving the choice between the two conformations with C2 symmetry. In the solid state, for the four compounds studied, the 1,2 alternate conformation is well established with a pseudo two-fold axis. Figure 2 gives the stereoview of the molecule of the compound **2** showing the 1,2 alternate conformation with its pseudo symmetry axis.

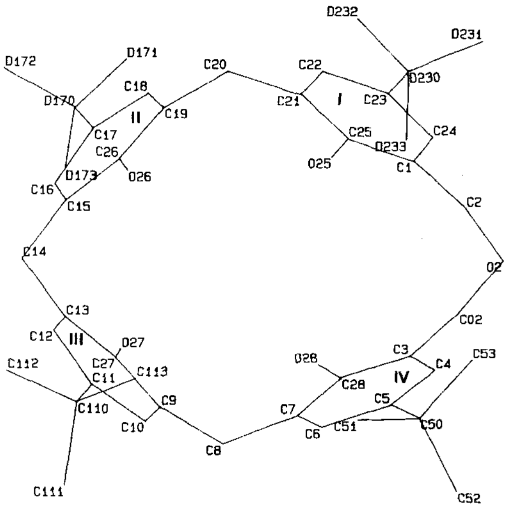


FIGURE 1 Numbering scheme of the macrocycle.

Table II gives the dihedral angles between the mean planes of the benzene rings versus the mean plane of the three methylene groups (M). The pseudo C2 symmetry for the four compounds is in accordance with the values of these angles.

Furthermore, for the compounds **1**,**2** and **4** two benzene rings are almost perpendicular to the plane M while the inclinations of the two others are large (values from 123.7(1)° to 145.0(1)°). The conformation of the compound **3** with allyl groups is more regular with the four values from 104.0(1)° to 112.9(1)°.

The main point is the geometry around the dimethyleneoxabridge which has great flexibility. Figure 3 shows that the oxygen atom of the bridge points outside the macrocycle for compounds **2** and **3** and inside the macroring for compound **4**. Compound **1** with methyl groups as substituents shows disorder as, said previously; the schemes of the two molecules show that the oxygen atom of the bridge points outside or inside the macrocycle. Therefore, these four calixarenes exhibit two conformations at the methylene bridge.

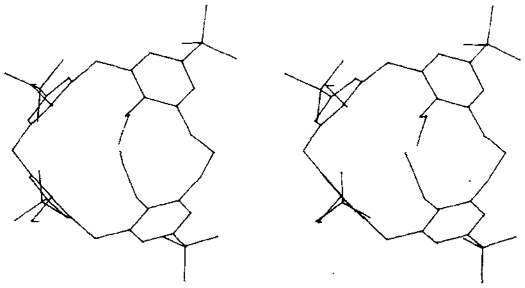


FIGURE 2 Stereoview of compound **2**.

TABLE II Dihedral angles between benzene rings and mean plane of methylene groups

	I	II	III	IV
CH_3	136.7(1)	95.9(1)	95.5(1)	124.5(1)
CH_2CH_3	133.7(1)	98.0(1)	94.5(1)	123.7(1)
$CH_2{-}CH{=}CH_2$	112.9(1)	105.5(1)	104.0(1)	107.5(1)
$\overset{O}{\overset{\|}{C}}{-}CH_3$	136.5(1)	93.8(1)	96.0(1)	145.0(1)

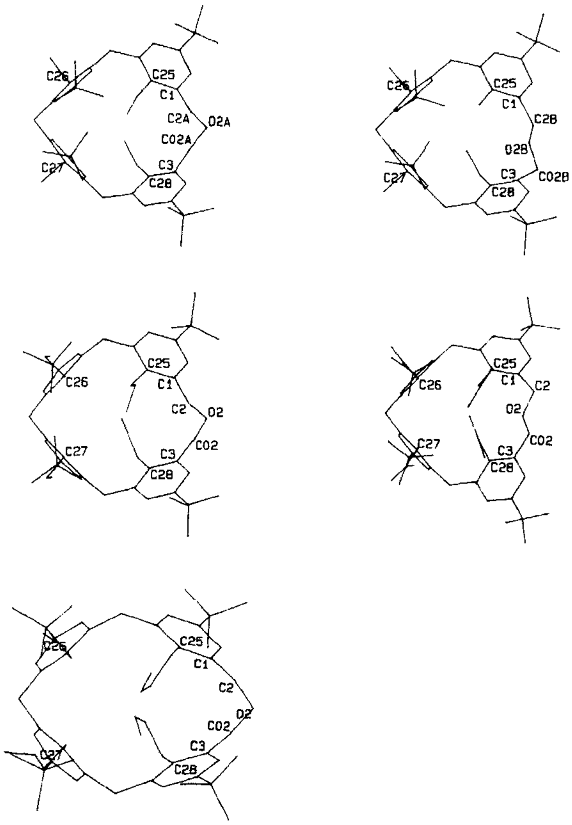


FIGURE 3 Views perpendicular to the plane C (8) – C (14) – C (20). In the first column successively compounds **1A**, **2**, **3**. In the second column compounds **1B**, **4**.

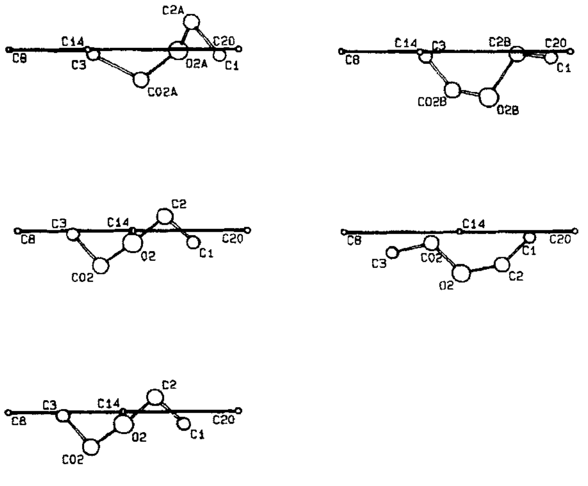
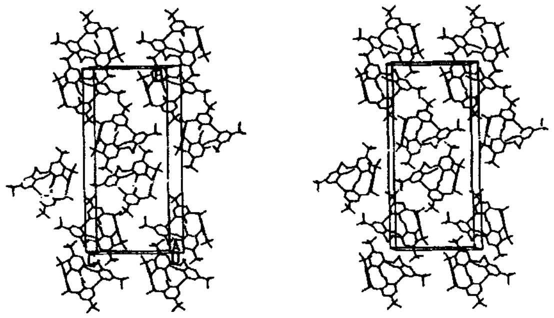


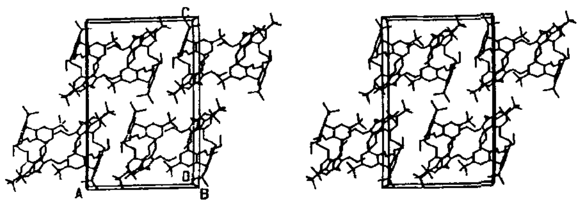
FIGURE 4 Geometry of the methyleneoxa bridge *versus* plane C (8) – C (14) – C (20). In the first column successively compounds **1A**, **2**, **3**. In the second column compounds **1B**, **4**.

Figure 4 shows a view of the bridge with the positions of the atoms C (1), C (3) and the three atoms of the bridge (C (02), O (1) and C (2)) versus the mean plane M of the three CH_2 groups (atoms called C (8), C (14) and C (20)). For compounds **2** and **3**, C (2) lies above the plane, O (2) very near the plane and C (02) under the plane. Distances are, respectively: + 0.663, – 0.133, – 0.948 Å for compound **2**; + 0.429, – 0.380, – 1.056 Å for compound **3**. Conformation A of compound **1** shows the same situation: + 0.82, – 0.041, – 0.92 Å. For the tetraacetate derivative the figure shows that all the atoms are on the

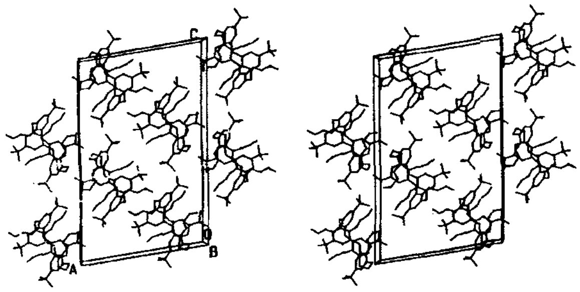


Compound 1

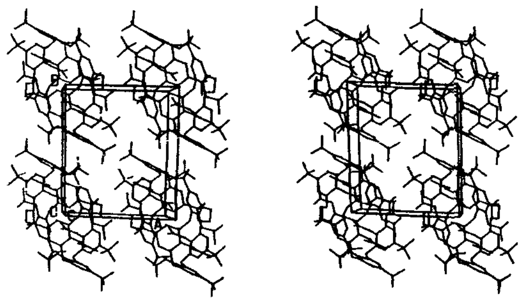
FIGURE 5 Stereoviews of the crystal structures of the four compounds.



Compound 2



Compound 3



Compound 4

FIGURE 5 (Continued).

same side *versus* the mean plane of the methylene groups: − 1.073, − 1.336, − 0.357 Å. The second conformation B of the methyl derivative gives the positions: − 0.06, − 1.38, − 1.15 Å, similar to compound **4**. The oxygen atoms lie very near the plane **1A**, **2** and **3** and farest for compounds **1B** and **4**.

CONCLUSION

Previously we described the conformation of *p*-tert-butyl dihomooxacalix [4] arene, empty form and complexed with various neutral molecules [1]; the bridge C (02) − O (2) − C (2) − C (1) shows two configurations, but the macrocycle was always in the cone shape. Concerning the compounds studied in this paper, the cone shape disappears due to the substituents at the OH groups and a 1, 2-alternate conformation is established. Two conformations of the dimethyleneoxabridge are found; they are different compared to those found previously [1] due to the C2 pseudo symmetry of the calixarenes.

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