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# A resorcinol derived calix[5]arene with $C_5$-symmetry

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**Condensation of 2,4-dihydroxy-3-hydroxymethyl benzophenone (4) in dioxane/$H_2SO_4$ gave the cyclic pentamer 5, a calix[5]arene with regular incorporation of the resorcinol units via their 2- and 6-positions. The structure follows from the $^1$H NMR and mass spectra and was further confirmed by single crystal X-ray analysis. Dynamic NMR in $C_2D_2Cl_4$ gave a surprisingly high barrier of $\Delta G^{\ddagger}$ = 17.3 kcal/mol for the cone-to-cone ring inversion.**



## INTRODUCTION

The importance of calixarenes[1] as host molecules and even more as building blocks for more elaborate structures[2] is unquestionable. Phenol derived calixarenes **1** usually are prepared by condensation of (mainly) p-tert-butylphenol with formaldehyde under alkaline conditions where different ring sizes (mainly 4, 6, or 8 phenolic units) are available. Resorcinol on the other hand can be reacted with aldehydes other than formaldehyde under acid catalysis to give exclusively the cyclic tetramer **2**, for which the name resorc[4]arene has been suggested. While the OH-groups are *endo* in **1** all OH-groups are *exo* in **2**.[3]

The nonplanar shape of all calixarenes and of resorcarenes opens up the way to various derivatives with inherent chirality,[4] most of which are asymmetric.[5] Of special interest, not only from an aesthetic point of view, are dissymmetric calixarenes with an n-fold symmetry axis. Calix[4]arenes with $C_4$-symmetry (**3**) are easily available from 3,4-dialkyl ($R^1$ = Me, i-Pr; $R^2$ = Me) or cycloalkyl ($R^1$–$R^2$ = $(CH_2)_3$, $(CH_2)_4$) phenols by $TiCl_4$ catalyzed condensation of their monohydroxymethyl derivatives in dioxane.[6] Due to the fourfold symmetry axis[7] all phenolic units are equivalent in **3**, which makes various O-alkyl derivatives readily available in an unambiguous way, as with the $C_{4v}$-symmetrical compounds **1**. Thus, racemization by the well known ring inversion becomes impossible, and some of these derivatives have been separated into the enantiomers by chromatography on chiral stationary phases.[8]

## SYNTHESIS

In order to obtain calix[4]arenes in which the chirality is "more pronounced" we tried (and try) to replace the alkyl (or cycloalkyl) substituents $R^1$ and $R^2$ in **3** by other (more different) functional groups. A suitable starting material for a similar synthesis seemed to be the resorcinol derivative **4** which is easily prepared in excellent yield (80–95%) by hydroxymethylation of the commercially available 2,4-dihydroxy-benzophenone.

A definite reaction of **4** failed under the conditions which usually are successful with 2- or 6-hydroxymethylated 3,4-dialkylphenols. This may be due to a "wrong" coordination of **4** via its second hydroxyl group or its keto function to the titanium atom. However, from condensation reactions of **4** in dioxane with $H_2SO_4$ as a catalyst a pure compound could be isolated by flash chromatography in 4–6% yield. Its $^1$H NMR spectrum is very simple showing three singlets in the ratio 1:1:1, which are easily attributed to two different OH-groups and to one of the Ar-H protons (5 Ar-H protons appear as a multiplet). A single pair of doublets (see also Figure 2) with geminal coupling for the Ar-$CH_2$-Ar protons further confirmed that a macrocyclic compound with regular incorporation of the resorcinol units was obtained.

It's FD mass spectrum surprisingly revealed, however, that **5** was not the expected tetramer but a pentamer. The molecular ion ($M^+$ = 1131.6) was found in 100% relative abundance, while no signals were found in the mass region of the tetramer nor at higher masses. The structure of a calix[5]arene was subsequently confirmed by a single crystal X-ray analysis (see below), proving again the regular incorporation of the resorcinol units. Up to now,

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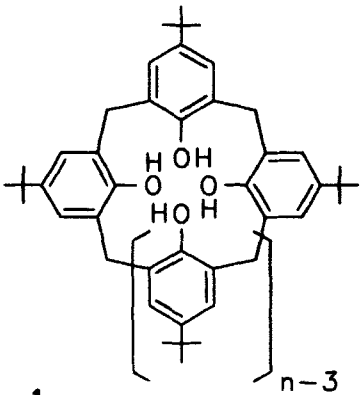
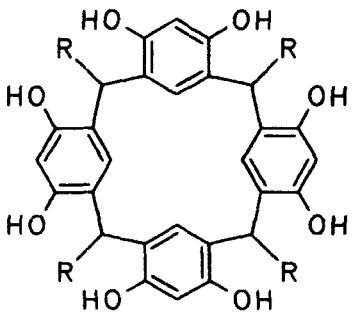



1

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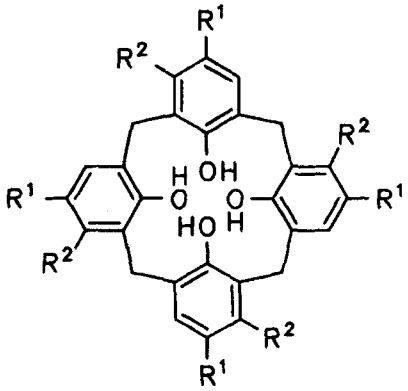



3

**5** was the only definite condensation product, which we could isolate. Attempts to obtain by variation of the reaction conditions a calix[4]arene or higher cyclic oligomers have failed so far.

For several reasons the formation of **5** seems remarkable:

a) Compound **5** represents the first calix[5]arene containing not only a resorcinol unit, but consisting entirely of resorcinol units.

b) In contrast to the "usual" resorc[4]arenes these resorcinol units are not linked by alkylidene bridges via their 4- and 6-positions but by methylene bridges via their 2- and 6-positions. Thus, the OH-groups are found not exclusively in *exo*-position but also in *endo*-position.

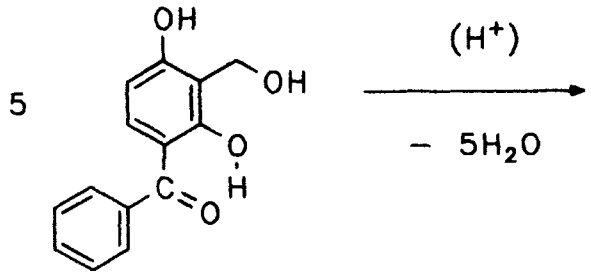
c) Compound **5** is not only the first dissymetric calix[5]arene but one of the rare examples with (inherent) $C_5$-symmetry at all.[9]

The points a) and b) demonstrate also, that the borderline between (phenol derived) calixarenes (in a narrow sense) and resorcarenes (resorcinol derived calixarenes) is fluent. It is suggested therefore, to use the expression "calixarene" also in a wider sense for all $1_n$-metacyclophanes.

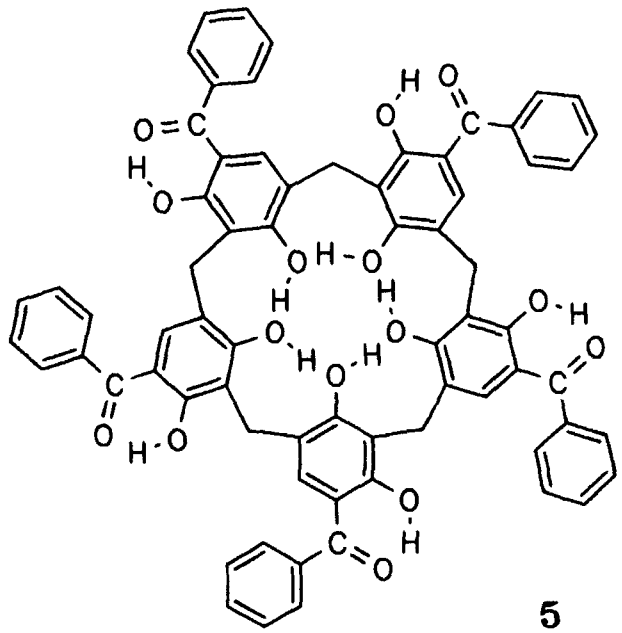
## CONFORMATIONAL PROPERTIES

The conformation in the crystalline state was determined by a single crystal X-ray analysis. Table 1 contains the fractional atomic coordinates of non-hydrogen atoms, selected structural parameters are collected in Table 2. All bond lengths and bond angles are found in the expected range.

As shown in Fig. 1, **5** assumes a cone-like conformation in the crystalline state in which the resorcinol units have dihedral angles between 121 and 139° with the molecular main plane (the best plane through the methylene carbons). This is also expressed by the torsion an-




4




5

**Table 1** Fractional atomic coordinates and equivalent isotropic temperature coefficients of the non hydrogen atoms (Å$^2$) U values are the mean-square deviations from equilibrium positions in Å$^2$. Ueq = (trace $\tilde{U}$)/3.

| | X | Y | Z | U(eq) |
|---|---|---|---|---|
| C(01) | 0.7230(3) | 0.3155(2) | 0.8300(3) | 0.0584(14) |
| C(02) | 0.7216(3) | 0.2626(2) | 0.8619(3) | 0.0605(14) |
| C(03) | 0.6634(3) | 0.2511(2) | 0.8978(2) | 0.0506(12) |
| C(04) | 0.6609(3) | 0.1924(2) | 0.9285(3) | 0.0568(13) |
| C(05) | 0.6013(3) | 0.1515(2) | 0.8760(2) | 0.0467(12) |
| C(06) | 0.6273(3) | 0.1260(2) | 0.8249(2) | 0.0490(12) |
| C(07) | 0.5740(3) | 0.0890(2) | 0.7745(2) | 0.0493(12) |
| C(08) | 0.4937(3) | 0.0731(2) | 0.7819(2) | 0.0493(12) |
| C(09) | 0.4659(3) | 0.0960(2) | 0.8348(2) | 0.0450(11) |
| C(10) | 0.3850(3) | 0.0724(2) | 0.8470(2) | 0.0481(12) |
| C(11) | 0.2981(3) | 0.0948(2) | 0.8009(2) | 0.0432(11) |
| C(12) | 0.2542(3) | 0.0713(2) | 0.7363(2) | 0.0466(11) |
| C(13) | 0.1701(2) | 0.0879(2) | 0.6944(2) | 0.0494(12) |
| C(14) | 0.1278(2) | 0.1278(2) | 0.7239(2) | 0.0506(12) |
| C(15) | 0.1698(2) | 0.1547(2) | 0.7877(2) | 0.0455(11) |
| C(16) | 0.1199(3) | 0.1971(2) | 0.8167(3) | 0.0512(12) |
| C(17) | 0.1139(3) | 0.2552(2) | 0.7845(1) | 0.0488(12) |
| C(18) | 0.0442(3) | 0.2701(2) | 0.7265(2) | 0.0513(12) |
| C(19) | 0.0374(3) | 0.3231(2) | 0.6929(2) | 0.0567(13) |
| C(20) | 0.1015(3) | 0.3640(2) | 0.7253(2) | 0.0589(14) |
| C(21) | 0.1709(3) | 0.3519(2) | 0.7862(2) | 0.0535(13) |
| C(22) | 0.2324(3) | 0.3990(2) | 0.8255(3) | 0.0609(15) |
| C(23) | 0.3124(3) | 0.4087(2) | 0.8049(2) | 0.0514(12) |
| C(24) | 0.3081(3) | 0.4376(2) | 0.7447(2) | 0.0513(12) |
| C(25) | 0.3824(3) | 0.4513(2) | 0.7271(2) | 0.0513(12) |
| C(26) | 0.4643(3) | 0.4389(2) | 0.7777(2) | 0.0538(13) |
| C(27) | 0.4724(3) | 0.4080(2) | 0.8388(2) | 0.0537(13) |
| C(28) | 0.5614(3) | 0.3981(2) | 0.8944(2) | 0.0573(14) |
| C(29) | 0.6141(3) | 0.3500(2) | 0.8799(2) | 0.0517(12) |
| C(30) | 0.6719(3) | 0.3587(2) | 0.8439(3) | 0.0582(14) |
| C(31) | 0.6081(3) | 0.2945(2) | 0.9038(2) | 0.0508(12) |
| C(32) | 0.5178(2) | 0.1380(2) | 0.8777(2) | 0.0451(11) |
| C(33) | 0.2565(2) | 0.1393(2) | 0.8238(2) | 0.0449(11) |
| C(34) | 0.1787(3) | 0.2966(2) | 0.8118(2) | 0.0503(12) |
| C(35) | 0.3953(3) | 0.3901(2) | 0.8485(2) | 0.0529(13) |
| C(36) | 0.7787(3) | 0.3245(2) | 0.7862(3) | 0.067(2) |
| C(37) | 0.7671(3) | 0.3747(2) | 0.7389(3) | 0.065(2) |
| C(38) | 0.6848(3) | 0.3948(3) | 0.6986(3) | 0.074(2) |
| C(39) | 0.6779(4) | 0.4405(3) | 0.6534(3) | 0.088(2) |
| C(40) | 0.7505(5) | 0.4663(3) | 0.6471(3) | 0.089(2) |
| C(41) | 0.8328(4) | 0.4460(3) | 0.6865(3) | 0.083(2) |
| C(42) | 0.8416(3) | 0.4001(2) | 0.7314(3) | 0.070(2) |
| C(43) | 0.5997(3) | 0.0651(2) | 0.7169(2) | 0.0614(14) |
| C(44) | 0.6797(3) | 0.0859(2) | 0.7040(3) | 0.062(2) |
| C(45) | 0.6970(3) | 0.1434(2) | 0.7006(3) | 0.067(2) |
| C(46) | 0.7735(4) | 0.1604(3) | 0.6898(3) | 0.086(2) |
| C(47) | 0.8328(4) | 0.1211(3) | 0.6836(3) | 0.093(2) |
| C(48) | 0.8147(4) | 0.0637(3) | 0.6852(3) | 0.096(3) |
| C(49) | 0.7375(3) | 0.0455(2) | 0.6937(3) | 0.074(2) |
| C(50) | 0.1253(3) | 0.0650(2) | 0.6237(2) | 0.0578(13) |
| C(51) | 0.1733(3) | 0.0352(2) | 0.5829(2) | 0.0518(12) |
| C(52) | 0.2570(3) | 0.0514(2) | 0.5854(3) | 0.068(2) |
| C(53) | 0.2957(4) | 0.0244(3) | 0.5417(3) | 0.089(2) |
| C(54) | 0.2531(4) | -0.0179(3) | 0.4961(3) | 0.087(2) |
| C(55) | 0.1697(4) | -0.0334(2) | 0.4929(3) | 0.070(2) |
| C(56) | 0.1297(3) | -0.0077(2) | 0.5358(2) | 0.0565(13) |
| C(57) | -0.0345(3) | 0.3373(2) | 0.6286(3) | 0.066(2) |
| C(58) | -0.1002(4) | 0.2930(2) | 0.5927(3) | 0.068(2) |
| C(59) | -0.0746(4) | 0.2411(2) | 0.5726(3) | 0.087(2) |
| C(60) | -0.1378(6) | 0.2013(3) | 0.5392(3) | 0.117(4) |
| C(61) | -0.2254(6) | 0.2121(3) | 0.5260(4) | 0.112(3) |
| C(62) | -0.2504(4) | 0.2642(3) | 0.5444(3) | 0.094(2) |
| C(63) | -0.1891(4) | 0.3048(2) | 0.5769(3) | 0.072(2) |
| C(64) | 0.3771(3) | 0.4808(2) | 0.6613(2) | 0.0580(13) |
| C(65) | 0.2916(3) | 0.4849(2) | 0.6018(3) | 0.0605(14) |
| C(66) | 0.2323(4) | 0.4395(2) | 0.5837(3) | 0.069(2) |
| C(67) | 0.1557(4) | 0.4454(2) | 0.5271(3) | 0.077(2) |
| C(68) | 0.1361(4) | 0.4951(3) | 0.4894(3) | 0.078(2) |
| C(69) | 0.1942(4) | 0.5400(2) | 0.5073(3) | 0.073(2) |
| C(70) | 0.2723(3) | 0.5350(2) | 0.5631(3) | 0.0610(14) |
| O(01) | 0.5471(2) | 0.28365(15) | 0.9364(2) | 0.0578(9) |
| O(02) | 0.4895(2) | 0.16639(14) | 0.9260(2) | 0.0547(9) |
| O(03) | 0.3027(2) | 0.16678(14) | 0.88619(15) | 0.0550(9) |
| O(04) | 0.2512(2) | 0.28195(15) | 0.8687(2) | 0.0595(9) |
| O(05) | 0.3987(2) | 0.35491(14) | 0.9045(2) | 0.0612(10) |
| O(06) | 0.7750(2) | 0.2195(2) | 0.8572(2) | 0.0763(12) |
| O(07) | 0.4413(2) | 0.03420(15) | 0.7384(2) | 0.0618(10) |
| O(08) | 0.0430(2) | 0.1428(2) | 0.6898(2) | 0.0695(11) |
| O(09) | 0.0973(3) | 0.41747(14) | 0.6987(2) | 0.0814(13) |
| O(10) | 0.5396(2) | 0.4563(2) | 0.7685(2) | 0.0711(11) |
| O(11) | 0.8352(3) | 0.2888(2) | 0.7859(3) | 0.0883(14) |
| O(12) | 0.5559(3) | 0.0269(2) | 0.6781(2) | 0.0790(12) |
| O(13) | 0.0445(2) | 0.0721(2) | 0.5942(2) | 0.0874(14) |
| O(14) | -0.0438(3) | 0.3862(2) | 0.6035(3) | 0.0932(15) |
| O(15) | 0.4421(3) | 0.5028(2) | 0.6530(2) | 0.0796(12) |
| C(1) | -0.0287(11) | 0.0882(6) | 0.9365(6) | 0.148(8) |
| Cl(11) | -0.0811(4) | 0.0688(2) | 0.9951(3) | 0.150(2) |
| Cl(12) | -0.0902(3) | 0.1062(2) | 0.8600(2) | 0.132(2) |
| Cl(13) | 0.0468(4) | 0.1431(3) | 0.9792(3) | 0.175(3) |
| C(2) | 0.4884(6) | 0.0809(4) | 0.4351(4) | 0.062(3) |
| Cl(21) | 0.3940(3) | 0.1106(3) | 0.4287(2) | 0.141(2) |
| Cl(22) | 0.5489(3) | 0.0740(3) | 0.5278(2) | 0.140(2) |
| Cl(23) | 0.5518(2) | 0.1245(2) | 0.3967(2) | 0.129(2) |
| Cl(31) | 0.3899(17) | 0.2514(7) | 0.7404(7) | 0.157(14) |
| Cl(32) | 0.4566(13) | 0.2534(12) | 0.7095(15) | 0.441(20) |
| Cl(33) | 0.7917(23) | 0.2750(8) | 1.1054(9) | 0.591(25) |
| Cl(34) | 0.3737(33) | 0.2821(21) | 0.6091(26) | 0.662(44) |
| Cl(35) | 0.3019(16) | 0.2558(9) | 0.6806(16) | 0.490(21) |
| Cl(37) | 0.4238(21) | 0.2004(16) | 0.6521(13) | 0.701(30) |

The chloroform occupancies are 0.538(4) for chloroform$_1$ and 0.536(4) for chloroform$_2$. The occupancies for Cl(31) to Cl(37) are: 0.21(2), 0.61(4), 0.70(3), 0.44(3), 0.69(3), 0.72(4).

gles $\phi$ and $\chi$ around Ar-$CH_2$-Ar bonds[10] which are defined including the carbon atoms carrying the *endo* OH-groups; values between 87 and 104° with alternating sign indicate a rather symmetrical cone conformation. All *exo* OH-groups form strong intramolecular hydrogen bonds (O. . .O separations 2.537 to 2.570 Å) to the carbonyl groups (the angles of C = O with the adjacent phenolic rings are between 4.1 and 16.9°, while those with the adjacent benzene rings vary between 34.7 and 52.6°). The O. . .O-distances of the *endo* OH-groups are 2.828 Å to 2.901 Å. Their average of 2.85 Å is, as usually found for calix[5]arenes,[11] somewhat larger than in calix[4]arenes; O-O-O angles between 106 and 111° (108° is the value for a regular pentagram) again demonstrate the regular shape.

There are three chloroform molecules incorporated in the crystal lattice, two of which are coordinated to carbonyl groups with CH. . .O distances of 3.306 Å and 3.317 Å, which is too large for hydrogen bonding. In the crystal lattice these solvent molecules are (partly occupied and disordered) in channels, which are parallel to the crystallographic y-axis and passing the origin and the

**Table 2** Selected structural data for compound **5** (distances in Å, angles in °)

| | | | | | |
|---|---|---|---|---|---|
| O..O-distances (endo-OH[a]) | 2.901 | 2.866 | 2.826 | 2.837 | 2.828 |
| O-O-O-angles (endo OH[b]) | 108.6 | 107.6 | 106.2 | 111.2 | 106.3 |
| inclination of phenyl rings δ[c] | 135.4 | 123.3 | 126.2 | 139.0 | 121.0 |
| torsion angle φ[d] | 92.8 | 100.1 | 101.2 | 92.0 | 102.2 |
| torsion angle χ[e] | -102.0 | -95.9 | -87.6 | -104.2 | -90.4 |
| O..O-distances C=O...exo-OH)[f] | 2.565 | 2.537 | 2.542 | 2.554 | 2.570 |
| angle between C=O and resorcinol ring[f] | 15.2 | 7.5 | 16.0 | 4.1 | 13.9 |
| angle between C=O and phenyl ring[f]) | 40.2 | 47.7 | 34.7 | 52.6 | 38.9 |
| angle between phenyl and resorcinol ring[f] | 46.2 | 48.9 | 43.8 | 53.3 | 45.2 |

a) in the order O(1)-O(2), O(2)-O(3), etc.
b) in the order O(5)-O(1)-O(2), O(1)-O(2)-O(3), etc.
c) with respect to the best plane through the methylene carbons; order I to V
d) Φ is defined as C(31)-C(3)-C(4)-C(5); C(32)-C(9)-C(10)-C(11); etc.
e) χ is defined as C(3)-C(4)-C(5)-C(32); C(9)-C(10)-C(11)-C(33); etc.
f) order I to V, and VI to X, respectively.

centre of the unit cell. A third chloroform molecule near the centre of the calixarene (distance 1.16 Å) is completely disordered. One can find only 6 shortly neighboured (1.41–1.90 Å) maxima of electron density. The reason is the entire mismatch between the large calixarene cavity and the comparatively small chloroform molecule.

Like other calix[5]arenes, **5** assumes a cone conformation also in solution. The weaker hydrogen bonding in comparison with calix[4]arenes (deduced in the crystalline state from the O. . .O separations) is reflected by the $^1$H NMR shift of 9.32 ppm found for the *endo* OH-groups in $CDCl_3$, while the *exo* OH-groups which form strong intramolecular OH. . .O = C hydrogen bonds appear at 13.03 ppm.

The cone-to-cone ring inversion on the other hand shows an energy barrier which is notably higher than in calix[4]arenes, although calix[5]arenes are usually more flexible.[1] Variable temperature $^1$H NMR spectra (200 MHz, $C_2D_2Cl_4$) show a coalescence temperature $T_c$ = 355 K (ν = 58.3 Hz, $^2J$ = 14.6 Hz) for the signals of the methylene protons (see. Fig. 2) which leads to $\Delta G^{\ddagger}$ = 17.3 kcal/mol. Energy barriers of $\Delta G^{\ddagger}$ = 14.6 kcal/mol and $\Delta G^{\ddagger}$ = 12.7 kcal/mol were found for instance for p-methyl calix[4]- and calix- [5]arene under similar conditions ($CDCl_3$, 500 MHz). The reason for this unusually high energy barrier for **5** is not yet entirely understood. It cannot be explained just by the presence of a m-hydroxyl substituent in each phenolic unit, since the m-methyl groups in calix[4]arenes **3** lead to a decrease of the energy barrier.[6b] It may be caused perhaps by the large ***and*** stiff (intramolecular OH. . .O = C hydrogen bond) hydroxybenzophenone units, but further studies are necessary to get a definite answer.

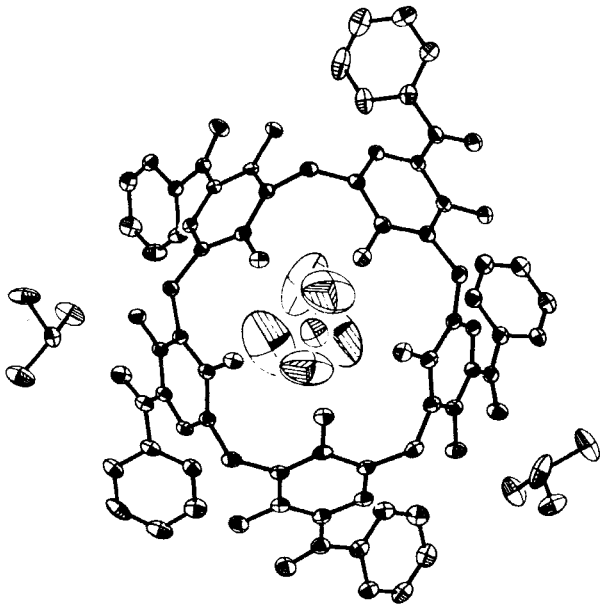


**Figure 1a** Molecular conformation of **5** seen from the "lower rim," the side of the *endo*-OH groups. (The $CHCl_3$ within the molecular cavity is completely disordered.)

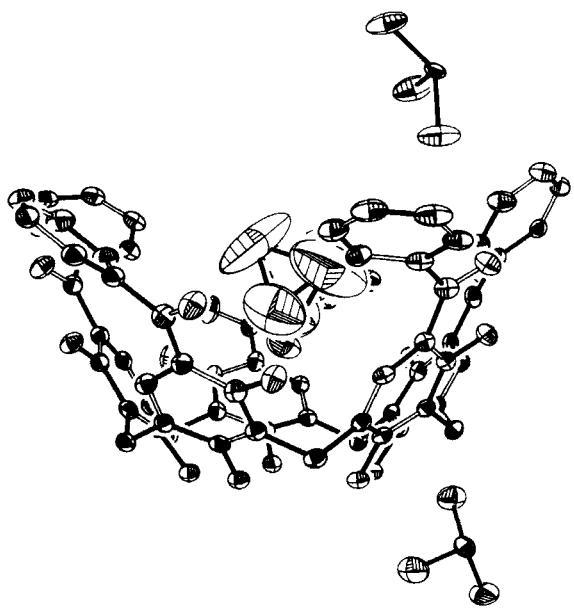
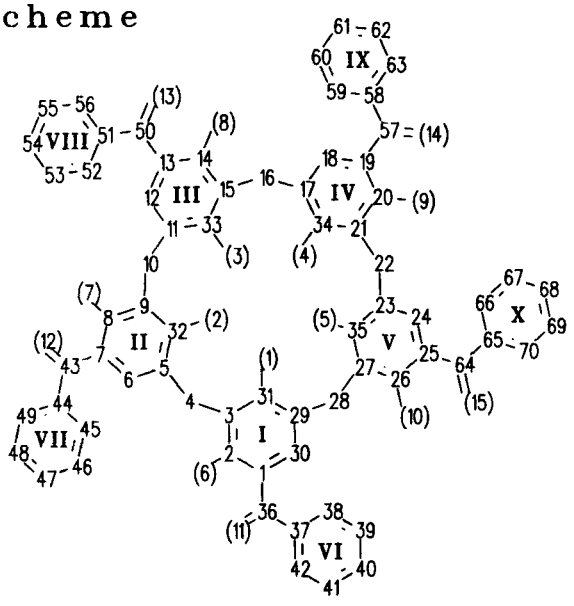


**Figure 1b** Molecular conformation of **5** showing the side of the calix. (The $CHCl_3$ within the molecular cavity is completely disordered.)

Numbering Scheme



## CONCLUSIONS

The energy barrier for the ring inversion, although for a calix[5]arene unusually high, is still not sufficient to separate and isolate the enantiomers of **5**. However, the equivalence of all phenolic units should make it easy in principle to introduce residues to the *endo* OH-groups which entirely hinder the conformational inversion (= racemization). The *exo* OH-groups and the keto groups are also capable of further derivatization. And finally, further analogues with substituted benzoyl residues (e.g. p-nitro- or 3,5-dinitrobenzoyl) should be available in a similar way. The easy access in two synthetic steps, makes these compounds attractive, even if the yield in the cyclisation step still leaves room for improvement.

## EXPERIMENTAL

2,4-Dihydroxy-3-hydroxymethylbenzophenone (**4**): 2,4-dihydroxybenzophenone (10.7 g, 0.05 mole) was dissolved in a cooled solution of NaOH (2 g, 0.05 mole) in 15–20 mL water. Formaldehyde (0.05 mole in form of its 35% aqueous solution) was added and the whole mixture was stirred at room temperature under argon atmosphere for 1–2 hours. The clear yellow solution was dripped with ice-cooling into a mixture of 15 mL acetic acid and 100 mL water. A yellow precipitate was filtered by suction, carefully washed with water and dried in a dessiccator over $P_2O_5$. The crude product thus obtained (80–95%, mp. 112–115 °C) was usually pure enough for the following reaction. An analytically pure sample was obtained by recrystallization from chloroform/acetone. M.p. 129 °C; $^1$H NMR (200 MHz, $CDCl_3$) δ = 13.03 (s, 1H, OH), 9.08 (s, 1H, OH), 7.62-7.44 (m, 5H, ArH), 7.43 (d, $^3J$ = 9.0 Hz, 1H, ArH), 6.38 (d, $^3J$ = 8.9 Hz, 1H, ArH), 5.15 (d, 2H, $ArCH_2$), 2.48 (t, 1H, $CH_2$ *OH*); EI-MS m/e = 244 ($M^+$, 34%), 226 ($M^+$-$H_2O$, 100%). Anal. calcd. for $C_{14}H_{12}O_4$: C, 68.83; H, 4.96. Found: C, 68.83; H, 5.05.

5,11,17,23,29-penta-benzoyl-4,10,16,22,28,31,32,33,34,35-decahydroxy-calix[5]arene (**5**): Compound 4 (2.4 g, 10 mmole) was dissolved in dry dioxane (250 mL) and slowly added (5 mL/h) to a boiling solution of 1 mL $H_2SO_4$ in dioxane (250 mL). After 96 h under reflux the dioxane was removed and the residue extracted by 300 ml boiling $CH_2Cl_2$. The organic solution was filtered, washed with water and dried over $MgSO_4$. A yellow oil was obtained after evaporation of the $CH_2Cl_2$ which was purified by column chromatography to give 135 mg of 5 as yellow needles, which decompose above 260°C. $^1$H NMR (200 MHz, $CDCl_3$) δ = 13.03 (s, 5H, OH), 9.32 (br s, 5H, OH), 8.17 (s, 5H, Ar-H), 7.68-7.46 (m, 25H, Ar-H), 4.03 and 3.73 ppm (d, $^2J$ = 14.5 Hz, 5H each, Ar-$CH_2$-Ar); (200 MHz, $C_2D_2Cl_4$) δ = 12.93 (s, 5H, OH), 9.23 (br s, 5H, OH), 8.10 (s, 5H, Ar-H), 7.62-7.42 (m, 25H, Ar-H), 4.00 and 3.60 ppm (d, $^2J$ = 14.6

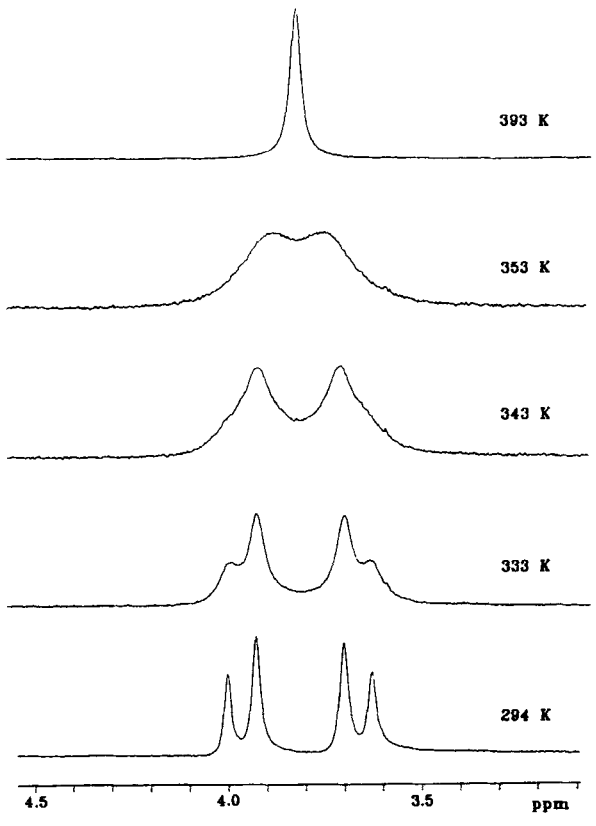



**Figure 2** Section of the methylene protons of **5** at various temperatures (200 MHz. $C_2D_2Cl_4$).

Hz, 5H each, Ar-$CH_2$-Ar); FD-MS m/e = 1131.6 ($M^+$, 100%)

**X-Ray structure analysis:**

Single crystals of **5**, suitable for an X-ray analysis were obtained by recrystallization from a mixture of cyclohexane and chloroform. A crystal of 0.9mm × 0.5mm × 0.5mm was sealed in a Lindemann glass capillary, 25 reflections with $\Theta > 5.2°$ for determining the cell dimensions, four circle computer controlled diffractometer (R3m/V, Siemens), $\lambda$(Mo-$K_\alpha$) = 0.7107 Å, $\Theta_{max}$ = 28°.

Crystal data: $C_{70}H_{50}O_{15}$ * 2.2 $CHCl_3$, MG = 1393.8, monoclinic, space group $P2_1/n$, Z = 4, a = 16.219(2), b = 23.558(4), c = 19.991(3) Å, $\beta$ = 109.44(1)°, V = 203.0 $Å^3$, $D_x$ = 1.285 $Mg/m^3$.

Further details: 13224 unique reflections, 6019 with $Fo > 4\sigma(Fo)$, solution of the phase problem by direct methods (SHELXS-90 and SHELXTL-PLUS)[12], minimization of $\Sigma w(Fo^2-Fc^2)^2$ with SHELXL-93[13], weighting scheme according to the counting statistics, 900 parameters, $wR_2$ = 0.33 (all reflections), $R_1$ = 0.095 (6019 reflections), S = 0.97; 10 largest maxima in the difference Fourier synthesis: 1.14 to 0.68 e/$Å^3$ (all in the region of chloroform molecules), absolute minimum: -0.46 e/$Å^3$. The relatively high unweighted $R_1$-value (0.093 for all reflections > 4σ) is due to three disordered $CHCl_3$ molecules with partial occupancy.

Lists of atom coordinates and thermal parameters and structure factors are deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH 76344 Eggenstein-Leopoldshafen 2. The full literature citation of this publication and the code number CSD-58409 should accompany the request.



## ACKNOWLEDGEMENT

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## REFERENCES

1. For reviews on calixarenes see: a) Gutsche, C.D., Calixarenes, Royal Society of Chemistry, Cambridge, **1989,** b) Vicens, J.; Böhmer, V. (Eds.); Calixarenes: A Versatile Class of Macrocyclic Compounds, Kluwer, Dordrecht, **1990**; c) Böhmer, V.; *Angew. Chem.* **1994**, in press.
2. Recent examples for elaborate structures are for instance, a) calixcrowns: King, A.M.; Moore, C.P.; Sandanayake, K.R.A.S.; Sutherland, I.O.; *J. Chem. Soc., Chem. Commun.* **1992,** 582–584; b) calixspherands: Dijkstra, P.J.; Brunink, J.A.J.; Bugge, K.-E.; Reinhoudt, D.N.; Harkema, S.; Ungaro, R.; Ugozzoli F.; Ghidini, E.; *J. Am. Chem. Soc.* **1989,** *111,* 7567–7575; c) double calixarenes: Arduini, A.; Manfredi, G.; Pochini, A.; Sicuri, A.R.; Ungaro, R.; *J. Chem. Soc., Chem. Commun.* **1991,** 936–937; d) annelated calix[4]arenes: Böhmer, V.; Dörrenbächer, R.; Vogt, W.; Zetta, L.; *Tetrahedron Lett.* **1992,** *33,* 769–772; e) bicyclic calix[4]arenes: Berger, B.; Böhmer, V.; Paulus, E.; Rodriguez, A.; Vogt, W.; *Angew. Chem. Int. Ed. Engl.* **1992,** *31,* 96–99.
3. Phenol derived calix[4]arenes with *exo* hydroxylgroups have also been obtained: a) Chasar, D.W.; *J. Org. Chem.* **1985,** *50,* 545–547; b) Pappalardo, S.; Ferguson, G.; Gallagher, J.F.; *J. Org. Chem.* **1992,** *57,* 7102–7109; see also reference 2d).
4. For a review on inherently chiral calixarenes see: Böhmer, V.; Kraft, D.; Tabatabai, M.; *J. Incl. Phenom. Mol. Recogn.*, in press.
5. For various examples of inherently chiral calix[4]arenes see: a) Zetta, L.; Wolff, A.; Vogt, W.; Platt, K.-L.; Böhmer, V.; *Tetrahedron* **1991,** *47,* 1911–1924. b) Böhmer, V.; Wolff, A.; Vogt. W.; *J. Chem. Soc., Chem. Commun.* **1990,** 968–970; c) Pappalardo, S.; Caccamese, S.; Giunta, L.; *Tetrahedron Lett.* **1991,** *32,* 7747–7750; d) Ferguson, G.; Gallagher, J.F.; Giunta, L.; Neri, P.; Pappalardo, S.; Pavisi, M.; *J. Org. Chem.*, **1994,** *59,* 42-53; e) Iwamoto, K.; Shimizu, H.; Araki, K.; Shinkai, S.; *J. Am. Chem. Soc.* **1993,** *115,* 3997–4006.
6. a) Wolff, A.; Böhmer, V.; Vogt, W.; Ugozzoli, F.; Andreetti, G.D.; *J. Org. Chem.* **1990,** *55,* 5665–5666; b) Andreetti, G.D.; Böhmer, V.; Jordan, J.G.; Tabatabai, M.; Ugozzoli, F.; Vogt, W.; Wolff, A.; *J. Org. Chem.* **1993,** *58,* 4023–4032.
7. By controlled derivatization of resorcarenes **2** compounds were recently obtained which may have also $C_4$-symmetry: a) Markovsky, L.N.; Kal'chenko, V.I.; Rudkevich, D.M.; Shivanyuk, A.N.; *Mendeleev Commun.* **1992,** 106–108. b) Matsushita, Y.; Matsui, T.; *Tetrahedron Lett.* **1993,** *46,* 7433–7436.
8. Pickard, S.T.; Pirkle, W.H.; Tabatabai, M.; Vogt, W.; Böhmer, V.; *Chirality* **1993,** *5,* 310–314.
9. A cyclic pentapeptide, for instance, would also have $C_5$-symmetry, but would be chiral due to the L-amino acid residues.
10. Ugozzoli, F.; Andreetti, G.D.; *J. Incl. Phenom. Mol. Recogn.* **1992,** *13,* 337–348.
11. For X-ray structures of calix[5]arenes see: a) Coruzzi, M.; Andreetti, G.D.; Bocchi, V.; Pochini, A.; Ungaro, R.; *J. Chem. Soc., Perkin Trans. 2* **1982,** 1133–1138; b) Perrin, M.; Lecocq, S.; *J. Incl. Phenom. Molec. Recogn.* **1991,** *11,* 171–183; c) Juneja, R.K.; Robinson, K.D.; Orr, G.W.; Dubois, R.H.; Belmore, K.A.; Atwood, J.L.; Ripmeester, J.M.; Ratcliffe, C.I.; *J. Incl. Phenom. Molec. Recogn.* **1992,** *13,* 93–96; d) Gallagher, J.F.; Ferguson, G.; Böhmer, V.; Kraft, D.; *Acta Cryst.* C **1994,** *50,* 73–77.
12. Sheldrick, G.M., SHELXS-90, a FORTRAN-77 Program for the Solution of Crystal Structures from X-Ray or Neutron Diffraction Data and SHELXTL-PLUS, an Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. Universität Göttingen, **1990.**
13. Sheldrick, G.M., SHELXL-93, a FORTRAN-77 Program for the Refinement of Crystal Structures from Diffraction Data. Universität Göttingen, **1993.**