



Solution and X-Ray Crystal Structures of the Di- and Tetra-allyl Ether of *tert*-Butylcalix[4]arene*

SILVIA STUMPF, GUDRUN GORETZKI, KERSTIN GLOE and KARSTEN GLOE**

Institut für Anorganische Chemie, TU Dresden, D-01062 Dresden, Germany

WILHELM SEICHTER and EDWIN WEBER**

Institut für Organische Chemie, TU-Bergakademie Freiberg, D-09596 Freiberg, Germany

JAN W. BATS

Institut für Organische Chemie, J. W. Goethe Universität Frankfurt, D-60439 Frankfurt, Germany

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Abstract

The di- and tetra-allyl ethers of *tert*-butylcalix[4]arene **1** and **2** have been prepared by alkylation of *tert*-butylcalix[4]arene with allyl bromide and K_2CO_3 using different reaction times. Solution 1H NMR measurement of the di-allyl ether **1** and X-ray crystal structures of the complexes of **1** with chloroform (**1a**) or methanol (**1b**) indicate the cone conformation of **1** in which intramolecular hydrogen bonding can be maximized. The crystalline state conformers **1a** and **1b** are distorted in different grades depending on the solvent. While methanol is incorporated in the macrocycle, chloroform molecules do not occupy the cage. The solution 1H NMR spectra of tetra-allyl ether **2** show the co-existence of the cone and partial cone conformation. The partial cone conformer of **2** was investigated by X-ray crystallography. In this compound hydrogen bonding is not existent. The conformer distribution is likely affected by steric and template effects.

Introduction

Due to their particular structure, calix[4]arenes have proved to be a very useful tool in supramolecular chemistry [1]. Although calix[4]arenes preferentially exist in the cone conformation, they are conformationally flexible compounds. At room temperature they interconvert at a rate of around 100 s^{-1} [2]. The energy barrier ΔG^\ddagger of the interconversion from the cone to the inverted cone conformation in chloroform at room temperature is 14.9 kcal/mol for calix[4]arene and 15.7 kcal/mol for *tert*-butylcalix[4]arene [3]. In solution as well as in the solid state the cyclic tetramer exists preferentially in the cone conformation in which intramolecular hydrogen bonding can be maximized. Changing the solvent from chloroform to pyridine causes a decrease of the energy barrier of interconversion for *tert*-butylcalix[4]arene from $\Delta G^\ddagger = 15.7$ kcal/mol to 13.4 kcal/mol, suggesting interference with the intramolecular hydrogen bonding system [4]. A mechanism proposed for the interconversion of the calix[4]arene-skeleton which is called the “broken-chain” describes the interconversion as a flipping of one phenolic unit through the calix[4]arene ring followed by the other

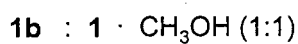
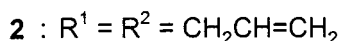
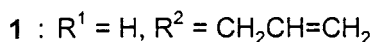
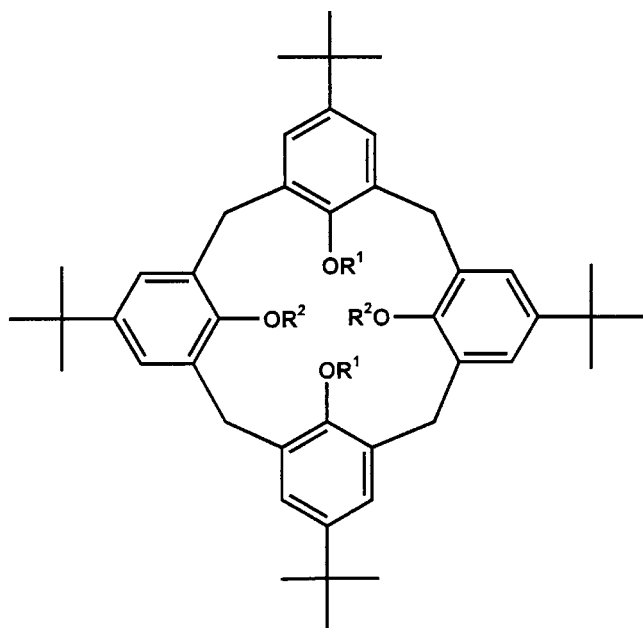
units. This leads to three more conformers: partial cone, 1,2-alternate and 1,3-alternate that can not be isolated [3].

Another important feature of calix[4]arenes is the feasibility of structural modification at both the lower (reaction at the OH groups) and the upper rim (reaction at the para position of the aromatic rings) of the molecule [5–8]. While the upper rim substituents almost do not affect the ring inversion, the lower rim substituents obviously exercise an influence. If the substituents attached to the four phenolic oxygens of calix[4]arene are larger than ethyl groups a conformationally rigid molecule results which can exist in the already mentioned four different conformations. The conformer distribution is remarkably affected by the metal cation present in the base used for the alkylation reaction [9–12]. Since calix[4]arenes form complexes with alkali and alkaline earth metal cations, these ions can act as templates to freeze the motion of the terminal groups in the calix[4]arene skeleton, giving rise to a cone conformer. In the absence of a templating metal ion, the partial cone becomes the major product. The yield of partial cone conformer increases in the order $Na_2CO_3 < K_2CO_3 < Cs_2CO_3$.

The partially etherified calix[4]arenes are less conformationally flexible than their fully etherified counterparts. Here both hydrogen bonding and steric interference reduce the conformational mobility. The reaction of *tert*-butylcalix[4]arene with alkyl bromide in the presence of K_2CO_3 normally yields di-O-alkylation, even in the pres-

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** Authors for correspondence.



Scheme 1. Compounds studied.

ence of excess alkyl bromide [13–15]. Only very much longer reaction times lead to the tetra-alkylation product which is a conformationally inflexible compound [16]. Thus in addition to intramolecular H-bond interactions, non-bonded steric hindrance must also play a part in determining the degree of conformational rigidity in these compounds [17, 18].

Etherified calix[4]arenes that contain a variable number of allyl substituents are regarded as important precursor compounds for the synthesis of particular calix[4]arene derivatives [1, 5]. Hence it is very helpful to know their conformational behaviour. In this connection we report synthesis and conformational properties of compounds **1** and **2** (Scheme 1) being the di- and tetra-allyl ethers of calix[4]arene. The structural description involves solution NMR studies and X-ray crystal structure analyses including host-guest complexes of **1** with $CHCl_3$ (**1a**) [**1**· $CHCl_3$ (1:2)] and $MeOH$ (**1b**) [**1**· $MeOH$ (1:1)].

Experimental

Synthesis

Compounds **1** and **2** were obtained from *tert*-butylcalix[4]arene and allyl bromide in the presence of K_2CO_3 [2, 19–24] after 3 and 72 h of reaction, respectively.

25, 27-Diallyloxy-*tert*-butylcalix[4]arene (1). Colorless solid, m.p. 181–182 °C 1H NMR ($CDCl_3$) δ 7.44 (s, 2H, OH); δ 7.03 (s, 4H, ArH); δ 6.81 (s, 4H, ArH); δ 6.25 (m, 2H, CH); δ 5.71 (d, $J = 17.16$ Hz, 2H, =CH₂); δ 5.35 (d, $J = 10.56$ Hz, 2H, =CH₂); δ 4.51 (d, $J = 5.23$ Hz, 4H, OCH₂); δ 4.25 (d, $J = 12.97$ Hz, 4H, ArCH₂Ar); δ 3.29 (d, $J = 13.05$ Hz, 4H, ArCH₂Ar); δ 1.27 (s, 18H, *t*-Bu); δ 0.97 (s, 18H, *t*-Bu).

25, 26, 27, 28-Tetraallyloxy-*tert*-butylcalix[4]arene (2). Colorless solid, m.p. 186–189 °C 1H NMR ($CDCl_3$) [**cone conformation**] δ 6.76 (s, 8H, ArH); δ 6.44 (m, 4H, CH); δ 5.25 (d, $J = 18.93$ Hz, 4H, =CH₂); δ 5.17 (d, $J = 10.3$ Hz, 4H, =CH₂); δ 4.45 (d, $J = 6.41$ Hz, 8H, OCH₂); δ 4.37 (d, $J = 12.53$ Hz, 4H, ArCH₂Ar); δ 3.12 (d, $J = 12.59$ Hz, 4H, ArCH₂Ar); δ 1.06 (s, 36H, *t*-Bu).

1H NMR ($CDCl_3$) [**partial cone conformation**] δ 7.28 (s, 2H, ArH); δ 7.09 (s, 2H, ArH); δ 6.88 (d, 2H, ArH); δ 6.60 (d, 2H, ArH); δ 6.23 (m, 2H, CH); δ 6.02 (m, 2H, CH); δ 5.36 (d, 2H, OCH₂); δ 5.28 (d, 2H, OCH₂); δ 5.22 (d, 1H , OCH₂); δ 5.18 (d, 1H , OCH₂); δ 4.93 (d, 2H, OCH₂); δ 4.10 (d, 2H, ArCH₂Ar); δ 3.74 (d, 2H, ArCH₂Ar); δ 3.68 (d, 2H, ArCH₂Ar); δ 3.09 (d, 2H, ArCH₂Ar); δ 1.42 (s, 9H, *t*-Bu); δ 1.36 (s, 9H, *t*-Bu); δ 1.08 (s, 18H, *t*-Bu).

X-ray crystallographic determination

Crystals of compounds **1a** and **1b**, suitable for X-ray diffraction studies, were grown by slow solvent evaporation of solutions of **1** in chloroform or methanol. Intensity data were collected with a SIEMENS SMART diffractometer at 141 and 144 K for **1a** and **1b**, respectively. Repeatedly measured reflections remained stable. In case of **1a**, an empirical absorption correction with program SADABS (Sheldrick 2000) gave a correction factor between 0.898 and 1.000. No absorption correction was made for **1b**. Equivalent reflections were averaged. The R(I) internal for **1a** is 0.086 and for **1b** 0.092. The structures were solved by direct methods using SHELXS-97 [25]. The H atoms were geometrically positional and treated as riding atoms. Referring to **1a**, the non-H atoms were refined with anisotropic thermal parameters. One of the two chloroform molecules was found to be disordered. Chlorine atoms Cl(4), Cl(5) and Cl(6) were refined with a split atom model. The occupancy factors are 0.811(4) for Cl(4), Cl(5) and Cl(6) and 0.189(4) for Cl(4'), Cl(5') and Cl(6'). In **1b**, two *tert*-butyl groups showed very large displacement parameters and were rotationally disordered. Split atoms were used for C(41), C(42) and C(43). Two partly occupied atoms [C(46') and C(47')] were required to describe residual density near the *tert*-butyl group attached to C(25). The O atom of the methanol group is distributed over two possible positions: a major position labeled O(51) and a minor position labeled O(53). The structures were refined on F_2 values using program SHELXL-97 [26]. The final difference densities are between -1.14 and $+0.91$, and -0.46 and $+0.52$ eÅ⁻³ for **1a** and **1b**, respectively.

A crystal of compound **2** suitable for the X-ray analysis was grown up from *n*-hexane solution. Data were collected at 211 K with a CAD4 Enraf-Nonius diffractometer using graphite-monochromated $CuK\alpha$ -radiation. Cell con-

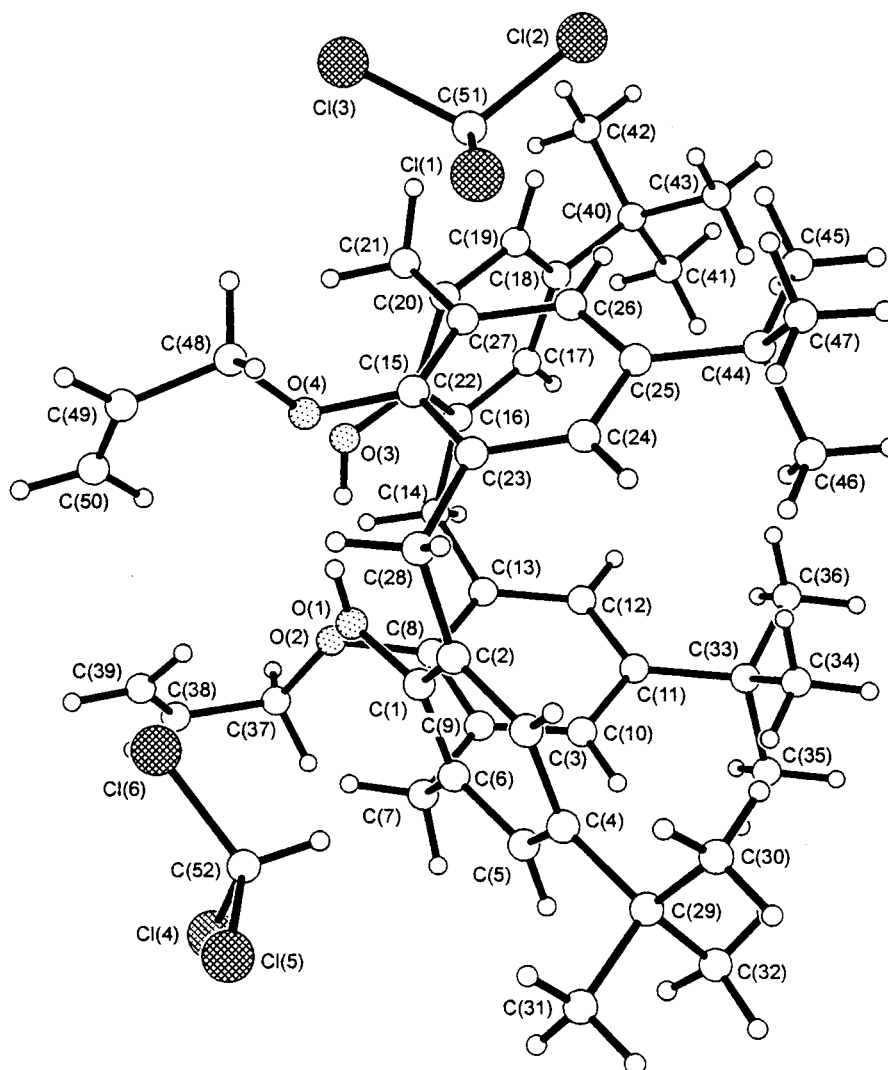


Figure 1. Perspective view of compound **1a** including the atomic numbering scheme. Hetero atoms are shaded.

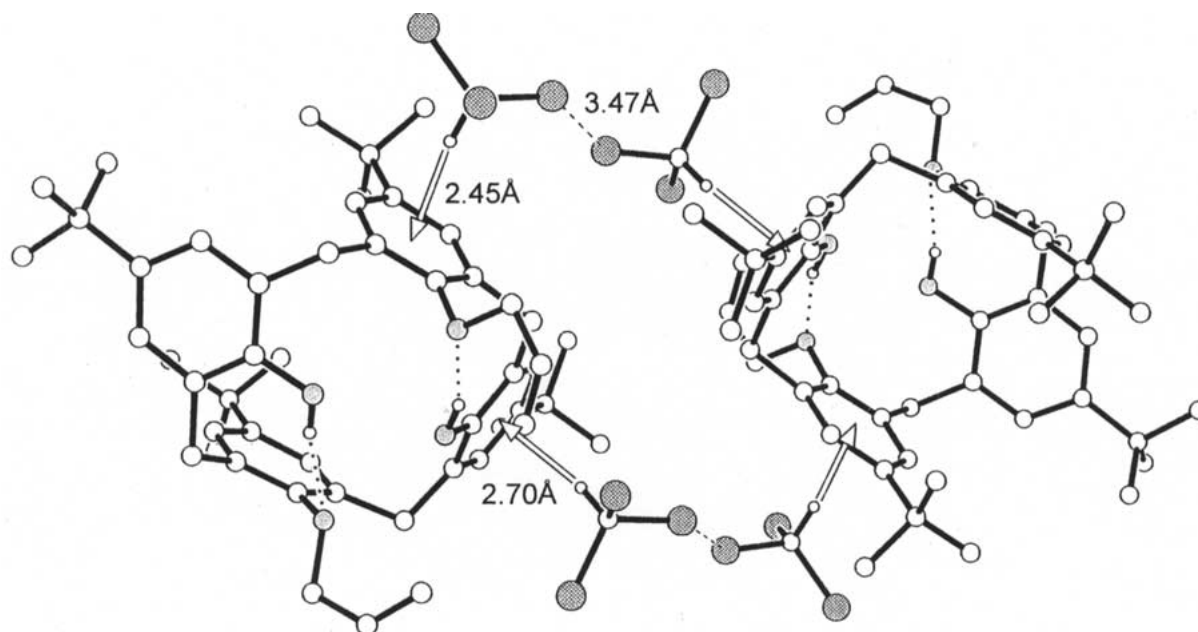


Figure 2. Dimer unit constituting the supramolecular building block of the crystal structure of **1a**. Hetero atoms are shaded. Dotted and dashed lines represent O-H...O and interhalogen interactions. Hollow arrows indicate C-H... π interactions.

Table 1. Crystal data, experimental parameters and selected details of the refinement calculations for **1a**, **1b** and **2**

Compound	1a	1b	2
Empirical formula	C ₅₀ H ₆₄ O ₄ · C ₂ H ₂ Cl ₆	C ₅₀ H ₆₄ O ₄ · CH ₄ O	C ₅₆ H ₅₈ O ₄
Formula weight	967.75	761.05	795.02
Temperature/K	141(2)	144(2)	193(2)
Wavelength/Å	0.71073	0.71073	1.5418
Crystal system	Monoclinic	Trigonal	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>R</i> 3	<i>Pna</i> 2/1
Unit cell dimensions			
<i>a</i> /Å	16.642(2)	43.960(6)	20.554(2)
<i>b</i> /Å	12.962(3)	43.960(6)	10.628(2)
<i>c</i> /Å	25.520(4)	12.692(2)	23.140(3)
α /deg	90	90	90
β /deg	100.27(1)	90	90
γ /deg	90	120	90
Cell volume/Å ³	5417.0(14)	21241(6)	5055(3)
<i>Z</i>	4	18	4
<i>D</i> _c /gcm ⁻³	1.187	1.071	1.045
μ /mm ⁻¹	0.357	0.3067	0.498
<i>F</i> (000)	2048	7452	1704
Crystal size/mm	0.50 × 0.34 × 0.28	0.80 × 0.19 × 0.14	0.50 × 0.40 × 0.30
θ range for data collection/deg	1.24 to 29.84	1.6 to 28.11	3.82 to 64.94
Index ranges: min/max <i>h</i> , <i>k</i> , <i>l</i>	−21/22, −16/17, −34/34	−58/58, −52/53, 16/16	0/24, 0/12, −27/0
Reflections collected/unique	65125/13910	79238/10489	4418/4418
<i>R</i> (int)	0.0856	0.0892	0.0
Absorption correction	Empirical (SADABS, Sheldrick, 2000)	–	–
Max. and min. transmission	1.0000 and 0.8977	–	–
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	13910/0/574	10489/0/552	4418/538
Goodness-of-fit on <i>F</i> ²	1.071	1.067	0.961
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.1292 <i>wR</i> 2 = 0.2692	<i>R</i> 1 = 0.0868 <i>wR</i> 2 = 0.1988	<i>R</i> 1 = 0.0773 <i>wR</i> 2 = 0.2138
<i>R</i> indices (all data)	<i>R</i> 1 = 0.2298 <i>wR</i> 2 = 0.3194	<i>R</i> 1 = 0.1704 <i>wR</i> 2 = 0.2445	<i>R</i> 1 = 0.1036 <i>wR</i> 2 = 0.2453
Largest diff. peak and hole/eÅ ⁻³	0.910 and −1.136	0.520 and −0.460	0.75 and 0.30

stants and orientation matrix were refined by least-square fits of 25 reflections in the θ -range 8.60–19.47°. Three standard reflections were measured after 1 h showing no decay of the crystal during the data collection. The SHELXTL version 5.10 program package was used for the structure solution and refinement. The crystal structure was solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. H atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. The allyl group of ring B exhibits partial disorder. Refinement of C(13) shows, that this atom occupies two positions with the occupation factors 0.7 and 0.3.

Crystal data and further details of the refinement calculations of **1a**, **1b** and **2** are summarized in Table 1.

Results and discussion

The reaction between *tert*-butylcalix[4]arene and allyl bromide in the presence of K₂CO₃ was monitored during 72 h.

Analytical and spectroscopic data confirmed that the product after 3 hs reaction time corresponds to the di-allyl ether **1**. After 72 h of reaction, the product represents a composition of compounds indicating various stages of alkylation with the di-alkylated derivative **1** being of negligible quantity and the tetra-alkylated calix[4]arene **2** being the main compound.

Structure of compound **1** (or **1a** and **1b**, respectively)

Solution ¹H NMR data established compound **1** to exist in the cone conformation, which is also represented in the crystal structures of **1a** and **1b**, although these compounds contain stoichiometric ratios of solvents in the crystal structure, thus being designated as inclusion compounds with chloroform (**1a**) and methanol (**1b**).

More strictly speaking in the crystal of **1a** [1·CHCl₃ (1:2)] the calixarene molecule adopts a rather distorted cone conformation (Figure 1). This is related by the dihedral angles involving the plane defined by the four bridging methylene C atoms and the planes of the individual benzene

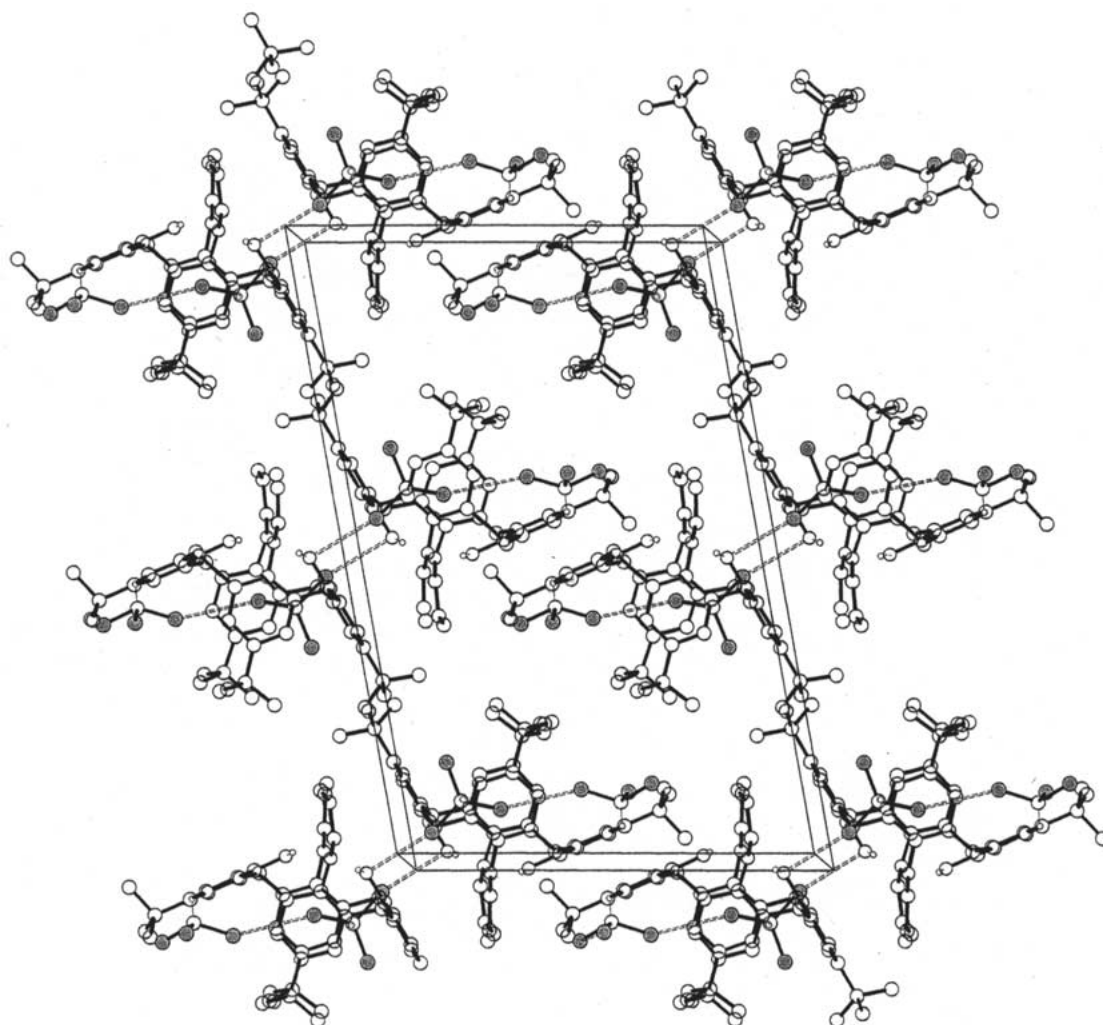


Figure 3. Crystal packing of **1a**, showing the Cl \cdots Cl and Cl \cdots O supramolecular interactions. Hetero atoms are shaded.

rings. The two benzene rings bearing the allyl ether groups are almost parallel to each other. The interplanar angle formed by these rings is 14.2 in contrast to 83.0° for the other two aromatic rings. To draw a parallel, in unsubstituted *tert*-butylcalix[4]arene which is arranged in undistorted cone conformation the respective dihedral angle is 123° leading to O \cdots O distance of 2.670(9) Å [27]. However, in **1a** the O(2) \cdots O(4) and O(1) \cdots O(3) distances are 4.765 and 3.283 Å, respectively. The allyl ether groups are pointing inward to the centre of the molecule. This arrangement allows the generation of intramolecular hydrogen bonds between the proximal hydroxy and ether functional groups O(1) \cdots O(4) and O(3) \cdots O(2) (Table 2). Figure 1 also shows that two chloroform molecules are involved in formation of the crystal. The real building block of the crystal packing consists of a centrosymmetric arrangement of two calixarene and four chloroform molecules interconnected via Cl \cdots Cl and C–H \cdots π (Ar) interactions (Figure 2). These dimers are linked together by Cl \cdots π (Ar) and Cl \cdots O contacts including the proximal hydroxy group of the calixarene. As a result, supramolecular strands are formed that run in the crystallographic *x*-direction (Figure 3).

The crystal structure of compound **1b** [1·CH₃OH (1:1)] is shown in Figure 4. Against all expectations no hydrogen bond interaction between the protic methanol and the acceptor atoms of the di-allyl ether is observed. Instead the methanol molecule is connected by one O–H \cdots π and two weak C–H \cdots π interactions involving three different aromatic rings. Similar to **1a**, the macrocycle **1** in **1b** is also arranged in a distorted cone conformation. However, due to the accommodation of the methanol molecule into the cone interior, the macrocycle changes conformation as against **1a** (Table 2). The interplanar angle between the two aromatic rings bearing the allyl ether groups is increased (41.9 versus 14.2°) while the interplanar angle for the other two rings is decreased (71.8 versus 83.0°), giving rise to larger O(1) \cdots O(3) or smaller O(2) \cdots O(4) distances in **1b** (Table 2). As before, this arrangement also allows the generation of intramolecular hydrogen bonds between the proximal hydroxy and ether functional groups O(1) \cdots O(2) and O(3) \cdots O(4).

Compared with **1a**, incorporation of the guest molecule in **1b** leads to basically different packing structure. As shown in Figure 5, the basic motif of the crystal structure consist of a unit of three calixarene molecules which are

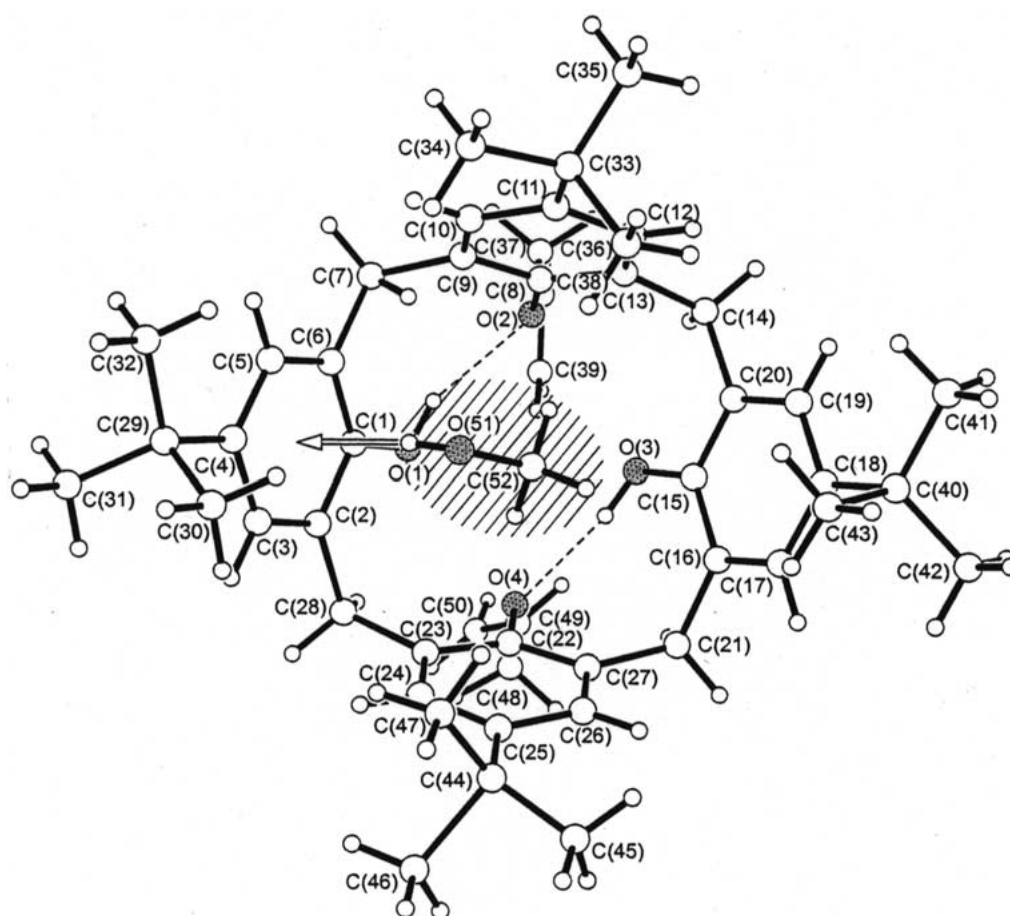


Figure 4. Perspective view of compound **1b** including the atomic numbering scheme. Hetero atoms are shaded. Dashed lines represent the intermolecular H bonds.

Table 2. Distances and angles of non-covalent interactions in **1a** and **1b**

Atoms involved	Symmetry	Distances/Å		Angle/°
		D...A	H...A	D-H...A
1a				
O(1)–H(01)···O(4)	x, y, z	2.837	2.033	160.2
O(3)–H(03)···O(2)	x, y, z	2.858	2.031	160.2
C(51)–H(51a)···centroid(4)*	x, y + 1, z	3.489	2.524	162.8
C(52)–H(52a)···centroid(1)*	x, 0.5 – y, 0.5 + z		2.420	166.5
C(51)–Cl(3)···O(3)	–x, –y + 1, –z	3.095		164.2
C(51)–Cl(1)···Cl(5)	–x + 1, –0.5 + y, 0.5 – z		3.468	133.6
C(52)–Cl(5)···Cl(1)				134.3
C(51)–Cl(1)···centroid(2)*	x, y, z		3.395	112.2
		D...A	H...A	D-H...A
1b				
O(3)–H(03)···O(4)	x, y, z	2.807	1.980	169.0
O(1)–H(01)···O(2)	x, y, z	2.830	2.032	158.9
O(51)–H(51)···centroid(1)*	x, y, z	3.465	2.663	160.8

* Centroid means the centre of the respective aromatic ring. [ring 1: C(1)···C(6), ring 2: C(8)···C(13), ring 4: C(22)···C(27)].

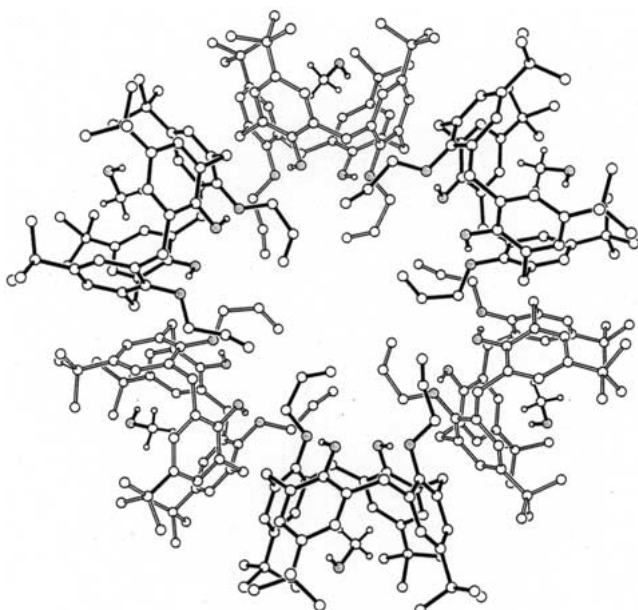


Figure 5. Structural motif typical of the crystal structure of **1b**. Hetero atoms are shaded.

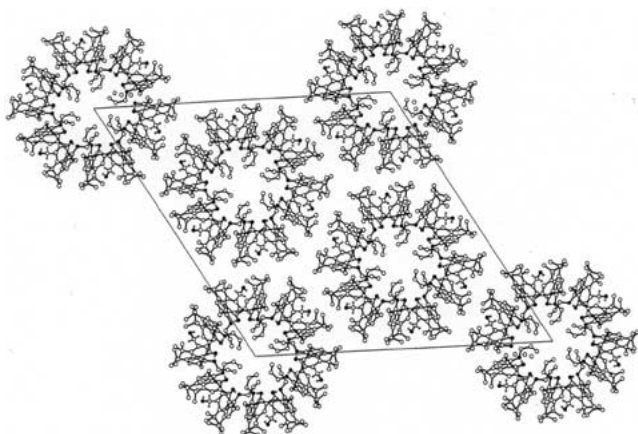


Figure 6. Crystal packing of **1b**, showing trigonal arrangement of columnar subunits. Hetero atoms are shaded.

arranged around the crystallographic C3 axis. These units are stacked together forming a column-like structure. The loosely packed core region of the columns are formed by the allyl groups leaving a small channel of dimensions of 3.5 Å. The exterior of the column is formed exclusively by the *tert*-butyl groups, which therefore produce the main contribution of the interaction between the columns of the packing structure (Figure 6).

Structure of compound **2**

The tetra-allyl compound **2** obtained from long-time reaction was identified from solution ^1H and ^{13}C NMR data to be a mixture of cone and partial cone conformers of approximately 1:1 ratio. The appearance of the two conformers can be established by steric and template effects. On the one hand, the template effect of K^+ arising from the presence of K_2CO_3 during the reaction is not strong enough to dominate over the cone conformation of **2**, while on the other hand the steric crowding on the narrow lower rim of the calixarene

2 is reduced by inversion of one aromatic ring to form the partial cone conformer.

The structure of this particular conformer of compound **2**, which has been solved by X-ray diffraction, is illustrated in Figure 7. It shows a distorted partial cone conformation defined by the dihedral angles listed in Table 2. All of the calix[4]arene *tert*-butylphenyl moieties are pointing outward from the centre of the molecule. Their orientation may be determined by the formation of van der Waals contacts $\text{H}\cdots\text{H}$ with distances 2.74–2.88 Å. This arrangement is similar to those found in the literature for the tetra-methylated and tetra-ethylated *tert*-butylcalix[4]arenes [28]. Shinkai *et al.* [9] and Grootenhuis *et al.* [28] explain this formation as a result of steric effects in the narrow calix[4]arene ring. The angle between the opposite aromatic rings B and D in **2** is 42.8°, and for the rings A and C it is 11.1°. This angle is smaller than the one for the di-allyl ether **1**, where hydrogen bonding fixes the conformation of the compound. Hence the opposite phenyl rings cannot approach the parallel orientation. Since compound **2** does not involve intra- or intermolecular hydrogen bonding, only the steric interference of the allyl groups determines this conformation. In the crystal packing of **2** the calixarene molecules form a layer structure in which the allyl- and *tert*-butyl groups constitute the hydrophobic area between the layers (Figure 8).

Conclusion

The reaction of *tert*-butylcalix[4]arene with allyl bromide in the presence of K_2CO_3 was found to be kinetically controlled. While after 3 h reaction time transformation proceeded to the di-allyl calixarene **1**, long reaction time led to the tetra substituted compound **2**.

Due to the strong intramolecular H bonding the di-allyl ether **1** is definitely in the cone conformation, whatever distortion may be, regardless whether the molecule is in solution (**1**) or in a solvated crystalline state (**1a**, **1b**). Thus, even the protic solvent methanol such as in **1b** does not interfere with the intramolecular H bonding that determines the cone conformation. Only distortion of the cone is affected by the solvent. By way of contrast, the tetra-allyl ether **2** is a mixture of cone and partial cone conformers determined by steric and template effects. In the solid state the partial cone conformation seems to be preferred because of additional hydrophobic interactions in the crystal packing. Actually this finding is important to the conformational orientation and selective synthesis of desired derivatives of *tert*-butylcalix[4]arene related to **1** or **2**.

Acknowledgements

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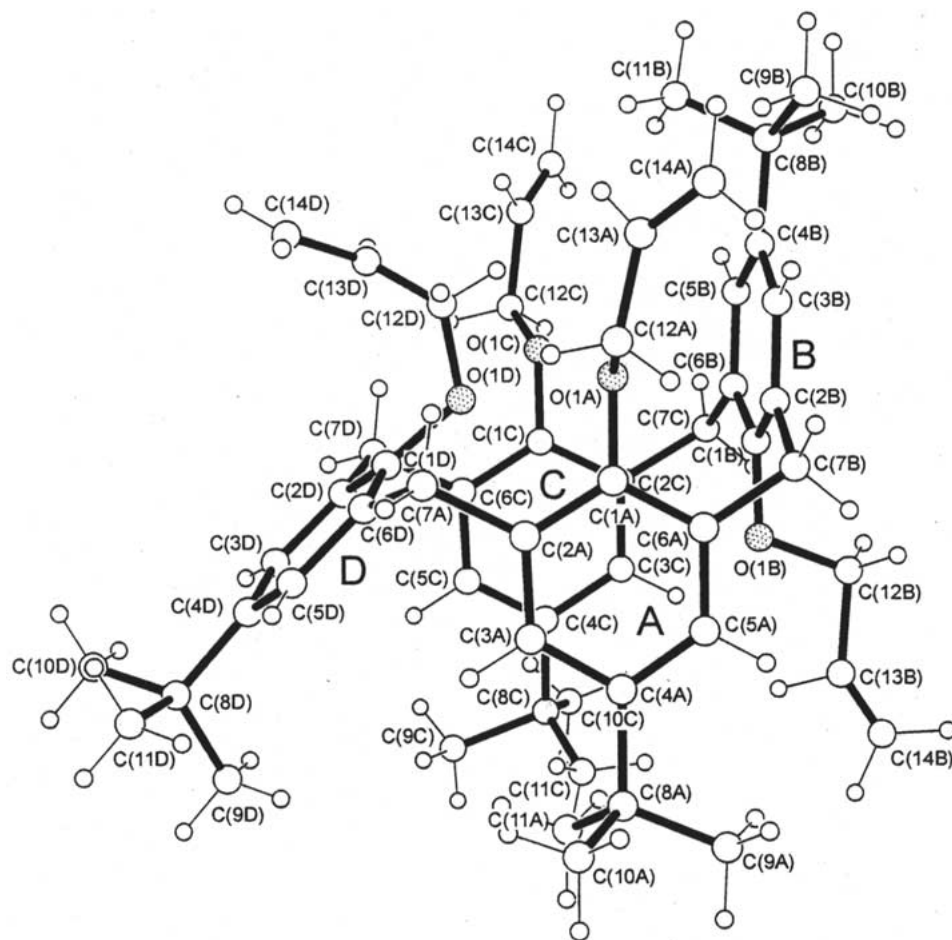


Figure 7. Perspective view of compound **2** including the atomic numbering scheme. Hetero atoms are shaded.

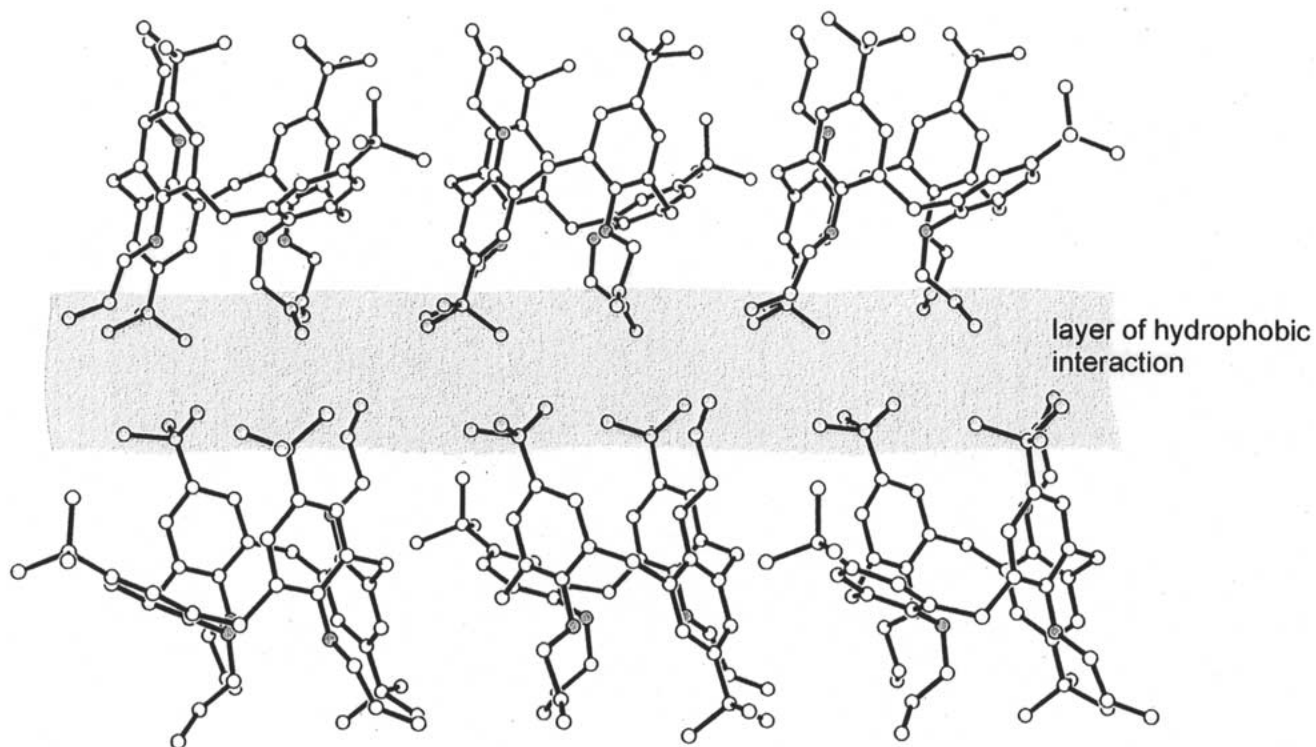


Figure 8. Crystal packing of **2**, showing the layer structure. O atoms are shaded.

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