



HAL
open science

Crystal Structures of a Calix[4]arene Controlled by Two Affixed Pyrene Units

Tobias Gruber, Wilhelm Seichter, Edwin Weber

► **To cite this version:**

Tobias Gruber, Wilhelm Seichter, Edwin Weber. Crystal Structures of a Calix[4]arene Controlled by Two Affixed Pyrene Units. *Supramolecular Chemistry*, 2008, 20 (08), pp.753-760. 10.1080/10610270701854945 . hal-00513527

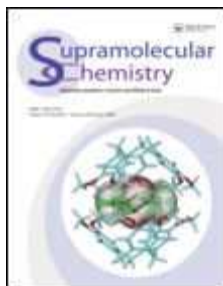
HAL Id: hal-00513527

<https://hal.science/hal-00513527>

Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Crystal Structures of a Calix[4]arene Controlled by Two Affixed Pyrene Units

Journal:	<i>Supramolecular Chemistry</i>
Manuscript ID:	GSCH-2007-0155
Manuscript Type:	Special Issue Paper
Date Submitted by the Author:	07-Dec-2007
Complete List of Authors:	Gruber, Tobias; TU Bergakademie Freiberg, Organische Chemie Seichter, Wilhelm; TU Bergakademie Freiberg, Organische Chemie Weber, Edwin; TU Bergakademie Freiberg, Organische Chemie
Keywords:	Calixarenes, Crystalline inclusion compound, Supramolecular interactions, Pyrene stacking , X-ray crystal structures



Only

1
2
3
4
5
6
7 **Crystal Structures of a Calix[4]arene Controlled by Two**
8
9
10 **Affixed Pyrene Units**
11

12
13
14
15
16 TOBIAS GRUBER, WILHELM SEICHTER, EDWIN WEBER*

17
18
19 *Institut für Organische Chemie, Technische Universität Bergakademie Freiberg,*
20 *Leipziger Str. 29, D-09596 Freiberg/Sachs., Germany*
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52

53
54 _____
55 *Author for correspondence. Fax: +49-3731-393170. Email: edwin.weber@chemie.tu-freiberg.de
56
57
58
59
60

1
2
3 *Keywords:* Calixarenes; Crystalline inclusion compound; X-ray crystal structures;
4
5
6 Supramolecular interactions; Pyrene stacking;
7
8
9

10 Abstract

11
12 **The synthesis and crystal structures of a calix[4]arene (1) with two affixed pyrene**
13 **units and its corresponding inclusion compound with chloroform (1a) are**
14 **reported. In both cases, stacking structures resulting from the influencing control**
15 **of the pyrene units are observed. Dependent on the absence or presence of the**
16 **included guest solvent, infinite or dimeric stack motifs of the pyrene units are**
17 **concerned, respectively.**
18
19
20
21
22
23
24
25
26
27
28
29
30
31

32 INTRODUCTION

33
34
35
36 Calixarenes are a particular class of supramolecular compounds obtained from
37
38 condensation between phenols and formaldehyde [1]. Due to their calix-shaped hollow
39
40 structure, they have proven extremely useful in forming host-guest inclusion
41
42 compounds [2]. On the other hand, owing to its restricted conformational mobility, the
43
44 calix framework has been found a functional platform to create more complex
45
46 supramolecular constructions and devices [3]. This is demonstrated by a great number
47
48 of calixarenes providing functional side arms for supramolecular interaction or the
49
50 attachment of a sensing unit [4]. While the function of a side arm, being designed for
51
52 the specific interaction with a guest molecule or mutually between the calixarene
53
54 molecules, very often make use of hydrogen bonding [5], the $\pi\cdots\pi$ -stacking mode of
55
56 interaction is far less considered [6, 7]. In particular the pyrene moiety, which is
57
58 generally known to be inclined to stacking formation [8], is given reference only in a
59
60

1
2
3 few recent cases [9, 10, 11]. The present dipyrène-substituted calix[4]arene **1** (Scheme
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

few recent cases [9, 10, 11]. The present dipyrène-substituted calix[4]arene **1** (Scheme 1) is included by a short communication but concentrating especially on the fluorescent property [12]. Here, we now report in detail on the preparation and crystal structures of the calixarene **1** and its inclusion compound **1a** with chloroform, showing specific control of the pyrene units both in the molecular and packing structure.

RESULTS AND DISCUSSION

Synthesis and Conformational Characterization

The title compound **1** (Scheme 1) was synthesized from calix[4]arenedicarboxylic acid **3** via chlorination with thionyl chloride, followed by reaction with 1-(hydroxymethyl)pyrene. Beside **1**, this esterification process yielded also the monopyrene derivative **2**. Compound **3** was prepared in three steps from conventional tetra-*t*-butylcalix[4]arene [13] involving propylation, reaction with ethyl bromoacetate and subsequent hydrolysis of the respective ester [14, 15]. The inclusion compound of **1** with chloroform (**1a**) has been obtained by crystallization of **1** from a chloroform solution.

The solution conformational behaviour of the propoxy groups in **1** and **2** has been studied using NMR technique. In the solution proton NMR spectrum of compound **2**, the resonance signals of the two propoxy OCH₂ groups appear as two multiplets at 3.62 and 3.87 ppm in a 1:1 ratio, indicating limited rotability of the O-C bond. Evidence of the chemical non-equivalence of the respective methylene protons is given by the

1
2
3 splitting in the COSY spectrum (Fig. 1). A corresponding splitting is not observed for
4
5 compound **1** due to the molecular symmetry.
6
7
8
9

10 11 12 **X-ray structural study** 13

14
15
16
17 X-ray crystal structures of compound **1** as well as the inclusion compound **1a** [**1**·CHCl₃
18 (1:2.5)] have been studied (Table I). Perspective views of the molecular structures
19 together with illustrations of the crystal packings are displayed in Figures 2-6. Usually,
20 the conformation of a calix[4]arene framework is described by a set of interplanar
21 angles that defines the inclination of the aromatic rings with respect to the basis plane
22 given by the methylene atoms C(7), C(14), C(21) and C(28). These data are included in
23 Table II while parameters of intramolecular contacts are listed in Table III. In the
24 present crystal structures, the calixarene skeleton is highly ordered whereas a part of the
25 *tert*-butyl and propoxy substituents is disordered over two positions. In case of the
26 structure **1**·CHCl₃ (1:2.5), one of the guest molecules has proven to be difficult to model
27 and show significant residue electron density around the molecule.
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45

46 In the solvent-free crystal structure of **1**, the calixarene framework adopts a rather
47 typical pinched cone conformation (Fig. 2) with the aromatic rings (A and C) that
48 contain the pyrene units exhibiting a nearly orthogonal arrangement, whereas the other
49 pair of opposite rings (B and D) is almost parallel. As a result of this conformational
50 fact, the upper rim cavity is too small for accommodation of a guest molecule (5.30 Å
51 centroid-to-centroid distance of rings B and D). The torsion angles of the two ester
52 pendants [ranging between 161.3(2) and 175.5(2)°] give rise to an almost linear overall
53 conformation while the conformations around C-C-O-C [64.1(2) and 68.3(2)°] and O-
54
55
56
57
58
59
60

1
2
3 C-C-C [179.8(2) and 176.5(2)°] having reference to the connection between the pendant
4
5 moieties and the calixarene or pyrene units, can be described as gauche and anti,
6
7 respectively (Table II). Both pyrene units deviate only slightly from a coplanar
8
9 arrangement [5.89(1)°], exhibiting an average distance of about 3.5 Å, but are also
10
11 rotated about 57.0° due to the inherent twofold crystallographic symmetry of the
12
13 calixarene molecule in the crystal structure and the connection of pyrene in the 1-
14
15 position. Nevertheless, the two pyrene units show a significant overlapping of their π -
16
17 systems. Previously, with regard to excimer formation, a similar situation involving two
18
19 pyrene units of analogous calix[4]arenes has been observed in solution [10, 11, 12].
20
21
22
23
24
25
26

27 Owing to the absence of strong hydrogen bond donors, the intermolecular
28
29 interactions in the crystal are dominated by a zipper-like infinite stacking of the pyrene
30
31 pairs along the crystallographic *b*-axis (Fig. 3). It is worth to note that the pyrene
32
33 overlap in this stacking is higher in intermolecular than in intramolecular fashion. This
34
35 might be attributed to the space required by the ester subunit, partly facing the pyrene
36
37 group of a neighbouring calixarene, in order to make possible C-H...O(C=O) and C-
38
39 H... π (pyrene) contacts thus allowing a maximum of interactions along the appended
40
41 side arms. Moreover, due to the head-to-head orientation of the calixarene part of the
42
43 molecules, a bilayer-like structure is formed in the crystal packing with calixarene
44
45 molecules shifted half a translation unit along the *b*-axis. According to their
46
47 hydrophobic nature, these domains are stabilized through van der Waals interactions. In
48
49 a comparison of resemblance, while bilayers formed of amphiphilic molecules are
50
51 typical of a clear separation of polar and apolar regions, the present structure is
52
53 composed of molecules featuring segments that are proportionally poorer and richer in
54
55 the arene constituents.
56
57
58
59
60

1
2
3 As in the unsolvated calixarene **1**, the asymmetric unit of its crystalline 1:2.5
4 inclusion compound with chloroform (1:2.5) **1a** contains one molecule of calixarene but
5
6 in addition two and a half molecules of chloroform. One of these chloroform molecules
7
8
9 is located at the special position $1, \frac{1}{2}, \frac{1}{4}$, i.e. occupying two alternative orientations with
10
11 side occupation factors of 0.5 (Fig. 4). As a result of the weak donor/acceptor property,
12
13 the guest molecules show a high degree of mobility which makes determination of their
14
15 positions difficult. The geometry of the calixarene backbone differs only slightly from
16
17 that in the unsolvated compound **1**. Nevertheless, conformational changes arise from the
18
19 orientation of the aromatic ring C with regard to the mean plane defined by the bridging
20
21 methylene groups, thus explaining the increase of the interplanar angle A/C. However,
22
23 the inclusion of chloroform causes a drastic conformational change of the lower rim
24
25 substituents, especially regarding the aliphatic ester segment, the torsion angles of
26
27 which $[C(1)-O(1)-C(33)-C(34) = -57.4(5), C(16)-C(15)-O(5)-C(63) = -113.8(3)^\circ]$
28
29 proved to be noticeably different from those of the apo-host **1** $[-97.7(2)$ and $-68.3(2)^\circ$,
30
31 respectively]. The two pyrenyl units are inclined by $56.9(1)$ and $57.5(1)^\circ$ towards the
32
33 least-squares plane of the bridging methylene carbons showing distinct loss of
34
35 molecular symmetry. In the present structure, the pyrene rings are also almost parallel in
36
37 their orientation $[0.88(21)^\circ]$, but the intramolecular distance between these groups has
38
39 increased to approximately 7.1 \AA . As contrasted with the unsolvated compound **1**, in **1a**
40
41 a pair of calixarene molecules is interlocked through pyrene units leading to a dimer
42
43 stack such as illustrated in Fig. 5. Moreover, edge-to-face interactions are displayed
44
45 between the pyrenyl groups of neighbouring dimers, giving rise to a C-H... π (centroid)
46
47 distance of 2.83 \AA . This packing behaviour resembles the reported structure of
48
49 crystalline pyrene [16], showing both face-to-face and edge-to-face relationship. The
50
51 solvent molecules in **1a** are located interstitially in the voids of the host lattice (Fig. 6).
52
53 While one of the solvent molecules is encircled by the voluminous *tert*-butyl groups and
54
55
56
57
58
59
60

1
2
3 seems to have no interaction with the calixarene, the other two chloroform molecules
4
5 either interact with their acidic hydrogen to one of the carbonyl oxygen atoms of the
6
7 calixarene [C(1A)-H(1A)···O(6)] or are engaged in a C-H··· π interaction involving an
8
9 aromatic ring of the calixarene. Furthermore, a host/guest interaction including C(14)-
10
11 H(14A)···Cl(2B) and additional contacts between chlorine atoms of the chloroform
12
13 molecules are found.
14
15
16
17
18
19
20
21

22 CONCLUSION

23
24
25
26
27 A calix[4]arene **1**, featuring two propoxy groups and two substituents carrying terminal
28
29 pyrene units in alternate lower rim positions of the calixarene framework, shows
30
31 crystalline packing behaviour largely controlled by the preference of the pyrene units to
32
33 form stacks. Accordingly, this is verified in the structure by an obvious bilayer-type of
34
35 infinite stacking, being subject to the glide plane symmetry of the calixarene molecules.
36
37 Inclusion of the chloroform molecules in **1a** leads to a change of the distance between
38
39 the calixarene molecules, involving the loss of the glide plane symmetry. As a
40
41 consequence, the infinite stacking mode of the pyrene groups in **1** turns into separate
42
43 dimer stacks of interlocked pyrene units in **1a**, connected with some conformational
44
45 change of the side arms, while the geometry of the calixarene backbone remains
46
47 virtually constant. Hence, aside from the purpose of fluorescent activity [17], pyrene
48
49 groups peripherally attached to a calixarene framework may also be considered a useful
50
51 controlling factor in the engineering of a desired crystalline packing structure.
52
53
54
55
56
57
58
59
60

EXPERIMENTAL

General

Melting points are uncorrected. NMR spectra were recorded on a Bruker AVANCE DPX 400 at 25 °C. Chemical shifts are reported in ppm with TMS as an internal standard ($\delta = 0$ ppm). IR spectra were obtained using a Perkin-Elmer 1600 FT-IR instrument. The elemental analyses were performed with a Heraeus CHN rapid analyzer. Mass spectra were obtained on an Applied Biosystems (Applera) Mariner ESI-TOF. Analytical TLC was performed on precoated silica gel plates (Merck, 60 F₂₅₄), and column chromatography was performed with silica gel (Merck, particle size 0.040-0.063 mm, 230-240 mesh). The calix[4]arenedicarboxylic acid **3** [14, 15] and 1-(hydroxymethyl)pyrene [18] were synthesized according to literature procedures.

Preparation of compounds 1 and 2

The calix[4]arenedicarboxylic acid **3** (1.0 g, 1.18 mmol) was stirred under reflux in thionyl chloride (5.8 ml, 80.00 mmol) for 3 h. Subsequently, the excess thionyl chloride was distilled off. In order to remove remaining traces of thionyl chloride, the residue was dissolved in dry dichloromethane (5 ml). The solvent was evaporated under reduced pressure, the resulting solid dried under high vacuum conditions for 2 h, and subsequently dissolved in dry dichloromethane (30 ml). This solution was added dropwise to a stirred mixture of 1-(hydroxymethyl)pyrene (600 mg, 2.6 mmol) and pyridine (1.0 ml, 5.2 mmol) in 50 ml dry dichloromethane. Stirring was continued for 24 h. Afterwards, the solvent was removed under reduced pressure, the residue

dissolved in chloroform (30 ml) and washed with water (30 ml). The organic layer was separated, dried over sodium sulphate and evaporated. The oily crude product was purified by column chromatography on silica gel with CH₂Cl₂/acetone using an elution gradient, increasing stepwise from 20:1 to 5:2 ratio of the solvent mixture, to yield compounds **1** and **2** as separate fractions. Specific details are given for each compound.

5,11,17,23-Tetra-tert-butyl-25,27-bis[(1-pyrenylmethoxycarbonyl)methoxy]-26,28-dipropoxycalix[4]arene (1)

Stirring of the colourless oil, obtained from column chromatography, with *n*-hexane for 1 h yielded a precipitate which was isolated to give a white solid of compound **1** (440 mg, 30 %), mp = 185-186 °C (lit. [12] mp = 189 °C). TLC: R_f = 0.14 [SiO₂, CH₂Cl₂/acetone (20:1)]. IR (KBr, cm⁻¹) 3047, 2966, 2905, 2869 (CH), 1734 (C=O), 1631 (C=C), 1481 (CH), 1395, 1363, 1303, 1238, 1202, 1135, 1067, 967, 946, 850; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, 6 H, *J* = 7.6 Hz, CH₂CH₂CH₃), 0.89 (s, 18 H, C(CH₃)₃), 1.21 (s, 18 H, C(CH₃)₃), 1.86 (m, 4 H, CH₂CH₂CH₃), 3.09 (d, 4H, *J* = 12.8 Hz, ArCH₂Ar), 3.68 (t, 4 H, *J* = 7.2 Hz, OCH₂CH₂), 4.27 (d, 4 H, *J* = 12.8 Hz, ArCH₂Ar), 5.02 (s, 4 H, OCH₂CO), 5.74 (s, 4 H, COOCH₂Ar), 6.51 (s, 4 H, ArH), 6.93 (s, 4 H, ArH), 7.91 (m, 12 H, pyrene), 8.06 (m, 6 H, pyrene); ¹³C NMR (100 MHz, CDCl₃) δ 10.5 (CH₂CH₃), 23.4 (CH₂CH₃), 31.2, 31.6 (C(CH₃)₃), 31.8 (ArCH₂Ar), 33.6, 34.0 (C(CH₃)₃), 64.4 (COOCH₂Ar), 70.4 (OCH₂CO), 77.2 (OCH₂CH₂), 122.7, 124.4, 124.5, 124.7, 125.3, 125.4, 125.6, 125.9, 127.2, 127.3, 127.6, 127.9, 128.6, 129.3, 130.6, 131.1, 131.5, 132.4, 134.6, 144.2, 145.1, 153.2, 153.3 (Ar), 170.5 (CO)); MS (ESI-TOF) *m/z* Calcd for C₈₈H₉₂O₈: 1300.66. Found: 1300.67 [M+Na⁺]. Anal. Calcd for C₈₈H₉₂O₈: C, 82.72; H, 7.26. Found: C, 82.21; H, 7.25.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

5,11,17,23-Tetra-tert-butyl-25-carboxymethoxy-27-[(1-pyrenylmethoxycarbonyl)methoxy]-26,28-dipropoxycalix[4]arene (2)

Column chromatography yielded **2** (400 mg, 32 %) as a white solid, mp = 147-148 °C. TLC: R_f = 0.03 [SiO₂, CH₂Cl₂/acetone (20:1)]. IR (KBr, cm⁻¹) 3043, 2960, 2903, 2872 (CH), 1765, 1745 (C=O), 1631 (C=C), 1486 (CH), 1388, 1367, 1305, 1243, 1205, 1129, 1062, 964, 855; ¹H NMR (400 MHz, CDCl₃) δ 0.83 (s, 18 H, C(CH₃)₃), 0.90 (t, 6 H, J = 7.6 Hz, CH₂CH₂CH₃), 1.33 (s, 9 H, C(CH₃)₃), 1.35 (s, 9 H, C(CH₃)₃), 1.87 (m, 4 H, CH₂CH₂CH₃), 3.15 (d, 2 H, J = 12.8 Hz, ArCH₂Ar), 3.22 (d, 2 H, J = 12.8 Hz, ArCH₂Ar), 3.62 (m, 2 H, OCH₂CH₂), 3.87 (m, 2 H, OCH₂CH₂), 4.26 (d, 2 H, J = 12.4 Hz, ArCH₂Ar), 4.59 (s, 2 H, OCH₂COOH), 4.87 (d, 2 H, J = 12.4 Hz, ArCH₂Ar), 5.03 (s, 2 H, OCH₂COCH₂), 5.03 (s, 2 H, OCH₂CO), 5.95 (s, 4 H, COOCH₂Ar), 6.49 (d, 2 H, J = 2 Hz, ArH), 6.57 (d, 2 H, J = 2 Hz, ArH), 7.12 (s, 2 H, ArH), 7.17 (s, 2 H, ArH), 8.17 (m, 6 H, pyrene), 8.42 (m, 3 H, pyrene), 11.51 (s, 1 H, COOH); ¹³C NMR (100 MHz, CDCl₃) δ 10.3 (CH₂CH₂CH₃), 23.0 (CH₂CH₂CH₃), 31.1, 31.3, 31.6, 31.7 (C(CH₃)₃, ArCH₂Ar), 33.7, 34.1, 34.2 (C(CH₃)₃), 65.0 (COOCH₂Ar), 71.0, 72.8 (OCH₂CO), 78.4 (OCH₂CH₂), 123.4, 124.6, 124.7, 124.9, 125.3, 125.4, 125.9, 126.0, 127.4, 127.7, 127.7, 128.3, 128.9, 129.7, 130.9, 131.3, 131.7, 131.8, 132.6, 134.8, 135.4, 145.0, 145.8, 147.4, 151.0, 151.3, 154.5 (Ar), 169.9, 170.9 (CO); MS (ESI-TOF) m/z Calcd for C₇₁H₈₂O₈: 1086.39. Found: 1086.59 [M+Na⁺]. Anal. Calcd for C₇₁H₈₂O₈ · 2 CH₃COCH₃: C, 78.40; H, 8.03. Found: C, 78.80; H, 8.35.

X-ray Crystallography

Crystals of **1** and **1a** suitable for X-ray diffraction were obtained by slow evaporation of solutions of **1** in benzene or toluene for **1** and chloroform for **1a**.

1
2
3 The intensity data were collected on a Bruker APEX II diffractometer with MoK α
4 radiation ($\lambda = 0.71073 \text{ \AA}$) using ω - and φ -scans. Reflections were corrected for
5 background Lorentz and polarization effects. Preliminary structure models were derived
6 by application of direct methods [19] and were refined by full-matrix least squares
7 calculation based on F^2 for all reflections [20]. All hydrogen atoms were included in the
8 models in calculated positions and were refined as constrained to bonding atoms. The
9 crystal data and experimental parameters are summarized in Table I. Crystallographic
10 data for the structures in this paper have been deposited with the Cambridge
11 Crystallographic Data Centre as supplementary publication numbers CCDC-655309 and
12 CCDC-655310. Copies of the data can be obtained, free of charge, on application to
13 CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, E-mail:
14 deposit@ccdc.cam.ac.uk).

15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 **Acknowledgements**

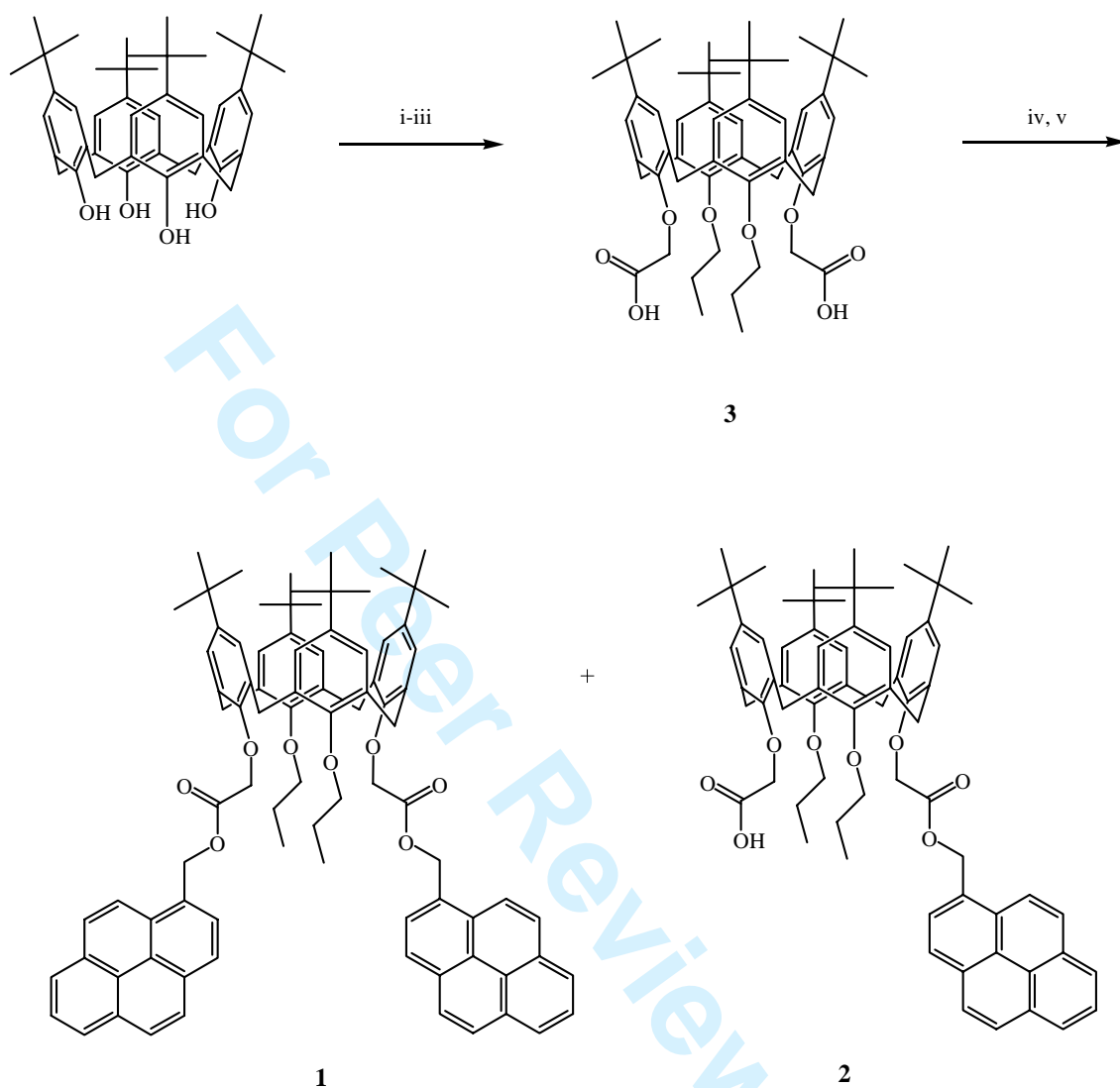
38
39
40
41 The authors are indebted to Dr. E. Brendler (Institute of Analytical Chemistry, TU
42 Bergakademie Freiberg) for recording the COSY NMR spectra. Financial support from
43 the German Federal Ministry of Economics and Technology (BMWi) under grant No.
44 16IN0218 'ChemoChips' is gratefully acknowledged.
45
46
47
48
49
50
51
52
53

-
- 54 [1] Gutsche, C. D. *Calixarenes Revisited, Monographs in Supramolecular*
55 *Chemistry*; Royal Society of Chemistry: Cambridge, UK, 1998; Vol. 6.
56
57 [2] Vicens, J., Böhmer, V., Eds. *Calixarenes - A Versatile Class of Macrocyclic*
58 *Compounds*; Kluwer: Dordrecht, 1991.
59
60 [3] Mandolini, L.; Ungaro, R., Eds. *Calixarenes in Action*; Imperial College Press:
London, 2000.

- 1
2
3
4
5
6 [4] Bren, V. A. *Russ. Chem. Rev.* **2001**, *70*, 1017.
7
8 [5] Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J., Eds. *Calixarenes 2001*;
9 Kluwer: Dordrecht, 2001.
10
11 [6] Li, X.-H.; Fang, P.-F.; Chen, Y.-Y. *Youji Huaxue* **2001**, *21*, 721.
12
13 [7] Hartley, J. H.; James, T. D.; Ward, C. J. *J. Chem. Soc., Perkin Trans. 1* **2000**,
14 3155.
15
16 [8] Tiekink, E. R. T.; J. Vittal, Eds. *Frontiers in Crystal Engineering*, Wiley:
17 Hoboken, 2006.
18
19 [9] Krebs, F. C.; Larsen, M.; Jørgensen, M.; Jensen, P. R.; Bielecki, M.;
20 Schaumburg, K. *J. Org. Chem.* **1998**, *63*, 9872.
21
22 [10] Kim, J.-M.; Min, S. J.; Lee, S. W.; Bok, J. H.; Kim, J. S. *Chem. Commun.* **2005**,
23 27, 3427.
24
25 [11] Kim, S. K.; Kim, S. H.; Kim, H. J.; Lee, S. H.; Lee, S. W.; Ko, J.; Bartsch, R.
26 A.; Kim, J. S. *Inorg. Chem.* **2005**, *44*, 7866.
27
28 [12] Aoki, I.; Sakaki, T.; Tsutsui, S.; Shinkai, S. *Tetrahedron Lett.* **1992**, *33*, 89.
29
30 [13] Gutsche, C. D.; Iqbal, M.; Stewart, D. *J. Org. Chem.* **1986**, *51*, 742.
31
32 [14] Murakami, H.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1993**, *20*, 1533.
33
34 [15] Murakami, H.; Shinkai, S. *Tetrahedron Lett.* **1993**, *34*, 4237.
35
36 [16] Frampton, C. S.; Knight, K. S.; Shankland, N.; Shankland, K. *J. Mol. Struct.*
37 **2000**, *520*, 29.
38
39 [17] Vicens, J.; Harrowfield, J., Eds. *Calixarenes in the Nanoworld*; Springer:
40 Dordrecht, 2007.
41
42 [18] Gruber, T.; Seichter, W.; Weber, E. *Acta Cryst.* **2006**, *E62*, o2569.
43
44 [19] Sheldrick, G. M. *SHELXS-97: Program for Crystal Structure Solution*;
45 University of Göttingen: Germany, 1990.
46
47 [20] Sheldrick, G. M. *SHELXL-97: Program for Crystal Structure Refinement*;
48 University of Göttingen: Germany, 1997.
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For Peer Review Only



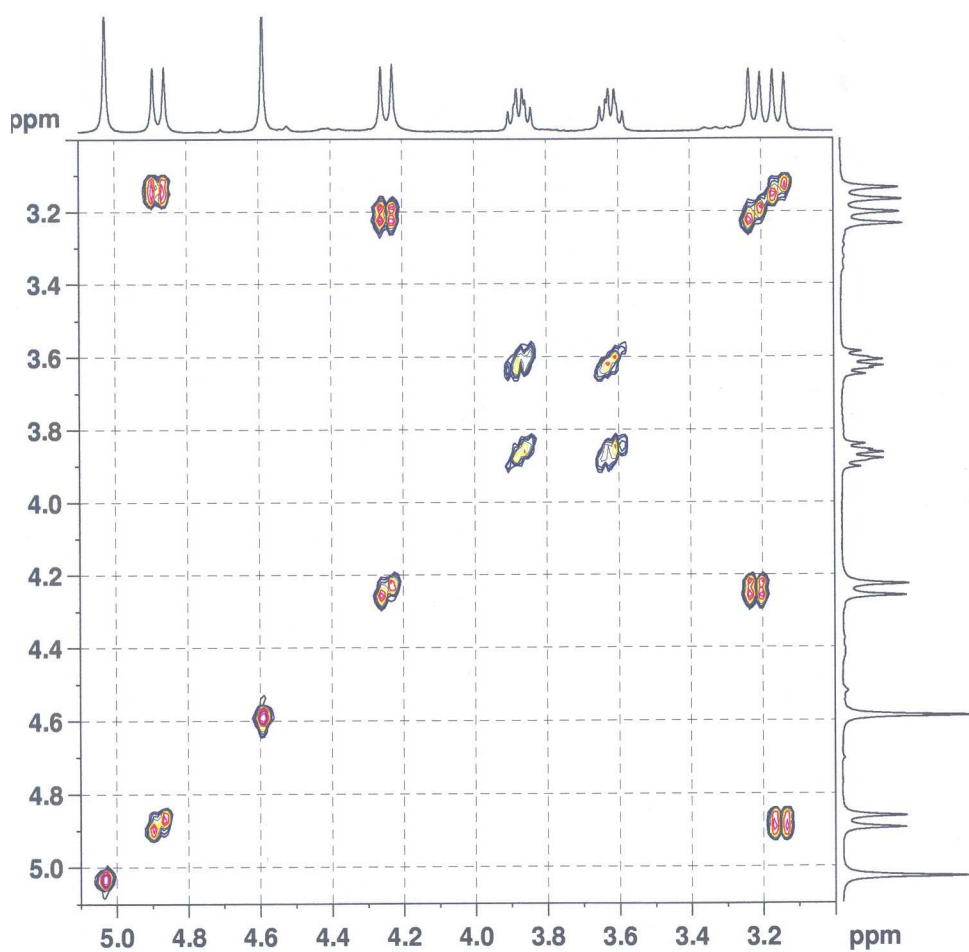
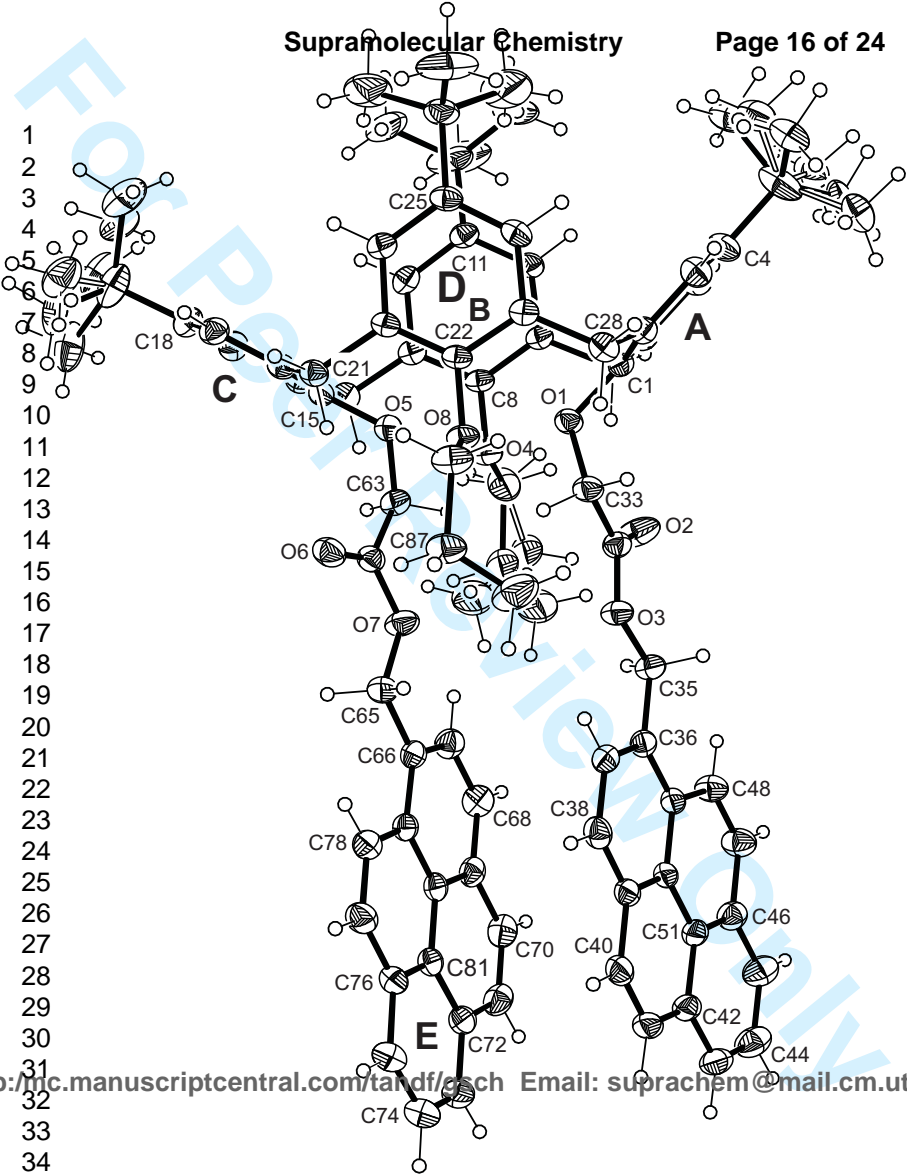


FIGURE 1 Section of the 400 MHz COSY spectrum (CDCl_3) of **2** where cross-signals between two species of propoxy methylene protons are found ($\delta_1 = 3.62$ ppm, $\delta_2 = 3.87$ ppm).



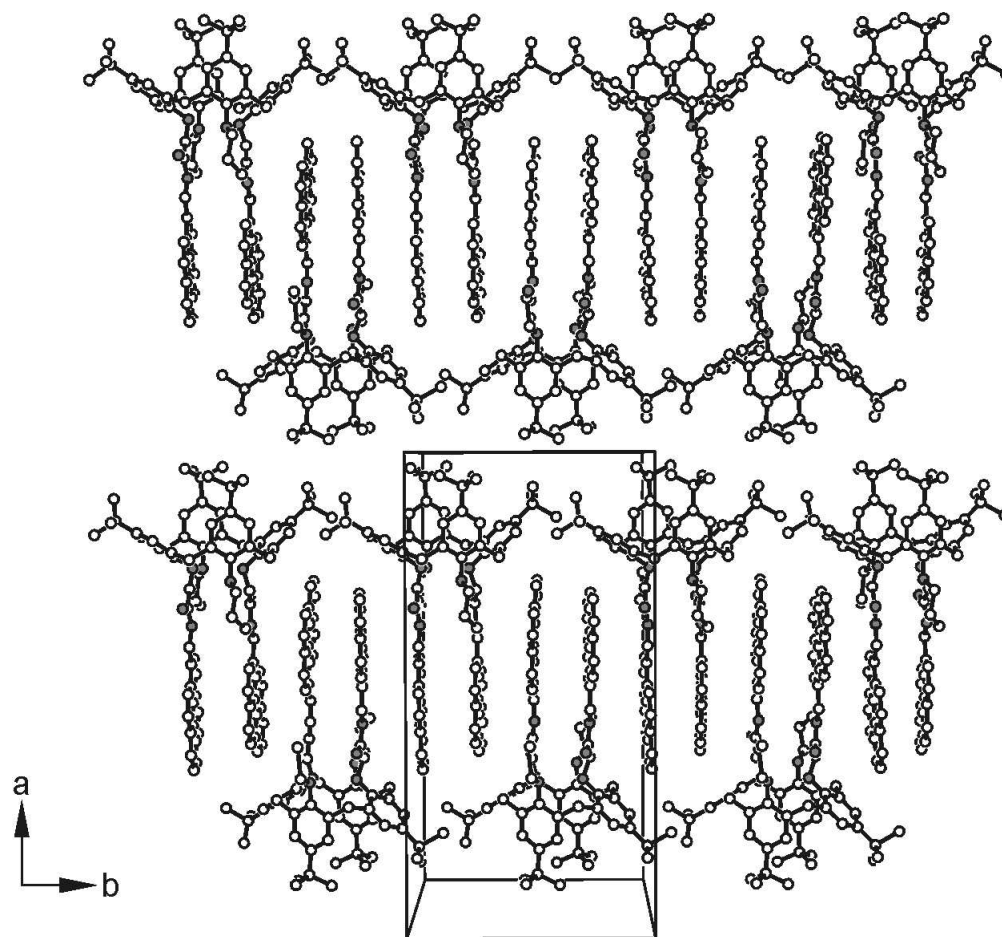


FIGURE 3 Packing motif of **1**, viewed along the *c* axis. Heteroatoms are indicated by shading, and hydrogens have been omitted for clarity.

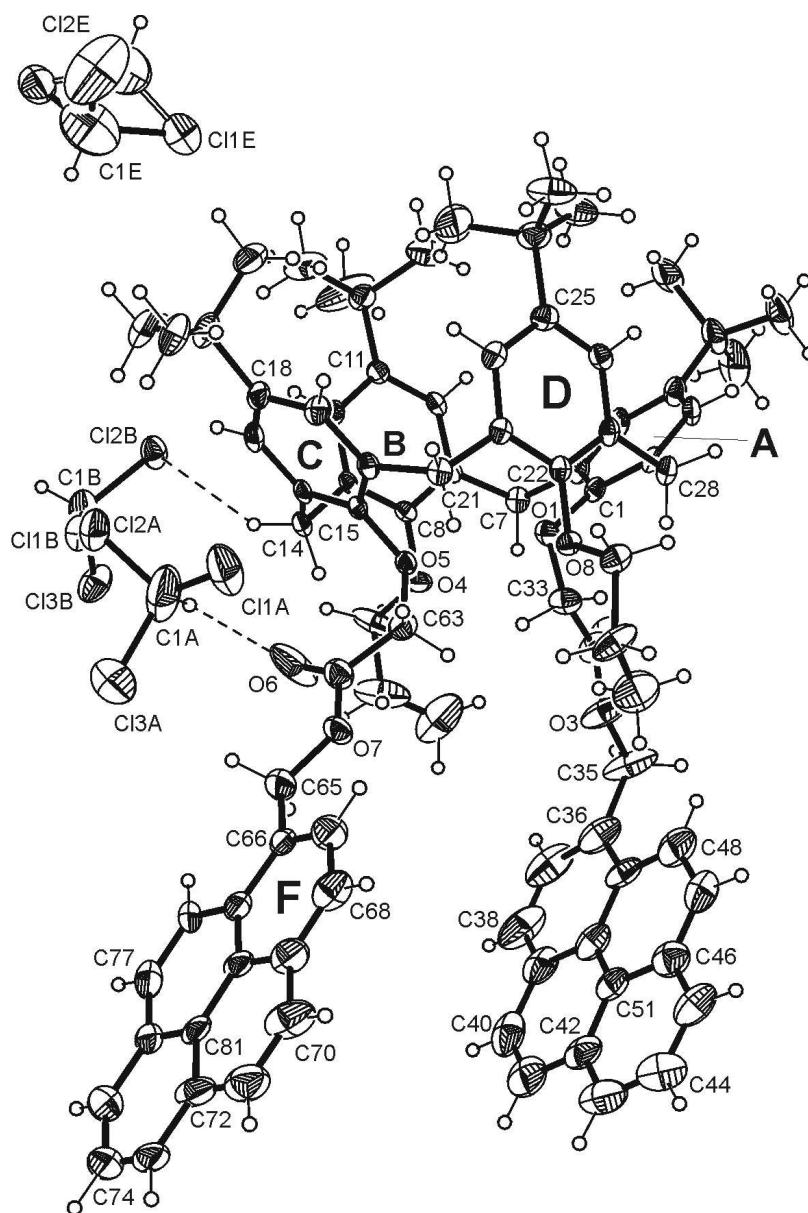
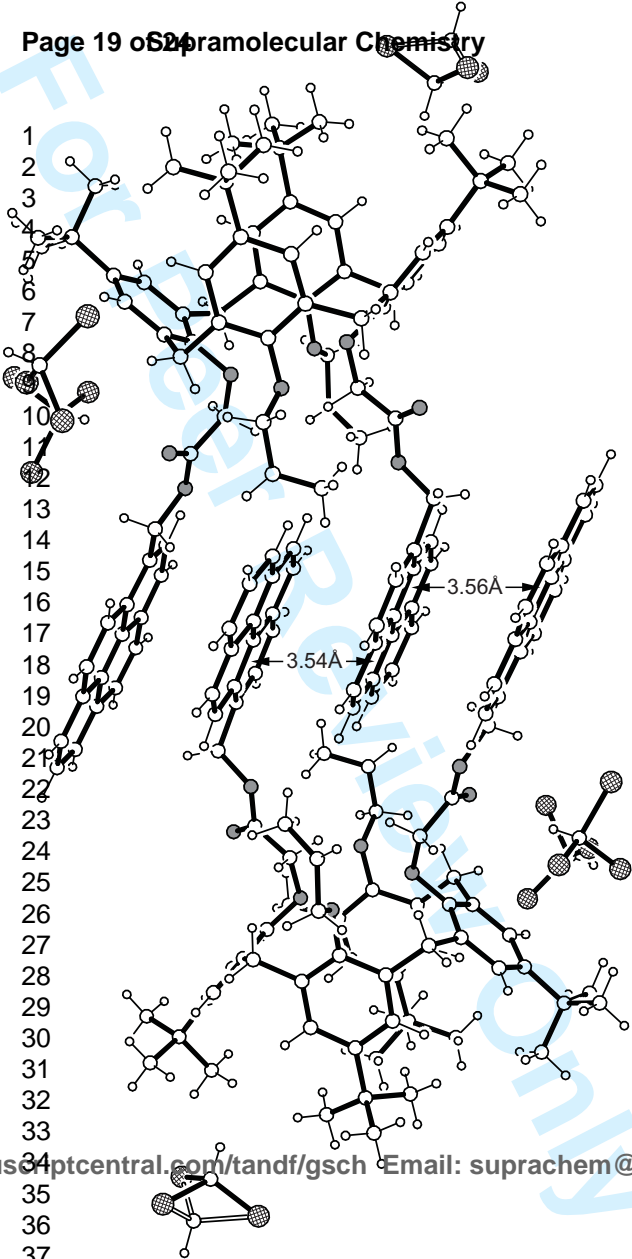


FIGURE 4 Molecular structure of the inclusion compound of **1** with CHCl₃ (1:2.5) showing 30% probability displacement representation and numbering scheme of the non-hydrogen atoms. Only one disorder site of the coordinated chloroform molecules is shown for clarity.



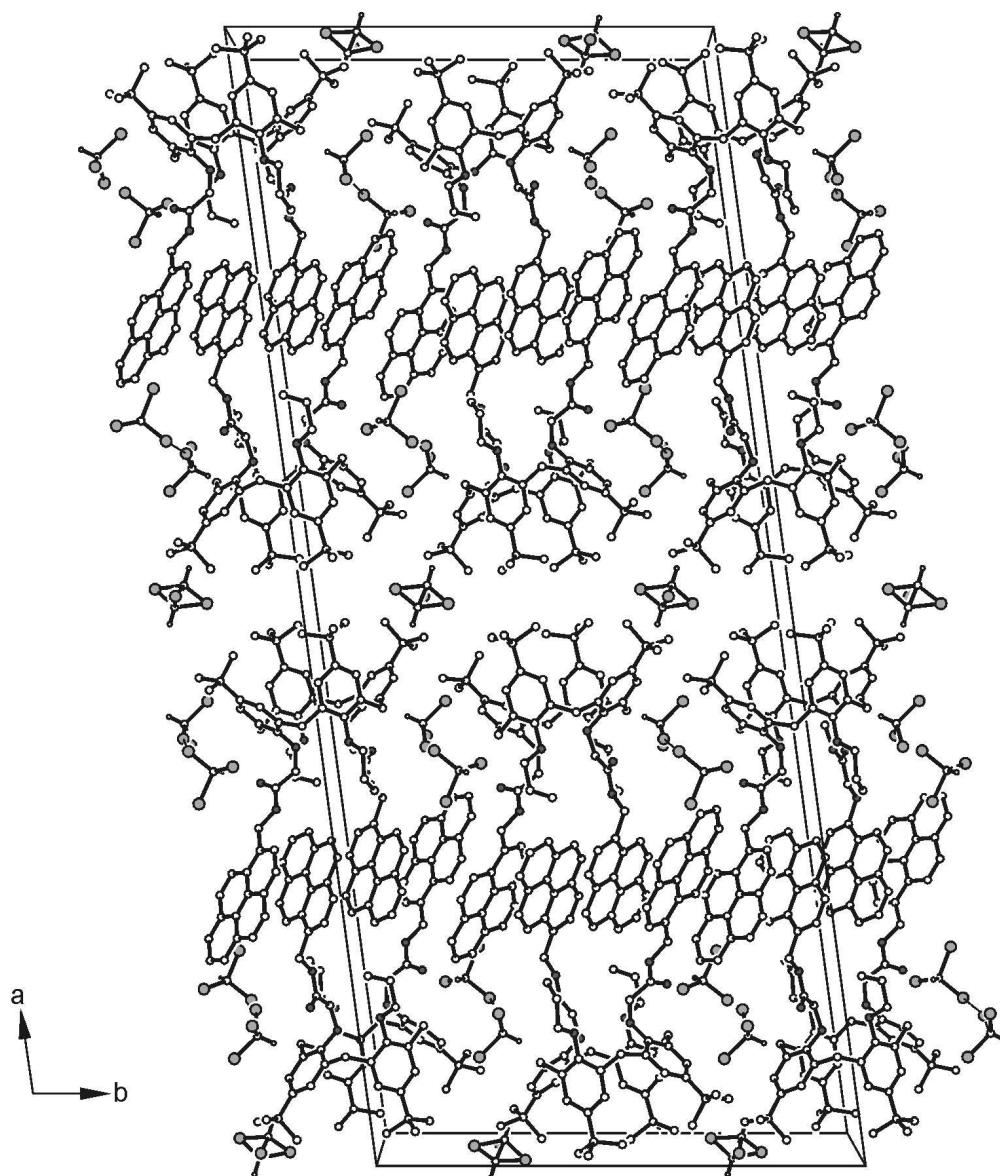


FIGURE 6 Packing illustration of **1a**, viewed along the *c* axis. Heteroatoms are indicated by shading, and hydrogen atoms, except for chloroform, have been omitted for clarity.

Compound	1	1a
Empirical formula	C ₈₈ H ₉₂ O ₈	C ₈₈ H ₉₂ O ₈ · 2.5 CHCl ₃
Formula weight	1277.62	1582.04
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	27.367(3)	61.9037(16)
<i>b</i> (Å)	14.0071(13)	10.0521(3)
<i>c</i> (Å)	19.1495(17)	26.3612(7)
α (°)	90.0	90.0
β (°)	92.226(6)	97.609(3)
γ (°)	90.0	90.0
<i>V</i> (Å ³)	7335.0(12)	16259.1(8)
<i>Z</i>	4	8
<i>F</i> (000)	2736	6656
<i>D</i> _c (Mg m ⁻³)	1.157	1.293
μ (mm ⁻¹)	0.072	0.317
Data collection		
Temperature (K)	153(2)	93(2)
No. of collected reflections	149661	188759
within the θ -limit (°)	1.5-28.5	1.6-29.4
Index ranges $\pm h$, $\pm k$, $\pm l$	-36/36, -18/18, -25/25	-85/85, -10/13, -36/36
No. of unique reflections	18389	22212
No. of refined parameters	949	1016
No. of F values used [<i>I</i> >2 σ (<i>I</i>)]	6919	10947
Final <i>R</i> -Indices		
<i>R</i> (= $\Sigma \Delta F / \Sigma F_o$)	0.051	0.1053
<i>wR</i> on <i>F</i> ²	0.1395	0.3593
<i>S</i> (=Goodness of fit on <i>F</i> ²)	0.927	1.024
Final $\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å ⁻³)	0.24/-0.27	2.02/-0.91

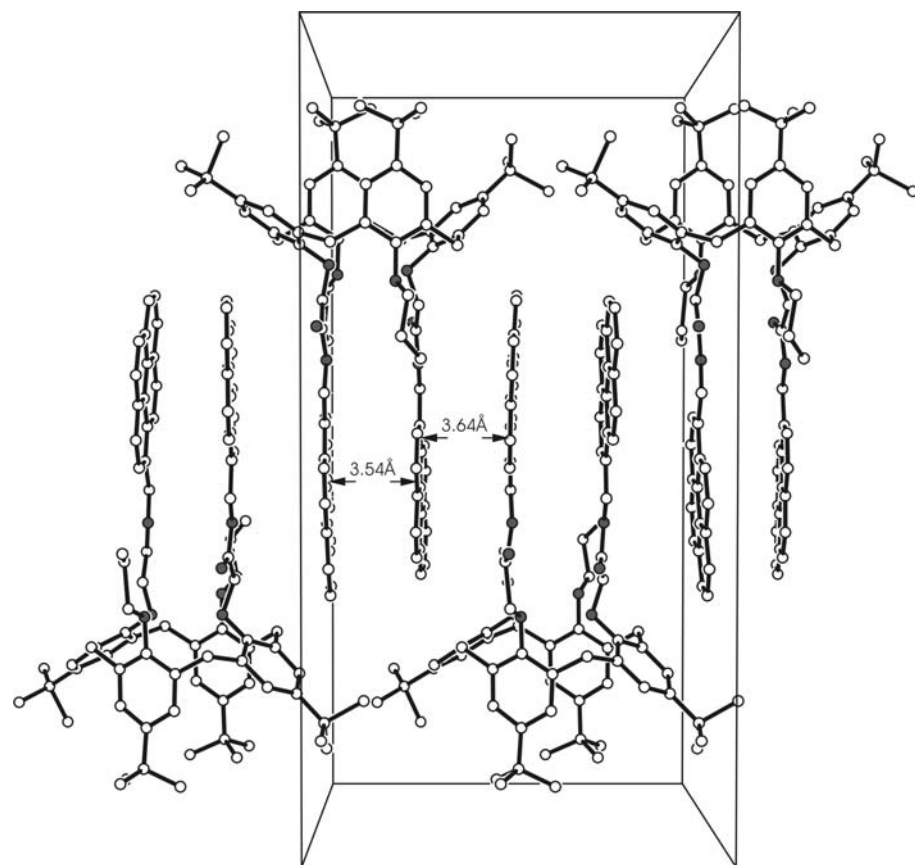
Compound	1	1a
Interplanar angles (°) ^a		
mpla ^b /A	43.04(5)	40.49(9)
mpla/B	87.54(5)	85.81(8)
mpla/C	33.44(5)	50.03(8)
mpla/D	86.00(5)	88.79(8)
A/C	83.87(6)	88.53(8)
B/D	2.38(9)	2.99(8)
Torsion angles (°)		
C(1)-C(2)-C(28)-C(27)	-70.6(3)	-69.1(5)
C(2)-C(28)-C(27)-C(22)	115.9(2)	117.5(4)
C(22)-C(23)-C(21)-C(20)	-119.1(2)	-114.1(4)
C(23)-C(21)-C(20)-C(15)	66.2(3)	76.5(4)
C(15)-C(16)-C(14)-C(13)	-64.6(3)	-83.7(4)
C(16)-C(14)-C(13)-C(8)	112.4(2)	117.1(4)
C(8)-C(9)-C(7)-C(6)	-114.7(2)	-109.5(4)
C(9)-C(7)-C(6)-C(1)	75.5(2)	70.4(4)
C(2)-C(1)-O(1)-C(33)	-64.1(2)	-68.5(5)
C(1)-O(1)-C(33)-C(34)	-97.7(2)	-57.4(5)
O(1)-C(33)-C(34)-O(3)	-164.6(2)	-174.7(4)
C(33)-C(34)-O(3)-C(35)	-173.8(2)	179.2(6)
C(34)-O(3)-C(35)-C(36)	-175.2(2)	-147.8(5)
O(3)-C(35)-C(36)-C(49)	179.8(2)	-71.5(8)
C(16)-C(15)-O(5)-C(63)	-68.3(2)	-113.8(5)
C(15)-O(5)-C(63)-C(64)	-87.4(2)	75.2(4)
O(5)-C(63)-C(64)-O(7)	-161.3(2)	-175.3(3)
C(63)-C(64)-O(7)-C(65)	-175.5(2)	-176.8(4)
C(64)-O(7)-C(65)-C(66)	171.5(2)	-174.3(4)
O(7)-C(65)-C(66)-C(79)	176.5(2)	-172.7(3)

^a Aromatic rings: ring A: C(1)...C(6); ring B: C(8)...C(13); ring C: C(15)...C(20); ring D: C(22) ...C(27);

^b Best plane through atoms C(7), C(14), C(21) and C(28).

Atoms involved	Symmetry	Distance (Å)		Angle (°)
		D...A	H...A	
1				
C(87)-H(87A)...O(2)	$x, 0.5-y, 0.5+z$	3.256(3)	2.53	129.6
C(35)-H(35A)...M(E)*	$1-x, 0.5+y, 0.5-z$	3.572(3)	2.78	137.4
1a				
C(1A)-H(1A)...O(6)	x, y, z	3.531(6)	2.62	151.3
C(1AA)-H(1AA)...O(6)	x, y, z	3.714(7)	2.80	152.3
C(1B)-H(1B)...M(A)*	$x, 1+y, z$	3.084(6)	2.37	127.3
C(1D)-H(1D)...M(A)*	$x, 1+y, z$	3.207(7)	2.33	145.3
C(77)-H(77)...M(F)*	$0.5-x, -0.5+y, 1.5-z$	3.760(8)	2.83	165.8
C(14)-H(14A)...Cl(2B)	$x, 1-y, 0.5+z$	3.724(6)	2.86	146.2
C(1B)-Cl(1B)...Cl(2A)	$x, 1-y, -0.5+z$	3.544(8)	-	162.1
C(1A)-Cl(2A)...Cl(1B)	$x, 1-y, 0.5+z$	3.544(8)	-	105.3

* M(A): ring centroid C(1)...C(6); M(B): ring centroid C(8)...C(13); M(C): ring centroid C(15)...C(20); M(D): ring centroid C(22)...C(27); M(E): ring centroid C(76)...C(81); M(F): ring centroid C(66)...C(69), C(79)...C(80).



Tobias Gruber, Wilhelm Seichter, Edwin Weber

Crystal Structures of a Calix[4]arene

Controlled by Two Affixed Pyrene Units

Review Only