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Crystal structures of a calix[4]arene controlled by two affixed pyrene units

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The synthesis and crystal structures of a calix[4]arene (**1**) with two affixed pyrene units and its corresponding inclusion compound with chloroform (**1a**) are reported. In both cases, stacking structures resulting from the influencing control of the pyrene units are observed. The occurrence of infinite or dimeric stack motifs of the pyrene units is dependent on the absence or presence of the included guest solvent.

Keywords: calixarenes; crystalline inclusion compound; X-ray crystal structures; supramolecular interactions; pyrene stacking

Introduction

Calixarenes are a particular class of supramolecular compounds obtained by the condensation of phenols and formaldehyde (*1*). Due to their calix-shaped hollow structure, they have proven extremely useful in forming host–guest inclusion compounds (*2*). On the other hand, owing to its restricted conformational mobility, the calix framework has been found a functional platform to create more complex supramolecular constructions and devices (*3*). This is demonstrated by a great number of calixarenes providing functional side arms for supramolecular interaction or the attachment of a sensing unit (*4*). While the function of a side arm, being designed for the specific interaction with a guest molecule or mutually between the calixarene molecules, very often makes use of hydrogen bonding (*5*), the $\pi\cdots\pi$-stacking mode of interaction is far less considered (*6*, *7*). In particular, the pyrene moiety, which is generally known to be inclined to stacking formation (*8*), is given reference only in a few recent cases (*9–11*). The present dipyrene-substituted calix[4]arene **1** (Scheme 1) is included in 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 structures.

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 tetramethylsilane (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 analyser. Mass spectra were obtained on an Applied Biosystems, Foster City, CA, USA (Applera), Mariner ESI-TOF. Analytical thin layer chromatography (TLC) was performed on precoated silica gel plates (Merck, Darmstadt, Germany, 60 F_{254}), 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** (*13*, *14*) and 1-(hydroxymethyl)pyrene (*15*) were synthesised 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 mmol) for 3 h. Subsequently, the excess thionyl chloride was distilled off. In order to remove the 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. Later, 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

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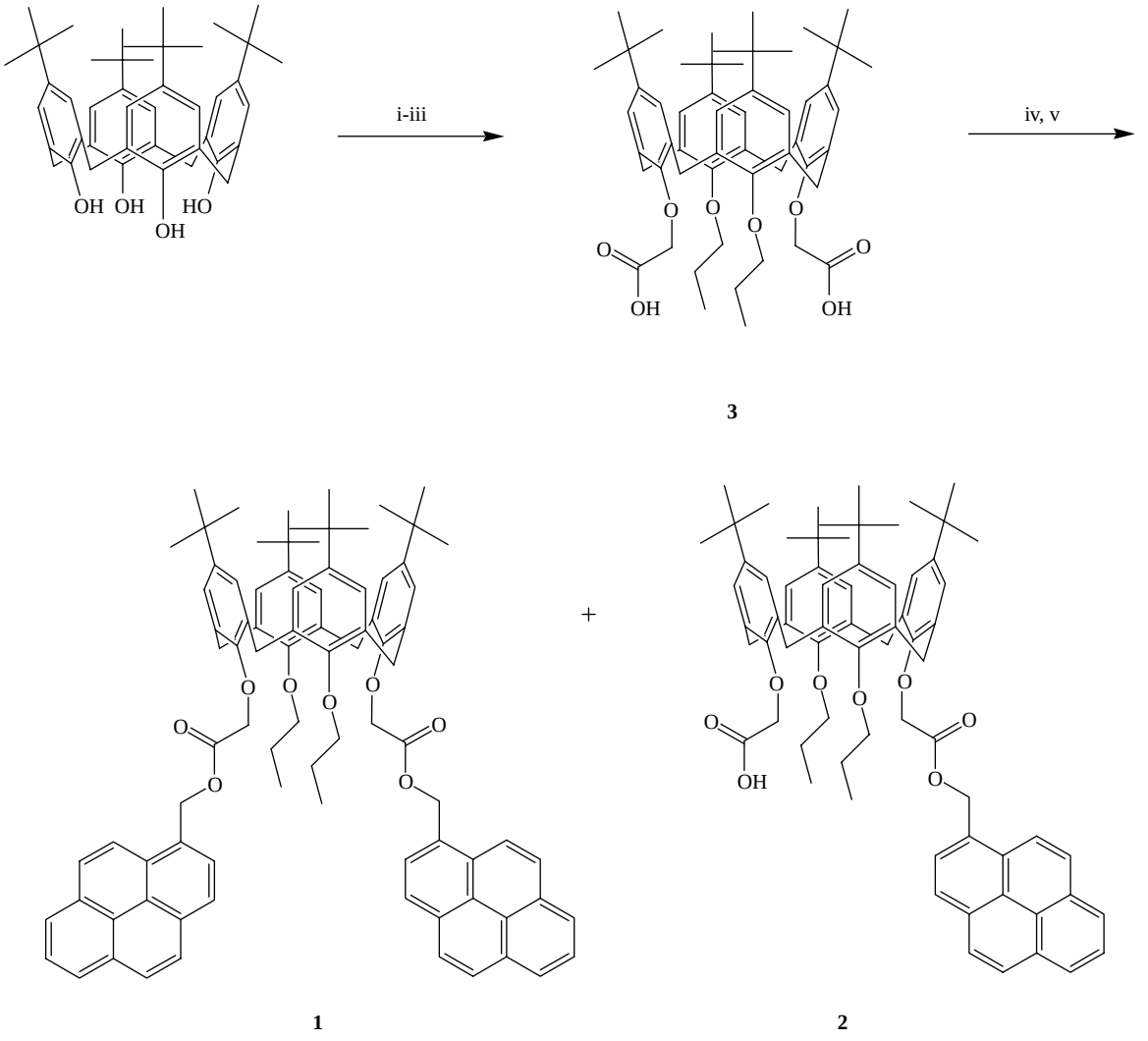

Scheme 1. Synthesis of calix[4]arenes **1** and **2**, showing different numbers of affixed pyrene units. (i) $BrCH_2CH_2CH_3$, K_2CO_3, DMF, 70°C, 24 h (87%); (ii) $BrCH_2COOEt$, NaH, THF, reflux, 7 h (83%); (iii) KOH, MeOH/EtOH, reflux, 7 h (87%); (iv) $SOCl_2$, reflux, 3 h (quant.); (v) 1-(hydroxymethyl)pyrene, pyridine/CH_2Cl_2, rt, 24 h (30 and 32%, respectively).

chromatography on silica gel with CH_2Cl_2/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-t-*butyl-25,27-bis[(1-pyrenylmethoxy-carbonyl)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: $R_f = 0.14$ [SiO_2, CH_2Cl_2/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; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 6H, $J = 7.6$ Hz, $CH_2CH_2CH_3$), 0.89 (s, 18H, $C(CH_3)_3$), 1.21 (s, 18H, $C(CH_3)_3$), 1.86 (m, 4H, $CH_2CH_2CH_3$), 3.09 (d, 4H, $J = 12.8$ Hz, $ArCH_2Ar$), 3.68 (t, 4H, $J = 7.2$ Hz, OCH_2CH_2), 4.27 (d, 4H, $J = 12.8$ Hz, $ArCH_2Ar$), 5.02 (s, 4H, OCH_2CO), 5.74 (s, 4H, $COOCH_2Ar$), 6.51 (s, 4H, Ar*H*), 6.93 (s, 4H, Ar*H*), 7.91 (m, 12H, pyrene), 8.06 (m, 6H, pyrene); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.5 (CH_2CH_3), 23.4 (CH_2CH_3), 31.2, 31.6 ($C(CH_3)_3$), 31.8 ($ArCH_2Ar$), 33.6, 34.0 ($C(CH_3)_3$), 64.4 ($COOCH_2Ar$), 70.4 (OCH_2CO), 77.2 (OCH_2CH_2), 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 (*C*O)); MS (ESI-TOF) *m/z* Calcd for $C_{88}H_{92}O_8$: 1300.66. Found: 1300.67 [M + Na^+]. Anal. Calcd for $C_{88}H_{92}O_8$: C, 82.72; H, 7.26. Found: C, 82.21; H, 7.25.

5,11,17,23-Tetra-t-*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: $R_f = 0.03$ [SiO_2, CH_2Cl_2/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; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (s, 18H, C(CH_3)$_3$), 0.90 (t, 6H, $J = 7.6$ Hz, $CH_2CH_2CH_3$), 1.33 (s, 9H, C(CH_3)$_3$), 1.35 (s, 9H, C(CH_3)$_3$), 1.87 (m, 4H, $CH_2CH_2CH_3$), 3.15 (d, 2H, $J = 12.8$ Hz, ArCH_2Ar), 3.22 (d, 2H, $J = 12.8$ Hz, ArCH_2Ar), 3.62 (m, 2H, OCH_2CH$_2$), 3.87 (m, 2H, OCH_2CH$_2$), 4.26 (d, 2H, $J = 12.4$ Hz, ArCH_2Ar), 4.59 (s, 2H, OCH_2COOH), 4.87 (d, 2H, $J = 12.4$ Hz, ArCH_2Ar), 5.03 (s, 2H, OCH_2-COCH$_2$), 5.03 (s, 2H, OCH_2CO), 5.95 (s, 4H, COOCH_2-Ar), 6.49 (d, 2H, $J = 2$ Hz, Ar*H*), 6.57 (d, 2H, $J = 2$ Hz, Ar*H*), 7.12 (s, 2H, Ar*H*), 7.17 (s, 2H, Ar*H*), 8.17 (m, 6H, pyrene), 8.42 (m, 3H, pyrene), 11.51 (s, 1H, COO*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.3 ($CH_2CH_2CH_3$), 23.0 ($CH_2CH_2CH_3$), 31.1, 31.3, 31.6, 31.7 (C(CH_3)$_3$, ArCH_2Ar), 33.7, 34.1, 34.2 (C(CH$_3$)$_3$), 65.0 (COOCH_2-Ar), 71.0, 72.8 (OCH_2CO), 78.4 (OCH_2CH$_2$), 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 (*C*O); MS (ESI-TOF) *m/z* Calcd for $C_{71}H_{82}O_8$: 1086.39. Found: 1086.59 [M + Na^+]. Anal. Calcd for $C_{71}H_{82}O_8$·2 CH_3COCH_3: 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**.

The intensity data were collected on a Bruker APEX II diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å) using ω- and ϕ-scans. Reflections were corrected for background Lorentz and polarisation effects. Preliminary structure models were derived by application of direct methods (*16*) and were refined by full-matrix least-squares calculation based on F^2 for all reflections (*17*). All hydrogen atoms were included in the models in calculated positions and were refined as constrained to bonding atoms. The crystal data and experimental parameters are summarised in Table 1. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as

Table 1. Crystal data and selected details of the data collection and refinement calculations of compounds **1** and **1a**.

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	$P2_1/c$	$C2/c$
a (Å)	27.367(3)	61.9037(16)
b (Å)	14.0071(13)	10.0521(3)
c (Å)	19.1495(17)	26.3612(7)
α (°)	90.0	90.0
β (°)	92.226(6)	97.609(3)
γ (°)	90.0	90.0
V (Å^3)	7335.0(12)	16,259.1(8)
Z	4	8
F(000)	2736	6656
D_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	149,661	188,759
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	18,389	22,212
No. of refined parameters	949	1016
No. of F values used [$I > 2\sigma(I)$]	6919	10,947
Final R-indices		
$R(= \Sigma\|\Delta F\|/\Sigma\|F_o\|)$	0.051	0.1053
wR on F^2	0.1395	0.3593
S (= Goodness of fit on F^2)	0.927	1.024
Final $\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.24/−0.27	2.02/−0.91

supplementary publication numbers CCDC 655309 and CCDC 655310. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, Email: deposit@ccdc.cam.ac.uk).

Results and discussion

Synthesis and conformational characterisation

The title compound **1** (Scheme 1) was synthesised from calix[4]arenedicarboxylic acid **3** via chlorination with thionyl chloride, followed by the reaction with 1-(hydroxymethyl)pyrene. Besides **1**, this esterification process also yielded the monopyrene derivative **2**. Compound **3** was prepared in three steps from conventional tetra-*t*-butylcalix[4]arene (*18*) involving propylation, reaction with ethyl bromoacetate and subsequent hydrolysis of the respective ester (*13*, *14*). The inclusion compound of **1** with chloroform (**1a**) has been obtained by crystallisation 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 OCH_2 groups appear as two multiplets at 3.62 and 3.87 ppm in a 1:1 ratio, indicating a limited rotability of the O—C bond. Evidence of the chemical non-equivalence of the respective methylene protons is given by the splitting in the correlated spectroscopy (COSY) spectrum (Figure 1). A corresponding splitting is not observed for compound **1** due to the molecular symmetry.

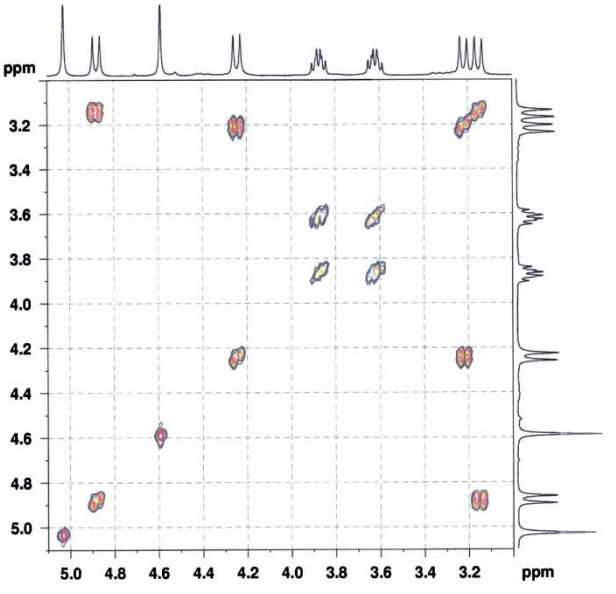

Figure 1. Section of the 400 MHz COSY spectrum ($CDCl_3$) of **2**, where cross-signals between two species of propoxy methylene protons are found ($\delta_1 = 3.62$ ppm, $\delta_2 = 3.87$ ppm).

X-ray structural study

X-ray crystal structures of compound **1** as well as the inclusion compound **1a** [**1**·$CHCl_3$ (1:2.5)] have been studied (Table 1). Perspective views on the molecular structures together with illustrations of the crystal packings are displayed in Figures 2–6. Usually, the conformation of a calix[4]arene framework is described by a set of interplanaric angles that defines the inclination of the aromatic rings with respect to the basis plane given by the methylene atoms C(7), C(14), C(21) and C(28). These data are included in Table 2, while parameters of intramolecular contacts are listed in Table 3. In the present crystal structures, the calixarene skeleton is highly ordered whereas, a part of the *t*-butyl and propoxy substituents is disordered over two positions. In the case of structure **1**·$CHCl_3$ (1:2.5), one of the guest molecules has proven to be difficult to model and show a significant residue electron density around the molecule.

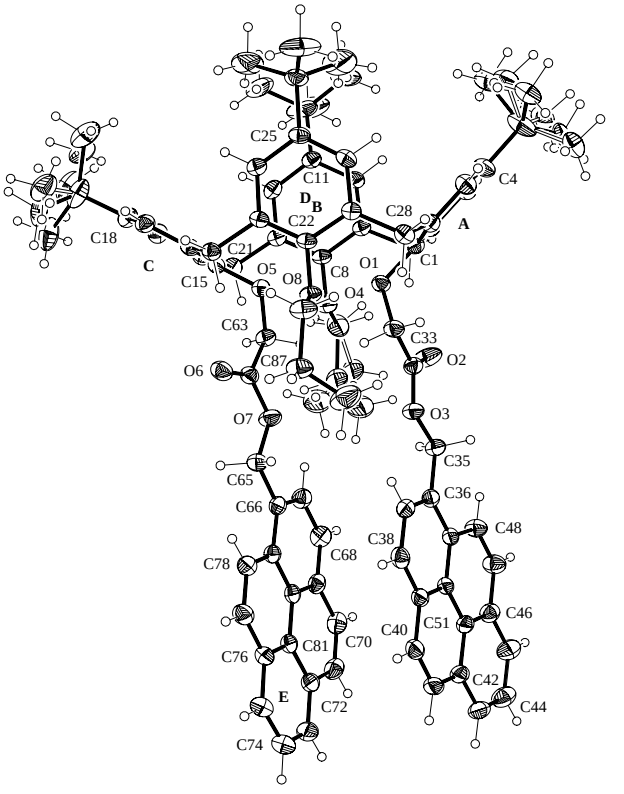

Figure 2. Molecular structure of the calix[4]arene **1** showing 30% probability displacement representation and numbering scheme of the non-hydrogen atoms.

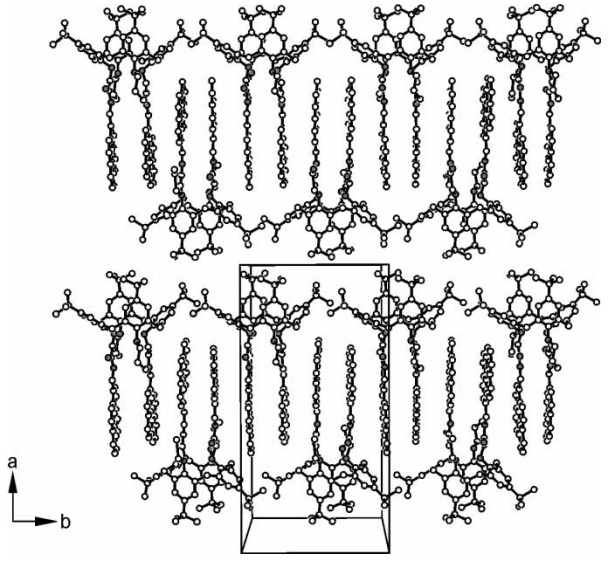

Figure 3. Packing motif of **1**, viewed along the *c*-axis. Heteroatoms are indicated by shading, and the hydrogen atoms have been omitted for clarity.

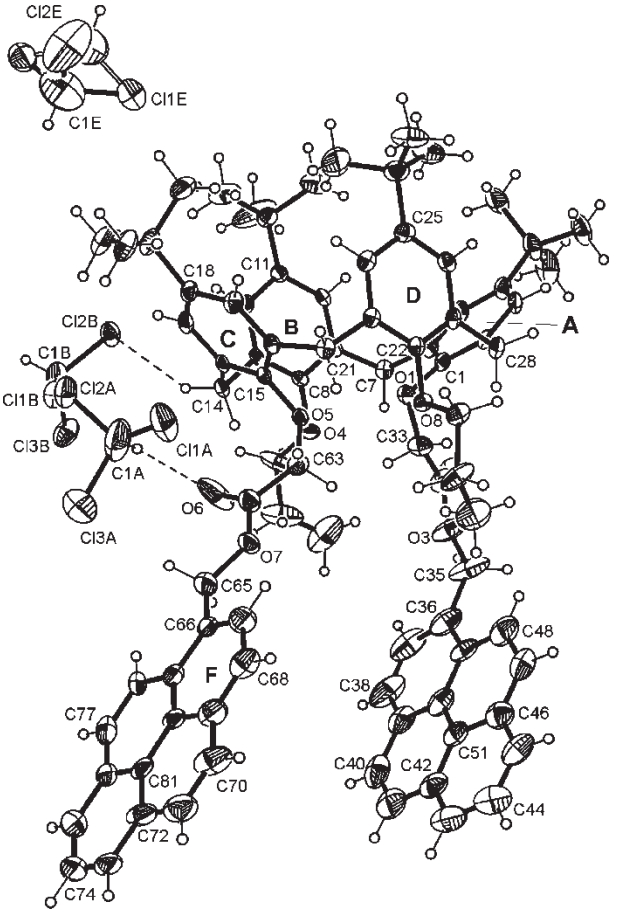

Figure 4. Molecular structure of the inclusion compound of **1** with $CHCl_3$ (1:2.5) showing 30% probability displacement representation and numbering scheme of the non-hydrogen atoms. Only one disorder site of the coordinated chloroform molecules has been shown for clarity.

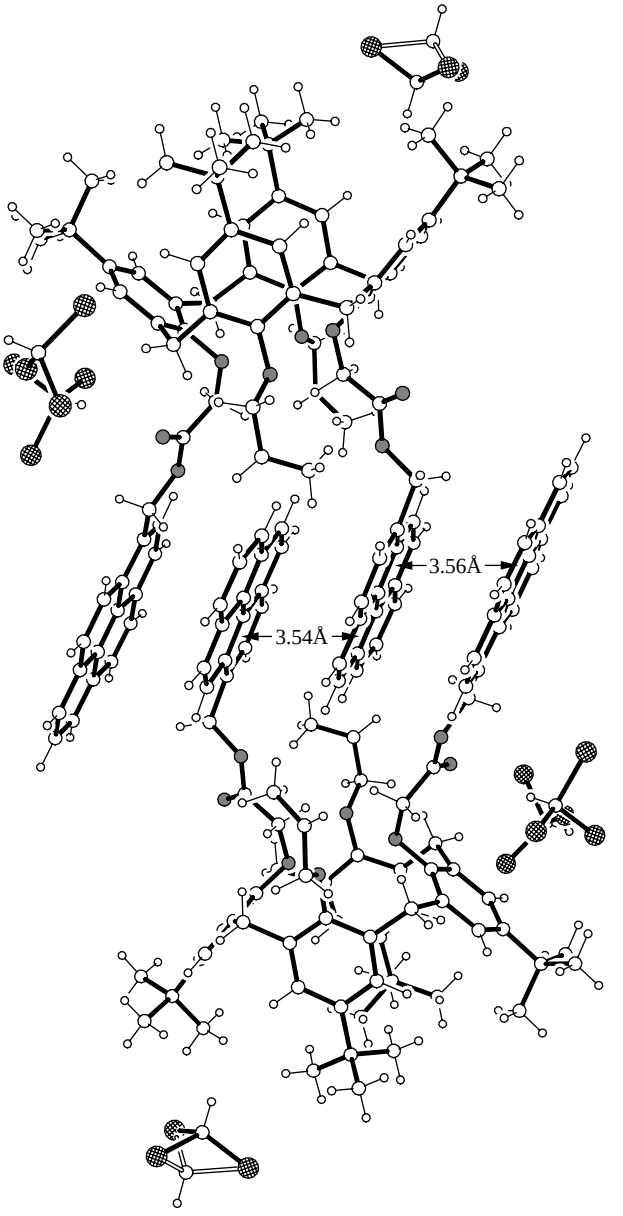

Figure 5. Formation of dimers in the crystal structure of **1a**. Heteroatoms are specified by shading. Disorder of the chloroform molecules is indicated by filled and hollow lines.

In the solvent-free crystal structure of **1**, the calixarene framework adopts a rather typical pinched cone conformation (Figure 2) with the aromatic rings (A and C) that contain the pyrene units exhibiting a nearly orthogonal arrangement, whereas the other pair of opposite rings (B and D) is almost parallel. As a result of this conformational fact, the upper rim cavity is too small for accommodating a guest molecule (5.30 Å centroid-to-centroid distance of rings B and D). The torsion angles of the two ester pendants [ranging between 161.3(2) and 175.5(2)°] give rise to an almost linear overall conformation, while, the conformations around

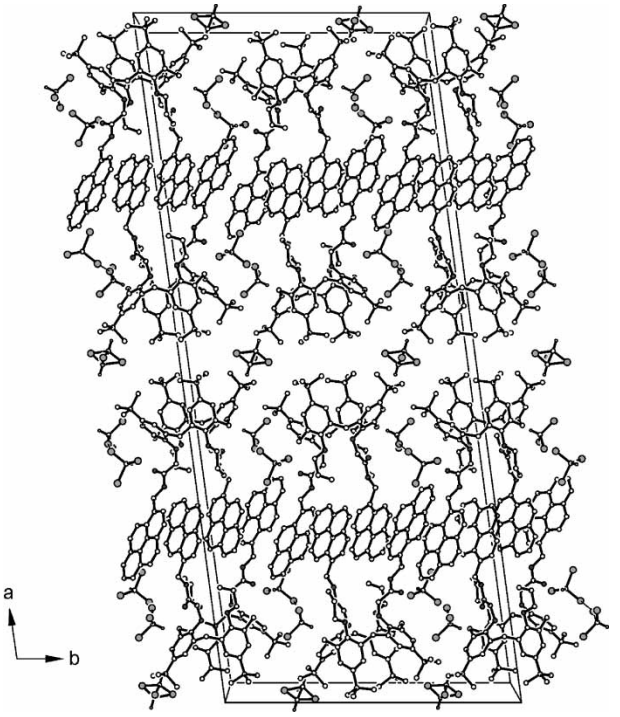

Figure 6. Packing illustration of **1a**, viewed along the *c*-axis. Heteroatoms are indicated by shading, and hydrogen atoms, except for chloroform, have been omitted for clarity.

Table 2. Selected conformational parameters of the calixarene molecule in the crystal structures of compounds **1** and **1a**.

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).

C—C—O—C [64.1(2) and 68.3(2)°] and O—C—C—C [179.8(2) and 176.5(2)°] having reference to the connection between the pendant moieties and the calixarene or pyrene units, can be described as *gauche* and *anti*, respectively (Table 2). Both pyrene units deviate only slightly from a coplanar arrangement [5.89(1)°], exhibiting an average distance of about 3.5 Å, but are also rotated about 57.0° due to the inherent two-fold crystallographic symmetry of the calixarene molecule in the crystal structure and the connection of pyrene in the 1-position. Nevertheless, the two pyrene units show a significant overlapping of their π-systems. Previously, with regard to excimer formation, a similar situation involving two pyrene units of analogous calix[4]arenes has been observed in solution (*10–12*).

Owing to the absence of strong hydrogen bond donors, the intermolecular interactions in the crystal are dominated by a zipper-like infinite stacking of the pyrene pairs along the crystallographic *b*-axis (Figure 3). It is worth noting that the pyrene overlap in this stacking is higher in the intermolecular than in the intramolecular fashion. This might be attributed to the space required by the ester subunit, partly facing the pyrene group of a neighbouring calixarene, in order to make possible C—H···O(C═O) and C—H···π(pyrene) contacts, thus allowing a maximum of interactions along the appended side arms. Moreover, due to the head-to-head orientation of the calixarene part of the molecules, a bilayer-like structure is formed in the crystal packing with calixarene molecules shifted half a translation unit along the *b*-axis. According to their hydrophobic nature, these domains are stabilised through van der Waals interactions. In a comparison of resemblance, while bilayers formed of amphiphilic molecules are typical of a clear separation of polar and apolar regions, the present structure is composed of molecules featuring segments that are proportionally poorer and richer in the arene constituents.

As in the unsolvated calixarene **1**, the asymmetric unit of its crystalline 1:2.5 inclusion compound with chloroform (1:2.5) **1a** contains one molecule of calixarene but in addition two and a half molecules of chloroform. One of these chloroform molecules is located at the special position 1, 1/2, 1/4, i.e. occupying two alternative orientations with side occupation factors of 0.5 (Figure 4). As a result of the weak donor/acceptor property, the guest molecules show a high degree of mobility, which makes determination of their positions difficult. The geometry of the calixarene backbone differs only slightly from that in the unsolvated compound **1**. Nevertheless, conformational changes

Table 3. Distances and angles of possible hydrogen-bond type interactions and selected intermolecular contact distances observed for compounds **1** and **1a**.

Atoms involved	Symmetry	Distance (Å) D···A	Distance (Å) H···A	Angle (°) D–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).

arise from the orientation of the aromatic ring C with regard to the mean plane defined by the bridging methylene groups, thus explaining the increase in the interplanaric angle A/C. However, the inclusion of chloroform causes a drastic conformational change of the lower rim substituents, especially regarding the aliphatic ester segment, the torsion angles of which [C(1)—O(1)—C(33)—C(34) = −57.4(5), C(16)—C(15)—O(5)—C(63) = −113.8(3)°] proved to be noticeably different from those of the apo-host **1** [−97.7(2) and −68.3(2)°, respectively]. The two pyrenyl units are inclined by 56.9(1) and 57.5(1)° towards the least-squares plane of the bridging methylene carbons showing distinct loss of molecular symmetry. In the present structure, the pyrene rings are also almost parallel in their orientation [0.88(21)°], but the intramolecular distance between these groups has increased to approximately 7.1 Å. As contrasted with the unsolvated compound **1**, in **1a**, a pair of calixarene molecules is interlocked through pyrene units leading to a dimer stack such as that illustrated in Figure 5. Moreover, edge-to-face interactions are displayed between the pyrenyl groups of neighbouring dimers, giving rise to a C—H···π(centroid) distance of 2.83 Å. This packing behaviour resembles the reported structure of crystalline pyrene (*19*), showing both face-to-face and edge-to-face relationships. The solvent molecules in **1a** are located interstitially in the voids of the host lattice (Figure 6). While, one of the solvent molecules is encircled by the voluminous *t*-butyl groups and seems to have no interaction with the calixarene, the other two chloroform molecules either interact with their acidic hydrogen to one of the carbonyl oxygen atoms of the calixarene [C(1A)—H(1A)···O(6)] or are engaged in a C—H···π interaction involving an aromatic ring of the calixarene. Furthermore, a host/guest interaction including C(14)—H(14A)···Cl(2B) and additional contacts between chlorine atoms of the chloroform molecules are found.

Conclusion

A calix[4]arene **1**, featuring two propoxy groups and two substituents carrying terminal pyrene units in alternate lower rim positions of the calixarene framework, shows crystalline packing behaviour largely controlled by the preference of the pyrene units to form stacks. Accordingly, this is verified in the structure by an obvious bilayer-type of infinite stacking, being subject to the glide plane symmetry of the calixarene molecules. Inclusion of the chloroform molecules in **1a** leads to a change in the distance between the calixarene molecules, involving the loss of the glide plane symmetry. As a consequence, the infinite stacking mode of the pyrene groups in **1** turns into separate dimer stacks of interlocked pyrene units in **1a**, connected with some conformational change of the side arms, while the geometry of the calixarene backbone remains virtually constant. Hence, aside from the purpose of fluorescent activity (*20*), pyrene groups peripherally attached to a calixarene framework may also be considered a useful controlling factor in the engineering of a desired crystalline packing structure.

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