Conformational behaviour and first crystal structures of a calix[4]arene featuring a laterally positioned carboxylic acid function in unsolvated and solvent complexed forms

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Electronic Supplementary Information

(ESI)

Table S1 ^{13}C NMR data of **1** in $CDCl_3$ at T=265 K

paco-1 (▲,▲´)		**paco-2** (..,´)		**1,2-alternate**(+)	**cone**(·)
173.64 (C-18▲)		179.82 (C-18)		180.03 (C, C-18+)	n.d.
154.80 (C_i-7▲) 154.23 (C_i-15▲)	155.19 (C_i-15▲´) 151.33 (C_i-7▲´)	154.66 (C_i-15) 154.38 (C_i-7)	154.47 (C_i-7´) 154.40 (C_i-15´)	154.60 (C_i -15+) 153.40 (C_i -7+)	n.d.
146.35 (C_i-4▲) 145.22 (C_i-12▲)	145.63 (C_i-4▲´) 145.61 (C_i-12▲´)	144.95 (C_i-4) 144.91 (C_i-12)	145.39 (C_i-4´) 143.37 (C_i-12´)	144.56 (C_i -12+) 144.33 (C_i -4+)	n.d.
135.22 (C_i-6▲) 133.92 (C_i-14▲) 132.67 (C_i-10▲) 129.91 (C_i-2▲)	135.76 (C_i-14▲´) 134.08 (C_i-6▲´) 132.03 (C_i-10▲´) 130.09 (C_i-2▲´)	135.29 (C_i-10) 133.63 (C_i-6) 133.08 (C_i-14) 130.32 (C_i-2)	132.99 (C_i-14´) 132.82 (C_i-10´) 132.29 (C_i-6´) 130.32 (C_i-2´)	135.03 (C_i -14+) 132.60 (C_i -6+) 132.43 (C_i -10+) 132.03 (C_i -2+)	n.d. 130.99 (br, C_i-2·)
126.94 (CH, C-5▲) 125.45 (CH, C-13▲) 124.98 (CH, C-11▲) 122.78 (CH, C-3▲)	128.90 (CH, C-5▲´) 127.15 (CH, C-3▲´) 125.83 (CH, C-13▲´) 125.63 (CH, C-11▲´)	126.15 (CH, C-5) 125.63 (CH, C-13) 125.09 (CH, C-11) 123.36 (CH, C-3)	127.15 (CH, C-5´) 126.54 (CH, C-13´) 126.23 (CH, C-11´) 123.59 (CH, C-3´)	127.75 (CH, C-5+) 125.85 (CH, C-11+) 125.45 (CH, C-13+) 123.75 (CH, C-3+)	126.5 (br, CH, C-11·) 124.7 (br, CH, C-13·) 124.5 (br, CH, C-5·) 123.0 (br, CH, C-3·)
61.07 (CH_3, C-16▲) 59.70 (CH_3, C-8▲)	60.68 (CH_3, C-16▲´) 59.84 (CH_3, C-8▲´)	61.71 (CH_3, C-8) 60.46 (CH_3, C-16)	60.15 (CH_3, C-8´) 58.16 (CH_3, C-16´)	60.89 (CH_3, C-8+) 59.90 (CH_3, C-16+)	61.7 (br, CH_3, C-8·) 61.3 (br, CH_3, C-16·)
58.35 (CH-1▲)		42.51 (CH, C-1)		41.08 (CH, C-1+)	43.1 (br, CH, C-1·)
31.35 (CH_2, C-17▲) 30.39 (CH_2, C-9▲)	36.31 (CH_2, C-9▲´)	36.35 (CH_2, C-17) 31.10 (CH_2, C-9)	37.96 (CH_2, C-9´) 37.96 (CH_2, C_i-9´)	36.75 (CH_2, C-9+) 30.09 (CH_2, C-17+)	n.d. 31.1 (CH_2, C-9·)
34.25 (C, C-4a▲) 33.88 (C, C-12a▲) 31.36 (C, C.4b▲) 31.25 (C, C-12b▲)	34.06 (C,C-4a▲´) 33.06 (C,C-12a▲´) 31.49 (CH_3,C-4b▲´) 31.36 (CH_3,C-12b▲´)	33.88 (C,C -4a) 33.88 (C,C -12a) 31.36 (CH_3,C-12b) 31.18 (CH_3,C-4b)	34.06 (C, C-4a´) 34.06 (C, C-12a´) 31.36 (C, C-4b´) 31.36 (C, C-12b´)	33.99 (C, C-12a+) 33.93 (C, C-4a+) 31.36 (CH_3,C-4b+) 31.29 (CH_3,C-12b+)	n.d.

Table S2 ^{13}C NMR data of **1** in TCl-d_2 at T=265 K

paco-1 (▲,▲′)		**paco-2** (.,′)		**1,2-alternate**(+)	**cone**(·)
174.602 (C-18▲)		178.98 (C-18)		178.90 (C, C-18+)	n.d.
155.05 (C_i-7▲) 154.42 (C_i-15▲)	155.32 (C_i-15▲′) 151.42 (C_i-7▲′)	154.87 (C_i-15) 154.64 (C_i-7)	154.47 (C_i-7′) 154.40 (C_i-15′)	154.81 (C, C-15+) 153.49 (C, C-7+)	n.d.
146.70 (C_i-4▲) 145.11 (C_i-12▲)	146.18 (C_i-4▲′) 145.93 (C_i-12▲′)	145.85 (C_i-12) 145.03 (C_i-4)	145.39 (C_i-4′) 143.37 (C_i-12′)	144.79 (C, C-12+) 144.60 (C, C-4+)	n.d.
135.97 (C_i-6▲) 134.12 (C_i-14▲) 132.75 (C_i-10▲) 129.87 (C_i-2▲)	136.31 (C_i-14▲′) 134.61 (C_i-6▲′) 132.37 (C_i-10▲′) 130.18 (C_i-2▲′)	n.d.	n.d.	n.d.	n.d.
127.61 (CH, C-5▲) 125.83 (CH, C-13▲) 125.23 (CH, C-11▲) 122.63 (CH, C-3▲)	129.37 (CH, C-5▲′) 127.41 (CH, C-3▲′) 126.14 (CH, C-13▲′) 126.08 (CH, C-11▲′)	126.85 (CH, C-5) 126.14 (CH, C-11) 125.60(CH, C-13) 123.97 (CH, C-3)	127.20 (CH, C-5′) 126.84 (CH, C-13′) 126.59 (CH, C-11′) 123.60 (CH, C-3′)	128.21 (CH, C-5+) 126.23 (CH, C-11+) 126.14 (CH, C-13+) 123.97 (CH, C-3+)	n.d.
61.52 (CH_3, C-16▲) 60.08 (CH_3, C-8▲)	61.11 (CH_3, C-16▲′) 60.38 (CH_3, C-8▲′)	62.37 (CH_3, C-8) 60.81 (CH_3, C-16)	60.49 (CH_3, C-8′) 58.51 (CH_3, C-16′)	61.25 (CH_3, C-8+) 60.27 (CH_3, C-16+)	n.d.
58.72 (CH-1▲)		42.60 (CH, C-1)		41.25 (CH, C-1+)	n.d.
31.54 (CH_2, C-17▲) 30.62 (CH_2, C-9▲)	36.60 (CH_2, C-9▲′)	36.60 (CH_2, C-17) 30.60 (CH_2, C-9)	38.49 (CH_2, C-9′)	37.10 (CH_2, C-9+) 30.15 (CH_2, C-17+)	n.d.
34.56 (C, C-4a▲) 34.13 (C, C-12a▲) 31.68 (C, C.4b▲) 31.61 (C, C-12b▲)	34.39 (C,C-4a▲′) 34.29 (C,C-12a▲′) 31.75 (CH_3,C-4b▲′) 31.67 (CH_3,C-12b▲′)	n.d. 31.54 (CH_3,C-4b)	n.d. 31.88 (C, C-12b′)	34.43 (C, C-12a+) 34.19 (C, C-4a+) n.d. n.d.	n.d.

Table S3 ^{1}H NMR data of **1** in $CDCl_3$ at T=265 K

paco-1 (▲,▲´)		**paco-2** (.,´)		**1,2-alternate**(+)	**cone**(˙)
9.3 (s, COOH)		12.0 (br, COOH)		12.0 (br, COOH)	12.0 (br, COOH)
7.14 ((d), 1H, H-5▲) 7.11 ((d), 1H, H-3▲) 6.92 (s, br, 1H, H-11▲) 6.74 ((d), 1H, H-13▲)	7.32 (d,^{4}J=2.2 Hz, 1H, H-5▲´) 7.28 (d,^{4}J=2.2 Hz, 1H, H-3▲´) 6.99 (s, 2H,H-11▲´,H-13▲´)	7.07 (s, br, 1H, H-3) 6.96 (s, br, 1H, H-13) 6.92 (s, br, 1H, H-11) 6.73 (s, br, 1H, H-5)	7.21 ((d), 1H, H-3´) 7.21 ((d), 1H, H-11´) 7.19 (s, br, 1H, H-13´) 7.08 (s, br, 1H, H-5´)	7.48 (d,^{4}J=2.3 Hz, 2H, H-3+) 7.16 (d,^{4}J=2.4 Hz, 2H, H-5+) 7.04 (d,^{4}J=2.1 Hz, 2H, H-11+) 6.83 (d,^{4}J=2.0 Hz, 2H, H-13+)	7.21 (br, H-11˙) 6.99 (br, H-3˙) 6.79 (br, H-5˙) 6.78 (br, H-13˙)
5.03 (s,1H, H-1▲)		5.69 (s, 1H, H-1)		5.97 (s, 1H, H-1+)	5.78 (s, br, H-1˙)
4.23 (d,^{2}J=12.6 Hz, 1H, H-9a▲) 4.20 (d,^{2}J=12.8 Hz, 1H, H-17a▲) 3.21 (d,^{2}J=13.1 Hz, 1H, H-17b▲) 3.25 (d,^{2}J=12.7 Hz, 1H, H-9b▲)	3.85 (d,^{2}J=17.9 Hz, 1H, H-9a▲´) 3.78 (d,^{2}J~ 18 Hz, 1H, H-9b▲´)	4.18 (d,^{2}J=12.2 Hz, 1H, H-9a) 3.82-3.74 (2H, H-17a,b) 3.18 (d,^{2}J=13 Hz, 1H, H-9b)	4.18 (d,^{2}J=14.4 Hz, 1H, H-9a´) 3.79 (d, 1H, H-9b´)	4.05 (d, ^{2}J=13.5 Hz, 1H, H-17a+) 3.90 (d, 2H, H-9a+) 3.79 (d, 2H, H-9b+) 3.13 (d, H-17b+)	4.29 (d, ^{2}J=12.7 Hz, H-9a˙) 3.18 (d, ^{2}J=13 Hz, H-9b˙) 3.82-3.74 (H-17a˙, b˙)
3.58 (s, 3H, H-8▲) 3.50 (s, 3H, H-16▲)	3.38 (s, 3H, H-16▲´) 1.33 (s, 3H, H-8▲´)	3.57 (s, 3H, H-8) 3.34 (s, 3H, H-16)	3.61 (s, 3H, H-8´) 2.11 (s, 3H, H-16´)	3.14 (s, 6H, H-8+) 2.89 (s, 6H, H-16+)	3.89 (s, H-8˙) 3.83 (s, H-16˙)
1.22 (s, 9H, H-4b▲) 1.10 (s, 9H, H-12b▲)	1.36 (s, 9H, H-4b▲´) 1.22 (s, 9H, H-12b▲´)	1.21 (s, 9H, H-12b) 1.05 (s, 9H, H-4b)	1.36 (s, 9H, H-12b´) 1.20 (s, 9H, H-4b´)	1.26 (s, 18H, H-4b+) 1.22 (s, 18H, H-12b+)	1.16 (s, H-12b˙) 1.07 (s, H-4b˙)

Table S4 ^{1}H NMR data of **1** in TCl-d_2 at T=265 K

paco-1 (▲,▲′)		**paco-2** (.,′)		**1,2-alternate**(+)	**cone**(˙)
9.0 (s, COOH)		11.8 (br, COOH)		11.8 (br, COOH)	n.d.
7.05 (d, ^{4}J=1.8 Hz, 1H, H-5▲) 6.90 ((d), 1H, H-3▲) 6.76 (d, ^{2}J=2.1 Hz, 1H, H-11▲) 6.58 (d, ^{2}J=2.1 Hz, 1H, H-13▲)	7.23 (d, ^{4}J=2.1 Hz, 1H, H-5▲′) 7.15 (d, ^{4}J=2.1 Hz, 1H, H-3▲′) 6.87 (s, 1H, H-13▲′) 6.85 (s, 1H, H-11▲′)	6.87 (br, H-3) 6.85 (s, H-13) 6.82 (s, H-11) 6.58 (s, H-5)	7.15 (br, H-3′) 7.08 (s, H-11′) 7.06 (s, H-13′) 6.96(s, H-5′)	7.34 ((d), H-3+) 7.05 ((s), H-5+) 6.87 (s, H-11+) 6.68 (s, H-13+)	n.d.
4.87 (s,1H, H-1▲)		5.58 (s, H-1)		5.81 (s, H-1+)	5.63 (br, H-1˙)
3.47 (s, 3H, H-8▲) 3.41 (s, 3H, H-16▲)	3.25 (s, 3H, H-16▲′) 1.17 (s, 3H, H-8▲′)	3.50 (s, H-8) 3.18 (s, H-16)	3.47 (s, H-8′) 1.71 (s, H-16′)	2.99 (s, H-8+) 2.76 (s, H-16+)	3.76 (s, H-8˙) 3.69 (s, H-16˙)
4.10 (d, ^{2}J=12.5 Hz, 1H, H-9a▲) 4.05 (d, ^{2}J=12.8 Hz, 1H, H-17a▲) 3.09 (d, ^{2}J=13.0 Hz, 1H, H-17b▲) 3.15 (d, ^{2}J=12.8 Hz, 1H, H-9b▲)	3.77 (1H, H-9a▲′) 3.70 (1H, H-9b▲′)	n.d.	n.d.	n.d.	n.d.
1.11 (s, 9H, H-4b▲) 0.96 (s, 9H, H-12b▲)	1.26 (s, 9H, H-4b▲′) 1.11 (s, 9H, H-12b▲′)	1.11 (s, H-12b) 0.90 (s, H-4b)	1.25 (s, H-12b′) 1.08 (s, H-4b′)	1.16 (s, H-4b+) 1.12 (s, H-12b+)	n.d.

Table S5 Selected conformational parameters of the calixarene molecule in the compounds studied

Compound	**1**	**1a**	**1b**
Interplanar angles (°)[a]			
mpla[b]/A	28.8(1)	77.6(1)	77.2(1)
mpla/B	86.0(1)	46.3(2)	46.6(1)
mpla/C	51.6(1)	79.6(1)	79.4(1)
mpla/D	74.2(1)	81.4(1)	80.8(1)
A/C	99.9(1)	23.0(3)	23.5(2)
B/D	19.8(1)	35.1(2)	34.2(1)
Distance (Å) methoxy O from 3 O plane	1.932	3.268	3.267
Angle (°) turned phenyl from 3 O plane	83.0(1)	62.2(3)	61.5(2)

[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)

Table S6 Distances and angles of possible hydrogen-bond type interactions of the compounds studied

Atoms involved	Symmetry	Distances/Å		Angles/°
		D···A	H···A	D-H···A
1				
O(5)-H(5A)···O(6)	1-*x*, 2-*y*, -*z*	2.621(4)	1.82	166
C(48)-H(48A)···C(15)[b]	*x*, *y*, *z*	3.382(5)	2.52	149
C(48)-H(48B)···C(1)[b]	*x*, *y*, *z*	3.443(5)	2.58	149
C(40)-H(40C)···*centroid* (D)[a]	0.5-*x*, 0.5+*y*, 0.5-*z*	3.622(5)	2.79	145
1a				
O(1GA)-H(1G1)···O(4)	*x*, *y*, *z*	2.669(5)	1.88	154
O(1GB)-H(1G2)···O(4)	*x*, *y*, *z*	2.669(5)	1.91	149
O(5)-H(5)···O(1GA)	*x*, *y*, *z*	2.610(5)	1.77	180
C(40)-H(40B)···O(6)	-*x*, 1-y, 0.5+ *z*	3.486(5)	2.55	161
C(48)-H(48C)···*centroid* (A)[a]	*x*, *y*, *z*	3.165(5)	2.22	163
C(48)-H(48A)···*centroid* (C)[a]	*x*, *y*, *z*	3.184(5)	2.35	142
C(33)-H(33A)···*centroid* (B)[a]	-*x*,-*y*,0.5+*z*	3.424(5)	2.64	137
C(43)-H(43C)···*centroid* (D)[a]	0.5-*x*, *y*, -0.5+*z*	3.629(5)	2.91	135
1b				
O(1GA)-H(1G1)···O(4)	*x*, *y*, -1+*z*	2.672(8)	1.91	150
O(1HA)-H(1H1)···O(4)	*x*, *y*, -1+*z*	2.708(7)	1.92	156
O(5)-H(5)···O(1GA)	*x*, *y*, *z*	2.560(8)	1.73	169
O(5)-H(5)···O(1HA)	*x*, *y*, *z*	2.658(7)	1.82	176
C(41)-H(41C)···O(6)	-*x*,1-*y*,0.5+*z*	3.557(8)	2.66	153
C(48)-H(48C)···*centroid* (A)[a]	*x*, *y*, *z*	3.176(8)	2.30	152
C(48)-H(48A)···*centroid* (C)[a]	*x*, *y*, *z*	3.179(8)	2.29	153
C(33)-H(33A)···*centroid* (B)[a]	-*x*, -*y*, 0.5+*z*	3.452(8)	2.68	136
C(43)-H(43C)···*centroid* (D)[a]	0.5-*x*, *y*, -0.5+*z*	3.622(8)	2.87	134

[a] Centroid means center of gravity of the respective aromatic ring: 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] In order to achieve reasonable hydrogen bond geometries carbon atoms instead of ring centroids were chosen as acceptor positions.

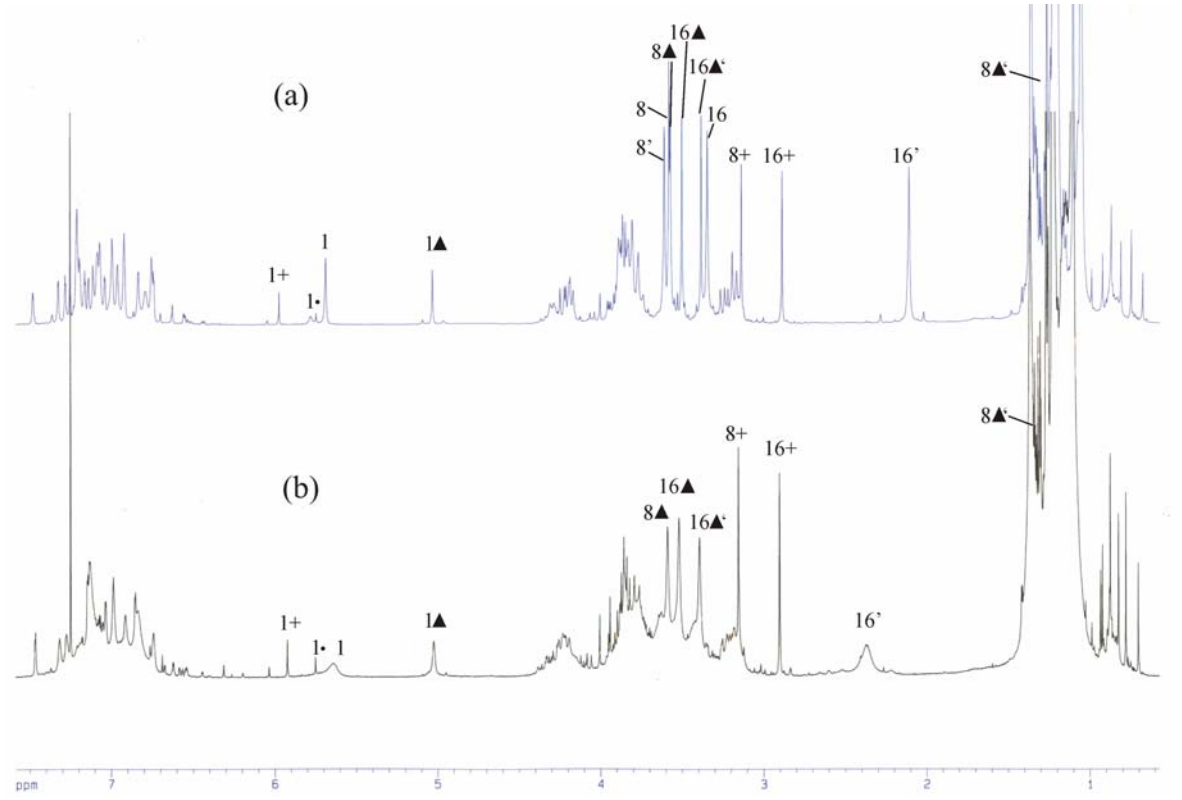

Fig. S1 ^{1}H NMR spectra of **1** in TCl-d_2 at 269 (a) and 295K (b).

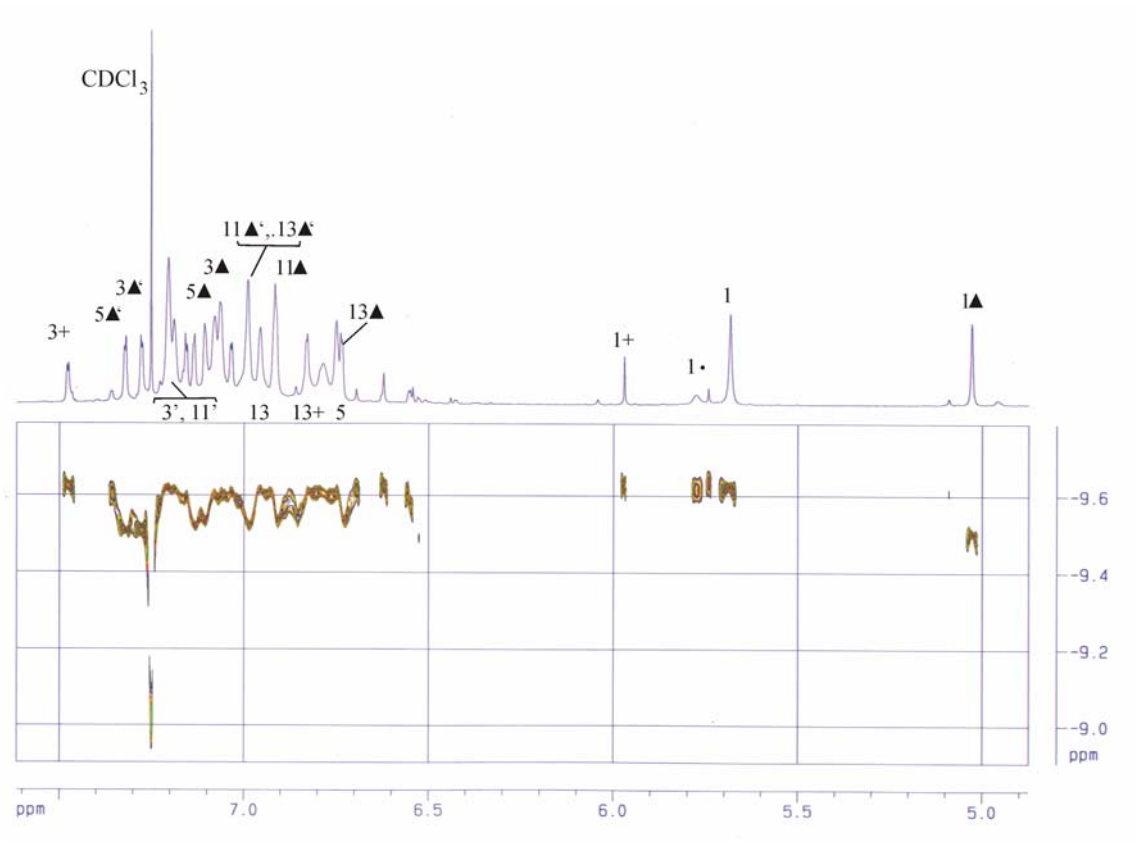

Fig. S2 DOSY spectrum of **1** in $CDCl_3$ at 269 K.

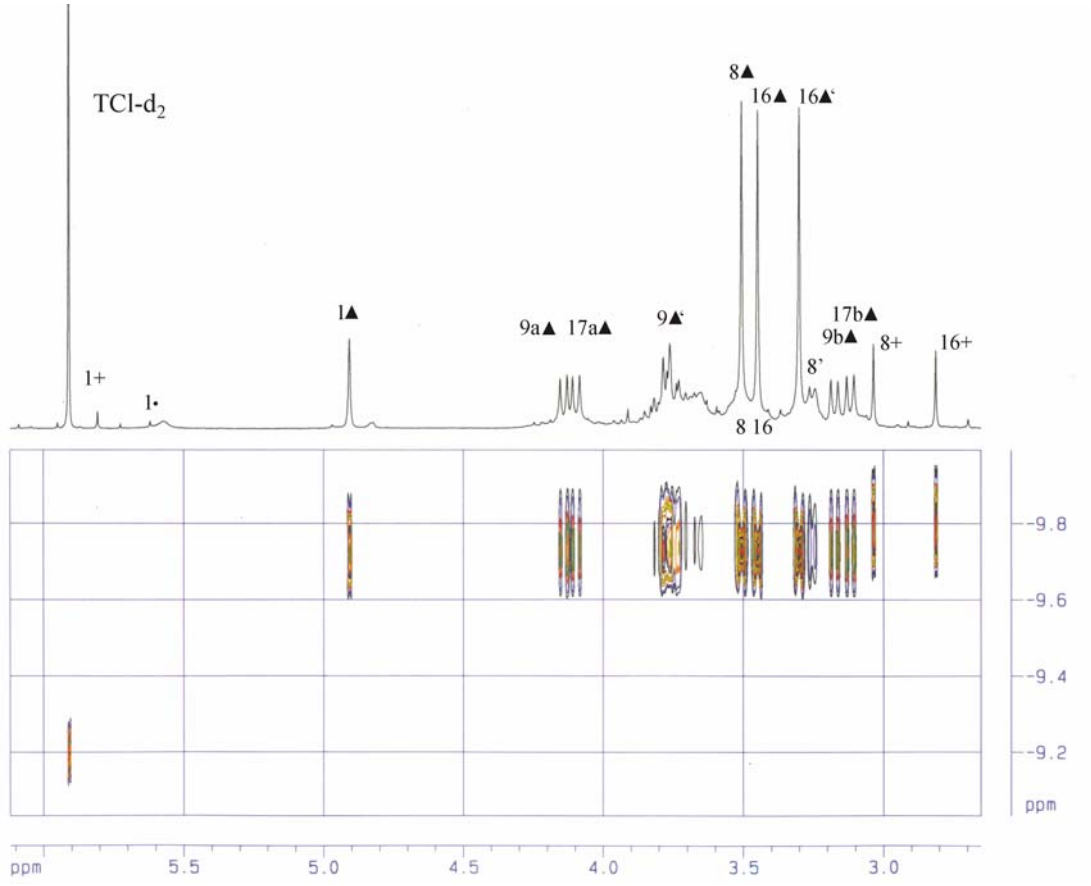

Fig. S3 DOSY spectrum of **1** in TCl-d_2 at 295 K.

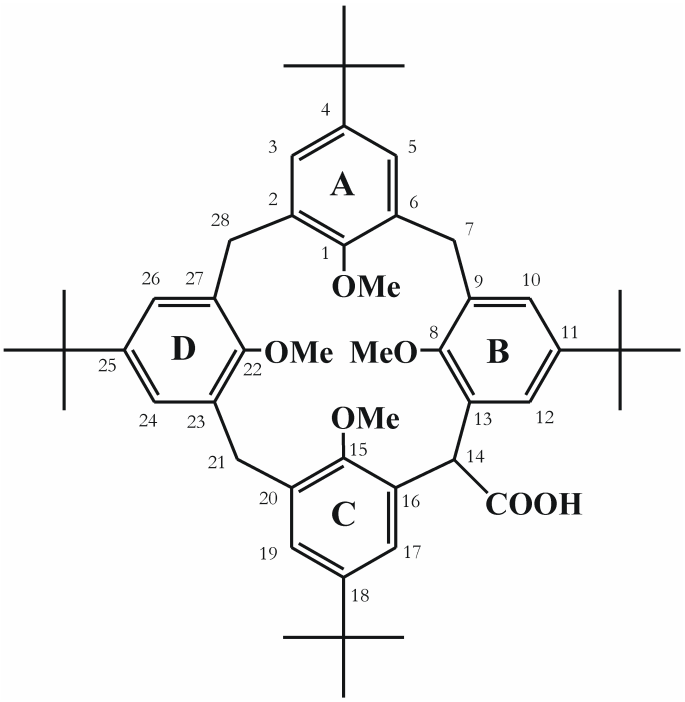

Fig. S4 Denotation of atoms of **1** used for X-ray analysis.

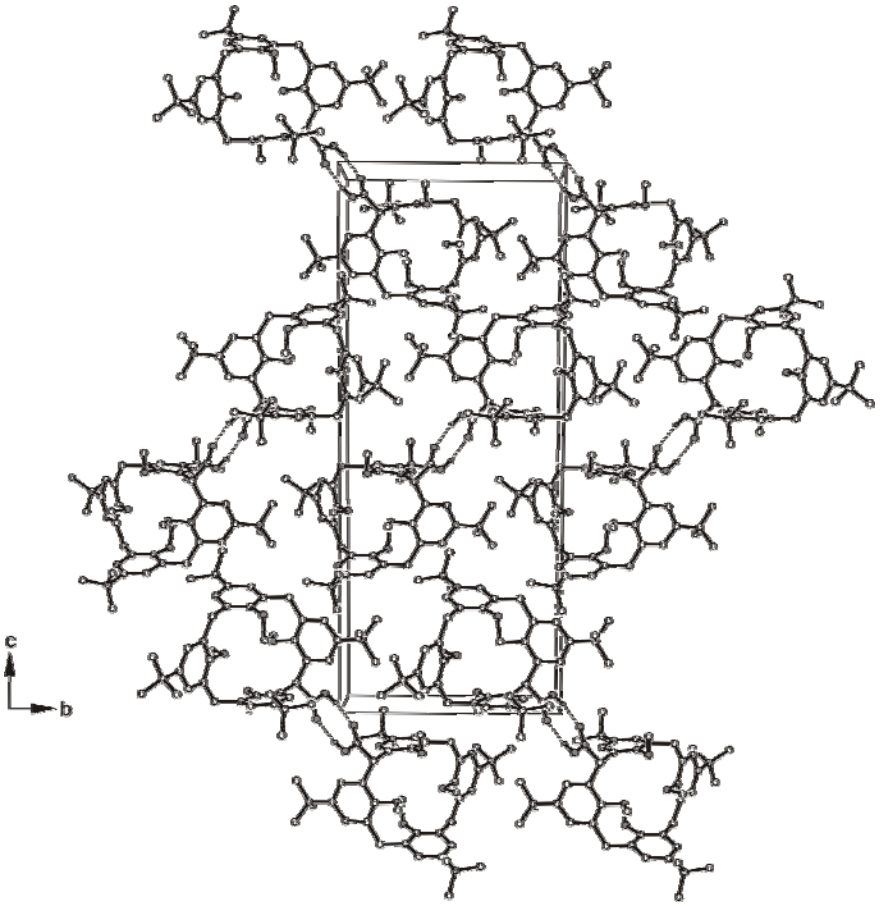

Fig. S5 Packing diagram of calix[4]arene **1** viewed down the crystallographic *a*-axis. With the exception of the carboxy hydrogen all other hydrogen atoms are omitted for clarity. Oxygen atoms are distinguished by shading. Broken lines represent hydrogen bonds.

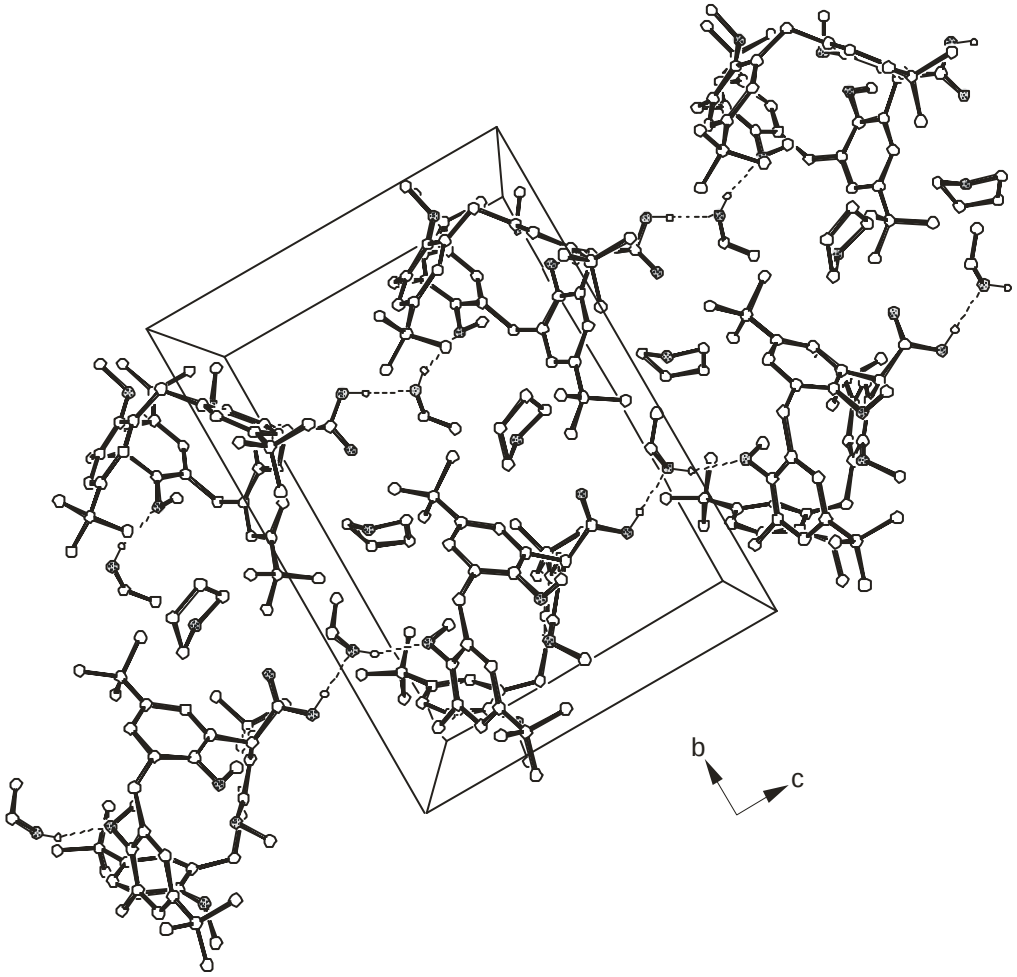

Fig. S6 Packing diagram of **1b** [**1** · EtOH · THF (1:1:1)] viewed down the crystallographic *a*-axis. Only one disorder position of the guest molecules is depicted. All hydrogens not involved in non-covalent bonding are omitted for clarity. Oxygen atoms are distinguished by shading. Broken lines represent hydrogen bond interactions.

(a) **(b)**

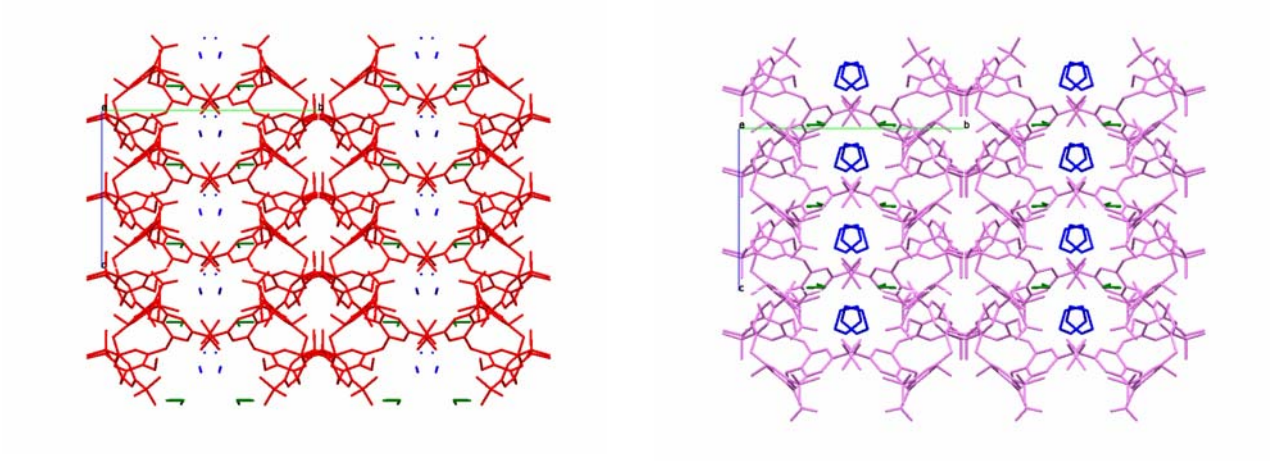

Fig. S7 Packing diagrams of **1a** (a) and **1b** (b) viewed along the crystallographic *a* axis, showing the solvent molecules in the inter-calixarene space. In (a), the calixarene, EtOH and H_2O molecules are given in red, green and blue colour, respectively; in (b), the calixarene, EtOH and THF molecules are given in violet, green and blue colour, respectively. The isostructurality of the host molecules (homostructurality) can well be observed.

a) **b)**

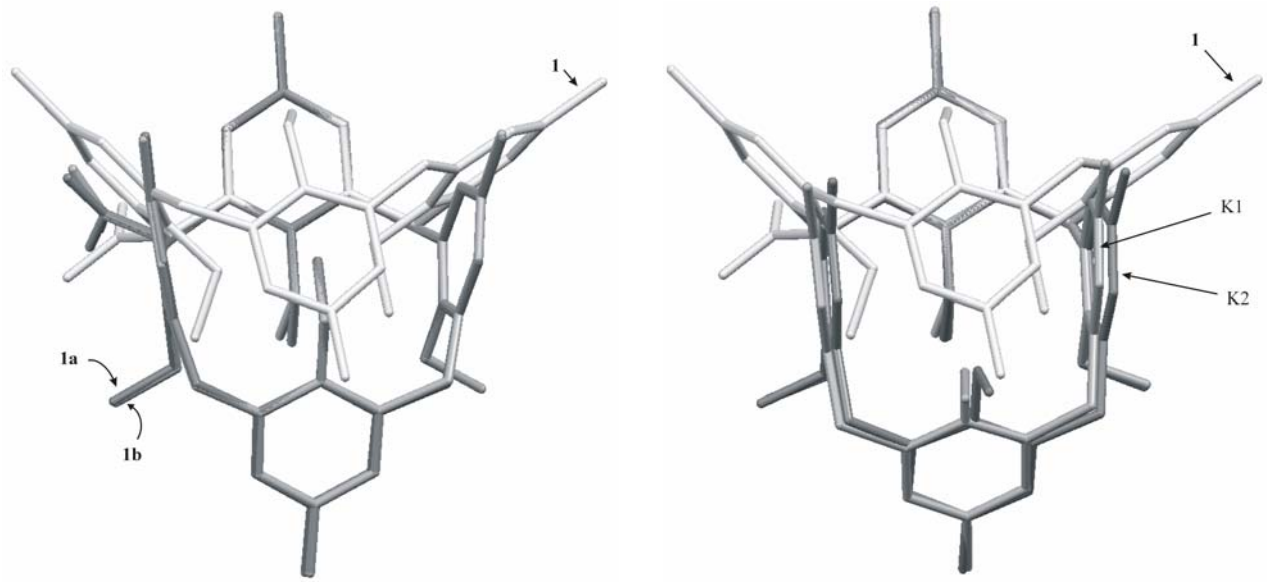

Fig. S8 Superimposed conformations of the calixarene molecules as found in the crystal structures of (a) the unsolvated compound **1** as well as the solvent complexes **1a** and **1b**, and (b) the unsolvated compound **1** and the two crystallographically independent unsubstituted calixarene molecules from KEVXUE (K1 and K2). In order to enhance the differences in the molecular conformation, one phenyl ring of each calixarene molecule is fitted. Methyl groups of the *tert*-butyl units are omitted for clarity.

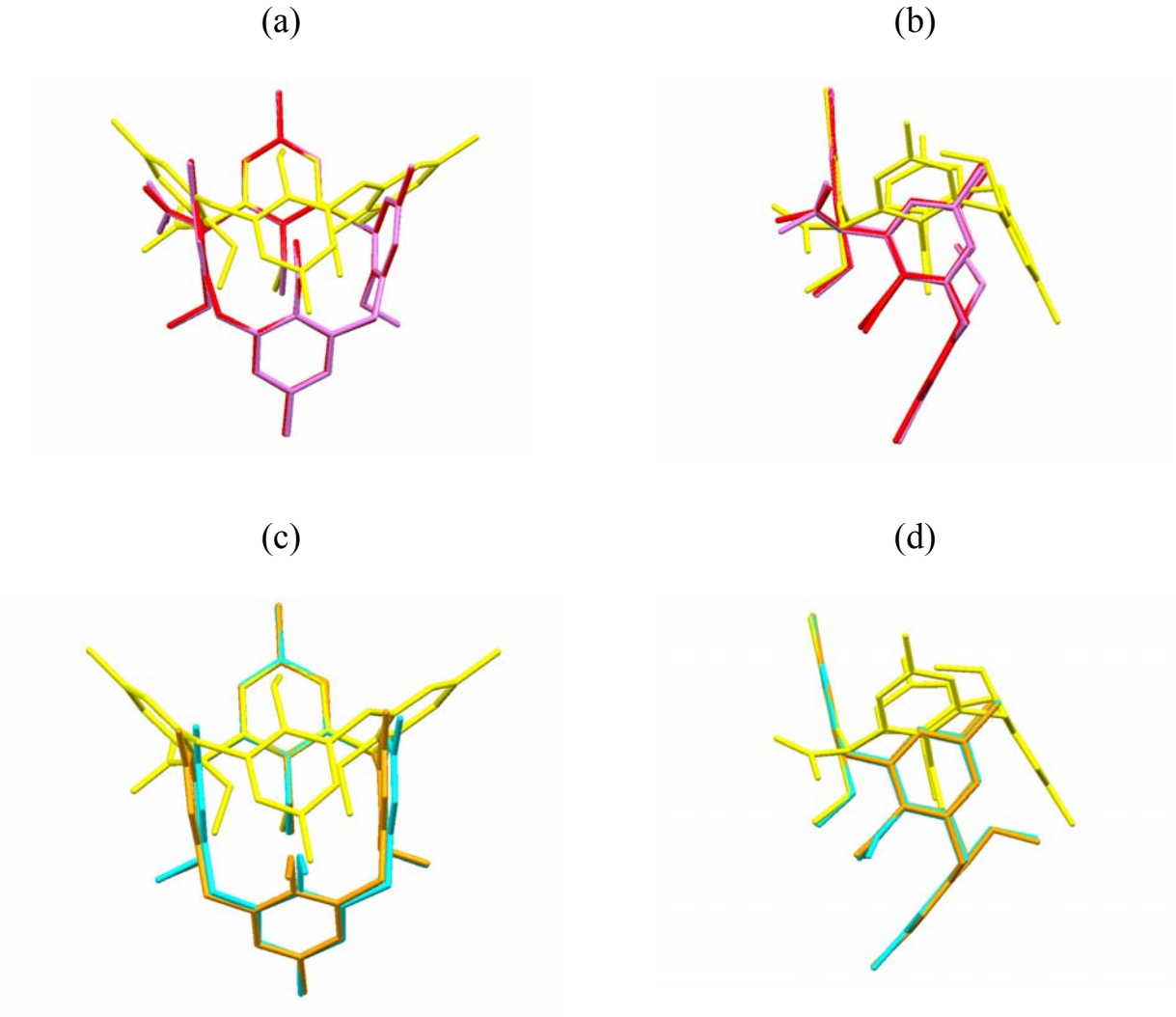

Fig. S9 Superimposed conformations of the calixarene molecules as found in the crystal structures of the unsolvated compound **1** (yellow) as well as the solvent complexes **1a** (red) and **1b** (violet) from two different viewing points: (a) front and (b) side view. Superimposed conformations of the calixarene molecules from the crystal structures of the unsolvated compound **1** (yellow) and the unsubstituted calixarene (KEVXUE1 and KEVXUE2; orange and blue) from two different viewing points: (c) front and (d) side view. In order to enhance the differences in the molecular conformation, one phenyl ring of each calixarene molecule is fitted.