DESIGN AND PREPARATION OF MESOGENIC CAVITANDS

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Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday in recognition of his outstanding contributions to supramolecular chemistry.

Mesogenic cavitands have been prepared for the first time. They form uniaxial disordered columnar mesophases (D_{hd}). The structure requirements for mesophase formation have been identified: (i) macrocyclic cores with thickness below 5 Å and (ii) four large (3,4,5-tris-{[4-(dodecyloxy)benzyl]oxy}benzoyl)oxy groups at the upper rim. The orientation of the molecules within the columns is random, excluding the formation of intracolumnar cavities of molecular dimensions in the mesophase.

Keywords: Cavitands; Liquid crystals; Self-organization; Calixarenes; Resorcinarenes; Macrocycles; X-ray diffraction.

The generation of new materials endowed with molecular recognition properties is highly pursued nowadays. Liquid crystalline materials are ideal candidates, due to their self-organization properties, which enables the amplification of molecular recognition phenomena[1]. So far, the efforts have been mainly devoted to the induction of mesophases as macroscopic expression of molecular recognition events between complementary components[2]. The induction/amplification of mesomorphic behaviour via host–guest interactions has received less attention. The few examples reported in the literature regard the induction of liquid crystallinity in crown ether derivatives by metal ion complexation[3], the suppression of columnar ordering in metallocalixarenes via DMF inclusion[4], and the mesophase induction in molecular clips by conformational control of the glycoluril core, obtained

via resorcinol complexation[5]. A particular mention deserves the guest-induced formation of liquid crystalline polymeric capsules, where the capsules self-assemble only in the presence of a suitable guest[6].

In this paper we report the design and preparation of mesogenic cavitands. Our previous work on liquid crystalline resorcinarenes[7] has highlighted the major factors affecting columnar mesophase formation in this class of macrocycles: (i) the presence of at least twelve side chains radiating from the core; (ii) the thickness of the core (related to the bulkiness of the R substituents); (iii) the conformational mobility of the macrocyclic core. Particularly intriguing is the observed alternating sequence of head-to-head and tail-to-tail intracolumnar organization[8] which, if retained in the presence of a rigid preorganized core, could lead to intracolumnar cavities of molecular dimensions.

RESULTS AND DISCUSSION

The main structural limitation encountered in designing mesogenic cavitands concerns the bridging units. Methylene and ethylene bridges have been selected because they comply with two conflicting molecular requirements: limiting the thickness of the resorcinarene core and forming a rigid, preorganized cavity. Besides, the eight phenolic OHs engaged in bridging are not available for side chains functionalization. Therefore the side chains must be positioned in the four apical positions of the core and each substituent must bear at least three long alkyl chains to reach the appropriate number of lateral substituents.

3,4,5-Trialkoxybenzoyl Tetrasubstituted Cavitands

According to these requirements three different classes of cavitands were prepared, in the order of decreasing thickness of the rigid core. In all cases four 3,4,5-trialkoxybenzoic acid residues in the apical positions of the cavitand core are present. For each class the core thickness can be quantitatively evaluated from the crystal structures of the cavitand precursors[9] **4**, **12** (Figs 1 and 2) and the methyl-footed derivatives[10] of **4**. The macrocyclic core thickness (*h* in Fig. 3) is progressively reduced from 5.36 Å (R = CH_3, methylene bridge)[10] to 3.83 Å (**4**, R = H, methylene bridge) and to 3.27 Å (**12**, R = H, ethylene bridge). These values have been calculated considering the mean distance between the least-square planes passing through the R groups and through the carbon atoms of the methyl groups at the upper rim. In the last compound the cavity is wider and shallower than in the for-

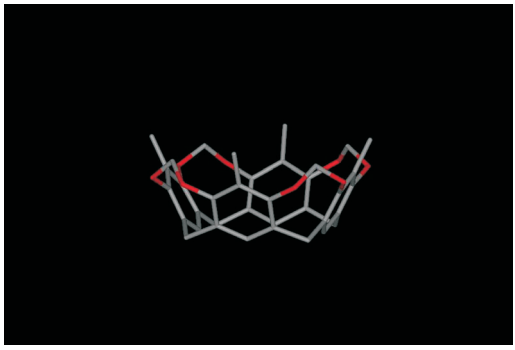


FIG. 1
Crystal structure of cavitand **4**

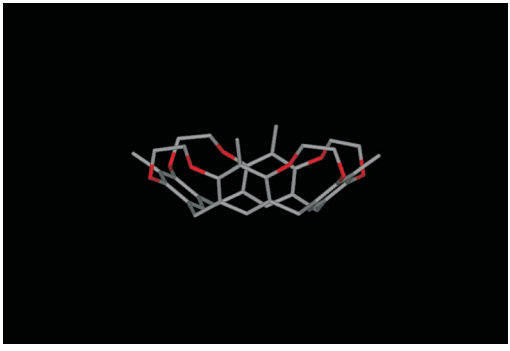
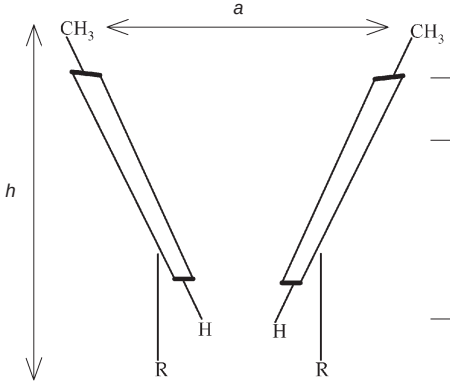


FIG. 2
Crystal structure of cavitand **12**



Cavitand	*a*, Å	*h*, Å
Methyl-footed derivative of **4** (**R = CH_3**)[10]	9.09	5.36
4 (R = H)	9.43	3.83
12 (R = H)	9.48–11.94	2.75–3.80

FIG. 3
General drawing of the three cavitand platforms, their thickness (*h*) and cavity width (*a*)

mer two and the macrocycle presents a limited degree of conformational mobility. In the solid state **12** assumes a "pinched-cone" conformation, while in solution the observed C_{4v} symmetry cone structure is the result of the rapid interconversion of two equivalent pinched-cone conformations. The cavity width (*a* in Fig. 3) is calculated as the mean value of the distances between opposite methyl groups.

Synthesis

The preparation of cavitands **2** and **3** requires the condensation of 3,4,5-tris(octyloxy)benzoic acid (in the case of **2**) and 3,4,5-tris(dodecyloxy)-benzoic acid (in the case of **3**) with tetrol cavitand[11] **1**. The reaction was carried out using the mild DCC (1,3-dicyclohexylcarbodiimide)/DMAP (4-(dimethyl-amino)pyridine) procedure (Scheme 1). The purification of the final products turned out to be critical, reducing the yields of the desired compounds. Trace amounts of trifunctionalized cavitands were also obtained.

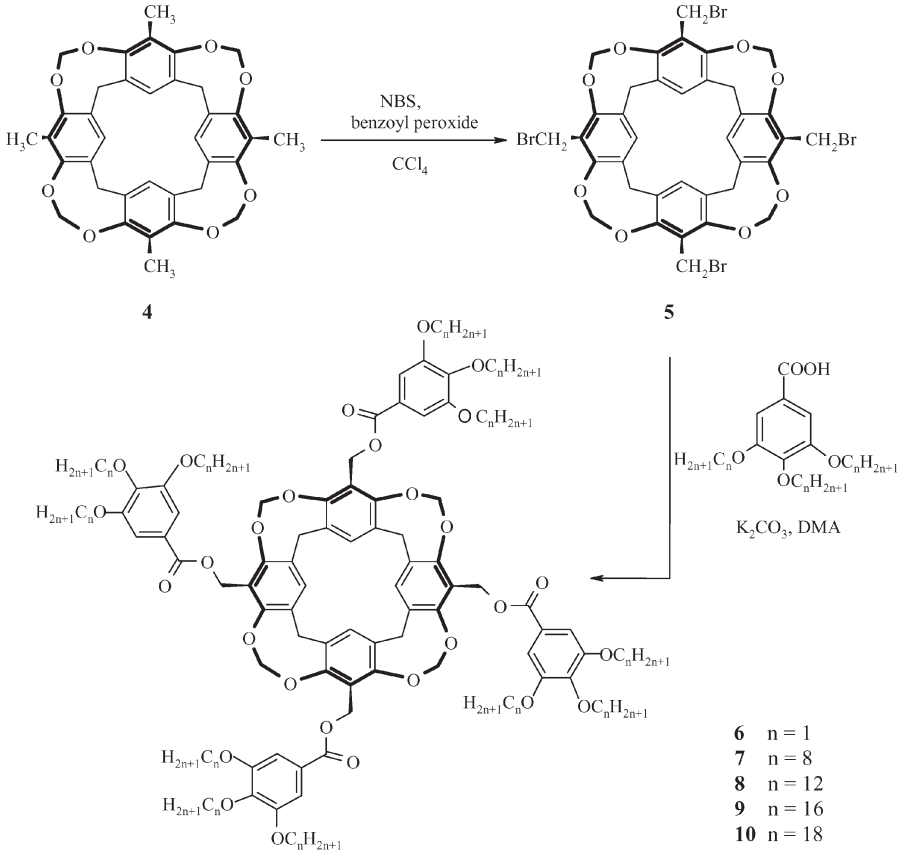
The synthetic route to cavitands **6**–**10** is shown in Scheme 2. The first step was the radical bromination of the methyl groups in the apical position of cavitand[9] **4**, following the Sorrell procedure with NBS and dibenzoyl peroxide[12]. The reaction gave cavitand **5** in high yields, which is the molecular platform for the synthesis of compounds **6**–**10**. Fourfold acyloxy-dehalogenation of **5** with 3,4,5-trialkoxybenzoic acids under alkaline conditions afforded cavitands **6**–**10**. Increasing the length of the alkyl chains made the purification more difficult and reduced the yields of the final products.

For the synthesis of ethylene-bridged cavitands **14** and **15**, the same procedure of Scheme 2 was followed (Scheme 3), after the bridging reaction of resorcinarene[13] **11** to give cavitand **12**.

Thermal Behaviour: Differential Scanning Calorimetry and Optical Microscopy

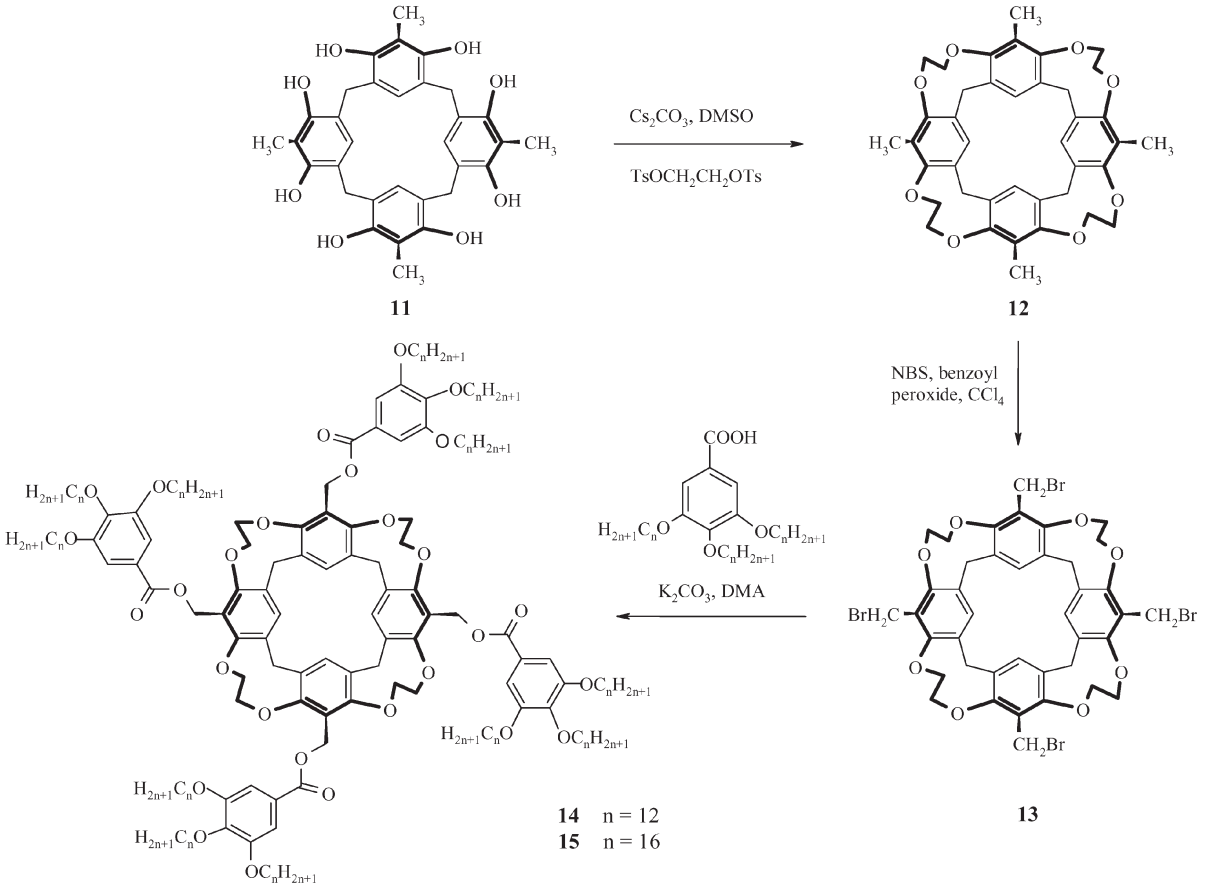
Thermal properties of 3,4,5-trialkoxybenzoate substituted cavitands were studied using differential scanning calorimetry (DSC) and optical microscopy (OM). All solid cavitands exhibited a single isotropic liquid-crystal transition (I-K) upon cooling with a strong overcooling effect. This effect is typical of high-molecular-weight compounds and is strongly influenced by the cooling rate. Cavitands **2**, **3** and **7** are isotropic liquids at room temperature. DSC measurements al low temperature (–35 °C) did not show any phase transition. The isotropic liquid phase of these cavitands is stable over

SCHEME 1



SCHEME 2

time: no formation of a crystal phase was observed after months. Cavitand **8** showed an intermediate behaviour: upon heating a solid sample melting occurred at 64 °C (Table I). Crystallization turned out to be kinetically very slow: **8** formed spherulitic domains only after two days at room temperature (seen by OM). Cavitand **9** exhibited a complex thermal behaviour upon heating presenting a first fusion at 41 °C (K-I), immediately followed by crystallization at 44 °C and final melting of the K_1 form at 85 °C. Cavitands **10**, **14** and **15** exhibited only K-I and I-K transitions with no evidence of mesophase formation (Table I).


11
Cs2CO3, DMSO
TsOCH2CH2OTs
12
NBS, benzoyl peroxide, CCl4
13
K2CO3, DMA
14 n = 12
15 n = 16

SCHEME 3

(3,4,5-Tris{[4-(dodecyloxy)benzyl]oxy}benzoyl)oxy Tetrasubstituted Cavitands

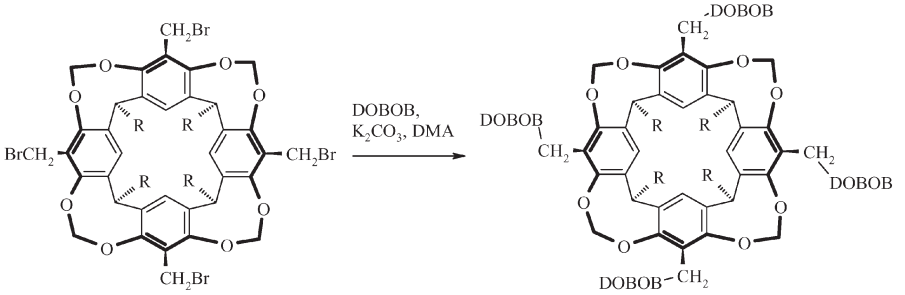
The lack of mesogenic properties in all cavitands prepared, despite of the different thickness of the macrocyclic core, forced us to reconsider the role of the peripheral substituents. We reasoned that the presence of twelve aliphatic chains radiating from the upper rim apical positions was not sufficient to assure an optimal space filling around the macrocyclic cores. To test this hypothesis we resorted to the large and roughly triangular (3,4,5-tris{[4-(dodecyloxy)benzyl]oxy}benzoyl)oxy (DOBOB) group, a potential columnarogenic unit[14]. Four of these units were introduced onto each of the three macrocyclic cores employed above via nucleophilic substitution of the benzylic bromides in the apical positions (Schemes 4 and 5). The MS characterization of these compounds turned out to be particularly challenging. The normal chemical ionisation technique, successful for the other cavitands, proved to be ineffective in this case. The DOBOB group has a strong tendency to fragment by losing the [4-(dodecyloxy)benzyl]oxy

TABLE I
Transition temperatures for cavitands **2**–**15**[a]

Compound	Transition[b]	*T*, °C	Transition[c]	*T*, °C
2 (*n* = 8)	I[d]	–	I[d]	–
3 (*n* = 12)	I[d]	–	I[d]	–
7 (*n* = 8)	I[d]	–	I[d]	–
8 (*n* = 12)	K-I	64	I[e]	–
9 (*n* = 16)	K-I I-K_1 K_1-I	41 45 85	I-K	43
10 (*n* = 18)	K-I	47	I-K	34
14 (*n* = 12)	K-I	75	I-K	28
15 (*n* = 16)	K-I	42	I-K	22

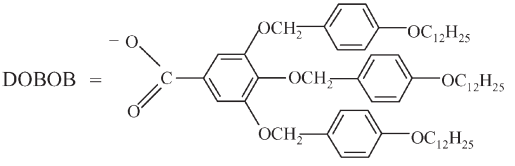
[a] These results refer to DSC measurements at 10 °C/min between –35 and 150 °C. K and K_1, crystal forms; I, isotropic liquid. [b] Heating run. [c] Cooling run. [d] The isotropic phase is stable over the entire temperature range. Below 20 °C the isotropic phase became progressively frozen. [e] Crystallization occurred after two days at room temperature (OM observations).

moiety. Using the MALDI-TOF technique at low ionising laser energy, the molecular ion of the fragment without two of the twelve [4-(dodecyloxy)-benzyl]oxy units has been detected as $[M + Na]^+$ for **17**, **18** and **19**.

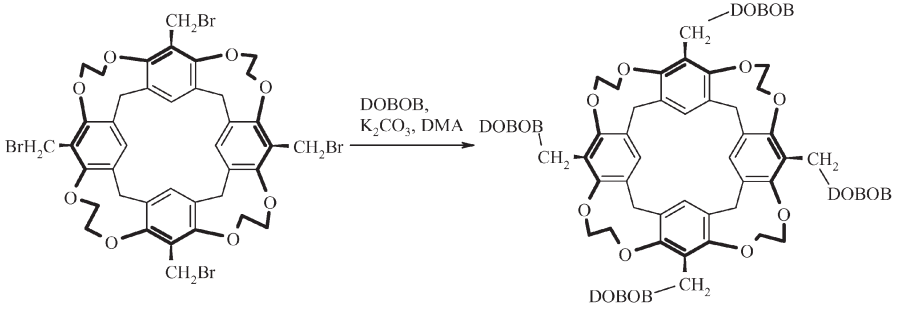


5 R = H
16 R = CH_3

17 R = H
18 R = CH_3



SCHEME 4



13 **19**

SCHEME 5

The mesogenic properties of high-molecular-weight cavitands **17**, **18** and **19** were assessed via DSC, OM and X-ray diffraction. Under the microscope, a virgin sample of **17** exhibited a fan-shaped texture typical of hexagonal columnar arrangements at room temperature. Upon heating the mesophase disappeared gradually between 85 and 100 °C (93–98.5 °C by DSC, Table II). On slow cooling, the mesophase formed gradually, while fast cooling led to

the formation of an amorphous glass which remained unchanged for several weeks. The optical observations were confirmed by DSC measurements performed at slow rate (Table II). In the DSC cooling trace, the crystallization transition was not observed, even at low temperatures (–35 °C). The mesophase remained frozen at low temperature.

Cavitand **19** formed a monotropic D_h mesophase on first heating of virgin samples (miscible with that formed by **17**). Once the isotropic phase was formed, no more transitions were observed in the subsequent cooling and heating runs, both by DSC and OM. At low temperatures, the isotropic phase turned into an amorphous glass. The residual conformational mobility of the macrocyclic core due to the ethylene bridges contributes to the suppression of phase transitions.

Cavitand **18** is an isotropic liquid at room temperature. DSC measurements at low temperature (–35 °C) did not show any phase transition. Its thermal behaviour resembled that of cavitands **2** and **3**, having the same core. In this case the use of DOBOB did not lead to mesophase formation.

Mesophase X-ray Diffraction

X-ray diffraction experiments were performed on cavitand **17**. The X-ray pattern does not change significantly with temperature. Only two rings of diffractions were present: the inner ring corresponds to a mean spacing of 41–42 Å and the outer one to 4.5 Å. A comparison with OM observations

TABLE II
Transition temperatures for cavitands **17**–**19**[a]

Compound	Transition[b]	*T*, °C	Transition[c]	*T*, °C
17	D_h-I	93–98.5 (maximum 96.5)	I-D_h[d]	82–75 (maximum 79)
18	I[e]	–	I[e]	–
19	K-D_h[f]	60	I[e]	–
	D_h-I	99		

[a] These results refer to DSC measurements at 5 °C/min between –35 and 150 °C. K, crystal form; D_h, columnar mesophase; I, isotropic liquid. [b] Heating run. [c] Cooling run. [d] The mesophase became progressively frozen below 20 °C (OM observations). [e] The isotropic phase is stable over the entire temperature range. Below 20 °C the isotropic phase became progressively frozen. [f] Transitions observed only in the first heating runs of virgin samples (confirmed by OM observations).

showed that the mesophase is growing very slowly at every temperature. By stretching the sample, the aligned sublayer turned out to be very thin. By annealing the sample five days at 70 °C the inner ring became sharper and moved slightly toward larger angles. However, no extra rings appeared at larger angles and therefore, in principle, it is impossible to distinguish between a columnar and a smectic mesophase. Given the molecular architecture, the mesophase is a columnar one, a uniaxial hexagonal columnar phase D_h with spacing 47.3 Å. The mean area per column is consistent with the molecular dimensions. Assuming a density of about 1 g cm^{-3}, the mean distance between two molecules along the column is about 4 Å. There is no sharp interface between the aromatic and aliphatic media, as testified by the absence of high order reflections for the hexagonal lattice.

The asymmetric shape of the rigid cavitand core, which presents two nonequivalent concave and convex surfaces, has interesting consequences regarding the nature of intracolumnar molecular packing. Both head-to-tail and head-to-head/tail-to-tail molecular organizations are possible. In the last case, intracolumnar cavities can be formed with potential molecular inclusion capabilities. Experimentally, contrary to mesogenic resorcinarenes[8], no intracolumnar ordering was observed. No regular head-to-head and tail-to-tail arrangement is present, as there is no evidence of a period being equal to twice the mean distance between two molecules. The high level of disorder observed is consistent with the coexistence of head-to-tail and head-to-head/tail-to-tail arrangements.

Guest-induced core dimerization within the columns was attempted by addition of suitable bifunctional guests to **17**. Guest–**17** mixtures at different stoichiometry were prepared by dissolving both components in dichloromethane, followed by slow evaporation of the solvent[5c]. The guests employed were those having “acid” methyl groups at both ends, capable of interaction with the π-basic cavity of **17** [10]. Hexane-2,5-dione, dimethyl oxalate and 1,3-dimethylurea were selected for the purpose. Charged guests like hexane-1,6-diamine dihydrochloride were not miscible with the cavitand. The molar ratios spanned from **17**/guest 2:1 to **17**/guest 1:2. The effective molar ratios **17**/guest were checked for all mixtures via ^{1}H NMR integration of selected peaks. The mixtures, analyzed via DSC and OM, did not show any significant change of texture or transition temperatures. In the case of dimethyl oxalate, guest segregation was observed at high concentrations. Probably CH–π interactions are not sufficiently strong to change the statistical columnar ordering of **17**, overcoming a large number of dispersion interactions among lateral substituents. This is conceivable

considering that the cavitand core is surrounded by four very large DOBOB groups.

CONCLUSIONS

Three cavitand platforms have been decorated at the upper rim with appropriate substituents to induce the formation of columnar mesophases. Two structural factors have been found essential for the mesophase induction: (i) the thickness of the rigid macrocyclic core must be lower than 5 Å to allow columnar packing; (ii) four DOBOB groups at the periphery of the core are necessary to assure an optimal space filling. Only cavitands **17** and **19** fulfil these rather demanding structural requirements, forming discotic hexagonal disordered (indexed as D_{hd}) mesophases. No intracolumnar ordering of the macrocyclic cores has been observed, jeopardizing the possibility of inducing/stabilizing liquid crystallinity by host–guest interactions. Because of their high molecular weight, the molecules have a low diffusion coefficient and, consequently, the isotropic liquid-to-columnar-mesophase transition is very slow and crystallization is often inhibited.

EXPERIMENTAL

Melting points of nonmesogenic compounds were determined on a Gallenkamp apparatus and are uncorrected. Mass spectra were recorded on a Finnigan MAT 8400 (Chemical Ionization mode) and a Micromass MALDI-TOF spectrometers. ^{1}H NMR spectra were recorded on a Brucker AC 300 and AMX 400 spectrometers. Chemical shifts, δ, are given in ppm ($\delta_{TMS} = 0$) using the residual solvent peak referred to TMS as internal reference; coupling constants, *J*, are given in Hz. OM was performed using a Leitz–Wetzlar polarizing microscope equipped with a Leitz–Wetzlar hot stage. Thin samples were observed between two untreated cover slips of ordinary glass. DSC measurements were performed with a Perkin–Elmer DSC 7 thermal analyser. The powder diffraction patterns of unoriented mesophases of compounds **17** and **19** were recorded on a Siemens D 500 TH-TH diffractometer with Ni-filtered radiation (λ_2-Kα = 1.5418 Å). IR spectra (ν in cm^{-1}). Elemental analyses were carried out with a Carlo Erba Model 1106 elemental analyser. Resorcinarene **11** [13], cavitands **1** [11], **4** [9], **16** [12] and 3,4,5-tris{[4-(dodecyloxy)benzyl]oxy}benzoic acid[14] were prepared according to published literature procedures. All 3,4,5-tris(dodecyloxy)benzoic acids used were prepared via alkylation of gallic acid methyl ester, followed by saponification of the ester group.

Cavitand **2**

Cavitand **1** (0.316 g, 0.44 mmol), 3,4,5-tris(octyloxy)benzoic acid (2.246 g, 4.43 mmol), DMAP (0.542 g, 4.43 mmol) and DCC (0.914 g, 4.43 mmol) were dissolved in dry CH_2Cl_2 (200 ml) and dry DMA (13 ml). The reaction was stirred at room temperature for 3 days, then extracted with 2 M HCl and saturated $NaHCO_3$ and NaCl solutions. The organic layer was dried over anhydrous Na_2SO_4. After solvent evaporation, the residue was purified by col-

umn chromatography (Florisil, CH_2Cl_2) giving compound **2** as an oil (0.189 g) in 16% yield. For $C_{164}H_{248}O_{28}$ (2667.7) calculated: 73.84% C, 9.37% H; found: 73.49% C, 9.59% H. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.88 t, 36 H, $(CH_2)C\mathbf{H}_3$, J = 6.4; 1.28 bs, 96 H, $(C\mathbf{H}_2)_4CH_3$; 1.45 m, 24 H, CH_2^{γ}; 1.68–1.84 m, 36 H, $CHC\mathbf{H}_3$ + CH_2^{β}; 3.99 m, 24 H, OCH_2^{α}; 4.39 d, 4 H, CH_{in}, J = 7.2; 5.00 q, 4 H, ArCHAr, J = 7.5; 5.16 s, 8 H, $ArCH_2$; 5.99 d, 4 H, CH_{out}, J = 7.2; 7.19 s, 8 H, ArH; 7.32 s, 4 H, ArH. MS (CI, *m/z*): 2667 (M^-, 100).

Cavitand **3**

Cavitand **1** (0.140 g, 0.19 mmol), 3,4,5-tris(dodecyloxy)benzoic acid (0.794 g, 1.18 mmol), DMAP (0.144 g, 1.18 mmol) and DCC (0.244 g, 1.18 mmol) were dissolved in dry CH_2Cl_2 (60 ml). The reaction was stirred at room temperature for 3 days, then extracted with 2 M HCl and saturated $NaHCO_3$ and NaCl solutions. The organic layer was dried over anhydrous Na_2SO_4. After solvent removal, the residue was purified by column chromatography (Florisil, CH_2Cl_2) giving compound **3** as an oil (0.203 g) in 31% yield. For $C_{212}H_{344}O_{28}$ (3341.0) calculated: 76.21% C, 10.38% H; found: 76.02% C, 10.69% H. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.89 t, 36 H, $(CH_2)C\mathbf{H}_3$, J = 6.8; 1.27 bs, 192 H, $(C\mathbf{H}_2)_8CH_3$; 1.48 m, 24 H, CH_2^{γ}; 1.68–1.85 m, 36 H, $CHC\mathbf{H}_3$ + CH_2^{β}; 4.00 m, 24 H, OCH_2^{α}; 4.41 d, 4 H, CH_{in}, J = 7.2; 5.00 q, 4 H, ArCHAr, J = 7.4; 5.18 s, 8 H, $ArCH_2$; 6.00 d, 4 H, CH_{out}, J = 7.2; 7.20 s, 8 H, ArH; 7.33 s, 4 H, ArH. MS (CI, *m/z*): 3340 (M^-, 100).

Cavitand **5**

To a solution of cavitand **4** (0.830 g, 1.40 mmol) in a mixture of CCl_4 (80 ml) and $CHCl_3$ (20 ml), NBS (1.0 g, 5.74 mmol) and a catalytic amount of dibenzoyl peroxide were added under argon atmosphere. The resulting solution was refluxed for 4 h, after 2 h more NBS (0.053 g, 0.30 mmol) was added. A white precipitate was formed and after stirring at room temperature overnight, the solvent was removed and the residue was purified by column chromatography (silica gel, CH_2Cl_2) to give cavitand **5** (1.022 g) in 80% yield. M.p. 320 °C (dec.). ^{1}H NMR (DMSO-d_6, 300 MHz): 3.44 d, 4 H, $ArCH_{eq}Ar$, J = 12.1; 4.25 d, 4 H, $ArCH_{ax}Ar$, J = 12.1; 4.42 s, 8 H, CH_2Br; 4.50 d, 4 H, CH_{in}, J = 7.7; 6.04 d, 4 H, CH_{out}, J = 7.7; 7.65 s, 4 H, ArH. IR (KBr): 2934 ($C–H_{arom}$), 1247 (Ar–O), 1075 (CH_2–O), 555 (C–Br). MS (CI, *m/z*): 909 (M^-, 100).

Cavitand **6**

Potassium carbonate (0.189 g, 1.37 mmol) was added to a solution of cavitand **5** (0.207 g, 0.23 mmol) and 3,4,5-trimethoxybenzoic acid (0.290 g, 1.37 mmol) in dry DMA (40 ml). The reaction mixture was stirred at room temperature for 24 h. The formation of a solid was observed, which increased after addition of H_2O (200 ml) and 12 M HCl. The white precipitate was filtered off, dried and purified by column chromatography (silica gel, CH_2Cl_2/acetone 96:4) to give cavitand **6** (0.132 g) in 40% yield. M.p. 175–180 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.33 d, 4 H, $ArCH_{eq}Ar$, J = 12.2; 3.86 s, 24 H, OCH_3; 3.88 s, 12 H, OCH_3; 4.45 d, 4 H, CH_{in}, J = 7.3; 4.54 d, 4 H, $ArCH_{ax}Ar$, J = 12.2; 5.19 s, 8 H, $ArCH_2$; 5.99 d, 4 H, CH_{out}, J = 7.3; 7.20 s, 8 H, ArH; 7.22 s, 4 H, ArH. IR (KBr): 1718 (C=O), 1217 (C–O), 1128 (ν_{as} C–O), 964 (O–CH_2–O). MS (CI, *m/z*): 1434 (MH^+, 100).

Cavitand **7**

Potassium carbonate (0.110 g, 0.80 mmol) was added to a solution of cavitand **5** (0.170 g, 0.19 mmol) and 3,4,5-tris(octyloxy)benzoic acid (0.420 g, 0.80 mmol) in dry DMA (50 ml). The reaction mixture was stirred at room temperature for 24 h, then it was poured into 400 ml of H_2O acidified with 12 M HCl and extracted with CH_2Cl_2. The organic layer was washed with a saturated solution of NaCl, then dried over anhydrous Na_2SO_4. After solvent removal, the crude product was purified by column chromatography (silica gel, CH_2Cl_2 and CH_2Cl_2/hexane 9:1) to give cavitand **7** as an oil (0.202 g) in 41% yield. For $C_{160}H_{240}O_{28}$ (2611.6) calculated: 73.58% C, 9.26% H; found: 73.65% C, 9.01% H. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.87 t, 36 H, CH_3, J = 6.8; 1.28 m, 96 H, $(CH_2)_4CH_3$; 1.44 m, 24 H, CH_2^{γ}; 1.77 m, 24 H, CH_2^{β}; 3.32 d, 4 H, $ArCH_{eq}Ar$, J = 12.3; 3.97 m, 24 H, OCH_2^{α} 4.43 d, 4 H, CH_{in}, J = 7.2; 4.53 d, 4 H, $ArCH_{ax}Ar$, J = 12.3; 5.15 s, 8 H, $ArCH_2$; 5.96 d, 4 H, CH_{out}, J = 7.2; 7.17 s, 8 H, ArH; 7.19 s, 4 H, ArH. IR (KBr): 2920 (C–H_{arom}), 1715 (C=O), 1220 (C–O), 1110 (ν_{as} C–O), 957 (OCH_2). MS (CI, *m/z*): 2613 (MH^+, 100).

Cavitand **8**

Potassium carbonate (0.120 g, 0.87 mmol) was added to a solution of cavitand **6** (0.170 g, 0.19 mmol) and 3,4,5-tris(dodecyloxy)benzoic acid (0.564 g, 0.84 mmol) in dry DMA (45 ml). The reaction mixture was stirred at room temperature for 24 h. The mixture was poured into 400 ml of H_2O acidified with 12 M HCl. The white precipitate formed was filtered off, washed with water and concentrated to dryness. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/hexane 9:1 and 7:3) to give cavitand **8** as a white solid (0.169 g) in 27% yield. For $C_{208}H_{336}O_{28}$ (3284.9) calculated: 76.05% C, 10.31% H; found: 75.88% C, 10.69% H. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.87 t, 36 H, CH_3, J = 6.8; 1.26 m, 192 H, $(CH_2)_8CH_3$; 1.44 m, 24 H, CH_2^{γ}; 1.75 m, 24 H, CH_2^{β}; 3.31 d, 4 H, $ArCH_{eq}Ar$, J = 12.2; 3.97 m, 24 H, OCH_2^{α}; 4.44 d, 4 H, CH_{in}, J = 7.3; 4.53 d, 4 H, $ArCH_{ax}Ar$, J = 12.2; 5.15 s, 8 H, $ArCH_2$; 5.97 d, 4 H, CH_{out}, J = 7.3; 7.18 s, 8 H, ArH; 7.19 s, 4 H, ArH. IR (KBr): 2924 (C–H_{arom}), 1718 (C=O), 1209 (C–O), 1116 (ν_{as} C–O), 967 (OCH_2). MS (CI, *m/z*): 3285 (M^+, 100).

Cavitand **9**

Potassium carbonate (0.090 g, 0.65 mmol) was added to a solution of cavitand **5** (0.135 g, 0.15 mmol) and 3,4,5-tris(hexadecyloxy)benzoic acid (0.550 g, 0.65 mmol) in a mixture of dry DMA (50 ml) and dry toluene (60 ml). After 5 h of stirring at room temperature, the second addition of 3,4,5-tris(hexadecyloxy)benzoic acid (0.060 g, 0.07 mmol) was carried out and the solution was stirred for 7 h. The mixture was poured into 600 ml of H_2O acidified with 12 M HCl and extracted with CH_2Cl_2. The organic layer was washed with a saturated solution of NaCl, then dried over anhydrous Na_2SO_4. After solvent removal, the crude product was purified by column chromatography (silica gel, CH_2Cl_2 and CH_2Cl_2/hexane 7:3) to give cavitand **9** as a white solid (0.057 g) in 10% yield. For $C_{256}H_{432}O_{28}$ (3958.2) calculated: 77.68% C, 11.00% H; found: 77.51% C, 10.69% H. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.87 t, 36 H, CH_3, J = 6.8; 1.25 m, 288 H, $(CH_2)_{12}CH_3$; 1.46 m, 24 H, CH_2; 1.76 m, 24 H, CH_2^{β}; 3.32 d, 4 H, $ArCH_{eq}Ar$, J = 12.2; 3.97 m, 24 H, OCH_2^{α}; 4.43 d, 4 H, CH_{in}, J = 7.3; 4.53 d, 4 H, $ArCH_{ax}Ar$, J = 12.2; 5.15 s, 8 H, $ArCH_2$; 5.96 d, 4 H, CH_{out}, J = 7.3; 7.17 s, 8 H, ArH; 7.20 s, 4 H, ArH. IR (KBr): 2990 (C–H_{arom}), 1724 (C=O), 1204 (C–O), 1111 (ν_{as} C–O), 960 (OCH_2). MS (CI, *m/z*): 3958 (M^+, 100).

Cavitand **10**

Potassium carbonate (0.059 g, 0.43 mmol) was added to a solution of cavitand **5** (0.089 g, 0.10 mmol) and 3,4,5-tris(octadecyloxy)benzoic acid (0.400 g, 0.43 mmol) in a mixture of dry DMA (40 ml) and dry toluene (50 ml). The reaction mixture was stirred at room temperature for 12 h, then it was poured into 500 ml of H_2O acidified with 12 M HCl and extracted with CH_2Cl_2. The organic layer was washed with a saturated solution of NaCl and dried over anhydrous Na_2SO_4. After solvent removal, the crude product was purified by column chromatography (silica gel, CH_2Cl_2/hexane 8:2 and CH_2Cl_2/hexane 7:3) to give cavitand **10** as a white solid (0.016 g) in 14% yield. For $C_{280}H_{480}O_{28}$ (4294.9) calculated: 78.30% C, 11.26% H; found: 77.92% C, 11.58% H. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.88 t, 36 H, CH_3, J = 6.8; 1.24 m, 336 H, $(CH_2)_{14}CH_3$; 1.47 m, 24 H, CH_2^{γ}; 1.75 m, 24 H, CH_2^{β}; 3.31 d, 4 H, $ArCH_{eq}Ar$, J = 12.5; 3.97 m, 24 H, OCH_2^{α}; 4.43 d, 4 H, CH_{in}, J = 7.1; 4.53 d, 4 H, $ArCH_{ax}Ar$, J = 12.5; 5.14 s, 8 H, $ArCH_2$; 5.96 d, 4 H, CH_{out}, J = 7.1; 7.16 s, 8 H, ArH; 7.20 s, 4 H, ArH. IR (KBr): 2980 (C–H_{arom}), 1730 (C=O), 1207 (C–O), 1126 (ν_{as} C–O), 971 (OCH_2). MS (CI, *m/z*): 4294 (M^-, 20).

Cavitand **12**

To a solution of **11** (3.000 g, 6.50 mmol) in dry DMSO (200 ml), ethylene glycol ditosylate (16.320 g, 44.05 mmol) and Cs_2CO_3 (14.350 g, 44.00 mmol) were added under argon atmosphere. The reaction mixture was refluxed for 2 days, then ethylene glycol ditosylate (0.750 g, 2 mmol) and Cs_2CO_3 (0.650 g, 2.00 mmol) were added, the solution was heated for another 3 days, then poured into H_2O (700 ml) acidified with 12 M HCl. A brown precipitate formed which was filtered off and purified by column chromatography (silica gel, CH_2Cl_2/acetone 98:2) to give cavitand **12** in 70% yield (2.503 g) as a white solid. M.p. 244 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.17 s, 12 H, CH_3; 3.21 d, 4 H, $ArCH_{eq}Ar$, J = 12.6; 3.52 m, 8 H, CH_{in}; 4.28 m, 8 H, CH_{out}; 4.80 d, 4 H, $ArCH_{ax}Ar$, J = 12.6; 7.24 s, 4 H, ArH. IR (KBr): 2927 (C–H_{arom}), 1267 (Ar–O), 1082 (CH_2–O). MS (CI, *m/z*): 649 (M^+, 100).

Cavitand **13**

To a solution of tetramethyl cavitand **12** (1.893 g, 2.90 mmol) in a mixture of CCl_4 (60 ml) and $CHCl_3$ (60 ml), NBS (2.088 g, 1.20 mmol) and a catalytic amount of dibenzoyl peroxide were added under argon atmosphere. The solution was refluxed for 4 h, after 2 h NBS (0.052 g, 0.30 mmol) was added and the solvent was evaporated. The residue was washed with cold CH_2Cl_2 to give cavitand **13** (3.365 g) in 84% yield. M.p. 300 °C (dec.). ^{1}H NMR ($CDCl_3$, 300 MHz): 3.26 d, 4 H, $ArCH_{eq}Ar$, J = 12.7; 4.18 m, 8 H, CH_{in}; 4.63 m, 8 H, CH_{out}; 4.73 s, 8 H, CH_2Br; 4.85 d, 4 H, $ArCH_{ax}Ar$, J = 12.7; 7.46 s, 4 H, ArH. IR (KBr): 1090 (CH_2–O), 557 (C–Br). MS (CI, *m/z*): 964 (M^-, 100).

Cavitand **14**

Potassium carbonate (0.102 g, 0.74 mmol) was added to a homogeneous solution of cavitand **13** (0.162 g, 0.17 mmol) and 3,4,5-tris(dodecyloxy)benzoic acid (0.500 g, 0.74 mmol) in a mixture of dry DMA (40 ml) and dry CH_2Cl_2 (10 ml). After 48 h of stirring at room temperature, the reaction mixture was poured into 600 ml of H_2O acidified with 12 M HCl and extracted with CH_2Cl_2. The organic layer was washed with a saturated solution of NaCl

and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (silica gel, hexane/THF 8:2) to give cavitand **14** as a pink solid (0.074 g) in 14% yield. $C_{212}H_{344}O_{28}$ (3341.0) calculated: 76.21% C, 10.38% H; found: 75.86% C, 10.03% H. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.87 t, 36 H, CH_3, J = 6.8; 1.24 m, 192 H, $(CH_2)_8CH_3$; 1.43 m, 24 H, CH_2^{γ}; 1.73 m, 24 H, CH_2^{β}; 3.32 d, 4 H, $ArCH_{eq}Ar$, J = 12.9; 3.68 m, 8 H, CH_{in}; 3.92 m, 16 H, OCH_2^{α}; 3.97 m, 8 H, OCH_2^{α}; 4.37 m, 8 H, CH_{out}; 4.89 d, 4 H, $ArCH_{ax}Ar$, J = 12.9; 5.35 s, 8 H, $ArCH_2$; 7.12 s, 8 H, ArH; 7.51 s, 4 H, ArH. IR (KBr): 2922 ($C–H_{arom}$), 1715 (C=O), 1210 (C–O), 1110 (ν_{as} C–O), 404 (OCH_2). MS (CI, *m/z*): 3341 (M^+, 60).

Cavitand **15**

Potassium carbonate (0.137 g, 0.99 mmol) was added to a homogeneous solution of cavitand **13** (0.217 g, 0.23 mmol) and 3,4,5-tris(hexadecyloxy)benzoic acid (0.835 g, 0.99 mmol) in a mixture of dry DMA (50 ml) and dry CH_2Cl_2 (20 ml). After 12 h of stirring at room temperature, the reaction mixture was refluxed for 5 h. After cooling to room temperature, the mixture was poured into 600 ml of H_2O acidified with 12 M HCl and extracted with CH_2Cl_2. The organic layer was washed with a saturated solution of NaCl and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (silica gel, hexane/THF 8.5:1.5) to give cavitand **15** as a white solid (0.380 g) in 42% yield. For $C_{260}H_{440}O_{28}$ (4014.3) calculated: 77.79% C, 11.05% H; found: 77.50% C, 10.69% H. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.87 t, 36 H, CH_3, J = 6.8; 1.25 m, 288 H, $(CH_2)_{12}CH_3$; 1.43 m, 24 H, CH_2^{γ}; 1.73 m, 24 H, CH_2^{β}; 3.31 d, 4 H, $ArCH_{eq}Ar$, J = 12.9; 3.68 m, 8 H, CH_{in}; 3.91 m, 16 H, OCH_2^{α}; 3.97 m, 8 H, OCH_2^{α}; 4.37 m, 8 H, CH_{out}; 4.88 d, 4 H, $ArCH_{ax}Ar$, J = 12.9; 5.34 s, 8 H, $ArCH_2$; 7.12 s, 8 H, ArH; 7.50 s, 4 H, ArH. IR (KBr): 2920 ($C–H_{arom}$), 1718 (C=O), 1208 (C–O), 1118 (ν_{as} C–O), 406 (OCH_2). MS (CI, *m/z*): 4013 (M^-, 100).

Cavitand **17**

3,4,5-Tris{[4-(dodecyloxy)benzyl]oxy}benzoic acid (0.460 g, 0.46 mmol) was added to a solution of **5** (0.100 g, 0.10 mmol) and K_2CO_3 (0.070 g, 0.53 mmol) in dry DMA (40 ml). The mixture was stirred at room temperature for 24 h, then poured into water (300 ml) and acidified with HCl to neutral reaction. The precipitate was filtered off and purified by column chromatography (silica gel, CH_2Cl_2/acetone 99:1) to give cavitand **17** (0.130 g) in 27% yield. For $C_{292}H_{408}O_{40}$ (4558.4) calculated: 76.94% C, 9.02% H; found: 77.21% C, 8.86% H. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.87 t, 36 H, CH_3, J = 6.8; 1.26 bs, 216 H, $(CH_2)_9CH_3$; 1.74 m, 24 H, OCH_2CH_2; 3.34 d, 4 H, $ArCH_{eq}Ar$, J = 12.0; 3.91 m, 24 H, OCH_2; 4.44 d, 4 H, CH_{in}, J = 7.0; 4.56 d, 4 H, $ArCH_{ax}Ar$, J = 12.0; 4.95 s, 8 H, $ArCH_2OAr$, 4.97 s, 16 H, $ArCH_2OAr$; 5.16 s, 8 H, $ArCH_2$DOBOB; 5.95 d, 4 H, CH_{out}, J = 7.0; 6.70 d, 8 H, ArH, J = 8.5; 6.83 d, 16 H, ArH, J = 8.5; 7.19 d, 8 H, ArH, J = 8.5; 7.22 s, 4 H, ArH; 7.29 d, 16 H, ArH, J = 8.5; 7.30 s, 8 H, ArH. MS (MALDI-TOF, DHB matrix, *m/z*): 3998 [M – 2 $OCH_2PhOC_{12}H_{25}$ fragments + Na^+, 100].

Cavitand **18**

3,4,5-Tris{[4-(dodecyloxy)benzyl]oxy}benzoic acid (0.500 g, 0.50 mmol) was added to a solution of **16** (0.115 g, 0.11 mmol) and K_2CO_3 (0.080 g, 0.59 mmol) in dry DMA (40 ml). The mixture was stirred at room temperature for 24 h, then poured into water (300 ml), acidified with HCl to neutral reaction and extracted with CH_2Cl_2. After solvent evaporation the crude product was purified by column chromatography (silica gel, CH_2Cl_2/acetone 99:1) to give ca-

vitand **18** (0.130 g) in 25% yield. For $C_{296}H_{416}O_{40}$ (4614.5) calculated: 77.04% C, 9.09% H; found: 77.41% C, 9.19% H. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.86 t, 36 H, CH_3, *J* = 6.8; 0.98 d, 12 H, CHC**H**$_3$, *J* = 7.5; 1.26 bs, 216 H, (C**H**$_2$)$_9$CH$_3$; 1.75 m, 24 H, OCH$_2$C**H**$_2$; 3.89 m, 24 H, OCH_2; 4.40 d, 4 H, CH_{in}, *J* = 7.0; 4.93 s, 8 H, $ArCH_2OAr$; 4.97 s, 16 H, $ArCH_2OAr$; 5.06 q, 4 H, C**H**CH$_3$, *J* = 7.5; 5.16 s, 8 H, ArCH$_2$DOBOB; 5.96, d, 4 H, CH_{out}, *J* = 7.0; 6.70 d, 8 H, ArH, *J* = 8.5; 6.84 d, 16 H, ArH, *J* = 8.4; 7.18 d, 8 H, ArH, *J* = 8.5; 7.25 s, 4 H, ArH; 7.29 d, 16 H, ArH, *J* = 8.4; 7.30 s, 8 H, ArH. MS (MALDI-TOF, DHB matrix, *m/z*): 4054 [M – 2 $OCH_2PhOC_{12}H_{25}$ fragments + Na^+, 100].

Cavitand **19**

3,4,5-Tris{[4-(dodecyloxy)benzyl]oxy}benzoic acid (0.550 g, 0.55 mmol) was added to a solution of **13** (0.125 g, 0.13 mmol) and K_2CO_3 (0.086 g, 0.62 mmol) in dry DMA (50 ml). The mixture was stirred at room temperature for 24 h, then poured into water (400 ml) and acidified with HCl to neutral reaction. The precipitate was filtered off and purified by column chromatography (silica gel, CH_2Cl_2/acetone 99:1) to give cavitand **19** (0.145 g) in 25% yield. For $C_{296}H_{416}O_{40}$ (4614.5) calculated: 77.04% C, 9.09% H; found: 76.81% C, 9.38% H. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.88 t, 36 H, CH_3, *J* = 6.8; 1.28 bs, 216 H, (C**H**$_2$)$_9$CH$_3$; 1.75 m, 24 H, OCH$_2$C**H**$_2$; 3.32 d, 4 H, $ArCH_{eq}Ar$, *J* = 12.0; 3.65 m, 8 H, CH_{in}; 3.90 m, 24 H, OCH_2; 4.35 m, 8 H, CH_{out}; 4.91 d, 4 H, $ArCH_{ax}Ar$, *J* = 12.0; 4.94 s, 8 H, $ArCH_2OAr$; 4.95 s, 16 H, $ArCH_2OAr$; 5.35 s, 8 H, ArCH$_2$DOBOB; 6.72 d, 8 H, ArH_f, *J* = 8.5; 6.85 d, 16 H, ArH, *J* = 8.5; 7.20 d, 8 H, ArH_g, *J* = 8.5; 7.25 s, 4 H, ArH; 7.26 d, 16 H, ArH, *J* = 8.5; 7.53 s, 8 H, ArHc. MS (MALDI-TOF, DHB matrix, *m/z*): 4054 [M – 2 $OCH_2PhOC_{12}H_{25}$ fragments + Na^+, 100].

X-ray Crystal Structure of Cavitand **12**

The molecular structure of compound **12** was determined by single-crystal X-ray diffraction methods (Fig. 4). Intensity data and cell parameters were recorded at room temperature

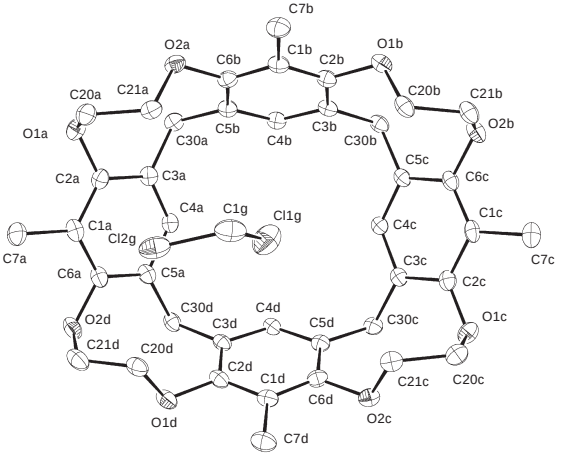


FIG. 4
ORTEP view of the molecular structure of **12** together with the atomic numbering system. Termal ellipsoids are drawn at 10% probability level

(25 °C) on a Siemens AED diffractometer using a graphite monochromatized CuKα radiation and a θ/2θ scan technique. Crystallographic and experimental details for the structure are summarized in Table III. Intensities were corrected for Lorentz and polarization; also an empirical correction for absorption[15] was made (maximum and minimum values for the transmission coefficient are 1 and 0.418). The structure was solved by direct methods using the SIR92 program[16] and refined by full-matrix least-squares procedures (based on F_o^2), using the SHELXL97 program[17]. All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were included in the refinement at idealized geometry (C–H 0.95 Å) and refined "riding" on the corresponding parent atoms. The weighting scheme used in the last cycle of refinement was $w = 1/[\sigma^2 F_o^2 + (0.2000P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Molecular geometry calculations were carried out using the PARST97 program[18]. CCDC 226085 contains the supplementary crystallographic data for this paper. These data

TABLE III
X-ray crystallographic data for **12**

Formula	$C_{40}H_{40}O_8 \cdot 2CH_2Cl_2$
M_w	818.6
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, Å	18.157(5)
b, Å	16.982(5)
c, Å	12.640(5)
Z	4
D_{calcd}, g cm^{-3}	1.395
Linear absorption coeff., mm^{-1}	3.202
F(000)	1712
Crystal size, mm	0.14 × 0.18 × 0.22
Index ranges	$-22 \le h \le 22$, $-20 \le k \le 20$, $-1 \le l \le 15$
θ range for data collection, °	1.64–25.66
Reflections collected	4098
Independent reflections	4098
Observed reflections [$I > 2\sigma(I)$]	2932
Data/restraints/parameters	4098/0/495
Goodness-of-fit on F^2 [a]	1.297
Final *R* indices (obs. data)[b]	$R_1 = 0.0975$, $wR_2 = 0.2829$
R indices (all data)[b]	$R_1 = 0.1128$, $wR_2 = 0.3191$
Largest diff. peak and hole, e Å^{-3}	0.375 and –0.648

[a] Goodness-of-fit $S = [\Sigma\, w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters. [b] $R_1 = \Sigma\, ||F_o| - |F_c||/\Sigma\, |F_o|$, $wR_2 = [\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma\, wF_o^4]^{1/2}$.

can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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