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Polyether-bridged cyclophanes incorporating bisphenol A units as neutral receptors for quats: synthesis, molecular structure and binding properties

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epoc ABSTRACT: Two novel neutral polyoxyethylene bridged cyclophanes (**2a** and **2b**) incorporating bisphenol A units were synthesized and characterized by means of x-ray crystal structure determination. The binding properties of **2a** and **2b** toward tetramethylammonium, *N*-methylpyridinium, and acetylcholine cations were evaluated by means of ^{1}H NMR spectroscopy. Consistent with indications provided by the molecular structure, the cavity in the basket-like cyclophanes is large enough to accommodate the given guest cations conveniently. Circumstantial evidence was obtained that 1,1,2,2-tetrachloroethane is too large to enter the cavity of the smaller cyclophane **2a**, but can be included in the cavity of the larger cyclophane **2b**. Copyright © 2001 John Wiley & Sons, Ltd.
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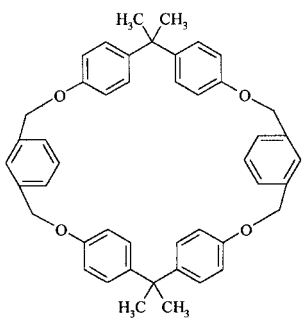
KEYWORDS: cyclophanes; molecular recognition; cation–π interactions; supramolecular chemistry; x-ray crystal structures

INTRODUCTION

The importance of non-covalent interactions between aromatic compounds and positively charged species (cation–π interactions) in the molecular recognition of quats and other cations in both biological and artificial systems is well recognized.[1] Because of the strong desolvation penalty suffered by the reaction partners upon complexation, efficient binding of quats in solution, in the absence of other stabilizing interactions, can only be achieved through multiple interactions with a number of strategically positioned aromatic units. Much work has been devoted in recent years to the design and synthesis of neutral receptors for quats, such as cyclophanes belonging to various structural types,[2–5] cryptophanes,[6] calixarenes,[7] homooxacalixarenes[8] and cyclic peptides incorporating arene units.[9]

We have recently reported[4a] that simple cyclophanes incorporating bisphenol A units such as **1** bind to quats in chloroform solution with low affinity, which was ascribed to the high conformational mobility of these receptors. It was felt that reduction of the conformational mobility of the cyclophane structure by means of polyoxyethylene bridges would hopefully result in a higher level of preorganization of the toroidal cavity defined by the cyclophane structure itself and, consequently, in a substantial improvement of the binding properties towards quats. We therefore synthesised the polyether bridged cyclophanes **2a** and **2b**, determined their x-ray crystal structures and compared their binding properties with those of **1** towards tetramethylammonium (TMA), *N*-methylpyridinium (NMP) and acetylcholine (ACh) salts.



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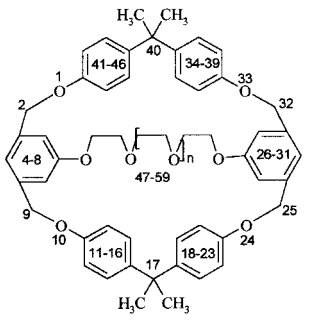

2a n = 1
2b n = 2

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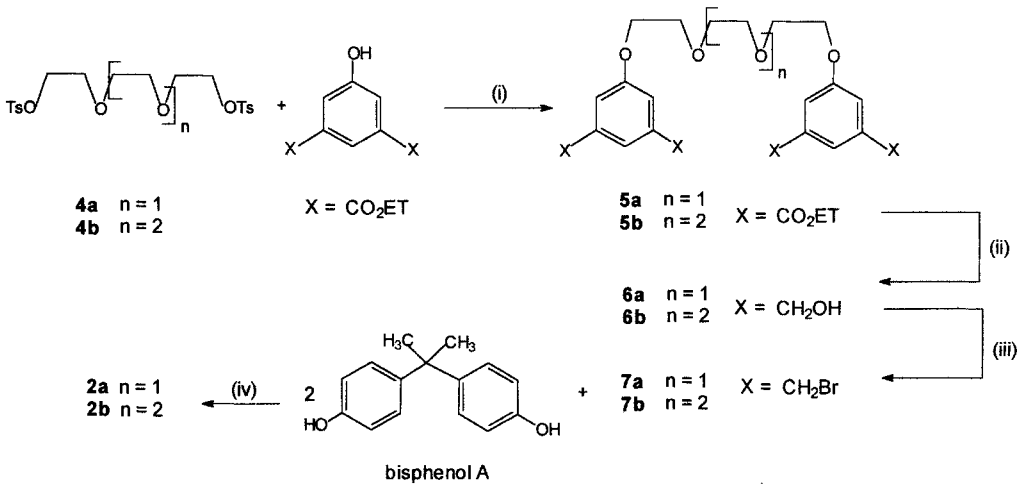

Scheme 1. Synthesis of cyclophanes **2a** and **2b**. (i) K_2CO_3, CH_3CN; (ii) $LiAlH_4$, THF; (iii) PBr_3, dioxane; (iv) KOH, DMSO, high dilution

RESULTS

Syntheses and crystal structures

Cyclophanes **2a** and **2b** were obtained in low yields by reacting 2 mol equiv. of bisphenol A with the corresponding tetra(bromomethyl) compounds **7a** and **7b** under high dilution conditions. The observed low yields are not surprising, because of the occurrence of two intermolecular and two intramolecular covalent bond formations in a single reaction step. Intermediates **7a** and **7b** were prepared by alkylation of the diethyl ester of 5-hydroxyisophthalic acid with tri- and tetraethylene glycol ditosylate, respectively, followed by standard group transformations, as shown in Scheme 1.

Suitable crystals for x-ray diffraction studies of **2a** were obtained by slow diffusion of CH_2Cl_2 into hexane, and of **2b** from a 1:1 mixture of methanol and chloroform. The crystal data are presented in Table 1. In the solid state both cyclophanes adopt a similar, basket-like conformation with the crown ether chains forming the handle and the aromatic moieties the bottom of the basket (Fig. 1). Both cyclophanes crystallize out with a solvent molecule included into the basket-like cavity (CH_2Cl_2 in **2a** and $CHCl_3$ in **2b**). Solvent inclusion is facilitated by weak hydrogen bonding of the solvent molecules to the ether oxygens. In **2a** the dichloromethane interacts weakly with O47, O53 and O56 [C100···047 = 3.596(3), C100···O53 = 3.322(3) and C100···O56 = 3.482(4) Å] and in **2b** the chloroform is weakly hydrogen

Table 1. Crystallographic data for cyclophanes **2a** and **2b**

	2a	**2b**
Empirical formula	$C_{52}H_{54}O_8 \cdot CH_2Cl_2 \cdot 0.5\ C_6H_{14}$	$C_{54}H_{58}O_9 \cdot CHCl_3$
M (g mol^{-1})	934.96	970.37
T (K)	173.0 (2)	173.0 (2)
Crystal system	Triclinic	Monoclinic
Space group	P-1 (No. 2)	$P2_1/c$ (No. 14)
Crystal size (mm)	0.20 × 0.40 × 0.60	0.05 × 0.10 × 0.15
D_{calc} (mg m^3)	1.226	1.292
a (Å)	11.9628(4)	17.3565(6)
b (Å)	15.7064(5)	12.2683(5)
c (Å)	15.9992(3)	24.8724(9)
α (°)	105.442(2)	90
β (°)	108.658(2)	109.669(2)
γ (°)	105.464(1)	90
V (Å^3)	2533.4(1)	4987.2(3)
Z	2	4
μ(mm^{-1})	0.182	0.240
Reflections collected	13501	11626
Unique reflections	8814	11626
R_{int}	0.019	0.000
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.578, −0.239	0.500, −0.347
$R1$, $wR2$ [$I > 2\sigma I$]	0.049, 0.113	0.076, 0.1362
S	1.046	0.987

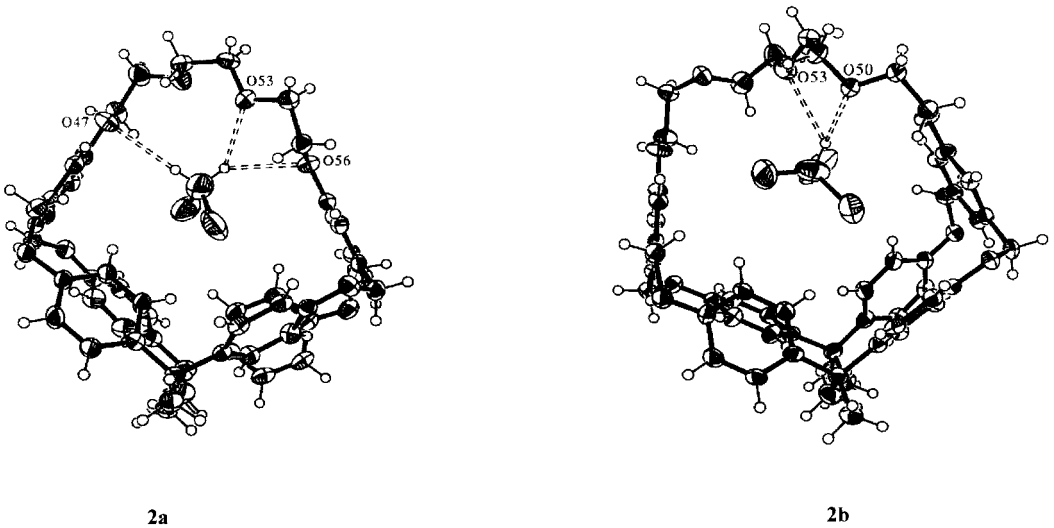

Figure 1. Molecular structures of **2a** and **2b** showing thermal ellipsoids at the 50% probability level. The weak hydrogen bonds of the included dichloromethane and chloroform (only the most populated orientations are shown), respectively, are shown with dotted lines

bonded to O50 and O53 [C100···O50 = 3.273(6) and C100···O53 = 3.407(6) Å]. Both cyclophanes pack into dimeric pairs held together via weak intermolecular C—H···O hydrogen bonds. In **2b** the crown ether chain forms a loop, which is self-complementary to the space between the handle and the bottom of the adjacent basket, giving tennis ball-like dimers (Fig. 2, right). Closest contacts are observed from methylene carbon C2 to O56 and O59 (3.23 and 3.34 Å, respectively). Carbon C2 is located between the electron-withdrawing ether oxygen and aromatic unit, thus giving it a slightly electropositive character and therefore facilitating weak hydrogen bonding with ether oxygens. In addition to these weak interactions between the hosts, the steric efficiency of the packing contributes significantly to dimer formation. The dimers pack into continuous chains with additional close C—H···O contacts between the neighbouring cyclophanes (O10···C55* = 3.33, O1···C2** = 3.35 Å), stabilizing the packing. The shorter crown ether chain of **2a** is not able to assemble itself into the space between the handle and the bottom. Instead, the chain is in close contact with the aromatic ring C34—C39 of the adjacent molecule, giving an arrangement in which the cavities are exactly facing and not slightly shifted as is found in the tennis ball-like structure (Fig. 2, left). The *n*-hexane molecules fill the interstices of the crystal lattice.

Binding studies

Owing to the magnetic anisotropy of the cyclophane aromatic units, ^{1}H NMR spectroscopy is an ideal tool for the detection and measurement of the inclusion of guest species in the cyclophane cavity.[10] Binding studies were carried out by addition of increasing amounts of a very dilute stock solution of quaternary salt to a weighed amount of cyclophane contained in an NMR tube. Maximum host concentrations allowed by solubility

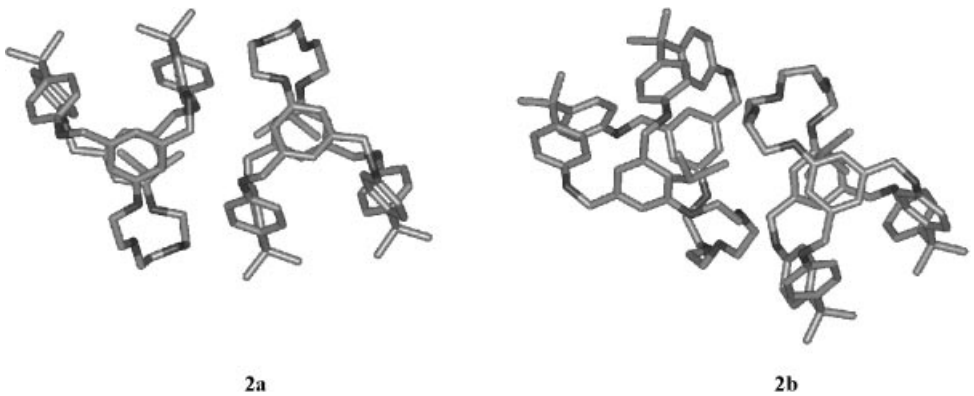

Figure 2. The dimeric packing of **2a** and **2b**. The dimerization of **2b** is tennis ball-like whereas with **2a** the cavities are exactly facing. Hydrogen atoms and *n*-hexane molecules are excluded for clarity

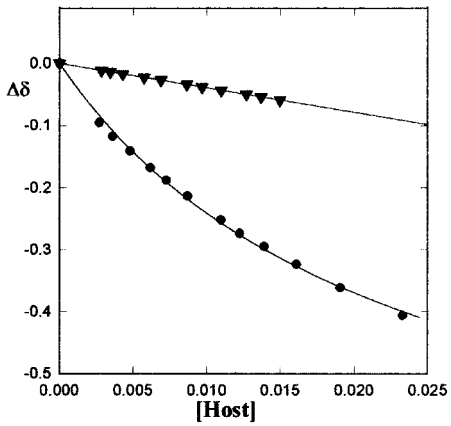

Figure 3. Titration of ACh iodide with host **1** (▼) and host **2a** (●) NCH_3 protons. Points are experimental and curves are calculated

were 25 mM for **2a** and **2b** and 15 mM for **1**. In no case were separate signals for free and bound guest observed. In chloroform solution the signals of the quat protons remained sharp during titration, but substantial line broadening was observed in the experiments carried out in 1,1,2,2-tetrachloroethane. Titration plots obtained with hosts **2a** and **2b** showed in all cases a definite tendency to saturation and were translated into equilibrium constants (K) and limiting upfield shifts ($-\Delta\delta_\infty$) as previously reported.[11] With host **1**, the titration plots showed no appreciable curvature, thus indicating that the fraction of complexed guest was in all cases very small, i.e. $K < 5\ \text{M}^{-1}$. Typical titrations curves are shown in Fig. 3. The results of the titration experiments are summarized in Table 2.

DISCUSSION

The mere inclusion of solvent molecules into their cavity (Fig. 1) clearly indicates the suitability of cyclophanes **2a** and **2b** to host other small molecules of similar size. Indeed, we found (Table 2) that both **2a** and **2b**, unlike **1**, form complexes of definite stability with TMA, NMP and ACh cations, clearly showing that the polyoxyethylene bridges have a profound influence on the preorganization of the cyclophane receptors and, consequently, on their binding abilities toward quats.

The longer polyoxymethylene bridge in **2b** compared with **2a** renders the size of the cavity in the former slightly larger than in the latter, as can be appreciated by visual inspection of the van der Waals surfaces of the crystal structure (Fig. 4), and also shown by the fact that the distance between the bridging benzene rings is 9.52 Å in **2b** and 8.59 Å in **2a**. The above difference does not appear to have a significant influence on the stability of complexes formed by the two cyclophane hosts in chloroform solution (Table 2). The large negative values of the complexation-induced shifts indicate that inclusion of the guests into the host cavity is extensive in all cases. Interestingly, the shift induced in the TMA protons upon complexation with **2a** is larger than that with **2b**, which indicates that the cavity of **2a** is large enough to accommodate the TMA cation conveniently. A similar situation holds for the inclusion of NMP. Here the observed shift patterns suggest that all part structures of the guest are similarly exposed to the shielding zones of the arene units, which is consistent with the idea of a loose host–guest complex,[6] in which the guest retains substantial rotational freedom. The shift patterns observed for the ACh complexes, which are comparable to those observed in analogous complexes with cryptophanes,[6] homooxacalixarenes[12] and calix[5]arenes,[11] suggest that the trimethylammonium head is more deeply buried into the host cavity, whereas the acetoxy tail points towards the exterior. Presumably, the much larger shifts suffered by the NCH_3 and CH_3CO signals of ACh upon complexation with **2b** indicate deeper penetration of ACh into the cavity of the larger cyclophane **2b**.

Enhanced stabilities are seen in 1,1,2,2-tetrachloroethane solution (see footnotes e and f in Table 2) for the complexes of **2a** and **2b** with NMP. Enhancements of host–guest interactions in solvents that are too bulky to solvate the host cavity are well precedented[13] (see also

Table 2. Stability constants (K, M^{-1})[a] and limiting upfield shifts ($-\Delta\delta_\infty$, ppm) for the complexes of hosts **2a** and **2b** with quats in $CDCl_3$ at 30 °C

	TMA[b]		NMP[c]		ACh[d]	
Host	K	$-\Delta\delta_\infty$	K	$-\Delta\delta_\infty$	K	$-\Delta\delta_\infty$
2a	41 ± 2	1.48 (NCH_3)	45 ± 7[e]	1.10 (NCH_3), 1.31 (αCH), 1.63 (γCH)	40 ± 8	0.79 (NCH_3), 0.83 (αCH_2), 0.70 (βCH_2), 0.21 (CH_3CO)
2b	25 ± 4	1.08 (NCH_3)	42 ± 3[f]	1.07 (NCH_3), 1.05 (αCH), 1.03 (βCH), 1.12 (γCH)	35 ± 4	1.38 (NCH_3), 0.73 (CH_3CO)

[a] Errors calculated as $\pm 2\sigma$ (95% confidence limit).
[b] Picrate salt, 1.4×10^{-4} M.
[c] Iodide salt, 1.0×10^{-3} M.
[d] Iodide salt, 2.0×10^{-4} M.
[e] In $(CDCl_2)_2$ $K = 410 \pm 22$, $-\Delta\delta_\infty = 0.90$ (NCH_3).
[f] In $(CDCl_2)_2$ $K = 65 \pm 7$, $-\Delta\delta_\infty = 0.97$ (NCH_3), 1.06 (αCH), 0.99 (βCH), 1.10 (γCH).

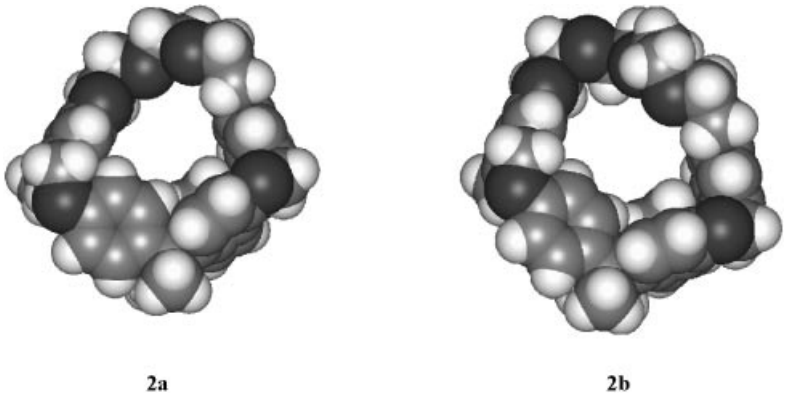

Figure 4. Van der Waals presentation of the empty cavities of **2a** and **2b**

Ref. 11 and references cited therein). These stability enhancements are believed to arise from the lower desolvation penalty suffered by the host upon complexation when the host itself is poorly solvated. On going from chloroform to 1,1,2,2-tetrachloroethane, the complex of NMP with **2a** experiences a 10-fold increase in stability, whereas the corresponding increase for the analogous complex with **2b** is very small. In other words, in marked contrast to the complete lack of selectivity observed in chloroform, in the bulkier 1,1,2,2-tetrachloroethane host **2a** binds to NMP much more strongly than its higher homologue **2b**. This remarkable solvent effect provides a strong indication that the cavity of the smaller cyclophane **2a** undergoes a much stronger desolvation than that suffered by **2b**, which implies that the cavity in **2b**, unlike that in **2a**, is large enough to accommodate a bulky 1,1,2,2-tetrachloroethane molecule. It appears, therefore, that 1,1,2,2-tetrachloroethane acts as a probe providing information about the cavity size in the given cyclophanes.

EXPERIMENTAL

Cyclophane **1** and *N*-methylpyridinium iodide were available from a previous investigation.[4a] Tetramethylammonium picrate was obtained from the corresponding iodide salt by anion exchange with silver picrate. Tri(ethylene glycol) ditosylate (**4a**) and tetra(ethylene glycol) ditosylate (**4b**) were prepared according to a literature method.[14] All other chemicals were reagent-grade commercial samples and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer and TMS was used as an internal standard. Electrospray mass spectra were obtained on a Fisons Instrument VG-Platform benchtop mass spectrometer.

*Compounds **5a** and **5b**.* A mixture of diethyl 5-hydroxyisophthalate (15 g, 63 mmol) and K_2CO_3 (9.3 g, 67 mmol) in 100 ml of CH_3CN was refluxed for 15 min under argon. A solution of the corresponding ditosylate **4** (31 mmol) in 30 ml of CH_3CN was then added and heated at reflux for 16 h. The mixture was poured into water (400 ml) and extracted with $CHCl_3$ (3 × 250 ml). The organic layer was washed with 5% aqueous KOH (6 × 130 ml), dried (Na_2SO_4) and evaporated to give **5** in virtually quantitative yield.

*Tri(ethylene glycol) bis(3,5-diethoxycarbonyl)phenyl ether (**5a**).* ^{1}H NMR ($CDCl_3$), δ 1.41 (t, J = 7.1 Hz, 12 H), 3.78 (s, 4H), 3.91 (m, 4H), 4.23 (m, 4H), 4.40 (q, J = 7.1 Hz, 8H), 7.77 (d, J = 1.4 Hz, 4H), 8.28 (t, J = 1.3 Hz, 2H).

*Tetra(ethylene glycol) bis(3,5-diethoxycarbonyl)phenyl ether (**5b**).* ^{1}H NMR ($CDCl_3$), δ 1.31 (t, J = 7.4 Hz, 12H), 3.66–3.74 (m, 8H), 3.86 (m, 4H), 4.19 (m, 4H), 4.36 (q, J = 7.4 Hz, 8H), 7.74 (s, 4H), 8.24 (s, 2H).

*Compounds **6a** and **6b**.* $LiAlH_4$ (0.76 g, 20 mmol) was added in small portions to a solution of tetraester **5** (4.7 mmol) in dry tetrahydrofuran (250 ml) at room temperature. The mixture was stirred at reflux for 8 h, cooled and quenched first with portions of $Na_2SO_4 \cdot 10H_2O$ and then with H_2O. The inorganic precipitate was removed by filtration and the solvent was evaporated from the filtrate. The residue, a yellow oil, was chromatographed [silica gel, $CHCl_3$–MeOH (85:15)] to give the desired pure product.

*Tri(ethylene glycol) bis(3,5-hydroxymethyl)phenyl ether (**6a**).* This compound was obtained in 66% yield, m.p. 94–95 °C. ^{1}H NMR $(CD_3)_2SO$, δ 3.38 (s, 4H), 3.58 (m, 4H), 3.88 (m, 4H), 4.30 (d, J = 2.3 Hz, 8H), 5.08 (t, J = 2.3 Hz, 4H), 6.63 (bs, 4H).

*Tetra(ethylene glycol) bis(3,5-hydroxymethyl)phenyl ether (**6b**).* This compound was obtained in 73% yield as a yellow oil. ^{1}H NMR $(CD_3)_2SO$, δ 3.65 (m, 8H), 3.83 (m, 4H), 4.17 (m, 4H), 4.56 (d, J = 1.2 Hz, 8H), 5.24 (t, J = 1.2 Hz, 4H), 6.84 (bs, 4H), 6.94 (bs, 2H).

Compounds ***7a*** *and* ***7b***. A solution of PBr_3 (12.97 g, 57 mmol) in dioxane (20 ml) was added at room temperature to a stirred solution of tetraol **6** in dioxane (30 ml). When the addition was complete, stirring at room temperature was continued for 24 h. The mixture was poured in 20 ml of water and stirred for 1 h at 0 °C. It was then extracted with $CHCl_3$ (2 × 100 ml). The organic layer was washed with aqueous $NaHCO_3$, dried and concentrated to give a yellow oil that was chromatographed [silica gel, $CHCl_3$–MeOH (99:1)].

*Tri(ethylene glycol) bis(3,5-dibromomethyl)phenyl ether (****7a****).* This compound was obtained in 72% yield as a solid, m.p. 109–110 °C. ^{1}H NMR ($CDCl_3$), δ 3.74 (s, 4H), 3.84–3.87 (m, 4H), 4.11–4.14 (m, 4H), 4.45 (s, 8H), 6.87 (m, 4H), 6.98 (m, 2H).

*Tetra(ethylene glycol) bis(3,5-dibromomethyl)phenyl ether (****7b****).* This compound was obtained in 63% yield as a yellow oil. ^{1}H NMR ($CDCl_3$), δ 3.67-3.72 (m, 8H), 3.80–3.83 (m, 4H), 4.07–4.10 (m, 4H), 4.38 (s, 8H), 6.84 (m, 4H), 6.96 (m, 2H).

Macrocyclization procedure. A solution of bisphenol A (0.73 g, 3.24 mmol) and 85% KOH (0.43 g, 6.6 mmol) in 120 ml of Me_2SO was kept under stirring at 62 °C for 30 min. A solution of **7a** or **7b** (1.60 mmol) in 40 ml of Me_2SO was added dropwise over 2 h. The mixture was stirred for an additional 7 h at 62 °C, after which it was poured in 250 ml of H_2O and extracted with 450 ml of CCl_4. The organic layer was then washed with water (5 × 400 ml), dried and concentrated.

Cyclophane ***2a***. The crude product was chromatographed twice on neutral alumina, first with hydroquinone-free tetrahydrofuran and then with tetrahydrofuran–hexane, to afford 103 mg (0.128 mmol) of a white solid, 8% yield, m.p. 198–201 °C. ^{1}H NMR ($CDCl_3$), δ 1.55 (s, 12H), 3.69 (s, 4H), 3.80 (m, 4H), 4.01–4.03 (m, 4H), 5.07 (s, 8H), 6.66–6.71 (m, 8H), 6.80 (bs, 4H), 6.88 (m, 2H), 6.99–7.04 (m, 8H). ^{13}C NMR ($CDCl_3$), δ 31.2, 41.5, 67.7, 70.0, 11.3, 114.9, 116.2, 127.6, 140.4, 143.0, 156.5, 159.6. ES-MS, *m/z* 829.4 $(M\ Na)^+$. Calculated for $C_{52}H_{54}O_8$: C 77.44; H 6.69. Found: C 77.27; H 6.58%.

Cyclophane ***2b***. The crude product was chromatographed [silica gel, $CHCl_3$–$(CH_3)_2CO$ (95:5)] to afford 82.5 mg (0.097 mmol) of a white solid, 6% yield, m.p. 75.2–78.6 °C. ^{1}H NMR ($CDCl_3$), δ 1.59 (s, 12H), 3.64 (s, 8H), 3.77–3.79 (m, 4H), 4.01–4.04 (m, 4H), 5.04 (s, 8H), 6.68–6.71 (m, 8H), 6.79 (bs, 4H), 6.85 (m, 2H), 6.99–7.02 (m, 8H). ^{13}C NMR $(CDCl_3)_2$, δ 30.9, 41.5, 67.3, 69.5, 69.8, 70.6, 70.8, 111.6, 114.7, 116.5, 127.5, 139.8, 143.2, 156.3, 159.4. ES-MS, *m/z* 873.43 $(M\ Na)^+$. Calculated for $C_{54}H_{58}O_9 \cdot 2H_2O$: C 73.11, H 7.04. Found: C 73.00, H 6.82%.

Single-crystal x-ray diffraction. The crystallographic data were collected on a Nonius Kappa CCD area-detector diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Lattice parameters were determined from 10 images recorded with 1° φ scans and subsequently refined on all data. The data collections were performed using φ and ω scans with 1° or 2° steps (**2b** and **2a**, respectively), an exposure time of 15 s per frame for **2b** and 30 s per frame for **2a** and a crystal-to-detector distance fixed at 35 mm. The data were processed using DENZO-SMN v0.93.0.[15] No absorption correction was applied.

The structures were solved by direct methods using SHELXS-97[16] and refined on F^2 using SHELXL-97.[17] The hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the carbon temperature factor) and refined as riding atoms. Two chlorine atoms of the included chloroform molecule in **2b** are disordered over two positions with site occupancies of 0.455:0.545. In the structure of **2a** the chlorine atoms of the included dichloromethane and ethyl chain C51—C52 of the cyclophane are disordered over two positions with the occupancies of 0.427:0.573 and 0.698:0.302, respectively.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-153052 and CCDC-153053. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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