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Experimental and Computational Study of Complexes Between Quats and Naphthalenophanes

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A number of neutral cyclophanes incorporating either a 2,6- or a 2,7-dioxynaphthalene unit have been synthesised and their binding properties toward tetramethylammonium and N-methylpyridinium picrates assessed by means of a ^{1}H NMR spectroscopic technique. A parallel computational study based on molecular mechanics and molecular dynamics calculations has been carried out. There is at least a rough agreement between complexation phenomena based on cation–π interactions in solution and molecular mechanics calculations in the gas phase, in that the stability trend seen across the series of naphthalenophane/tetramethylammonium complexes is satisfactorily reproduced. Furthermore, there is a clear corre-spondence between the magnitude of the observed upfield shifts upon complexation and the calculated structures of host-guest complexes.

Keywords: Cation–π; Molecular mechanics; Quat recognition; Naphthalenophanes

INTRODUCTION

There is currently a wide interest in the investigation of cation-π interactions [1], principally on account of the well-recognised role played in the biological recognition of a variety of cationic substrates, including the neurotransmitter acetylcholine [2]. A number of neutral cyclophane hosts have been reported to act as receptors for quaternary ammonium and iminium cations (quats) in lipophilic media, where the cation–π interaction is the sole driving force for association [3]. We have reported [3c] that a number of diphenylmethane based cyclophanes, such as **1a** and **1b**, bind to quats in chloroform solution with low to moderate affinity, which was believed to arise mainly from the high conformational looseness of the hosts. We felt that replacement of one of the diphenylmethane moieties of **1** (**a** or **b**) with more rigid aromatic moieties would substantially reduce the conformational mobility and hopefully enhance the binding properties of the resulting cyclophanes. Inspection of CPK molecular models showed that the thoroidal cavities of naphthalenophanes **2a**, **2b**, **3a**, and **3b** are still wide enough to easily

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accommodate a tetramethylammonium (TMA) cation.

We have therefore synthesised the above naphthalenophanes and investigated their binding properties toward TMA and N-methylpyridinium (NMP) picrates in chloroform solution by means of ^{1}H NMR technique. In order to shed light into the factors that determine the strength of complexation, a parallel computational study based on molecular mechanics and molecular dynamics calculations has been carried out.

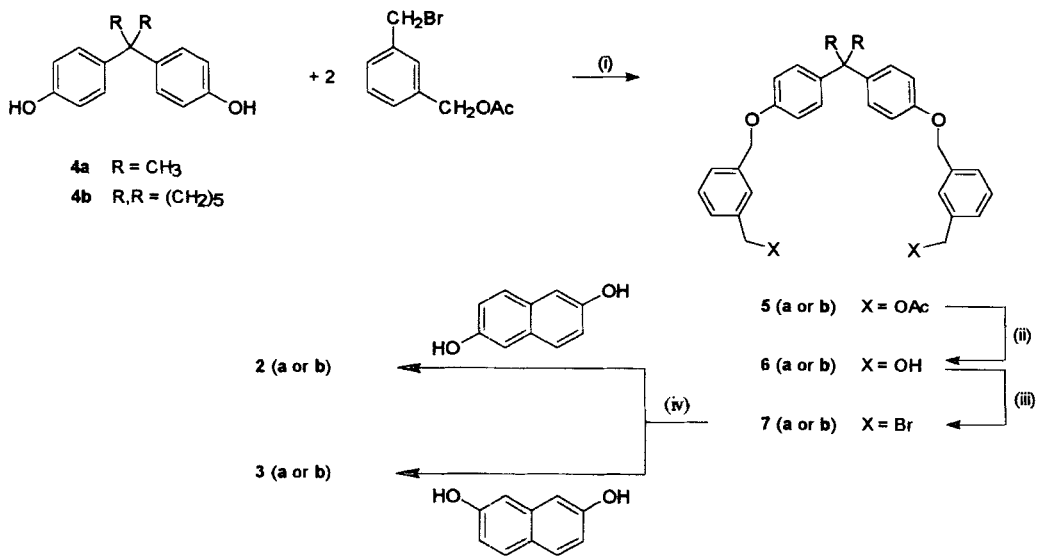
SYNTHESES AND EQUILIBRIUM MEASUREMENTS

The required naphthalenophanes **2** (**a** or **b**) and **3** (**a** or **b**) were obtained in low to moderate yields by reacting 2,6- and 2,7-dihydroxynaphthalene, respectively, with the appropriate α,ω-bifunctional precursor **7** (**a** or **b**). The latter compounds were synthesised by reacting the corresponding bisphenol **4** (**a** or **b**) with 3-bromomethylbenzyl acetate, followed by standard functional group transformation (Scheme 1).

All binding studies were carried out in $CDCl_3$ at 30.0°C by addition of increasing amounts of host solutions to an NMR tube containing a very dilute (0.5–0.7 mM) solution of quat (picrate salt). The final host concentrations were in the range of 21 to 27 mM. Addition of the host caused in all cases regularly increasing upfield shifts ($\Delta\delta$) of the N–Me proton resonances, thus indicating fast complexation on the ^{1}H NMR time scale. Titration data were fitted by means of a nonlinear least squares procedure to the standard binding isotherm of Eq. 1. Best fit values of the limiting upfield shift ($\Delta\delta_\infty$) and equilibrium constant (K_a) were obtained for hosts **2a**, **2b** and **3b** (Tab. I). With host **3a**, however, titration plots showed no significant curvature, indicating that in this case the product K_a[Host] was too small to affect the denominator in the right-hand term of Eq. (1) ($K_a < 5$).

$$\Delta\delta = \frac{\Delta\delta_\infty \mathrm{Ka[Host]}}{1 + \mathrm{Ka[Host]}} \qquad (1)$$

In a control experiment, TMA was titrated with 2,6-dimethoxynaphthalene. The very small



SCHEME 1 Synthesis of naphthalenophanes **2a**, **2b**, **3a** and **3b**. (i) K_2CO_3, KI, CH_3CN; (ii) NaOH, EtOH; (iii) PBr_3, C_6H_6; (iv) K_2CO_3, NaI, 18-crown-6, CH_3CN, high dilution.

TABLE I Stability constants (M^{-1}) and upfield shifts of the guest protons (p.p.m.) for the complexes of hosts **2a**, **3a**, **2b**, **3b** with TMA and NMP picrates in $CDCl_3$ at 30° C

	TMA			NMP		
Host	K_a[a]	$-\Delta\delta_{obs}$[b]	$-\Delta\delta_{\infty}$[c]	K_a[a]	$-\Delta\delta_{obs}$[b]	$-\Delta\delta_{\infty}$[c]
2a	6.2	0.13	1.0	6.0	0.17	1.3
3a	< 5	0.07	-	< 5	0.09	-
2b	9.6	0.35	1.8	9.1	0.35	1.9
3b	9.2	0.12	0.6	5.3	0.16	1.4

[a] Errors in the order of ± 10%.
[b] Observed upfield shift at 25 mM host concentration.
[c] Calculated limiting upfield shift.

chemical shift variations observed in this experiment ($\Delta\delta = -0.02$ p.p.m. at a titrant concentration of 27 mM), actually much smaller than those observed with the naphthalenophanes (Tab. I), rule out the possibility of mere external interactions of the cationic guests with the naphthalene moiety of the macrocyclic hosts.

COMPUTATIONAL PROCEDURE AND RESULTS

The molecular mechanics and dynamics calculations were carried out utilising the force field MM+, an extension of the MM2 force field [4] as implemented in the HyperChem, Release 4.5 for Windows, molecular modelling System [5].

Calculations were carried out *in vacuo* ($\varepsilon = 1.5$) and no cut off value for the nonbonded interactions was used. The nonbonded electrostatic interactions were calculated by using partial atomic charges. A series of molecular mechanics calculations on the benzene-TMA cation system were carried out in order to find the set of partial atomic charges which best reproduce the available energetic [6,7] and structural [7] data for the C–H···π interaction. In Table II results obtained with partial atomic charges calculated by different methods are reported together with experimental and computational data. From comparison of the MM+ results with the experimental ΔH° value and with the high-level *ab initio* complexation energies it appears that the best agreement is obtained with the AM1 charges. Moreover, the distance obtained with this set of charges compares quite well with the value from *ab initio* calculations. For these reasons the AM1 semiempirical method was

TABLE II Energetic and structural results for TMA-benzene interaction[a]

	MM+[b]					*ab-initio*[e]	*ab-initio*[f]
	GM	*AM1*	*PM3*	**OPLS**[c]	**AMBER**[d]	MP2 6-311+G**	MP2 6-31G[00]
ΔE	−4.1	−8.0	−7.1	−6.6	−11.2[g]	−10.2[g]	−9.1
d	4.40	4.25	4.24	4.19	4.10	4.22	4.16

[a] Energies in kcal/mol, distances d, from the nitrogen atom to the centroid of the benzene ring, in Å. The experimental ΔHo value is −9.4 kcal/mol (see Ref. 6 for details).
[b] This work, partial atomic charges obtained from the Gasteiger-Marsili method (Gasteiger, J. and Marsili, M. (1980). *Tetrahedron*, **36**, 3219), *GM*, and from Mulliken population analysis of *AM1* and *PM3* calculations.
[c] Ref. 7a.
[d] Ref. 7b.
[e] Ref. 7c.
[f] Ref. 7d.
[g] ΔH can be obtained from ΔE by adding ΔnRT and the translational, rotational, and vibrational energies. Values of ΔH = −9.9 and −9.5 are obtained from −11.2 and −10.2, respectively. See Refs. 7b and 7c for details.

used to evaluate partial atomic charges for all calculations of cyclophane-TMA complexes.

Additional parameters have been used for the Ar–O–C fragment, because the rotational barrier around the Ar–O bond is not well reproduced by the original MM+ parameters. The new parameters have been obtained by reproducing the rotational barrier around the Ph–O bond in anisole calculated at MP2 level of theory with 6–31G* basis set [8]. In Figure 1 the barriers calculated with our and original parameters are compared with those obtained from *ab initio*, AM1 and PM3 calculations. The new parameters, reported in the Appendix, have been introduced in the force field by defining a new atom type OA as an oxygen atom bound to an aromatic system.

The MM+ force field cannot treat correctly molecules with delocalized π electrons. Therefore the naphthalene moiety is treated in the MM+ force field by using the parameters of the benzene ring. Calculations performed on 2,7-dimetoxynaphthalene, a simple model of the naphthalene fragments present in the cyclophanes under study, gave a distance of 7.35 Å between the two oxygen atoms, which is very similar to the value of 7.31 Å found in the X-ray structure [9]. Since this is a most important feature for the structure of cyclophanes, original parameters of the MM+ force field have been used.

The conformational study of cyclophanes has been performed with the molecular dynamics module of the HyperChem program. For each cyclophane two MD simulations at high temperature (600 and 1200 K) were carried out. In each MD simulation the molecule, previously optimised to a root-mean-square (RMS) energy gradient less than 0.001 kcal mol^{-1} Å^{-1}, was heated up from 0 K to 600 K or from 0 K to 1200 K in 0.5 ps. Then the temperature was kept constant by coupling the system to a simulated bath [10] with a bath relaxation time of 0.5 ps. After an equilibration period of 1 ps, the MD simulation was continued for 100 ps. The coordinates were saved every 1 ps and each structure was cooled to 300 K and then optimised to an energy gradient less than 0.005 kcal mol^{-1} Å^{-1}. Among the 200 structures thus obtained, the lowest energy one was considered. A script program was written to automate the above procedure.

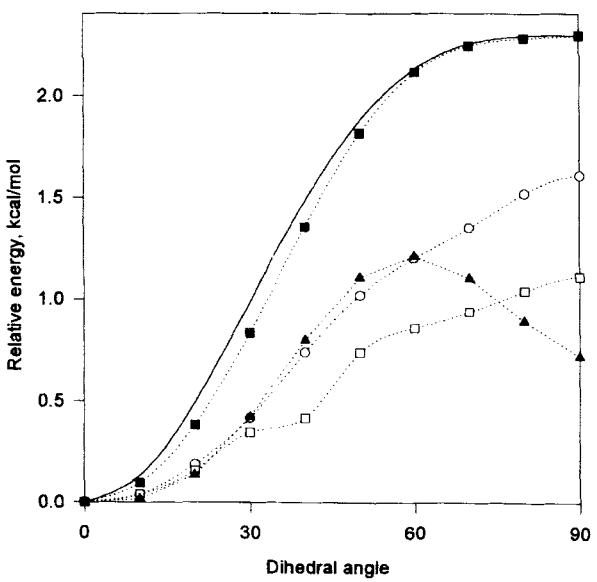


FIGURE 1 Rotational barrier around the Ph–O bond in anisole calculated at different levels of theory: -*ab initio* (MP2/6–31G*); O AM1; □ PM3; ▲ MM+ (AM1 charges, original MM+ parameters); ■ MM+ (AM1 charges, new parameters).

In order to carry out the conformational study of cyclophane-TMA complexes the following docking procedure was devised. The cyclophane was set inside an imaginary cube of side 8 Å and the TMA cation was put in 27 different positions, namely, at the centre of the cube, in the 8 vertices, in the 12 middle points of the edges and in the centres of the 6 faces of the cube. For each position, three orthogonal orientations were considered. The 81 starting geometries thus obtained were optimised to an energy gradient less than 0.01 kcal mol^{-1} $Å^{-1}$ and the lowest energy one was considered. Also in this case a script program was written to automate the above docking procedure.

The results obtained from the calculations are reported in Table III as total steric energies for the free hosts, free TMA cation and for their complexes. The total steric energies of the hosts and the guest in the conformations adopted in the complexes are also reported together with structural information for the complexes in terms of relevant distances [11], *i.e.*, lower than 4 Å, between the methyl carbon atoms of TMA and the centroid of the nearest aromatic rings. The lowest energy structures found for the four complexes are reported in Figure 2, where two orthogonal views of each complex are shown.

In order to discuss the energetic results we need to define two quantities that can be derived from the total steric energies obtained from our force field calculations and will be used to compare computational and experimental results. We define a "complexation energy" as the difference between the energy of the complex and those of the cyclophane and of the tetramethylammonium cation in their lowest energy conformation and an "interaction energy" as the difference between the energy of the complex and those of host and guest at infinite distance in

TABLE III Results obtained from the calculations[a]

	Steric energy	Complexation energy	Interaction energy	Induced strain	d[b]
2a free	−44.80	−27.22	−41.13	13.91	3.463
2a/TMA complex	−72.43				3.611
2a at infinity	−31.03				3.672
TMA at infinity	−0.27				3.740
					3.867
3a free	−51.23	−27.14	−30.48	3.34	3.654
3a/TMA complex	−78.78				3.667
3a at infinity	−47.98				3.684
TMA at infinity	−0.32				3.712
2b free	−21.41	−35.24	−43.74	8.50	3.374
2b/TMA complex	−57.06				3.394
2b at infinity	−13.10				3.432
TMA at infinity	−0.22				3.456
					3.566
					3.583
3b free	−21.55	−33.29	−40.00	6.71	3.369
3b/TMA complex	−55.25				3.652
3b at infinity	−15.09				3.633
TMA at infinity	−0.16				3.670
					3.706
					3.781
TMA free	−0.41				

[a] Energies in kcal/mol.
[b] Relevant Methyl C−π-centroid distances in the complexes, in Å.

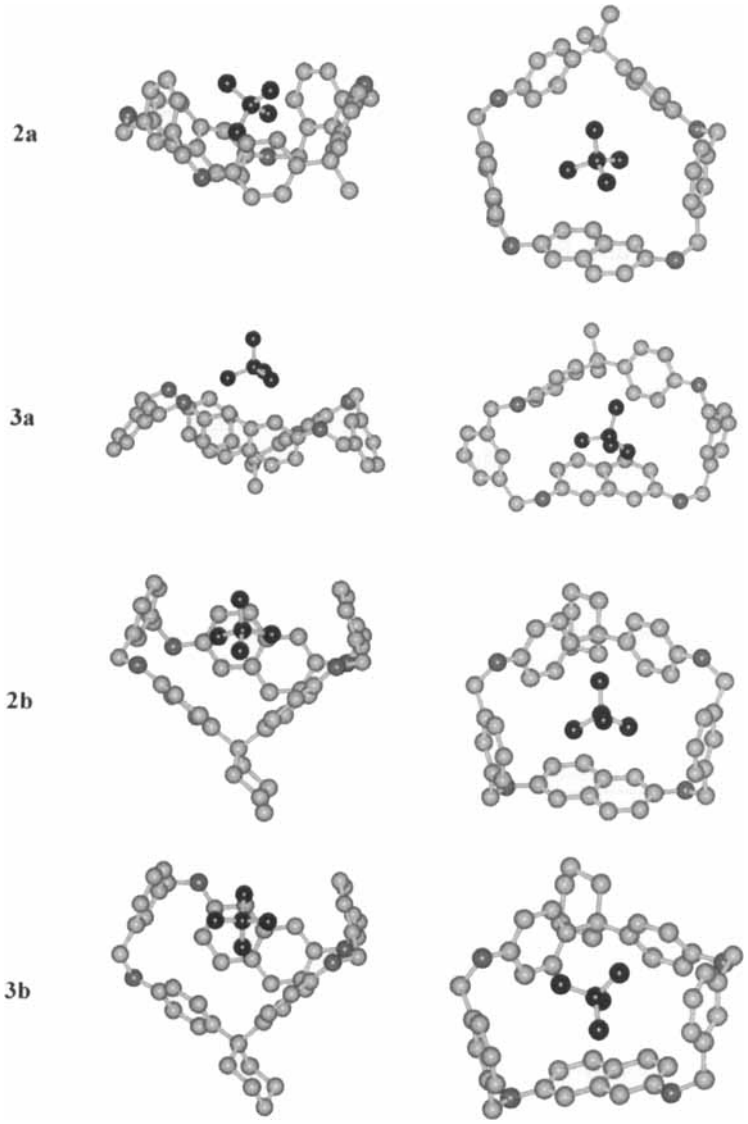


FIGURE 2 Side and top view of the TMA complexes of naphthalenophanes **2a**, **3a**, **2b**, and **3b**, top to bottom respectively (hydrogen atoms omitted, TMA atoms in black). (See Color Plate I).

the same conformation they adopt in the complex itself (see Fig. 3). A third quantity, which is obtained as the difference between the interaction and the complexation energy, is the "induced strain" on both host and guest upon complexation. Such a strain is an indication of how much host and guest have to pay to assume the right conformation for complexation. Also these three quantities are reported in Table III for each complex.

Host–guest complexation is entropically disfavoured not only because one supermolecule is formed from two separate molecules, but also on account of the expected loss of flexibility in the cyclophane host upon complexation. The latter effect has been evidenced by performing two molecular dynamics simulations on cyclophane **2a** and on its complex with TMA. The molecules have been kept at 300 K for 200 ps and the distances between oxygen atoms O1 and O3 and

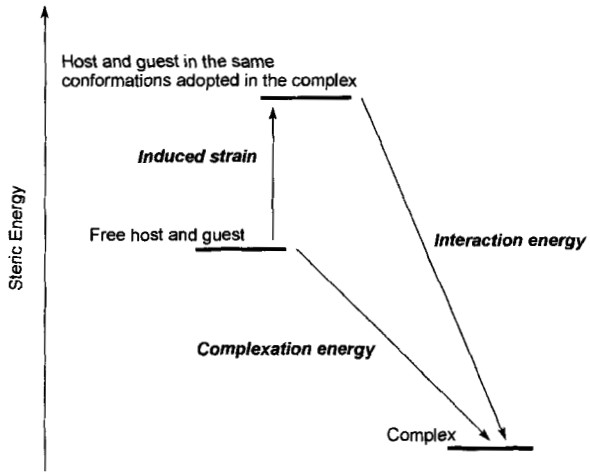


FIGURE 3 Relationship between complexation and interaction energy (see text for details).

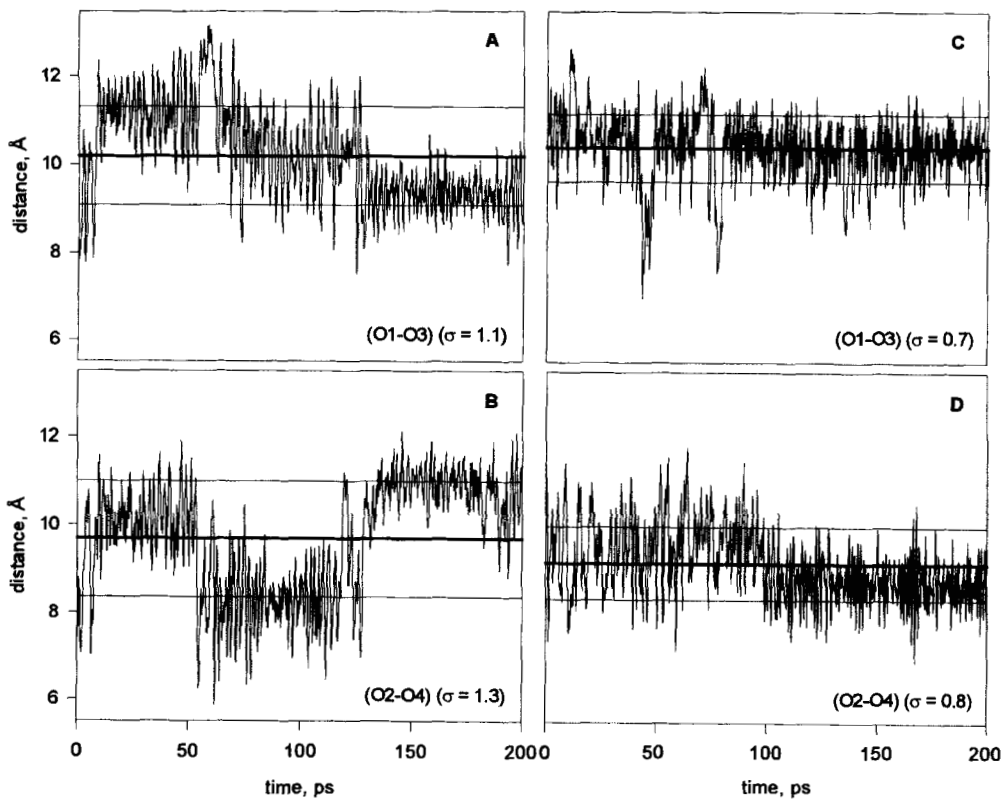


FIGURE 4 Time fluctuations of the O1–O3 and O2–O4 distances in the host **2a** (A and B) and in the complex **2a**/TMA (C and D) as obtained in 200 ps of MD at 300 K. The bold lines indicate the mean values whereas the thin upper and lower lines represent the standard deviation (σ).

between oxygen atoms O2 and O4 have been monitored. These distances and their standard deviations from the mean value are reported in Figure 4. It is evident that the standard deviations of these distances in the complex, 0.7 and 0.8 Å respectively, are smaller than in the

free host, 1.1 and 1.3 Å. Therefore these simulations confirm that the flexibility of the macrocycle is reduced by the presence of the guest.

DISCUSSION

In principle the complexation energy is the computed quantity that should be correctly compared with the experimental binding data. However, since solvent and entropy effects on complexation have not been taken into account in our calculations, it is more correct to compare trends rather than absolute values. In this respect the observed order of binding ability (**2b** $\geq$ **3b** > **2a** > **3a**) is satisfactorily reproduced by the complexation energies order. In particular, both calculations and experimental data confirm the previously observed [3c] favourable influence on complex stability of the closed pentamethylene chain compared with the *gem*-dimethyl group.

Whereas CPK molecular models suggest a complete inclusion of the guest in the thoroidal cavities of the hosts, in the calculated structures (Fig. 2) the guest is not placed completely inside the cavity of the host, but is nesting slightly above the plane of the macrocycle. In the calculated structures most aromatic rings orient their faces towards the TMA cation and this circumstance provides an explanation for the relatively high shielding effects observed in the titration experiments.

There are six relevant distances in the complex **2b**/TMA, which shows the greatest upfield shift. Conversely, the smallest upfield shift is observed in the complex **3a**/TMA, in which the relevant distances are only four, and are in all cases longer that those in **2b**/TMA. This is also evident in Figure 2, showing that the TMA cation sits well above the plane of the macrocycle **3a**.

In conclusion, this study has shown that inclusion phenomena based on cation–π interactions are fairly well simulated by the molecular mechanics calculations even with the simple approach presented in this paper, in which neither the guest's counterion nor the solvent is taken into account. For this reason, calculated energies as such are of limited significance, but the trend in the complexation ability of a related series of hosts is satisfactorily reproduced. Furthermore, the structural information obtained from the simulation is in general accord with the observed shifts.

EXPERIMENTAL SECTION

1,1-Bis(hydroxyphenyl)cyclohexane (**4b**) was available from a previous investigation [3c]. All other chemicals were reagent grade commercial samples and used as such. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer and TMS was used as an internal standard. ES-MS spectra were obtained on a Fisons Instrument VG-Platform benchtop mass spectrometer.

3-Bromomethylbenzyl Acetate

A solution of α,α'-dibromo-*m*-xylene (4.67 g, 17.7 mmol), sodium acetate (1.87 g, 22.8 mmol) and 18-crown-6 (0.40 g, 1.5 mmol) in CH_3CN (95 mL) was heated at reflux (77 h). Most of the solvent was distilled off, and the residue was dissolved in CH_2Cl_2 (110 mL) and washed twice with water. The organic phase was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed with CH_2Cl_2 on silica gel (230–400 mesh) to give the title compound (1.94 g, 45% yield) as a colourless liquid. δ_H(300 MHz, $CDCl_3$): 2.06 (s, 3H), 4.44 (s, 2H), 5.04 (s, 2H), 7.20–7.33 (m, 4H).

2,2-Bis[4-(3-acetoxymethylbenzyloxy) phenyl]propane (5a)

A solution of 3-bromomethylbenzyl acetate (2.39 g, 9.83 mmol), bisphenol A (**4a**) (1.12 g, 4.91 mmol), LiI (0.14 g, 1.0 mmol) and K_2CO_3

(2.83 g, 20.4 mmol) in CH_3CN (25 mL) was heated at reflux under N_2 (24 h). The mixture was then filtered and concentrated to give 2.65 g (98% yield) of the desired product as a colourless oil. δ_H(300 MHz, $CDCl_3$): 1.63 (s, 6H), 2.10 (s, 6H), 5.02 (s, 4H), 5.11 (s, 4H), 6.85–6.88 (d, J = 8.9 Hz, 4H), 7.13–7.16 (d, J = 9.1 Hz, 4H), 7.30–7.41 (m, 8H).

1,1-Bis[4-(3-acetoxymethylbenzyloxy) phenyl]cyclohexane (5b)

This compound was prepared from **4b** (1.07 g, 4.91 mmol) according to the same procedure described for the preparation of **5a**. A partially hydrolysed diester product (2.04 g) was obtained, that was used as such in the next step.

2,2-Bis[4-(3-hydroxymethylbenzyloxy) phenyl]propane (6a)

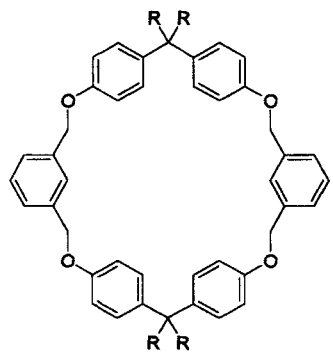
A solution of diacetate **5a** (2.65 g, 4.79 mmol), NaOH (1.93 g, 48.3 mmol) in EtOH (30 mL) was heated at reflux (3 h). After cooling, Et_2O (70 mL) was added, and the resulting solution was washed with water. The organic phase was dried and concentrated to afford 2.12 g (95% yield) of the pure diol as a colourless solid, m.p. 115.6–118.2°C. δ_H (300 MHz, $CDCl_3$): 1.63 (s, 6H), 4.70–4.72 (d, J = 5.9 Hz, 4H), 5.03 (s, 4H), 6.85–6.88 (d, J = 8.9 Hz, 4H), 7.12–7.15 (d, J = 8.9 Hz, 4H), 7.35–7.43 (m, 8H).

1,1-Bis[4-(3-hydroxymethylbenzyloxy) phenyl]cyclohexane (6b)

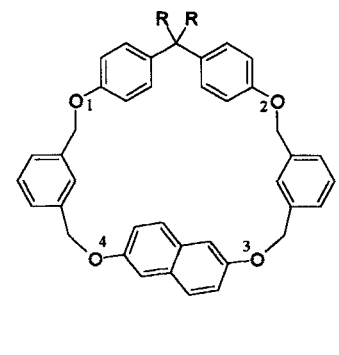
Diacetate **5b** was hydrolysed as described above to give the corresponding diol in 84% yield, m.p. 118.5–121.3°C. δ_H(300 MHz, $CDCl_3$): 1.43–1.55 (m, 6H), 2.19–2.21 (m, 4H), 4.69 (s, 4H), 4.71 (s, 2H), 5.00 (s, 4H), 6.85–6.88 (d, J = 8.9 Hz, 4H), 7.15–7.18 (d, J = 8.9, 4H), 7.30–7.42 (m, 8H).

2,2-Bis[4-(3-bromomethylbenzyloxy) phenyl]propane (7a)

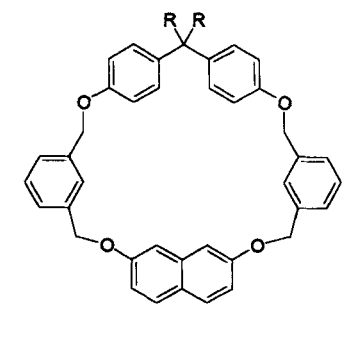
To a stirred solution of diol **6a** (2.12 g, 4.52 mmol) in dry benzene (115 mL) cooled at 0°C and kept under N2, a solution of PBr_3 (0.85 mL, 9.0 mmol) in dry benzene (5 mL) was added dropwise (40 min). When the addition was complete, stirring at room temperature was continued for 16 h. The solution was then washed with aqueous $NaHCO_3$, dried, and concentrated. The residue was chromatographed with $CHCl_3$ on silica gel (230–400 mesh) to give 2.05 g (77% yield) of **7a** as a white solid, m.p. 57.0–58.5° C. δ_H (300 MHz, $CDCl_3$): 1,63 (s, 6H), 4.50 (s, 4H), 5.01 (s, 4H), 6.85–6.88 (d, J = 8.8 Hz, 4H), 7.12–7.16 (d, J = 8.8 Hz, 4H), 7.35–7.45 (m, 8H).



1a R = CH_3
1b R,R = $(CH_2)_5$



2a R = CH_3
2b R,R = $(CH_2)_5$



3a R = CH_3
3b R,R = $(CH_2)_5$

1,1-Bis[4-(3-bromomethylbenzyloxy) phenyl]cyclohexane (7b)

This compound was prepared from diol **6b** in 64% yield according to the same procedure as for **7a**. M.p. 53.8–55.9° C. δ_H (300 MHz, $CDCl_3$): 1.54 (m. 6H), 2.22 (m, 4H), 4,49 (s, 4H), 5.00 (s, 4H), 6.85–6.88 (d, J = 8.9 Hz, 4H), 7.16–7.18 (d, J = 8.7 Hz, 4H), 7.34 (m, 6H), 7.43 (m, 2H).

General Macrocyclization Procedure

A solution of the dibromide (1.68 mmol), dihydroxynaphthalene (0.27 g, 1.7 mmol), NaI (0.30 g, 2.0 mmol), K_2CO_3 (2.87 g, 20.7 mmol), and 18-crown-6 (0.25 g, 0.95 mmol) in CH_3CN (35 mL) was heated at reflux for 24 h. The cooled mixture was filtered and the resulting clear solution was concentrated. The residue was chromatographed with $CHCl_3$ on silica gel to give the naphthalenophane product as a white solid.

Naphthalenophane 2a

This compound was prepared from **7a** and 2,6-dihydroxynaphthalene in 6.5% yield, m.p. 73.0–75.7° C. δ_H (300 MHz, $CDCl_3$): 1.59 (s, 6H), 5.01 (s, 4H), 5.20 (s, 4H), 6.60–6.63 (d, J = 8.7 Hz, 4H), 6.96–7.02 (m, 8H), 7.22–7.44 (m, 10H). δ_C (75 MHz, $CDCl_3$): 31.1, 41.7, 69.5, 70.4, 109.4, 114.7, 119.6, 125.9, 126.3, 127.6, 128.2, 128.7, 129.8, 137.7, 138.1, 143.2, 154.8, 156.2. ES-MS: m/z = 615.7 $(M+Na)^+$. Elemental analysis, Found: C, 82.95; H, 6.27. $C_{41}H_{36}O_4$ requires C, 83.07; H, 6.13.

Naphthalenophane 3a

This compound was prepared from **7a** and 2,7-dihydroxynaphthalene in 16% yield, m.p. 86.6–87.9° C. δ_H (300 MHz, $CDCl_3$): 1.43–1.49 (m, 6H), 2.17 (m, 4H), 5.02 (s, 4H), 5.21 (s, 4H), 6.65–6.68 (d, J = 8.9 Hz, 4H), 6.97–7.04 (m, 8H), 7.27–7.33 (m, 8H), 7.43–7.46 (m, 2H). δ_C (75 MHz, $CDCl_3$): 22.9, 26.4, 31.0, 37.4, 45.2, 69.6, 70.4, 109.4, 114.7, 119.5, 125.9, 126.1, 126.5, 128.0, 128.3, 128.7, 129.8, 137.8, 138.1, 141.1, 154.8, 156.2. ES-MS: m/z = 650.1 $(M+NH_4)^+$; 655.9 $(M+Na)^+$; 671.8 $(M+K)^+$. Elemental analysis, Found: C, 83.31; H, 6.41. $C_{44}H_{40}O_4$ requires C, 83.51; H, 6.38.

Naphthalenophane 2b

This compound was prepared from **7b** and 2,6-dihydroxynaphthalene in 4% yield, m.p. 205–207° C. δ_H (300 MHz, $CDCl_3$): 1.61 (s, 6H), 5.14 (s, 8H), 6.73–6.76 (d, J = 8.7 Hz, 4H), 6.99–7.06 (m, 9H), 7.31–7.36 (m, 5H), 7.62–7.65 (m, 4H). δ_C (75 MHz, $CDCl_3$): 30.6, 41.5, 69.8, 107.1, 114.9, 116.6, 124.5, 125.5, 126.1, 126.2, 127.6, 128.9, 129.2, 135.7, 137.5, 138.0, 143.5, 156.2, 157.1. ES-MS: m/z = 615.8 $(M+Na)^+$. Elemental analysis, Found C, 82.69; H, 6.27. $C_{41}H_{36}O_4$ requires C, 83.07; H, 6.13.

Naphthalenophane 3b

This compound was prepared from **7b** and 2,7-dihydroxynaphthalene in 11% yield, m.p. 220–221° C. δ_H (300 MHz, $CDCl_3$): 1.42–1.62 (m, 6H), 2.22 (m, 4H), 5.12–5.13 (m, 8H), 6.78–6.80 (d, J = 8.9 Hz, 4H), 7.00–7.15 (m, 8H), 7.61–7.64 (m, 2H). δ_C (75 MHz, $CDCl_3$): 22.9, 26.4, 36.9, 69.7, 69.8, 107.1, 114.4, 114.9, 116.7, 125.7, 126.2, 126.4, 127.9, 128.9, 129.1, 137.6, 137.9, 141.4, 156.2, 157.1. ES-MS: m/z = 655.9 $(M+Na)^+$; 671.4 $(M+K)^+$. Elemental analysis, Found: C, 83.14; H, 6.23. $C_{44}H_{40}O_4$ requires C, 83.51; H, 6.38.

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APPENDIX

In this appendix we give the additional parameters used in the molecular mechanics calculations (MM+ force field). The symbol OA represents a new atom type, defined as an oxygen atom bound to a benzene ring.

Stretching, bond (KS, L0, L1, dipole): OA–C4 (5.360, 1.420, 0.000, 0.440), OA–CA (6.000, 1.365, 0.000, 0.001). Bending, angle (KS, type 1, type 2, type 3): H–C4–OA (0.540, 106.700, 106.700, 106.700), C4–OA–CA (0.710, 110.000, 0.000, 0.000), CA–CA–OA (0.700, 121.000, 0.000, 0.000). Torsional, dihedral angle (V1, V2, V3): CA–CA–CA–OA (0.000, 16.250, 0.000), CA–CA–OA–C4 (3.530, 3.000, −2.530), H–C4–OA–CA (0.000, 0.000, 0.530), H–CA–CA–OA (0.000, 16.250, 0.000), OA–C4–CA–CA (0.000, 0.000, 0.000), CA–OA–C4–OA (0.000, 0.000, 0.400). Non bonded, atom type (r^*, ε): OA (1.7400, 0.0500). Out of plane, bond (COPB): OA–CA (0.050).