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A novel cyclophane–anthracene complex

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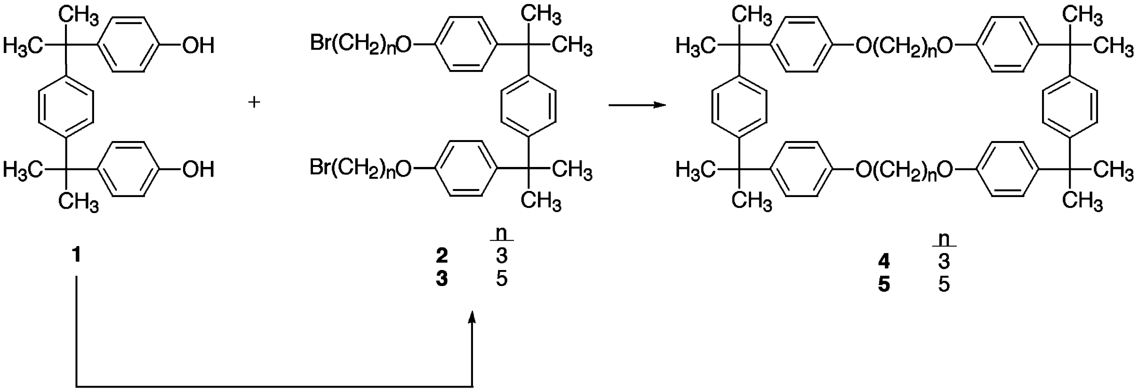
Abstract—A cyclophane host formed by connecting the oxygen atoms of two α,α′-di-(4-hydroxyphenyl)-1,4-diisopropylbenzene units with two pentamethylene spacers forms a unique solid-state complex with anthracene. © 2002 Elsevier Science Ltd. All rights reserved.

In the design and synthesis of new molecular receptors, cyclophanes play an important role.[1,2] Molecular guests are complexed within the central cavities of these macrocyclic receptors. We are using the relatively unexplored bisphenol **1**[3] (Scheme 1) as a π electron-rich, hydrophobic unit for the construction of a new family of cyclophanes.

In connecting the oxygen atoms of two molecules of **1** with two multi-methylene spacers, rigidity of the two α,α′-di-(4-oxyphenyl)-1,4-diisopropylbenzene units should provide open structures in which the dimensions of the central cavity can be systematically varied by changing the number of carbon atoms in the spacers. Complexation of aromatic guests within their central cavities should be facilitated by π interactions with the host molecules. Since it was envisioned that the aromatic guest would be contained within a walled enclosure, such cyclophane hosts are termed 'corrals'.[4]

Recently, we described the preparation of cyclophane host **4** and the solid-state structure for the complex of this corral with a *p*-xylene guest.[4] In this structure, the *p*-xylene guest was encapsulated within the central cavity of the cyclophane.

Changing the number of carbons in the multi-methylene spacers from three to five should expand the central cavity in the cyclophane so it can complex larger aromatic guest molecules. We now report the synthesis of host **5** and the solid-state structure of its complex with an anthracene guest.



Scheme 1. Two-step synthesis of cyclophane host **5**.

Keywords: host–guest; molecular recognition; solid-state structure.

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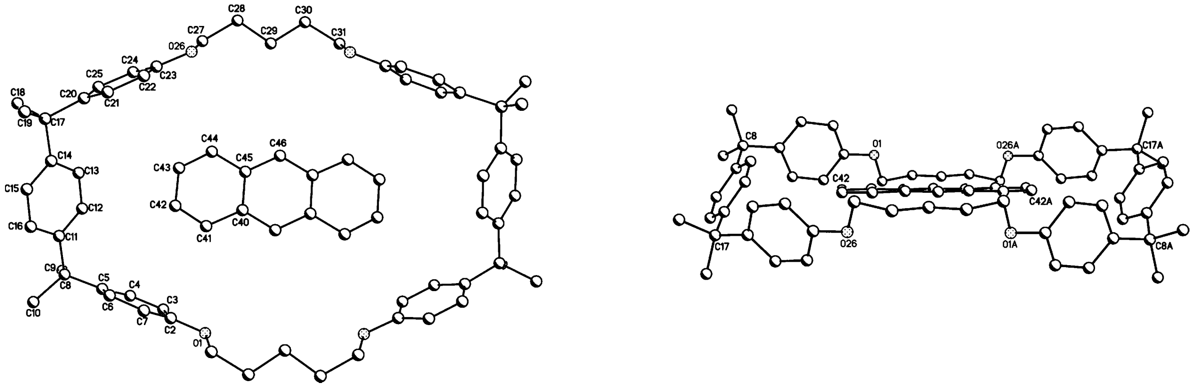
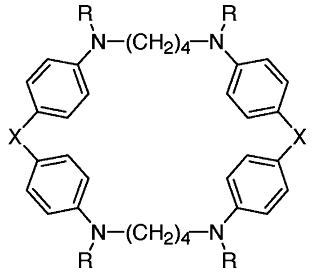


Figure 1. Top (left) and side (right) view for the solid-state structure of the **5**-anthracene complex.

Reaction of bisphenol **1** with a large excess of 1,5-dibromopentane and potassium carbonate in DMF at room temperature for 15 h gave an 80% yield of dibromide **3**.[5] A mixture of equivalent amounts of bisphenol **1** and dibromide **3** with cesium carbonate in DMF was stirred at 60–70°C for 6 days to provide a 70% yield of cyclophane **5**[7] as a white solid.

By ^{1}H NMR spectroscopy,[9] no complexation of toluene, *p*-xylene, or naphthalene molecules by cyclophane **5** in deuteriochloroform was evident. However, mixing of deuteriochloroform solutions of the cyclophane host and anthracene gave an immediate formation of a white crystalline precipitate with a melting point similar to that of host **5**. Under more controlled conditions, crystals were grown by slow evaporation of a chloroform–dichloromethane solution of equimolar cyclophane **5** and anthracene. Combustion analysis of the crystals revealed a one-to-one complex of host **5** and anthracene guest.[10] In contrast, no complexes were formed by slow evaporation of chloroform–dichloromethane solutions of **5** and naphthalene, phenanthrene, or pyrene. Crystals suitable for structure determination by X-ray diffraction were obtained by slow evaporation of the chloroform–dichloromethane solution of equimolar **5** and anthracene and the solid-state structure for the **5**-anthracene complex was determined.[11] Computer drawings of top and side views are shown in Fig. 1. As is readily evident, the anthracene guest is encapsulated within the cavity of the cyclophane host. The dihedral angles between the planes of the three benzene rings at each end of the cyclophane host are 73.9, 95.3, and 133.7° for ring 1–ring 2, ring 2–ring 3, and ring 1–ring 3 (ring 3 is the C20–C25 benzene ring). The dihedral angle between the least-squares planes of the host and guest is 18.8°. Both the host and the guest lie about the same inversion center. The cyclophane cavity has a rectangular shape with dimensions of approximately 15 Å (C12a···C13) for one side and approximately 10 Å (C3···O26) for the other. This provides sufficient space for the anthracene guest to lie nearly flat in the middle of the intramolecular cavity of the host with the terminal edges of the anthracene pointing toward the aromatic portions of the host. The distances from the centroid of ring 3 to the nearest proton of the guest is 3.01 Å (centroid of ring 3···H43) and the dihedral angles between the least squares plane of the guest and benzene rings 1, 2, and 3 are 77.5, 124.6, and 61.7°, respectively. This suggests edge-to-face π interactions[14,15] between the guest and benzene rings 1 and 3 of the host in the complex.



	X	R
6	CH_2	H
7	O	C_5H_{11}

Figure 2. Host molecules for reported cyclophane–aromatic quest complexes.

Koga and co-workers have determined the solid-state structure of a complex of durene[16] with related cyclophane **6** (Fig. 2) and assessed interactions of this cyclophane host with naphthalene in acidic aqueous solution.[17] In both the solid state and in solution, the aromatic guest was perpendicular to the plane of the host. A similar perpendicular arrangement was calculated for the complex of benzene with the *N*-alkylated analogue **7**.[18] Therefore, the nearly coplanar arrangement of the host and guest planes in the **5**-anthracene complex is quite unexpected. Studies to determine the causative factor(s) for this unusual orientation of the aromatic guest within the cyclophane host cavity are in progress.

Acknowledgements

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5. A mixture of bisphenol **1**[6] (1.73 g, 5.0 mmol), 1,5-dibromopentane (15.0 g, 0.10 mol), and freshly ground potassium carbonate (5.0 g) in DMF (50 ml) was stirred at room temperature for 15 h and filtered. The filtrate was evaporated to dryness in vacuo and the residue was dissolved in dichloromethane. The solution was washed twice with water, dried over $MgSO_4$, and evaporated in vacuo. Chromatography of the residue on silica gel with hexane–dichloromethane (1:1) as eluent gave an 80% yield of dibromide **3** as a white solid with mp 86–88°C. ^{1}H NMR (200 MHz) δ ($CDCl_3$)1.63 (s, 12H), 1.69–1.99 (m, 12H), 3.43 (t, 4H, $J=6.7$ Hz), 3.94 (t, 4H, 6.3 Hz), 6.78, 7.14 (dd, 8H, $J=8.8$ Hz), 7.09 (s, 4H). Anal. calcd for $C_{34}H_{44}Br_2O_2$: C, 63.36; H, 6.88. Found: C, 63.58; H, 6.77%.
6. Purchased from TCI America of Portland, OR, USA.
7. A mixture of dibromide **3** (0.65 g, 1.00 mmol), bisphenol **1** (0.35 g, 1.00 mmol), Cs_2CO_3[8] (2.15 g), and DMF (400 ml) was stirred at 60–70°C for 6 days under nitrogen. The mixture was evaporated in vacuo and dichloromethane and water were added to the residue. The organic layer was separated, washed with water, dried over $MgSO_4$, and evaporated in vacuo. Chromatography of the residue on silica gel with hexane–dichloromethane (1:1) as eluent provided a 70% yield of cyclophane **5** as a white solid with mp 234–238°C. ^{1}H NMR (200 MHz) δ ($CDCl_3$) 1.62 (s, 24H), 1.62–1.90 (m, 12H), 3.90 (t, 8H), 6.74, 7.08 (dd, 16H, $J=8.8$ Hz), 7.09 (s, 8H). Anal. calcd for $C_{58}H_{68}O_4$: C, 84.02; H, 8.27. Found: C, 84.02; H, 8.34%.
8. Purchased from Chemetall GMBH, marketed in the USA by CM Chemical Products, Inc. of Berkeley Heights, NJ, USA.
9. Wilcox, C. S. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J.; Dürr, H., Eds.; VCH: New York, 1991; pp. 123–143.
10. Mp 227–233°C. Anal. calcd for $C_{72}H_{78}O_4$: C, 85.84; H, 7.80. Found: C, 86.19; H. 7.52%.
11. Diffraction data for the single crystal (0.6×0.25×0.1 mm) were collected with a Siemens R3M/V automated diffractometer with Mo Kα radiation ($\lambda=0.71073$ Å). The structure was solved using the direct-methods program contained in the SHELXTL-PLUS program package.[12] Final refinement and display of the structures were performed using the SHELXTL PC program package.[13] Crystal data for **5**-anthracene: formula $C_{72}H_{78}O_4$, $F_w=1007.34$, monoclinic, space group $C2/c$, $a=44.78(2)$, $b=6.361(3)$, $c=21.103(8)$ Å, $\alpha=90$, $\beta=110.74(3)$, $\gamma=90°$, $V=5621(4)$ Å^3, $Z=4$, $D_{calcd}=1.190$ mg/m^3, $R_1=0.0633$, $wR_2=0.1046$ ($I>2\sigma(I)$). A CIF file with data for **5**-anthracene has been deposited, CCDC reference code: 181852.
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