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The Synthesis of a Novel Iptycene Containing the Triphenylene Unit

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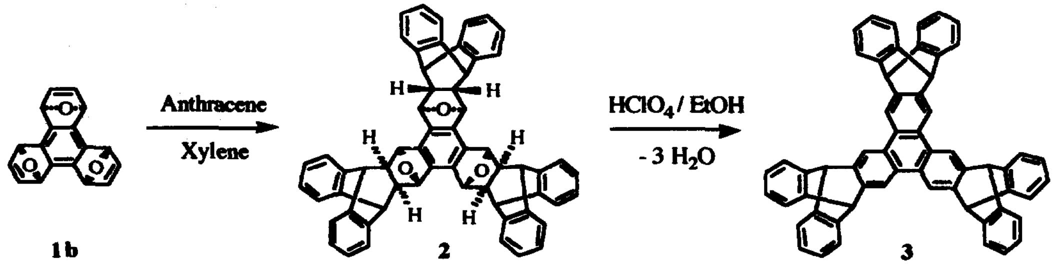
Abstract: A novel hydrocarbon composed of three 9,10-dihydroanthracene units fused to the three pairs of β positions on a central triphenylene ring has been synthesised. The molecule defines two large cup-shaped cavities lined with π-electron systems.

Iptycenes[1] are rigid molecules which contain several triptycene units. The synthesis and properties of numerous examples of this class have been described by Hart and coworkers[1,2] in the recent years. Iptycenes have been classified[3] on the basis of the number of different independent aromatic planes that are present in the molecule, and of the types of aromatic units bearing the 9,10-dihydroanthracene residues. Iptycenes containing naphthalene and anthracene have been synthesized previously.[1,2] Here we describe the synthesis of a heptiptycene based on the triphenylene nucleus.

The endocyclic double bond of 7-oxanorbornene - and of compounds that contain such a moiety - behaves as a dienophile and undergoes the Diels-Alder reaction with a variety of dienes with high facial diastereoselectivity.[4] A recently improved synthesis[5] of *syn* and *anti* triphenylenetrisendoxides **1a/b** encouraged us to explore the use of the *anti* isomer[6] **1b** for the rapid assembly of the hepiptycene **3** by means of a triple Diels-Alder reaction followed by acid-catalyzed triple dehydration (Scheme).



Scheme

The reaction of **1b** with 3.5 molar equivalents of anthracene (refluxing xylene, 48 h, under an argon atmosphere) gave the tris-adduct **2**, which was isolated (38% based on **1b**) by column chromatography (SiO_2, toluene/ethyl acetate 9/1) as the most chromatographically-mobile fraction after anthracene. The ^1H NMR spectrum[7] of **2** (300 MHz, C_6D_6) shows the two pairs of methine hydrogen atoms, belonging to the

7-oxanorbornane residues having the relative *syn* stereochemistry of the oxygen bridges, as two overlapping AB systems in which the A and the B parts are coupled only with a small coupling constant (2.7 Hz) with the adjacent oxymethine hydrogen atoms (2xABMX systems). The corresponding protons of the third 7-oxanobornane unit appear as broad signals. These data provide evidence[4] for the *endo* configuration of all the methine hydrogen atoms of the 7-oxanorbornane moieties of **2**. The ^{13}C NMR. spectrum (75.46 MHz, CDCl$_3$) shows 26 resonances, including four overlapping signals for the 30 heterotopic carbon atoms present in **2**.

The triple dehydration of **2** with acetic anhydride/hydrochloric acid gave a mixture of partially dehydrated and acetylated products, but proceeded satisfactorily when **2** was suspended in ethanol containing 20% of concentrated perchloric acid and refluxed for 12 h. Treatment of the crude mixture with aqueous sodium bicarbonate promoted the precipitation of a white solid which was filtered off, and subjected to column chromatography (SiO$_2$, hexane/toluene gradient) to give a white solid (40%) which was characterized as the heptiptycene **3**. The ^{1}H NMR spectroscopic data for **3** are consistent[8] with its D_{3h} symmetry showing only four types of resonances for the four sets of homotopic hydrogen atoms.

Heptiptycene **3** has some interesting features compared to other members of this class of compounds described in the literature: i) to the best of our knowledge, the central unit - triphenylene - is the largest aromatic polycyclic hydrocarbon ever included in the structure of higher iptycenes; ii) the molecule has two equivalent cup-shaped cavities lined with π-electron systems large enough to accommodate a six-membered ring; iii) the 9,10-dihydroanthracene moieties provide barriers that should impose steric selectivity upon the complexing ability of triphenylene[9] towards numerous aromatic compounds.

We are currently investigating the potential use of **3** as a host for aromatic substrates.

References and Notes

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2. (a) Shahlai K., Hart H., and Bashir-Hashemi A., *J.Org.Chem.*, **1991**, 56, 6912-6916; (b) Shahlai K. and Hart H., *J.Org.Chem.*, **1991**, 56, 6905-6912, and references therein.
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4. (a) Ashton P. R., Brown G. R., Isaacs N. S., Giuffrida D., Kohnke F. H., Mathias J. P., Slawin A. M. Z., Smith D. R., Stoddart J. F., and Williams D. J., *J.Amer.Chem.Soc.*, **1992**, 114, 6330-6353 and references therein; (b) Ashton P. R., Girreser U., Giuffrida D., Kohnke F. H., Mathias J. P., Raymo F. M., Slawin A. M. Z., Stoddart J. F., and Williams D. J., *J Amer.Chem.Soc.*, **1993**, in press, and references therein..
5. (a) Raymo F., Kohnke F. H., Cardullo F., Girreser U., and Stoddart J. F., *Tetrahedron*, **1992**, 48, 6827-6838; (b) The triphenylene trisendoxydes **1a/b** were previously synthesized by Stringer M. B. and Wege D., *Tetrahedron Lett.*, **1980**, 21, 3831-3834.

6. Both **1a** and **1b** can be used for the synthesis of **3**, since the relative stereochemistry of the oxygen bridges is lost in the dehydration step. However, **1b** is more readily available than **1a** (see ref. 5a).
7. ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ: 7.41-6.88 (24H, m), 4.87 (2H, bs), 4.83 (2H, bs), 4.78 (2H, s), 4.17 (2H, X part of 2xABMX systems, J_{AX}= 2.7, J_{BX} = 0, J_{MX} = 0 Hz), 4.05 (2H, bs), 3.92 (2H, M part of 2xABMX systems, J_{BM} = 2.7, J_{AM} = 0, J_{MX} = 0 Hz), 2.13 (2H, B part of 2xABMX systems, J_{AB} = 8, J_{BM} = 2.7, J_{BX} = 0 Hz), 1.84 (2H, A part of 2xABMX systems, J_{AB} = 8, J_{AM} = 0, J_{AX} = 2.7 Hz), 1.69 (2H, bs); ^{13}C NMR (CDCl$_3$, 75.46 MHz) δ: 143.8, 143.7, 143.7, 141.4, 141.3, 141.2, 135.3, 135.1, 135.01, 126.1, 126.0, 125.9, 125.8, 125.8, 125.6, 123.8, 123.7, 123.6, 123.5, 123.5, 123.4, 79.6, 79.6, 79.3, 48.7, 48.6, 48.5, 47.4, 47.3, 47.2; MS (EI): m/e= 810 (M$^+$); m.p from acetone: 406 °C (dec.).
8. ^{1}H NMR(CDCl$_3$, 300 MHz) δ: 8.57 (6H, s), 7.45-7.42 (12H, m), 7.02-6.99 (12H, m), 5,61 (6H, s); ^{13}C NMR (CDCl$_3$, 75.46 MHz) δ: 144.9, 143.1, 127.4, 125.3, 123.6, 117.8, 54.2; MS (positive ion FAB): m/e 756 (M$^+$); did not melt when heated up to 410°C.

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