Centropentaindan: Synthesis and Some Bridgehead Transformations of a Novel Regular Centropolyindan

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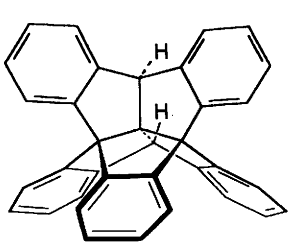
The synthesis of a novel centropentacyclic hydrocarbon, centropentaindan **1**, has been achieved by fourfold bromination of the readily available *difuso*-triindan **4** followed by $AlBr_3$-catalysed condensation with two molecules of benzene; functionalization of the two remaining tertiary bridgehead positions of **1** gives the strained, labile dibromide **6**, which has been converted into the dimethyl derivative **7**, the centrohexacyclic endoperoxide **8**, and, again by $AlBr_3$-catalysed condensation with benzene, into centrohexaindan **2**.

Among the regular centropolyindans,[1,2] all possible members have been synthesized in recent years except for one: centropentaindan **1**. This hydrocarbon, bearing five benzo nuclei at a centropentaquinane core, represents the next-lower congener of the highest member of the centropolyindan family, centrohexaindan, **2**, which has been obtained for the first time from tetrabenzo[5.5.5.5]fenestrane (fenestrindan) **3**[3,4] by bridgehead bromination and Lewis acid-catalysed condensation with two molecules of benzene.[5]

The parent centropentaquinane has remained unknown to date, and only very few organic compounds with centropentacyclic frameworks have been described.[6,7] Here, we report the first synthesis of the parent pentabenzo analogue, **1**, and some of its conversions at the two bridgehead positions, including the introduction of a single molecule of benzene to give centrohexaindan **2**.

The synthesis of **1** comprises only five steps starting from indan-1,3-dione. A three-step method leads to the *difuso*-triindan **4** as described in detail previously.[4,8] While selective bromination of the benzylic methine and methylene C–H bonds of **4** proved to be difficult,[9] we succeeded in converting it into a mixture of stereoisomeric tetrabromides **5** by using 4 equiv. of the reagent (Scheme 1). This is remarkable because of the inevitable presence of a *syn*-1,3-dibromo grouping in **5** which should be sterically unfavourable. In fact, attempts to introduce even more than four bromine substituents at the central neopentane core of **4** appears to be largely suppressed owing to steric reasons. Subsequent treatment of crude **5** with an excess of aluminium tribromide in benzene solution gives rise to a clean twofold incorporation of benzene giving the title compound **1**, which is isolated in excellent yield (88% based on **4**).



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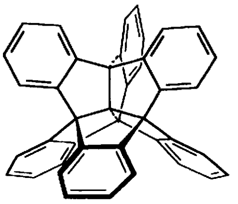
The identity of **1** is clearly confirmed by spectrometry.† In particular, the molecular C_{2v} symmetry of **1** effects the fourfold degeneracy of the arene ^1H and ^{13}C resonances of the fenestrindan subunit (*cf.* **3**) and twofold degeneracy of those of the remaining benzeno bridge as well as of the α-C atoms of the neopentane core. The nucleus of the unique *centro*-C of **1** resonates at δ 83.17, that is, nearly halfway between the chemical shifts for the lower and higher congeners (**3**, δ 71.93,[3,4] and **2**, δ 95.43[5]).

Besides the fenestrindan subunit, the structure of **1** comprises two mutually-fused tribenzotriquinacene moieties, which render its polycyclic skeleton highly rigid. As a consequence, the two remaining bridgehead benzhydrylic C–H bonds at C(8b) and C(16b) are oriented strictly *syn* within the plane containing the central C(16d) atom. Nevertheless, and much to our surprise, bromination of **1** with bromine (2 equiv.) may be achieved to give the 8*b*,16*b*-dibromocentropentaindan **6**. This dibromide is stable as a crystalline material stored for a few days under argon but decomposes readily in solution. The lability of **6** clearly reflects the unfavourable bis-functionalization of the two bridgehead positions with bulky bromine atoms.

In spite of the steric strain in **6**, several conversions of the bridgehead functionality were performed in analogy to



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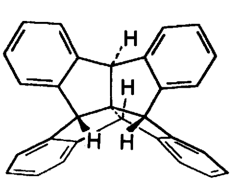

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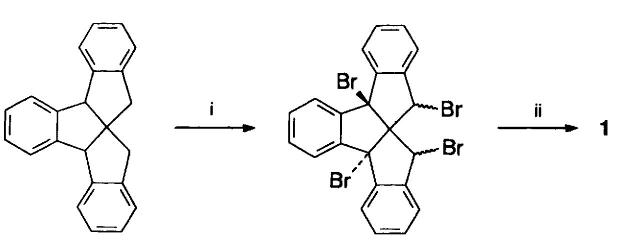
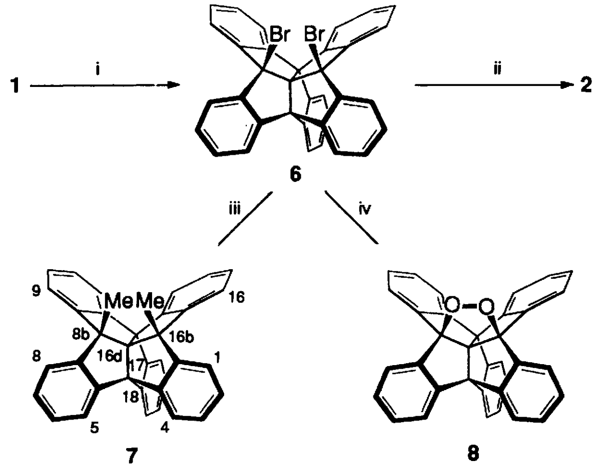


Scheme 1 *Reagents and conditions*: i, Br_2 (4 equiv.), CCl_4, hν, heat; ii, $AlBr_3$ (6 equiv.), benzene, 7 days, 25 °C (yield 88% from **4**)



Scheme 2 *Reagents and conditions*: i, Br_2 (2 equiv.), CCl_4, hν, heat; ii, $AlBr_3$, benzene, 5 days, 25 °C (yield 57% from **1**); iii, $AlMe_3$, *n*-hexane, 1 h, heat; iv, Bu^tOOH, $AgBF_4$, CH_2Cl_2, 30 min, 25 °C (yields of **7** and **8** both 55% from **1**)

previous results.[10] For example, **6** is quenched by treatment with trimethylaluminium in hexane to give 8*b*,16*b*-dimethylcentropentaindan **7** in good yield; similarly, Ag^{I}-assisted condensation of **6** with *tert*-butylhydroperoxide leads to endoperoxide **8** (Scheme 2), which represents another member of the growing family of topologically nonplanar organic compounds.[10–14]

While attempts to prepare centrohexaindan **2**, in analogy to the sequence **4** → **5** → **1**, by sixfold bromination of **4** and subsequent condensation with three molecules of benzene failed, **2** is obtained in good yield by Lewis acid-catalysed condensation of **6** with benzene (Scheme 2). Thus, the twofold sequential bromination/condensation approach **4** → **5** → **1** → **6** → **2** presented here provides a new, efficient synthesis of centrohexaindan **2**, which can be obtained now in seven steps and with 40% overall yield from indan-1,3-dione.[15]

The synthesis of centropentaindan **1**, as the last hitherto unknown regular centropolyindan, has been achieved following a remarkably short and efficient route. The facile accessibility of **1** promises the synthesis and investigation of a variety of interesting bridgehead functionalized derivatives bearing strictly 1,3-*syn* orientated substituents at the rigid framework as well as the synthesis of various 8b,16b-bridged, centrohexacyclic derivatives of **1**.

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Footnote

† All new compounds except **6** (see text) gave satisfactory combustional or high-resolution analyses. Selected physical data for **1**, **7** and **8**. [All ^{1}H NMR measured at 300 MHz ($CDCl_3$) and ^{13}C NMR at 75 MHz ($CDCl_3$) unless otherwise stated.]

1: mp 326 °C. ^{1}H NMR: δ 5.08 (s, 2 H, 8b-H, 16b-H), 7.16 and 7.66 [AA′BB′, 4 H, 20(21)-H and 19(22)-H, resp.], 7.21–7.31 [m, 8 H, 2(3,6,7,10,11,14,15)-H], 7.50 [d, ${}^{3}J$ 6.7 Hz, 4 H, 1(8,9,16)-H], 7.86 [d, ${}^{3}J$ 7.1 Hz, 4 H, 4(5,12,13)-H]; ^{13}C NMR: δ 61.8 [d, C-8b(16b)], 76.3 [s, C-4b(12b)], 83.2 (s, C-16d), 123.4 (d), 123.5 (d), 124.6 (d), 128.1 (d), 145.0 (s), 147.5 (s), 148.3 (s); MS (EI, 70 eV): *m/z* 442 (100, $M^{+\cdot}$), 365 (5), 221 (13).

7: mp 396–400 °C (subl.); ^{1}H NMR: δ 2.07 (s, 6 H, CH_3), 7.06 and 7.52 [AA′BB′, 4 H, 20(21)-H and 19(22)-H, resp.], 7.25–7.29 [m, 8 H, 2(3,6,7,10,11,14,15)-H], 7.43 [m, 4 H, 1(8,9,16)-H], 7.83 [m, 4 H, 4(5,12,13)-H]; ^{13}C NMR: δ 31.0 (q, CH_3), 64.0 [s, C-8b(16b)], 76.0 [s, C4b(12b)], 91.4 (s, C-16d), 123.0 (d), 123.2 (d), 127.8 (d), 128.0 (d), 145.7 (s), 148.4 (s), 150.3 (s); MS (EI, 70 eV): *m/z* 470 (42, $M^{+\cdot}$), 455 (100, $[M - Me]^{+}$), 440 (67, $[M - 2\,Me]^{+\cdot}$), 220 (30, $[M - 2\,Me]^{2+}$).

8: mp > 400 °C; ^{1}H NMR: δ 7.30 (overlapped) and 7.83 [AA′BB′, 4 H] 7.31 (t, overlapped, 4 H), 7.40 (t, ${}^{3}J$ 7.5 Hz, 4 H), 7.62 (d, ${}^{3}J$ 7.5 Hz, 4 H), 7.80 (d, ${}^{3}J$ 7.6 Hz, 4 H); ^{13}C NMR ([${}^{2}H_6$]DMSO): δ 69.1 [s, C-4b(8b)], 103.6 [s, C-8b(16b)], 106.8 (s, C-16d), 124.8 (d), 125.3 (d), 125.6 (d), 128.8 (d), 129.1 (d), 130.7 (d), 141.1 (s), 145.8 (s), 148.9 (s); MS (EI, 70 eV): *m/z* 472 (41, $M^{\cdot+}$), 456 (8, $[M - O]^{+}$), 440 (100, $[M - O_2]^{\cdot+}$), 220 (45, $[M - O_2]^{2+}$).

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