

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]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 pentabenz 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**.

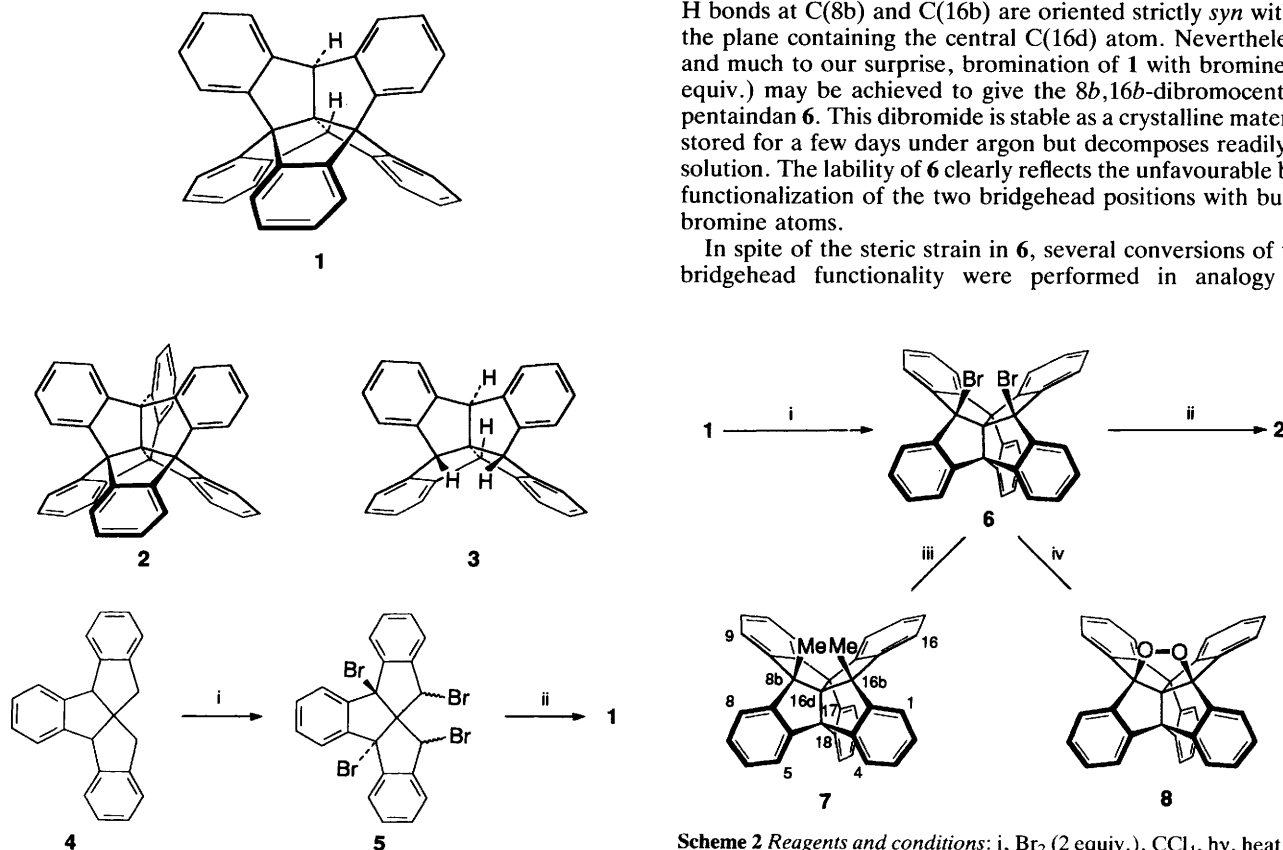
The synthesis of **1** comprises only five steps starting from indan-1,3-dione. A three-step method leads to the *difuso*-triindan **4** as described in detail previously.^{4,8} While selective bromination of the benzylic methine and methylene C-H bonds of **4** proved to be difficult,⁹ we succeeded 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**).

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 95.43⁵).

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 benzylic 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 8b,16b-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



Scheme 1 Reagents and conditions: i, Br_2 (4 equiv.), CCl_4 , hv, 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 , hv, 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*-dimethyl-centropentaindan **7** in good yield; similarly, AgI-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 centrohexasindan **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 centrohexasindan **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 8*b*,16*b*-bridged, centrohexasindan derivatives of **1**.

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Footnote

† All new compounds except **6** (see text) gave satisfactory combustion or high-resolution analyses. Selected physical data for **1**, **7** and **8**. [All ¹H NMR measured at 300 MHz (CDCl₃) and ¹³C NMR at 75 MHz (CDCl₃) unless otherwise stated.]

1: mp 326 °C. ¹H NMR: δ 5.08 (s, 2 H, 8*b*-H, 16*b*-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, ³J 6.7 Hz, 4 H, 1(8,9,16)-H], 7.86 [d, ³J 7.1 Hz, 4 H, 4(5,12,13)-H]; ¹³C NMR: δ 61.8 [d, C-8*b*(16*b*)], 76.3 [s, C-4*b*(12*b*)], 83.2 (s, C-16*d*), 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⁺), 365 (5), 221 (13).

7: mp 396–400 °C (subl.); ¹H NMR: δ 2.07 (s, 6 H, CH₃), 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]; ¹³C NMR: δ 31.0 (q, CH₃), 64.0 [s, C-8*b*(16*b*)], 76.0 [s, C-4*b*(12*b*)], 91.4 (s, C-16*d*), 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⁺), 455 (100, [M – Me]⁺), 440 (67, [M – 2 Me]⁺), 220 (30, [M – 2 Me]²⁺).

8: mp > 400 °C; ¹H NMR: δ 7.30 (overlapped) and 7.83 [AA'BB', 4 H] 7.31 (t, overlapped, 4 H), 7.40 (t, ³J 7.5 Hz, 4 H), 7.62 (d, ³J 7.5 Hz, 4 H), 7.80 (d, ³J 7.6 Hz, 4 H); ¹³C NMR ([²H₆]DMSO): δ 69.1 [s, C-4*b*(8*b*)], 103.6 [s, C-8*b*(16*b*)], 106.8 (s, C-16*d*), 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⁺), 456 (8, [M – O]⁺), 440 (100, [M – O₂]⁺), 220 (45, [M – O₂]²⁺).

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