

## Benzoannellated Centropolyquinanes. Part 21.<sup>1</sup> Centrohexasindane: Three Complementary Syntheses of the Highest Member of the Centropolyindane Family

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The syntheses of centrohexasindane **1**, a unique hydrocarbon bearing six mutually fused indane units in a centrohexasicyclic,  $T_d$  symmetrical, and topologically nonplanar framework is reported in full detail. Three independent and complementary synthetic routes have been developed making use of derivatives of the readily accessible centrotriindanes **9**, **10** and **11** ( $R = \text{CH}_3$ ) and centrotetraindane **13** (fenestrindane). The most efficient synthesis gives the title compound **1** in seven steps starting from indane-1,3-dione **15** in 40% yield, involving the 'broken' fenestrane **10** ('broken-fenestrane route'). Also starting from dione **15**, an even shorter route furnishes our target molecule **1** in six steps *via* triptindanetrione **24** in 25% yield ('propellane route'). Both of these routes surpass our first synthesis reported in 1988 *via* fenestrindane **13** which comprises eleven steps and gives a 7.5% overall yield from indanedione **15** ('fenestrane route'). The three routes allow the six benzene rings of compound **1** to be introduced in complementary ways, thus promising the synthesis of centrohexasindane derivatives with various substitution patterns. Particularly remarkable key steps of the syntheses of compound **1** are, *inter alia*: (i) single and two-fold condensation of benzene by  $\text{AlBr}_3$ -catalysed Friedel–Crafts reaction of cyclic 1,3-dibromides, (ii) unusual three-fold addition of phenyllithium to a 1,3,3'-triketone (compound **24**), (iii) two-fold and even three-fold cyclodehydration. Finally, a low-yield formation of compound **1**, among other products, has been observed upon cyclodehydrogenation of 10-methyl-1,4,7-triphenyltribenzotriquinacene **32**, which is obtained in two steps from 10-methyltribenzotriquinacene **11** ( $R = \text{Me}$ ), with Pd/C at 500 °C. The spectroscopic properties of compound **1** are presented along with some unique structural features of its rigid centrohexasicyclic framework.

Centrohexasicyclic compounds ('centrohexasicyclanes',<sup>2</sup> **a**) comprise molecular species bearing six mutually fused rings, all of them sharing a central carbon or hetero atom. The members of this unusual class of polycyclic compounds are characterized by some remarkable and rare structural features: the central tetracoordinated atom (Z) is bonded to four other tetracoordinated atoms (A), and this central unit,  $Z(\text{A}_4)$ , is bridged by six atomic groups or atoms (B) connecting the four outer atoms in a pairwise manner, according to the six edges of a tetrahedron (**b**), to give a highly condensed polycyclic  $Z(\text{A}_4)(\text{B}_6)$  arrangement of formal  $T_d$  symmetry. The connectivity of centrohexasicyclic species (**c**) corresponds to the graph  $K_5$ , a complete graph containing five mutually connected vertices.<sup>3</sup> As a particular feature,  $K_5$  graphs are topologically nonplanar; that is, any two of their edges (lines connecting a pair of vertices) must intersect when the graph is projected onto a plane, as illustrated in (**d**), for example<sup>3-6</sup> (see Fig. 1).

In organic chemistry, topologically nonplanar molecules are extremely rare. In 1981, Simmons III and Maggio<sup>7-9</sup> and Paquette and Vazeux<sup>10</sup> published the synthesis of the first organic  $K_5$  compound, the 'Simmons–Paquette molecule' **2**;<sup>4</sup> a little later, Walba reported on the synthesis of a Möbius strip-type polycycle,<sup>11</sup> yet another heterocyclic structure containing several ether groups, which corresponds to the likewise topologically nonplanar (*bipartite*) graph  $K_{3,3}$ .<sup>3-6</sup> In contrast, the related parent hydrocarbons, centrohexasindane **3**, and its congener, centrohexasindane **4**, have remained elusive, as reported by Simmons III and co-workers<sup>9</sup> and later in an extended work by Paquette *et al.*<sup>12</sup> However, hexacycles **3** and **4** have been studied by semiempirical calculations,<sup>2,13,14</sup> and partially benzoannellated centrohexasindanes† and a derivative of compound **4**<sup>17</sup> have been synthesized recently.

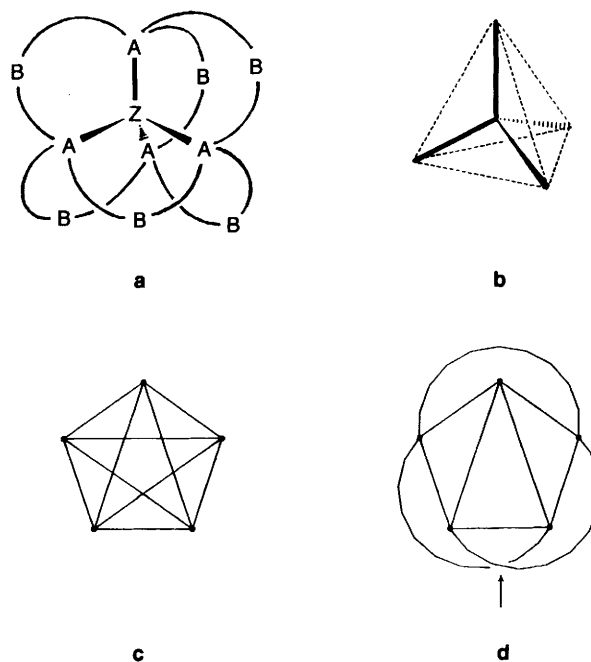
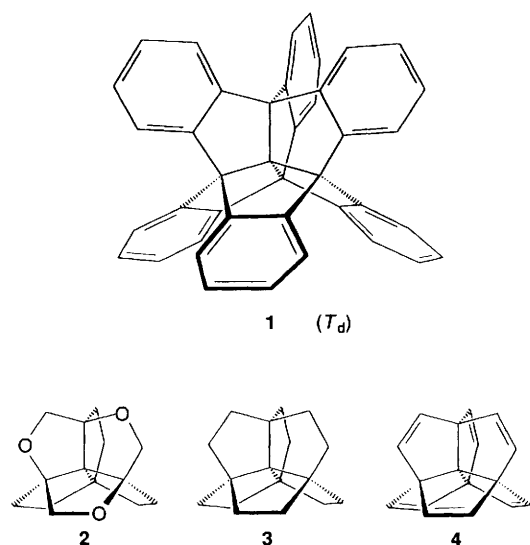


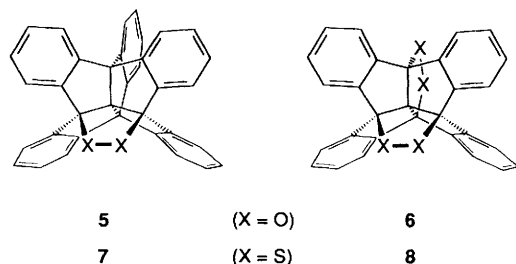
Fig. 1

The first topologically nonplanar hydrocarbon was the title compound, centrohexasindane **1**, synthesized in our laboratory for the first time in 1988.<sup>18</sup> This centrohexasicyclic core bears a neopentane core ( $Z = \text{A} = \text{carbon}$ ) bridged by six *o*-phenylene units ( $\text{B} = \text{o-C}_6\text{H}_4$  in **a**). This achievement has been the basis for our extensive synthetic research on both novel homocyclic<sup>15-17</sup> and novel heterocyclic centrohexasicyclanes such as compounds **5–8**, which have been described

† The pentabenzene and a 'propella-tribenzo' derivative of compound **3** have been synthesized recently.<sup>15,16</sup>



recently.<sup>15,19,20</sup> In the course of that work, two alternative syntheses of compound **1** were developed and have been communicated briefly.<sup>16,20</sup>



Inorganic and organo-element compounds with centrohexacyclic structures have been known since 1934 when Pauling and Sherman<sup>21</sup> suggested the  $Z(A_4)(B_6)$  arrangement for basic beryllium acetate  $O(Be_4)(OAc)_6$  containing six six-membered rings fused at the central  $O(Be_4)$  unit. Later, Tulinsky and Worthington<sup>22</sup> determined the detailed structure of this 'centropolysexane'<sup>2</sup> analogue, and, in the following years, related neutral species like dialkyl phosphorodithioates  $O(Zn_4)[S_2P(OR)_2]_6$  (e.g.,  $R = Pr^i$ )<sup>23</sup> and  $S(Zn_4)(S_2AsMe_2)_6$  and  $S(Cu_4)[(S_2AsMe_2)_6]$ <sup>24</sup> have been characterized. Moreover, heterometallic cluster anions containing a centrohexacyclic core of six four-membered rings (hence representing centrohexaquadrane<sup>2</sup> analogues) have been described in recent years by the groups of Clegg,<sup>25</sup> Müller,<sup>26</sup> and Sécheresse.<sup>27</sup> Also, carbide 'high-nuclearity' metal carbonyl clusters such as  $C[Fe_5(CO)_{15}]$ <sup>28</sup> and cluster anions such as  $\{C[Rh_6(CO)_6(\mu_2-CO)_9]\}^{2-}$ <sup>29</sup> may be considered topologically nonplanar polycyclic species.<sup>6,7</sup>

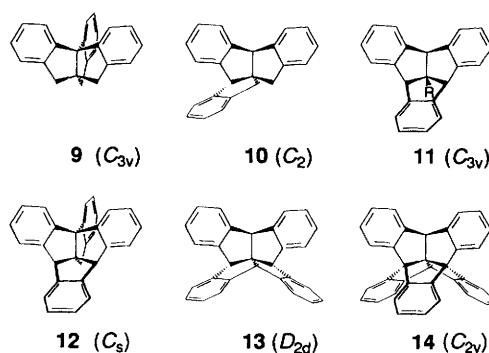
Although this short digression into general chemistry may not be complete, it does show that various molecular inorganic species are known bearing the centrohexacyclic (or ' $K_5$ ') structural unit. One reason for this may be the favourable self-aggregability of such microclusters from polar and/or charged components. In contrast to this, the generation of *organic* species with six rings fused in the highly spatially condensed centrohexacyclic manner requires perfect control of the stereochemistry during the synthetic (covalent) assemblage of the suitable synthons of low polarity. From an organic chemistry point of view, the fact that a centrohexacyclic molecule of type **a** would bear no fewer than four quaternary

$sp^3$ -hybridized carbon centres bonded to another, but one and the same, quaternary carbon atom and thus represents a derivative of tetrakis(*tert*-butyl)methane appeared to be a challenging outset for the synthesis of a centrohexacyclic hydrocarbon.

In this paper, a full report on the three syntheses of centrohexaindane **1**<sup>16,18,20</sup> is presented and some spectroscopic and structural properties of this unusual aliphatic hydrocarbon are discussed. Furthermore, the remarkable formation of compound **1** by three-fold cyclodehydrogenation of an easily accessible tribenzotriquinacene derivative is described, and some short remarks will be made on futile attempts to generate our target compound **1**. The three successful syntheses of compound **1** will be presented here in detail and contrasted with respect to the underlying strategies. Results obtained by X-ray structural analyses of compound **1**, which have been performed recently, are not included in this paper,<sup>‡</sup> but some experimentally confirmed structural features of this unique hydrocarbon will be presented briefly.

### Discussion—Synthetic Concepts

*Lower Centropolyindanes.*—Centrohexaindane represents the highest member of the family of regular centropolyindanes.<sup>30,31</sup> Its molecular framework comprises all of its lower congeners such as the three centrotriindanes **9–11**, *trifuso-* and *tetrafuso-*tetraindanes **12** and **13** (fenestrindane), respectively,



and centropentaindane **14**. Beyond the first synthesis of triptindane **9** by Thompson in 1966<sup>32</sup> and since our first communication on this topic in 1984,<sup>33</sup> we have developed efficient synthetic routes to all these centropolyindanes in recent years.<sup>1,16,18,20,34–40</sup> It will be shown in this paper that most of these hydrocarbons and/or closely related derivatives serve as synthetic intermediates for the construction of compound **1** following various complementary synthetic strategies.

*Retrosynthesis.*—Besides the C–C bonds of the six benzene rings, the  $C_{41}H_{24}$  hydrocarbon **1** contains four central and twelve 'lateral' C–C single bonds, corresponding to the A–B junctions in structure **a** (Fig. 1). Intuitively, these are the bonds to be formed with relative ease upon construction of the centrohexaquinane core of compound **1**. In other words, neither the C–C bonds of the central neopentane core nor those of the peripheral benzene rings would be generated in the last

<sup>‡</sup> Repeated attempts to grow solvent-free single crystals of compound **1** enabling a most accurate X-ray structural analysis have failed so far. Single crystals containing  $CH_2Cl_2$  or  $CHCl_3$  have been analysed and the analysis refined to  $R = 0.09$  (B. Neumann, H. Bögge and P. Jutzi, University of Bielefeld, and H. Pritzkow, University of Heidelberg).

<sup>§</sup> Regular centropolyindanes comprise those congeners which contain a truly aliphatic neopentane core (see structures **1**, **9–14**), not allowing any  $C^z$  atom to be fused to one of the benzo units. For irregular centropolyindanes, see ref. 31.

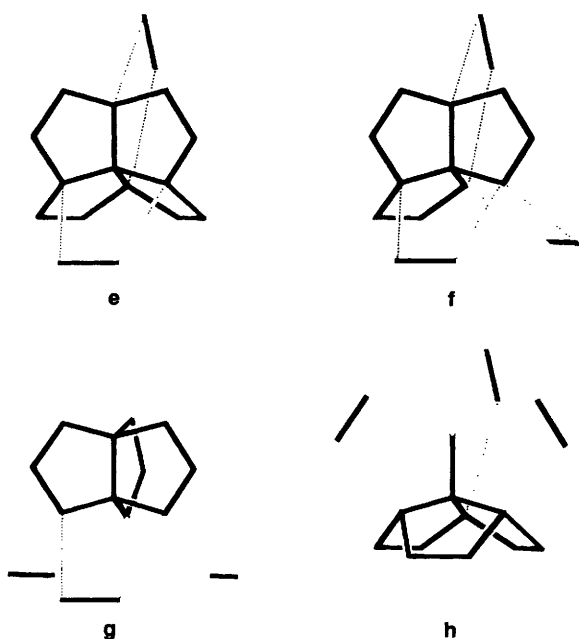


Fig. 2 Retrosynthetic pathways for the possible construction of the carbon framework of compound **1**

synthetic steps, which were expected to suffer most from the mutual steric hindrance of closely adjacent groups. In fact, four retrosynthetic pathways (e–h) have been envisaged, all of which include the cleavage of at least two pairs of lateral C–C bonds (Fig. 2). As will be seen, this renders the actual synthetic procedures highly efficient through a number of two-fold, three-fold, and, in several cases, even four-fold C–C bond-formation processes within the same synthetic conversion.

Cleavage according to e relies on the accessibility of a suitable [5.5.5]fenestrane and a derivative which may be treated with two synthons that contain the C<sub>2</sub> bridges missing from the centrohexaquinane centre. In fact, the chemistry of [5.5.5]-fenestrans has been developed continuously during the past 20 years,<sup>41–45</sup> and fenestrindane **13**, a stable, crystalline material promised to be a good starting point for the synthesis of compound **1** following the ‘fenestrane route’. Actually, this approach led to our first synthesis of compound **1**;<sup>18</sup> it represents the only strategy of our centrohexaquinane syntheses in which the six indane units of compound **1** are annelated by a [4 + 2] combination.

The retrosynthetic approach according to method f reduces the starting material to the angular (*difuso-*) triindane **10** and includes the introduction of three C<sub>2</sub> bridges. Triindane **10**, a ‘broken’ fenestrane, was the first centropolyindane synthesized in our laboratory; it is prepared much more easily than was the full fenestrane **13**. Nevertheless, its efficient convertibility into compound **1** has been discovered only recently since it relies decisively on the selective functionalization of the benzylic and benzydrylic C–H bonds. In fact, this ‘broken-fenestrane route’ has turned out to open a remarkably short and most efficient access to compound **1**, although the three C<sub>2</sub> bridges have to be introduced in two sequential, *viz.* [3 + 2 + 1], annelation steps.

Retrosynthetic analysis as illustrated in method g represents the ‘propellane route’ to compound **1**. In this case, a suitable benzoannellated [3.3.3]propellane derived from the C<sub>3</sub>-symmetrical *monofuso*-triindane **9** (‘triptindane’<sup>32</sup>) is extended by three synthons providing the C<sub>2</sub> bridges in one step only. This [3 + 3] annelation is highly efficient, too. It is noteworthy that retrosynthetic approach g was chosen by Simmons III<sup>7,8</sup> and by Paquette *et al.*<sup>10,12</sup> to synthesize triether **2** and to study

potential routes to centrohexaquinane **3**. Recently, the propellane route has been successfully used by us to synthesize the first tribenzocentrohexaquinane<sup>16</sup> as well as some methyl-substituted centrohexaquinanes.<sup>46</sup>

Finally, another retrosynthesis, illustrated by method h, leads to the *trifuso*-triindane subunit which has again to be completed by introduction of three C<sub>2</sub> fragments. Most synthetic possibilities according to this approach, based on various tribenzotriquinacenes of type **11**, have been considered or tested, but eventually discarded. Two related approaches, however, do lead to compound **1** and are discussed below (‘triquinacene route’). One of these represents a particularly short approach and corresponds to a [3 + 3] assemblage of the six indane units of compound **1**. It is based on the readily accessible *centro*-methyltribenzotriquinacene **11** (R = Me),<sup>33,37</sup> but the efficiency achieved so far has been very low.

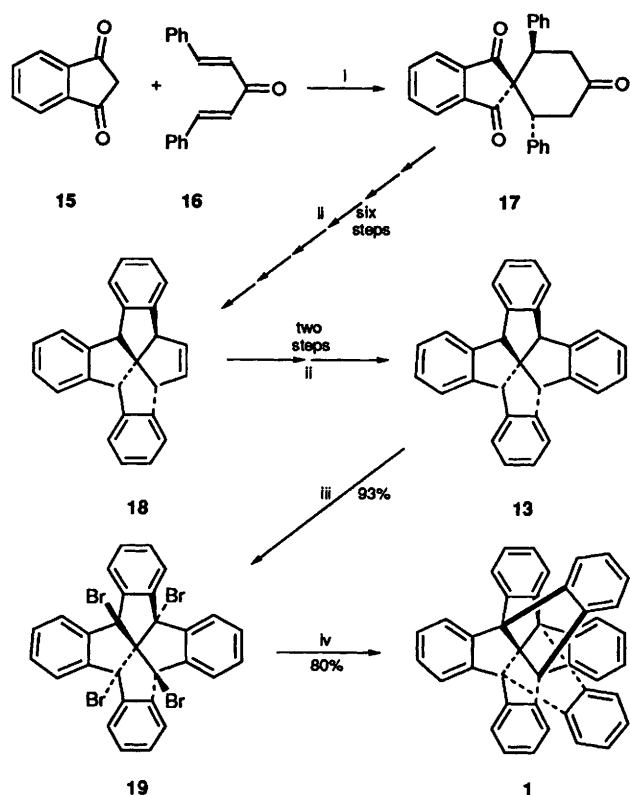
Besides the propellane route (g), two other retrosynthetic schemes (*viz.*, e and h) had already been envisaged by Simmons III<sup>8,9</sup> who analysed the potential synthetic routes to centrohexaquinane **3**, but the corresponding tri- and tetraquinane derivatives, potential starting materials on routes e and h, appeared extremely difficult to access. Even suitable [3.3.3]propellane derivatives (*cf.* g) required for studies aimed at the synthesis of compounds **2** and **3** turned out to be very difficult to prepare.<sup>8,47</sup> In the case of the benzoannellated analogues, the availability of several highly stable centrotri- and centrotetra-indanes proved to be a great advantage. Hence, our successful syntheses of centrohexaquinane **1** are based on the presence of the annelated benzene rings which stabilize the starting materials, reactive intermediates, and products. In the following paragraphs, the three syntheses of our target molecule **1** are discussed in detail and contrasted with respect to their respective potentials.

## Results

*Centrohexaquinane by the ‘Fenestrane Route’.*—The fenestrane route to compound **1** is the longest of all syntheses presented here. Of its eleven steps, most of which have been described recently in detail,<sup>40</sup> the first combines indane-1,3-dione **15** and dibenzylideneacetone **16** to give the double-Michael-addition product, *trans*-diphenylspirotriketone **17**, which had been reported previously by Freimanis and co-workers<sup>48</sup> and Ten Hoeve and Wynberg.<sup>49</sup> Six-step synthetic sequences (in two variants<sup>40</sup>) then led to the all-*cis*-tribenzo[5.5.5]fenestrane **18**, and two further steps furnish fenestrindane **13** (Scheme 1). Actually, this synthesis has been optimized to give compound **13** in ~10% total yield from indane-1,3-dione **15** and on a several-gram scale; nevertheless, among the centropolyindanes **9–14**, fenestrindane **13** is at present the most difficult one to prepare.

With its four equivalent benzydrylic C–H bonds, fenestrindane **13** is well suited for functionalization at the four ‘outer’ bridgehead positions. Similar to the tribenzotriquinacenes (see **11**, R = H, Me, Et, see below), which have been investigated by us at the same time,<sup>50,51</sup> compound **13** readily undergoes complete bromination of the benzydrylic positions to give 4b,8b,12b,16b-tetrabromofenestrindane **19** in excellent yield (93%). This halide is a stable, highly crystalline material which may be converted into a large number of interesting completely bridgehead-substituted fenestrans,<sup>19</sup> including the corresponding tetramethyl and tetrahydroxy<sup>50b,51</sup> derivatives and, furthermore, heterocyclic centrohexacyclanes<sup>15</sup> such as **6**

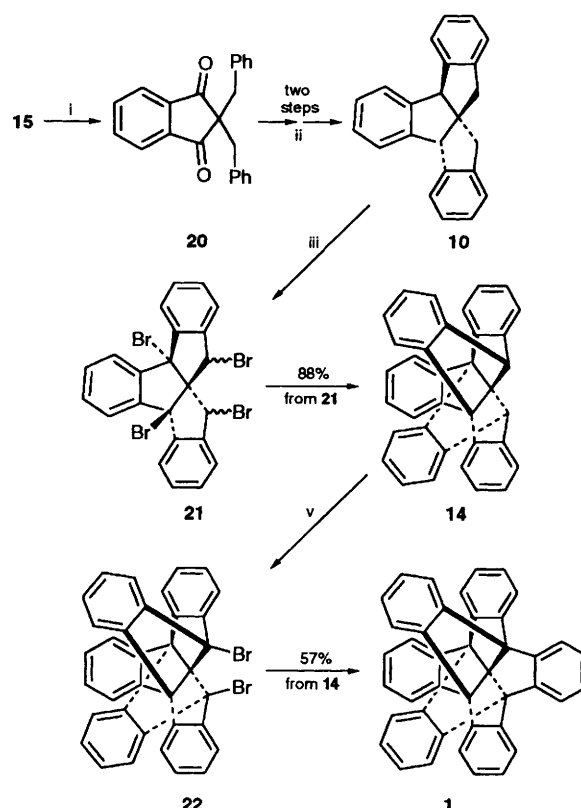
† Simmons III also envisaged the synthesis of the title compound **1**, then termed ‘hexabenzoc-K<sub>5</sub>’, *via* triptindane **9**.<sup>8</sup>



**Scheme 1** Reagents and conditions: i, HOAc (refs. 48, 49); ii, see ref. 40; iii, Br<sub>2</sub>, CCl<sub>4</sub>, reflux, *hv*; iv, AlBr<sub>3</sub>, benzene, reflux, 40 h

and **8**. The easy formation and the stability of compound **19** was surprising to us because of the fact that the two pairs of bulky bromine substituents above the two corrugated fenestrane 'faces' should suffer strong steric and probably dipolar repulsive interactions. In fact, this became evident by NMR spectrometry showing static behaviour of the two equivalent ground-state conformations.<sup>19</sup> Accordingly, X-ray analysis of compound **19** shows<sup>52</sup> a highly distorted, S<sub>4</sub>-symmetrical conformation with significant flattening of the geometry at the central tetracoordinate carbon atom.<sup>41-45,53-57</sup>

The final step of the fenestrane route to compound **1** consists of a Friedel-Crafts reaction by condensation of tetrabromide **19** with two molecules of benzene. Thus, benzene solutions of tetrabromide **19** are treated with equimolar amounts of aluminium tribromide at reflux temperature; after addition of about half of the catalyst, an orange-red precipitate is observed, suggesting the formation of an ionic adduct, which has not been characterized yet. This species is redissolved upon addition of the remaining Lewis acid, and centrohexaindane **1** is obtained in high yield (80%). The striking efficiency of this four-fold C-C bond formation may be traced to both the remarkable 'skeletal' stability of the multiply fused fenestrane framework of substrate **19** (no fragmentation products have been found) and the 'electronic' stability of the ionic intermediates involved owing to the four annelated benzene nuclei. Speculations on the intermediacy of dicationic species bearing a doubly charged isoindene moiety have not been substantiated to date. Such species have been generated from simpler, open-chain *o*-dibenzylbenzene dihalides<sup>58</sup> in superacidic media and may play a role in the first condensation step; however, in view of a similar condensation reaction (see **22** → **1**, Scheme 2), which involves the incorporation of one molecule of benzene into a 1,1'-dibromo[2.2']spirobiindane subunit, it appears reasonable simply to assume sequential formation, and conversion, of



**Scheme 2** Reagents and conditions: i, benzylation (see ref. 40); ii, see ref. 40; iii, 4 Br<sub>2</sub>, CCl<sub>4</sub>, reflux, *hv* (see ref. 1); iv, AlBr<sub>3</sub>, benzene, 25 °C, 7 days; v, 2 Br<sub>2</sub>, CCl<sub>4</sub>, reflux, *hv* (ref. 1); vi, AlBr<sub>3</sub>, benzene, 25 °C, 5 days

monocationic fenestrindane intermediates in a rather unusual kind of 'tandem' reaction.<sup>59</sup>

The fenestrane route to compound **1** represents an interesting example for the conversion of highly versatile benzoannulated fenestrans, *viz.* **13** and its derivatives, into a centrohexacyclic hydrocarbon, *i.e.* a fenestrane bridged by two other carbon (C<sub>2</sub>) units. Admittedly, it suffers from the long synthetic sequence of eleven steps starting from dione **15** and a low overall yield (~7.5%); nevertheless, it may be used favourably in certain cases to construct centrohexaindanes with pinpoint substituent pattern.

*Centrohexaindane via Centropentaindane: The 'Broken-fenestrane Route'.*—As compared with complete bridgehead bromination of fenestrindane **13** and *trifuso*-centrotriindane **11** (see below), partial bromination of most centropolyindanes has been found unsatisfactory since bromide mixtures were obtained and the yields and stability of the desired mono- and di-bromides are low in most cases.<sup>50b,60</sup> This holds also for *difuso*-centrotriindane **10**, although this hydrocarbon bears benzylic and benzhydrylic C-H bonds of different *a priori* reactivity. On the other hand, we found that 'exhaustive' bromination of all of the six aliphatic C-H bonds of hexacycle **10** cannot be achieved either; this would generate sterically unfavourable *syn*-1,3-interactions in three pairs of bromine substituents (*cf.* structure **19**). Thus, the idea to generate centrohexaindane **1** by subjecting the hypothetical hexabromo derivative of compound **10** to a Friedel-Crafts condensation with *three* molecules of benzene, similar to the strategy used in the fenestrane route, was tempting but found to be futile.

|| As a curiosity, the conversion **13** → **1** may be considered a synthesis creating two new fenestrane units around a given fenestrane skeleton.

Nevertheless, centrotriindane **10** was found to represent an excellent starting point for a new synthesis of compound **1**, the 'broken-fenestrane route' (Scheme 2), which turned out to be much more efficient than the fenestrane route itself.

As described previously,<sup>33,40</sup> centrotriindane **10** is obtained in three steps and with high yield from indane-1,3-dione **15** via diketone **20**. Careful treatment of compound **10** with four mole equivalents of bromine in tetrachloromethane yields a mixture of bromotriindanes which contains predominantly the stereoisomeric tetrabromides bearing one bromine substituent at each of the four C<sup>α</sup> atoms of the neopentane core, as shown in structure **21**. This follows from mass spectrometric analysis of the mixture but, most strikingly, from the subsequent conversion of tetrabromide **21** into centropentaindane **14** in excellent (88%) yield.<sup>1,20</sup> Alternative syntheses of this second-highest centropolyindane have been developed as well,<sup>1</sup> the more efficient one being a two-fold cyclodehydrogenation of benzhydryltribenzotriquinacene **11** (R = CHPh<sub>2</sub>)<sup>33,37</sup> (*cf.* 'triquinacene route', below). However, the bromination/condensation procedure **10** → **14** is by far the most efficient synthesis of compound **14**, representing a strict parallel to the incorporation of two *o*-phenylene bridges in the conversion **13** → **1**.

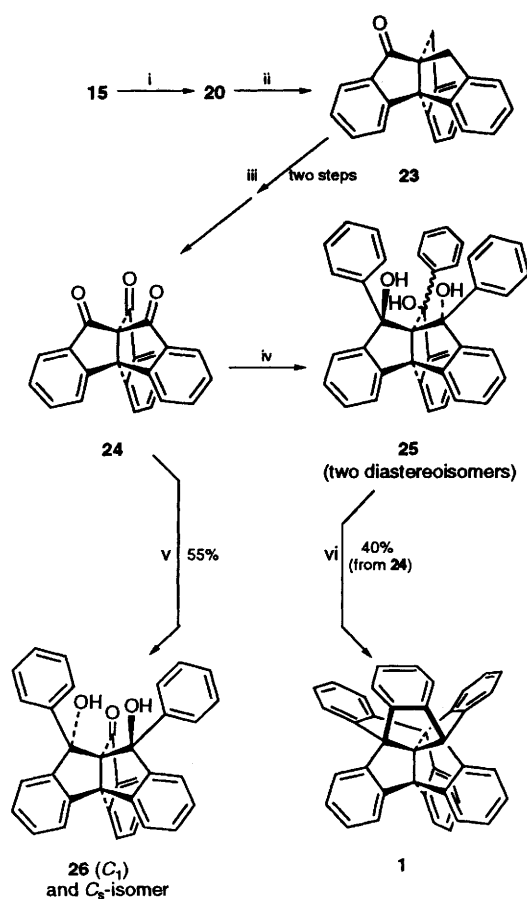
The two bridgehead C–H bonds remaining in centropentaindane **14** are orientated strictly 1,3-synplanar owing to the conformational rigidity of the centropentacyclic framework.<sup>1</sup> Consequently, introduction of two substituents at these positions should markedly increase the steric strain. Nevertheless, the benzylic activation of the C–H bonds is sufficient to allow the system to pick up two bromine atoms to give compound **22**.<sup>1</sup> And in fact, in spite of its remarkable lability, this dibromide incorporates the last benzene nucleus upon treatment with aluminium tribromide in benzene solution: if the reaction is carried out at room temperature and allowed to run smoothly for several days, a remarkable 57% yield of pure centrohexasindane **1** is obtained. Overall, this improves the synthetic access to compound **1** to a seven-step protocol and, starting from indane-1,3-dione **15**, to a total yield of 40%.

It may be noted at this point that, notwithstanding its close parallel to the fenestrane route, the *broken-fenestrane* route allows one to assemble the individual indane units of compound **1** in a completely independent manner. Again, this may be of interest if certain substituted derivatives of compound **1** have to be synthesized.

*Centrohexasindane by the 'Propellane Route'*.—Another, and even shorter, synthesis of compound **1** than that presented above has been developed making use of triptindane derivatives (*cf.* structure **9**) as the key intermediates for the construction of the centrohexasindane ring system. Historically, this 'propellane route' to compound **1** was the second access route discovered,<sup>36b</sup> and it allows the preparation of compound **1** in only six steps starting from indane-1,3-dione **15**. It should be kept in mind that this route (see structure **g** in Fig. 2) corresponds closely both to the approach used by Simmons III and Maggio<sup>7,8</sup> and by Paquette *et al.*<sup>10,12</sup> to synthesize trioxacentrohexaquinane **2** and their attempts directed toward centrohexasquinane **3**.

The overall sequence of the propellane route is illustrated in Scheme 3. The crucial intermediate of this synthesis is triptindane-9,10,11-trione **24**, the C<sub>3v</sub>-symmetrical tribenzo analogue of Conia's triketone;<sup>61</sup> it is synthesized in four steps from dione **15** via the corresponding monoketone **23** in 60% overall yield.<sup>36</sup>

Triptindanetrione **24** is a remarkable and highly versatile triketone since it contains a sterically fixed triacylmethane unit. Therefore, we were much surprised to find that trione **24** adds up to three mole equivalents of metalorganic reagents without



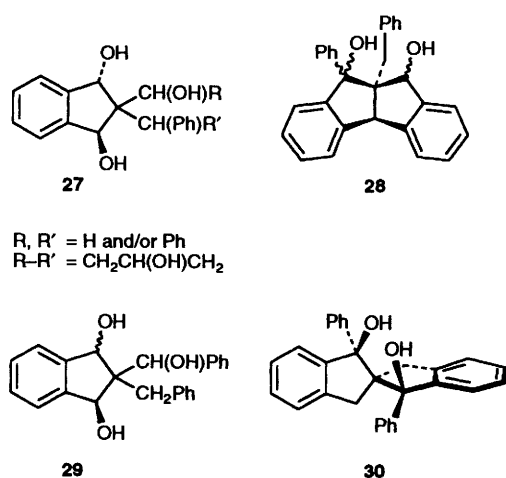
**Scheme 3** Reagents and conditions: i, benzylation (see ref. 40); ii, polyphosphoric acid (ref. 36); iii, see ref. 36; iv, PhLi (20 mol equiv.), benzene–Et<sub>2</sub>O (85:15); v, PhLi (4 mol equiv.), THF–Et<sub>2</sub>O–benzene (80:14:6); vi, H<sub>3</sub>PO<sub>4</sub>, xylenes, 135 °C

cleavage of the triquinane skeleton.<sup>16,36</sup> Addition of an excess of phenyl Grignard or phenyllithium in ether solvents [containing predominantly diethyl ether or tetrahydrofuran (THF)] leads to two-fold addition of the reagent, and the unsymmetrical keto diol **26** is isolated from the mixture of stereoisomers in 55% yield. Another isomer formed in ~22% yield is assumed to be the C<sub>s</sub>-symmetrical diastereoisomer bearing the two phenyl substituents *syn* to the keto group, but this product has not been fully characterized. Products of three-fold addition are not formed under these conditions, as expected with regard to the highly encumbered residual keto group in the bis-alcoholates obtained before hydrolysis. As shown recently,<sup>38,39</sup> C<sub>s</sub>-diindane-9-ones bearing a 10β-phenyl substituent exhibit strong steric hindrance between the keto group and the phenyl group, the latter being orientated into the concave side of a diindane unit. Addition of two phenyl groups to the triptindane framework of trione **24** necessarily gives rise, in a two-fold manner, to such unfavourable steric interactions. In this respect, it is astonishing that, in spite of the unfavourable steric effects, the system does not escape by retroaldol-type cleavage of appropriate neopentane C–C bonds after the first addition of the nucleophile (which it neither does, by Grob-type fragmentation, on the triol level of compound **25**; see below). It may be noted here that indane-1,3-diones bearing two bulky substituents at C-2 do react by retro-aldol cleavage upon addition of phenyl Grignard.<sup>62</sup> On the other hand, non-enolizable 1,3-diketones derived from C<sub>s</sub>-diindane have been found to resist retro-aldol cleavage upon addition of phenyl Grignard reagent.<sup>38</sup> Obviously, stereoelectronic effects in the encumbered 'crown' of the triptindane framework overcome

the tendency to form a relatively stable bridgehead 1,3-dionate anion.

In the light of these considerations, it appears all the more surprising that, in fact, triptindanetrione **24** undergoes even three-fold addition of phenyllithium in one synthetic step under enforced conditions. Therefore, utilization of poorly solvating media such as benzene–diethyl ether mixtures drastically enhances the reactivity of organometallic species.<sup>63</sup> In fact, the addition of a large (~20-fold) excess of phenyllithium in diethyl ether–benzene to a suspension of the extremely poorly soluble triketone **24** in benzene yields a mixture of products which, according to mass and <sup>1</sup>H NMR analysis, contains the triol **25** as the major component. After removal of volatile by-products (mainly biphenyl), the crude product is obtained in high (96%) yield, and TLC and MS analyses suggest the presence of two diastereoisomers which were not separated (see Experimental section). So far, no observations as to the fragmentation of the [3.3.3]propellane framework have been made. Obviously, the favourable behaviour of triketone **24** with respect to the potential drawbacks envisaged for the addition of metalorganic reagents pertains in benzene solution, and the steric hindrance of the third addition step is overrun by the high reactivity of the barely solvated reagent and/or reaction intermediates.

Upon treatment with orthophosphoric acid in xylenes at reflux temperature, the crude triol mixture **25** undergoes a three-fold cyclodehydration to give centrohexaindane **1**. In this manner, the centrohexacycle is isolated in 40% yield, based on triptindanetrione **24**. All chemical and spectroscopic properties show that the product obtained *via* the propellane route is identical with those produced by the previous syntheses.

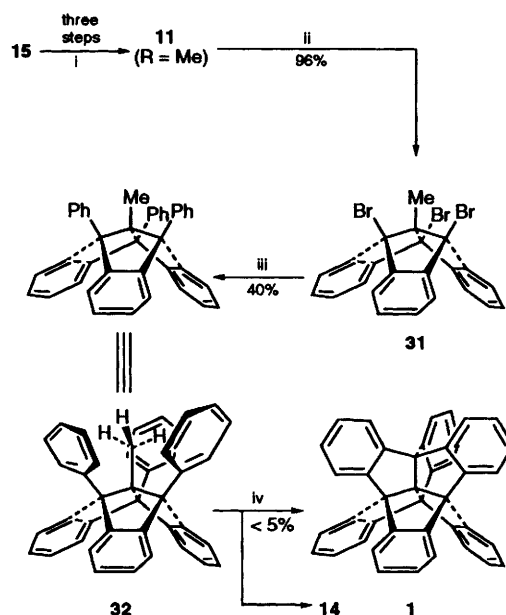


The three-fold cyclodehydration reaction **25**  $\rightarrow$  **1** deserves some special comments. First, it demonstrates the remarkable ease of the cyclization of 3-phenylpropan-1-ol groupings to indane units in the presence of other hydroxy groups in a 3-position to the reacting alkanol functionality. In fact, the syntheses of many centropolyindanes rely on the *two-fold* cyclodehydration of 2-benzyl- and 2-benzhydrylindane-1,3-diols such as **27** as a key step (*e.g.*, **10**, **11** and **13**). On the other hand, non-indane-type benzylic 1,3-diols such as *fuso*-diindane-diol **28**,<sup>38</sup> the 2-(hydroxybenzyl)indan-1-ol **29**<sup>63</sup> and *spiro*-diindanediol **30**<sup>64</sup> all undergo Grob-type fragmentation under acid catalysis, whereas triol **25**, being closely related to diol **28**, in particular, does not. It may be speculated that the three-fold cyclodehydration of triol **25** is stereospecific, in that only the  $C_3$ -symmetrical diastereoisomer is converted into compound **1** whereas the  $C_1$ -symmetrical (unsymmetrical) one might undergo fragmentation. This hypothesis would explain the relative low yield of product **1** obtained from the crude triol

mixture; however, fragmentation products could not be identified. To shed more light on this problem, the diastereoisomers would have to be isolated and subjected to attempted dehydration separately. In any case, the successful cyclodehydration of triol **25** may be ascribed to two factors: (i) the high degree of preorientation of the phenyl groups with respect to the alcohol centres, rendering the cyclization steps highly entropically favourable, and (ii) the stereoelectronic requirements for Grob fragmentation being poor in the 1,3,3'-trihydroxy unit of triol **25** owing to the considerably reduced mobility of the mutually locked substituents at the crown of the triptindane skeleton.

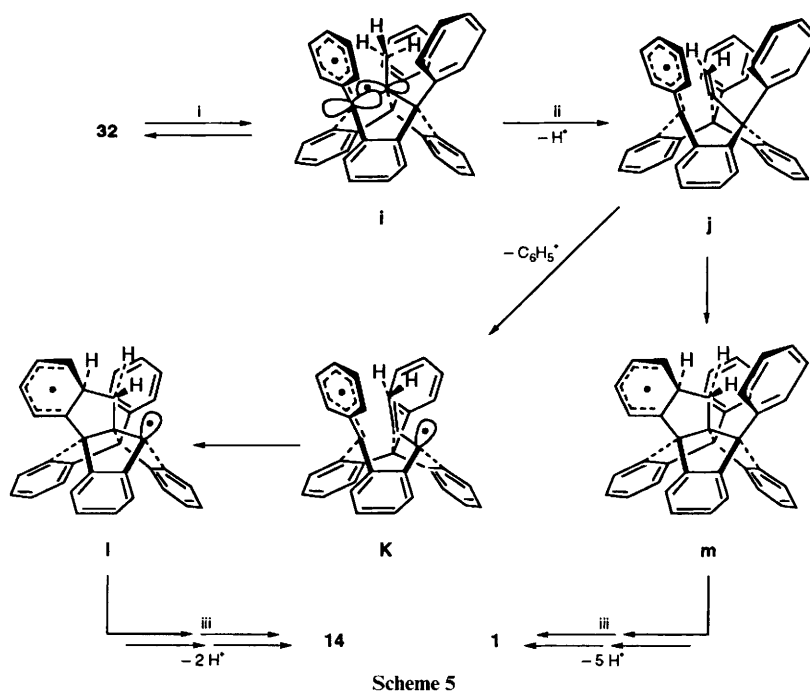
On the whole, the propellane route from indane-1,3-dione **15** to centrohexaindane **1** requires only six synthetic steps and furnishes the title compound in gram amounts and in 25% overall yield. It is therefore much superior to the 'fenestrane route' but is somewhat less efficient than the 'broken-fenestrane route' due to the low solubility of trione **24**. Hence, unfortunately, a scaled-up preparation is disfavoured in the last two steps (**24**  $\rightarrow$  **25**  $\rightarrow$  **1**; see Experimental section). Again, the assemblage of the six indane units should allow us to introduce individually substituted benzene rings in a way which may complement the two approaches described before.

*Centrohexaindane by the 'Triquinacene Route'.*—A fourth access to centrohexaindane **1**, corresponding to the cleavage **h** in the retrosynthetic view (Fig. 2), has been found very recently. Although far from being useful synthetically, this 'triquinacene route' (Scheme 4) represents a most remarkable approach since



**Scheme 4** Reagents and conditions: i, see ref. 37; ii,  $\text{Br}_2$ ,  $\text{CCl}_4$ , reflux, *h\nu*; iii,  $\text{AlBr}_3$ , benzene, 25 °C, 3 days; iv, Pd/C, 500 °C, 90 min

it involves the catalytic activation of a methyl group, the carbon atom of which is incorporated into three newly formed cyclopentane rings. As the propellane route described above, compound **1** is obtained in only six steps starting from the readily available *centro*-methyl-substituted tribenzotriquinacene **11** ( $R = \text{Me}$ ).<sup>33,37</sup> Bromination under standard conditions<sup>50</sup> (*cf.* also **13**  $\rightarrow$  **19**) gives the bridgehead tribromide **31** in almost quantitative yield and as a highly stable material.<sup>50a,65</sup> Similar to tetrabromide **19**, and besides a large number of other conversions of compounds **11** performed<sup>50</sup> *via* tribromide **31**, this multiple benzhydryl bromide may be used as an 'alkylation reagent' under Friedel–Crafts conditions. In



benzene solution, catalysis by aluminium tribromide leads to the formation of the corresponding 10-methyl-1,4,7-triphenyltribenzotriquinacene **32** in moderate yield.\*\*

It is noteworthy that four hydrocarbon substituents are locked in a strictly eclipsed orientation along the rigid triquinacene backbone of compound **32**, with each of the three peripheral phenyl groups being in close vicinity of the central methyl substituent. This particular situation and the fact that the only aliphatic C–H bonds in compound **32** are those of the encumbered methyl group encouraged us to subject this hydrocarbon to cyclodehydrogenation with palladium-on-charcoal at high temperatures. Whereas efficient cyclodehydrogenations are rare in araliphatic hydrocarbons and may need particular catalyst systems, as shown recently by Paquette *et al.*,<sup>66</sup> we found that cyclodehydrogenation of appropriate centropolyindanes may be performed favourably by utilizing conventional Pd/C catalyst at elevated temperatures (~450–550 °C). For example, as mentioned above, centropentaindane **14** can be synthesized in this way from *centro*-benzhydryl-substituted tribenzotriquinacene **11** (R = CHPh<sub>2</sub>).<sup>1</sup> Completion of the centrohexasindane structure by the route **14** → **22** → **1**, as described above as a part of the broken-fenestrane route, may be addressed as a (stepwise) variant of the triquinacene route (pathway **h**, Fig. 2).

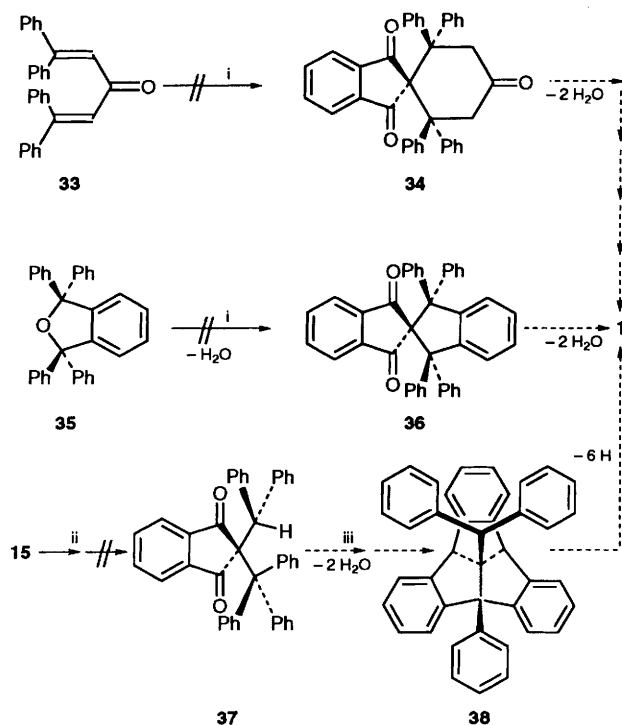
A more direct, albeit preliminary approach to compound **1** following the triquinacene route consists of three-fold ring closure in the fully bridgehead substituted tribenzotriquinacene **32**. In fact, heating of intimately mixed substrate **32** and Pd/C (~1:3 w/w) in a steel tube at 500–550 °C for 1.5–2.0 h gives a mixture of products among which centrohexasindane **1** and centropentaindane **14** are unequivocally identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy. At present, the yields of compound **1** obtained by this technique have been very low (a few percent), and the bulk of products formed has not been identified. Also, it is uncertain whether optimization of this reaction is possible. At this point of development we restrict ourselves noting that the three-fold cyclodehydrogenation

**32** → **1** may represent an unprecedented case in which an apparently electronically non-activated methyl group is attacked by the dehydrogenation catalyst. Being the only aliphatic group in the substrate, the methyl group appears to be *activated* toward C–H bond cleavage, rather than being sterically hindered, by the presence of the three vicinal bridgehead phenyl groups.

Mechanistically, the reaction may be supported by an unusually favourable anchimeric assistance by the phenyl groups or by a purely entropic proximity effect involving the incipient methylene radical and the *ortho*-carbon atom being attacked. Yet a more probable mechanism relies to the thermally induced homolysis of a central bisquaternary C–C bond (**32** ⇌ **i**, Scheme 5). The resulting intermediate biradical **i** is protected toward fragmentation of the triindane skeleton and will either collapse back to substrate **32** or undergo abstraction of a methyl hydrogen atom by the catalyst to give the triphenylmethyl radical **j**. This intermediate may undergo cyclization to radical **m**, which is followed by several readily occurring sequential hydrogen abstraction and cyclization steps to form target compound **1**. Alternatively, radical **j** may eliminate a phenyl radical to give an allyltriphenylmethyl-type biradical **k**; restoration of the triquinacene framework thus forming biradical **l**, followed by hydrogen abstraction/addition and a cyclization step, leads to centropentaindane **14**. Alternative mechanisms are conceivable, and detailed investigation is required to improve the efficiency and to clarify the mechanism of this intriguing approach to compound **1**.

*Some too Optimistic Ideas from Pencil-and-paper Chemistry.*—Cyclodehydration, a classical type of cyclization reaction, has proven a highly useful synthetic tool for the development of the centropolyindanes. All of the three syntheses of centrohexasindane **1** and even the ‘dehydrogenative’ triquinacene route include at least two—in the case of the propellane route even five—dehydrative cyclization processes. Thus, one may wonder whether the complex polycyclic framework of compound **1** might be accessible by still other approaches, which could be based on cyclodehydration in combination with other efficient C–C-coupling techniques such as the two-fold Michael addition and cyclodehydrogenation. Therefore, a short presentation of some attractive but,

\*\* Reaction of compound **31** with anisole, however, gives the corresponding tris(*p*-methoxyphenyl)methyltribenzotriquinacene in 80% yield.<sup>50b</sup>



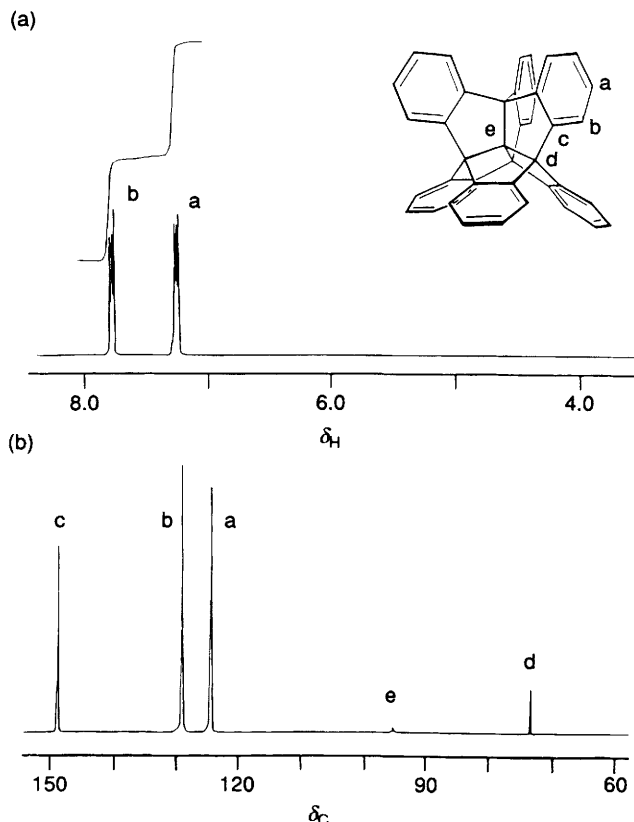
**Scheme 6** Reagents and conditions: i, compound **15**,  $H^+$ ; ii, see ref. 36; iii, reduction, then  $H^+$

eventually, futile ideas for the synthesis of the title compound may be documented briefly at this point.

In analogy to the synthesis of fenestrindane **13** (Scheme 1), an attractive route to compound **1** was envisaged starting from dibenzhydrylideneacetone **33**<sup>67</sup> and indane-1,3-dione **15**. Two-fold Michael addition of these components was hoped to lead to the spirotrione **34** which would undergo four-fold cyclization and could be elaborated to the target hydrocarbon **1** in analogy to the sequence **17**  $\rightarrow$  **13**. Unfortunately, the two-fold Michael addition performed under standard conditions in acetic acid<sup>48,49</sup> failed, probably due to the highly unfavourable steric situation in the overcrowded spirotrione **34**.

An even shorter route was tried involving the condensation of  $\alpha, \alpha'$ -dihydroxy- $\alpha, \alpha, \alpha', \alpha'$ -tetraphenyl-*o*-xylene<sup>68</sup> and the corresponding 1,1,3,3-tetraphenylphthalan **35**<sup>58</sup> and indane-1,3-dione **15**. Since  $\alpha, \alpha, \alpha', \alpha'$ -tetraphenyl-*o*-xylylene dications derived from compound **35** have been observed in superacidic solution,<sup>58</sup> this route could lead to the spirodione **36**, which possibly would undergo sequential multiple cyclodehydration to compound **1**. Again, to date, this idea turned out to be more of a dream than reality: the phthalan **35** proved to be too unreactive under the conditions used. Nevertheless, this reaction may become feasible provided a suitable (superacid or Lewis acid) medium would be found which allows the system to circumvent undesired condensation paths. Notably, the hypothetical sequence **15** + **35**  $\rightarrow$  **1** would represent a tandem reaction of unmatched efficiency.

Another experimental limit was encountered when we tried to synthesize 2-benzhydryl-2-tritylindane-1,3-dione **37**, bearing two extremely bulky geminal substituents. Whereas the synthesis of 2,2-ditrylindane-1,3-dione has been claimed,<sup>69</sup> we did not succeed in either reproducing this or preparing the slightly less sterically overcrowded dione **37**. As discussed previously,<sup>37</sup> the trityl group is both too sterically demanding and, as a cation, an excellent electrofuge. In fact, this excluded the possibility to generate the benzhydryl-phenyl-substituted tribenzotriquinacene **38** which could have been



**Fig. 3**  $^1H$  NMR spectrum (300 MHz;  $CDCl_3$ ) (a) and  $^{13}C$  NMR spectrum (75 MHz;  $CD_2Cl_2$ ) of compound **1** (b)

subjected to three-fold cyclodehydrogenation to give target compound **1**.

**Spectroscopic Properties of Centrohexasindane.**—Owing to its potential role as a prototype hydrocarbon, the NMR, mass, and UV spectra of centrohexasindane **1** will be discussed here in some detail. The high molecular symmetry ( $T_d$ ) of compound **1** gives rise to six equivalent indane subunits. Hence, as in indane itself, there are only five distinct resonances in the  $^{13}C$  NMR spectrum of this  $C_{41}H_{24}$  hydrocarbon (Fig. 3) which reflect the *ipso*, *ortho*, and *meta* positions of the benzene rings and those of the neopentane core. Of the latter, the central carbon atom is indicated by a singlet at  $\delta_c$  95.4 with remarkably low intensity due to inefficient magnetic relaxation. The unusually large downfield shift of this aliphatic carbon resonance may be traced to several factors: (i) the maximum possible degree of substitution at the  $\alpha$  and  $\beta$  positions with respect to the central atom, (ii) the high steric crowding, and (iii) the strictly in-plane orientation of the central carbon atom relative to the six aromatic rings (see below). In line with its molecular symmetry,  $^1H$  NMR spectrometry of compound **1** shows only two resonances, generating an AA'BB' spectrum for the six equivalent sets of benzo protons (Fig. 3). Of these, the *ortho* protons are distinctly more deshielded than the (peripheral) *meta* protons owing to the vicinity of two other arene rings of the same triphenylmethane subunit (*cf.*  $^1H$  NMR spectrum of compound **14**<sup>1</sup>).

In accord with the complete mutual fusion of the six indane units, the electron-impact mass spectrum of compound **1** is dominated by the molecular ion peak at  $m/z$  516 and is almost devoid of fragment-ion peaks. Besides minor signals corresponding to loss of  $H^+$  and of  $C_6H_5^+$ , a minor peak at  $m/z$  258 ( $< 10\%$  relative to  $M^+$ ) indicates the formation of doubly charged molecular ions.

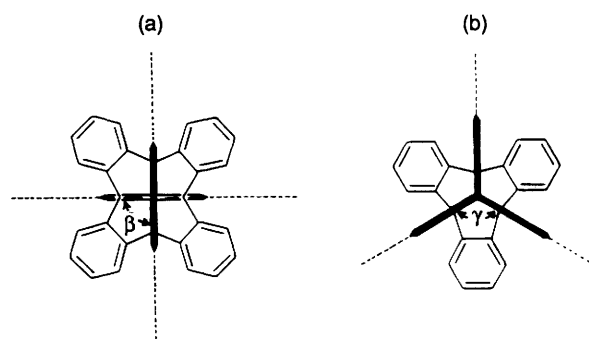
The UV spectrum of compound **1** is very similar to those of



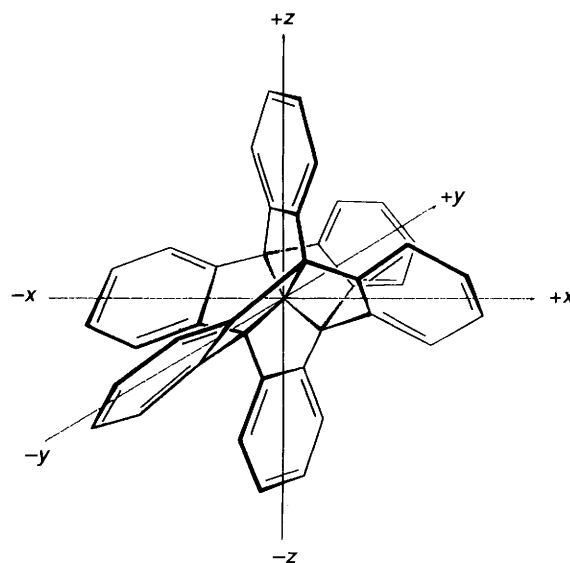
the lower centropolyindanes. As found for these, there is no evidence for a significant electronic interaction between the  $\pi$  systems of the adjacent aromatic rings: the lowest-energy absorption of the  $\alpha$  band is observed at  $\lambda_{\max} = 276.5$  nm ( $\epsilon \approx 5800$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), corresponding to a very small ( $\Delta\lambda_{\max} \approx +3$  nm) bathochromic shift relative to indane.<sup>70</sup> This corresponds to the spectra of other centropolyindanes containing a conformationally rigid framework, such as methyltribenzotriquinacene **11** (R = Me) showing  $\lambda_{\max} = 276.5$  nm,<sup>33,37</sup> trifuso-centrotetraindane **12** ( $\lambda_{\max} = 276.0$  nm)<sup>38</sup> and centropentaindane **14** ( $\lambda_{\max} = 276.5$  nm).<sup>1</sup> The extinction coefficients of these absorptions increase monotonically with the number of benzene rings fused in the polycyclic skeleton. Thus, the electronic excitation of compound **1** may be regarded as those of six combined but electronically isolated indane (or *o*-xylene) chromophores. It may be noted here that this holds also for those centropolyindanes which exist in two equilibrating conformations, *e.g.* compounds **9**, **10** and **13**, the only difference being that, in these cases, the slight bathochromic shift of the  $\alpha$  band is *not* observed with these congeners.<sup>32,34,40</sup> Similar to the centropolyindanes, benzoannulated [2.2.2]triblattanes, which contain several mutually fused 1,2-diphenylethane units instead of the diphenylmethane units of the former, do not show electronic interactions between the aromatic  $\pi$  electron systems.<sup>71</sup>

**Solid-state Structure of Centrohexaquinacene.**—As mentioned above, the X-ray structural analyses of compound **1** have not yielded satisfyingly accurate results to date. Therefore, only some preliminary results concerning the mutual spatial orientation of the six indane units of compound **1** will be discussed here. As expected, the structural analyses corroborate, to a good degree of approximation, the  $T_d$  symmetry of the rigid centrohexacyclic framework of compound **1**. The six C–C–C bond angles at the central carbon atom show values that are very close to the ideal tetrahedral angle (109.46°), the experimentally determined average value being  $\alpha = 109.4 (\pm 0.2)^\circ$ . Owing to the presence of four mutually fused tribenzotriquinacene units (see structure **11**, R = H), each being conformationally rigid in itself, the six five-membered rings of compound **1** do not show the usual half-envelope conformation of the indane skeleton; rather, each of the indane units is locked in the framework **1** in a completely planar conformation. As a consequence, the three 2,2'-spirobiindane units of compound **1** adopt linear conformations stretched along the  $C_{2v}$  axes, and they are orientated perfectly orthogonally to each other, *i.e.*  $\beta = 90.1 \pm 0.1^\circ$  [Fig. 4(a)]. For the same reason, the four triptindane units (structure **9**) in compound **1** are fixed in strict  $C_{3v}$ -symmetrical conformations, that is with arene–arene dihedral angles  $\gamma = 120.0 \pm 0.4^\circ$  [Fig. 4(b)]. This corresponds to the most unfavourable transition state for the 'concerted' conformational conversion of triptindane **9**.<sup>72</sup> Similarly, the three fenestrindane units (structure **13**) interfused in compound **1** are locked in a perfect  $D_{2d}$  conformation, again corresponding to the most unfavourable transition state of the concerted interconversion of the  $S_4$ -symmetrical conformers of moiety **13**.<sup>19,34,52</sup> These structural features provide the first experimental proof for the  $T_d$  symmetry of the carbon framework of a centrohexaquinacene derivative in its conformational ground state. This result was predicted for the parent centrohexaquinacene **4** by Ermer<sup>13</sup> on the basis of force-field calculations.

**Conclusions.**—Centrohexaquinacene **1**, a unique polycyclic hydrocarbon with  $T_d$  molecular symmetry and topologically nonplanar ( $K_5$ ) molecular skeleton, bears six indane units mutually fused at a common neopentane core and stretched along the six directions of space. It was synthesized by three



**Fig. 4** Orientation of the six indane units in compound **1**, as viewed along a spirobiindane  $C_{2v}$  axis (a) and along a triptindane  $C_{3v}$  axis (b, see text)



**Fig. 5** Fenestrane route  $-X + X/-Y + Y/-Z + Z$ ; propellane route  $-X/-Y - Z/+X + Y + Z$ ; broken-fenestrane route  $-X/-Y + Y/-Z + Z/+X$ ; triquinacene route  $-X/-Y + Z/+X + Y - Z$

independent and complementary routes, and its formation was observed by another approach which is being further developed at present. The syntheses including the latter approach are contrasted in Fig. 5 by sketching the framework of compound **1** along the axes of the three-dimensional space and denoting the synthetic sequence according to the site of the individual indane units in the coordinate system. Starting with the indane unit of indane-1,3-dione **15** at the negative moiety of the  $x$  axis (denoted by  $-X$ ), the fenestrane route, for example, continues by adding another indane at  $+X$ , then by incorporating two indanes at  $-Y$  and  $+Y$  and, finally, those at  $-Z$  and  $+Z$ .

Interestingly, the fenestrane route appears to be the simplest route but has turned out to be the longest and least efficient one (11 steps, 7.5% total yield) whereas the formally least straightforward access to compound **1**, *viz.* the broken-fenestrane route, is most efficient (seven steps, 40% yield). The two remaining approaches, the propellane and the triquinacene route, both involving the symmetrical incorporation of three indane units, are conceptually the shortest since they comprise only six steps. However, whereas the propellane route is only somewhat less efficient (total yield 25%), the triquinacene route has furnished only low yields (<5%) to date; more work is required to improve this approach.

In fact, our efforts to prepare compound **1** on the basis of lower centropolyindanes proved successful since three factors facilitated the synthesis of the hexabenzocentropolyindane analogue of the elusive centrohexaquinacene **3**: (i) the applicability of the

principles of electrophilic aromatic substitution chemistry, in particular of cyclodehydration of  $\gamma$ -functionalized alkylbenzenes; (ii) the generally experienced greater stability of arene-annelated substrates and also of the corresponding transient species as compared with their olefinic (non-benzoannelated) counterparts, and (iii) the tendency of condensed aromatic molecules to give readily crystallizing materials. All of these three aspects turned out to be, in fact, of great importance here, and it is hoped that experience gathered by these investigations will help to pave the way to a goal hidden in the background: centrohexaquinane **3**.<sup>16</sup>

## Experimental

**General.**—Mps (uncorrected): Büchi 512 and Electrothermal melting point apparatus. IR: Perkin-Elmer 841. UV: Beckman model 25. <sup>1</sup>H NMR: Bruker AM 300. <sup>13</sup>C NMR: Bruker AM 300 (*J*-modulated spin-echo experiments). *J*-Values are given in Hz. MS: Finnigan MAT 311 A, Finnigan CH 5 DF, Fisons VG Autospec; all run in the EI mode, 70 eV. Combustion analyses: Perkin-Elmer 240 and LECO CHNS-932 Analysator. MPLC: Besta E 100 and Besta UV 1; column dimensions 25 × 250 mm and 25 × 500 mm; eluent 6 cm<sup>3</sup> min<sup>-1</sup>; Kieselgel LiChroprep Si 60, 40–60  $\mu$ m (Merck), Matrex LC 60, 20–45  $\mu$ m and 35–70  $\mu$ m (Grace). TLC: Kieselgel 60 F<sub>254</sub> on Al foil (Merck).

**Centrohexaindane 1 from Compound 13 (Fenestrane Route).**—4b,8b,12b,16b-Tetrabromo-4b,8b,12b,16b-tetrahydro-dibenzo[a,f]dibenzo[2,3:4,5]pentaleno[1,6-cd]pentalene (Tetrabromofenestrindane **19**). A warm suspension of fenestrindane **13**<sup>40</sup> (368 mg, 1.00 mmol) in tetrachloromethane (100 cm<sup>3</sup>) was stirred while a 1.00 mol dm<sup>-3</sup> solution of bromine in the same solvent (4.00 cm<sup>3</sup>; 4.00 mmol) was added within 2 min. Upon addition of the first half of the reagent intense formation of hydrogen bromide was observed and the mixture became homogeneous. Continued addition gave a precipitate, and the reaction was completed by irradiation of the mixture with a 500 W photolamp. The solvent was removed under reduced pressure and the lemon-yellow residue was recrystallized from toluene to give tetrabromide **19** (635 mg, 93%) as needles, mp 341 °C (decomp.);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 3069, 3040, 1466, 1260, 1161, 1095, 1022, 1015, 877, 760, 735 and 652;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) ABCX spin system 7.95 (4 H, d, <sup>3</sup>*J* 7.4 and 7.54–7.45 (12 H, m);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 145.5 and 140.5 (quat. C), 130.3, 130.0, 127.2 and 123.2 (tert. C), 87.7 (q, C-16d) and 72.3 (q); *m/z* 601, 603, 605 and 607 (25/76/73/26%, [M – Br]<sup>+</sup>), 522, 524 and 526 (16/35/22, [M – 2 Br]<sup>+</sup>), 443 and 445 (37/43, [M – 3 Br]<sup>+</sup>), 365 (40), 364 (95), 363 (100), 262.5 (2) and 262 (4) (Found: C, 51.7; H, 2.3. C<sub>29</sub>H<sub>16</sub>Br<sub>4</sub> requires C, 50.9; H, 2.35%).

4b,12b[1',2']:8b,16b[1'',2'']Dibenzodibenzo[a,f]dibenzo-[2,3:4,5]pentaleno[1,6-cd]pentalene, Centrohexaindane **1**. Tetrabromofenestrindane **19** (500 mg, 730  $\mu$ mol) was dissolved in warm anhydrous benzene (100 cm<sup>3</sup>) and a 100 mmol dm<sup>-3</sup> solution of aluminium tribromide in benzene (10 cm<sup>3</sup>, 1.0 mmol) was added dropwise within 2 h at 40 °C. An orange-red complex was formed, which redissolved after complete addition of the reagent. The solution was heated to slight reflux for 40 h and then was hydrolysed by addition of water. The mixture was extracted with dichloromethane, the combined extracts were dried with sodium sulfate, and the solvent was removed under reduced pressure to leave a yellow solid, which was recrystallized from xylenes (20 cm<sup>3</sup>) to give the title compound **1** (300 mg, 80%) as needles, mp > 420 °C. Large crystals of compound **1** may be obtained from chloroform-methanol solutions using the vapour-diffusion technique

(MeOH  $\rightarrow$  CHCl<sub>3</sub>);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 3059, 3018, 1466, 1157, 1074, 752 and 618;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) AA'BB' spin system 7.79 (12 H) and 7.29 (12 H) [see Fig. 3(a)];  $\delta_{\text{C}}$ (75 MHz; CD<sub>2</sub>Cl<sub>2</sub>; Me<sub>4</sub>Si) 148.2 (quat. C), 128.5, 123.9 (tert. C), 95.0 (q, C-16d) and 73.0 (q, C-4b, -8b, -12b and C-16b) [see Fig. 3(b)]; *m/z* 516 (100%, M<sup>+</sup>), 515 (12), 439 (3) and 258 (4, M<sup>2+</sup>);  $\lambda_{\max}$ (heptane, *c* 4 × 10<sup>-5</sup> mol dm<sup>-3</sup>)/nm 276.5 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 5800), 269 (5000), 263 (3000) and 257sh (Found: C, 94.9; H, 5.1. C<sub>41</sub>H<sub>24</sub> requires C, 95.3; H, 4.7%).

**Centrohexaindane 1 from Compound 22 (Broken-fenestrane Route).**—Dibromocentropentaindane **22**, a labile material readily decomposing at ambient temperature under air, was prepared from centropentaindane **14** (442 mg, 1.00 mmol) and was recrystallized from toluene under argon as described previously.<sup>1</sup> The product obtained in this way was redissolved in anhydrous benzene (50 cm<sup>3</sup>) under argon, and the solution was stirred at room temperature while a solution of aluminium tribromide (330 mg, 1.24 mmol) in anhydrous benzene (20 cm<sup>3</sup>) was added dropwise within 1 h. Stirring of the orange-red mixture under argon was continued for 3–5 days while the reaction was monitored by TLC. The mixture was hydrolysed by addition of water and extracted with dichloromethane; the combined extracts were dried with sodium sulfate, and the solvent was removed under reduced pressure. The yellow-brown residue was redissolved in a little chloroform and the solution was filtered through a pad of silica gel. The residue obtained after evaporation of the solvent was recrystallized from xylenes to give the title compound **1** (290 mg, 57%), as identified by identical <sup>1</sup>H NMR and mass spectra with the material obtained from compound **13** (see above).

**Centrohexaindane 1 from Trione 24 (Propellane Route).**—10,11-Dihydroxy-10,11-diphenyl-9H,10H-4b,9a-([1,2]benzenomethano)indeno[1,2-a]inden-9-one **26**. A suspension of triptindane-9,10,11-trione **24** (336 mg, 1.00 mmol) in anhydrous THF (20 cm<sup>3</sup>) was stirred under nitrogen while a 0.85 mol dm<sup>-3</sup> solution of phenyllithium in diethyl ether-benzene (7:3; 5.00 cm<sup>3</sup>, 4.25 mmol) was added by syringe. After the addition was complete, the mixture started to warm to reflux temperature and turned red. It was stirred for 15 min, allowed to cool, and was then hydrolysed by addition of water to give a colourless mixture. Aq. ammonium chloride (20 cm<sup>3</sup>) was added, the mixture was extracted with diethyl ether, and the combined extracts were dried with sodium sulfate. Evaporation of the solvent gave a solid residue, which was subjected to MPLC [silica gel; CH<sub>2</sub>Cl<sub>2</sub>-EtOAc (98:2)] to remove by-products (mainly biphenyl). The first eluted isomer (**26**) was obtained pure (270 mg, 55%), mp 246 °C; the second fraction (110 mg, 22%) represented mainly another isomer, mp 250 °C (see Discussion section). Isomer **26** was assigned the unsymmetrical stereoorientation of the phenyl groups;  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 3825, 3381, 3065, 3029, 1703 and 756;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.85 (3 H, d, <sup>3</sup>*J* 7.6), 7.50–7.52 (4 H, m), 7.34 (2 H, t, <sup>3</sup>*J* 7.6), 6.90–7.18 (12 H, m), 6.79 (1 H, d, <sup>3</sup>*J* 7.6) and 4.79 (2 H, br s, OH); *m/z* 474 (50%, [M – H<sub>2</sub>O]<sup>+</sup>), 446 (12), 340 (11), 339 (34), 265 (10), 263 (19), 105 (100), 78 (12), 77 (86) and 76 (10) (Found: C, 85.2; H, 4.85. C<sub>35</sub>H<sub>24</sub>O<sub>3</sub> requires C, 85.35; H, 4.9%).

9,10,11-Triphenyl-9H,10H-4b,9a-([1,2]benzenomethano)indeno[1,2-a]indene-9,10,11-triol **25** (Mixture of Isomers).—A suspension of triptindane-9,10,11-trione **24** (3.36 g, 10.0 mmol) in anhydrous benzene (250 cm<sup>3</sup>) was stirred under nitrogen while a 0.85 mol dm<sup>-3</sup> solution of phenyllithium in benzene-diethyl ether (3:7; 250 cm<sup>3</sup>, 212 mmol) was added through a dropping funnel. The suspension was held at 40 °C, and the triketone dissolved slowly while some lithium hydroxide

precipitated *ca.* 1 h after the addition was complete. Stirring was continued for 5 h at 40 °C before the mixture was allowed to cool to room temperature and then hydrolysed by addition of water. The organic layer was diluted with diethyl ether and separated, the aqueous layer was extracted with the same solvent, and the combined organic solutions were washed with water, and dried with sodium sulfate. Removal of the solvent gave a residue, from which biphenyl was distilled off in a Kugelrohr apparatus at 100 °C (15 Pa). A brownish material (5.47 g, 96%) was obtained, showing only one spot on TLC,  $R_f$  0.25 [ $\text{CH}_2\text{Cl}_2$ -EtOAc (95:5)]. A solution of this crude product (300 mg) in ethyl acetate (*ca.* 10  $\text{cm}^3$ ) was filtered through silica gel and further subjected to MPLC [ $\text{CH}_2\text{Cl}_2$ -EtOAc (85:15);  $t_R(1)$  42 min,  $t_R(2)$  58 min] which showed it to contain two isomers. Both compounds showed identical mass spectra;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3556, 3070, 1058, 703 and 614;  $m/z$  570 (1%,  $\text{M}^{+}$ ), 552 (36,  $[\text{M} - \text{H}_2\text{O}]^+$ ), 553 (16), 475 (17), 458 (11), 457 (9), 105 (100), 106 (9), 91 (14) and 77 (39).

**Centrohexaindane 1.** The crude mixture of isomeric 9,10,11-triphenyltriptindane-9,10,11-triols **25** (9.60 mmol) obtained as described above was dissolved in xylenes (250  $\text{cm}^3$ ) (Merck, p.a.), orthophosphoric acid (85%, 5  $\text{cm}^3$ ) was added, and the mixture was stirred and heated to reflux in a reactor equipped with a Thiele-Pape extractor filled with pre-dried molecular sieves (4 Å). The cyclodehydration was completed after 25–30 h, as monitored by TLC. The mixture was allowed to cool, and the organic solution was decanted from the oily residue, washed with aq. sodium hydrogen carbonate, and dried with sodium sulfate. Removal of the solvent gave a brownish residue, which was redissolved in some chloroform and the solution was filtered through a pad of silica gel. Evaporation of the solvent yielded pure compound **1** (1.98 g, 40%) as crystals, the spectroscopic data of which were identical with those given above.

**Centrohexaindane 1 from Compound 11 (Triquinacene Route).**—4b,8b,12b-Tribromo-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene, 1,4,7-Tribromo-10-methyltribenzotriquinacene **31**. To a stirred solution of methyltribenzotriquinacene **11** (R = Me) (294 mg, 1.00 mmol) in slightly heated anhydrous tetrachloromethane (50  $\text{cm}^3$ ) was slowly added a 1.00 mol  $\text{dm}^{-3}$  solution of bromine in the same solvent (3.30  $\text{cm}^3$ , 3.30 mmol). The mixture is irradiated with a 500 W photolamp. Initially, the reaction proceeded rapidly as indicated by efficient absorption of the reagent and strong effervescence of the solution by the hydrogen bromide evolved. After the reaction had slowed down, irradiation was continued for 15 min at reflux temperature. The product began to precipitate as fine needles after two-thirds of the reagent solution had been added. Finally, the solvent and excess of bromine were removed, and the residue was recrystallized from toluene (100  $\text{cm}^3$ ) to yield tribromide **31** (509 mg, 96%) as extremely (up to 4 cm) long needles, mp 340 °C (decomp.);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3073, 3033, 2988, 1472, 1459, 1271, 1214 and 750;  $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  AA'BB' spin system 7.70 (6 H), 7.32 (6 H) and 2.32 (3 H, s);  $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  143.4 (quat. C), 130.4 and 125.6 (tert. C), 80.2 (q), 75.1 (q, C-12d) and 36.9 (s);  $m/z$  449, 451 and 453 (49/100/49%,  $[\text{M} - \text{Br}]^+$ ), 369 and 371 (15/17,  $[\text{M} - (\text{Br}, \text{HBr})]^+$ ), 291 (70), 289 (46), 276 (30), 274 (15), 184.5 and 185.5 (13/13,  $[\text{M} - (\text{Br}, \text{HBr})]^2+$ ) and 145 (26) (Found: C, 52.85; H, 2.8.  $\text{C}_{23}\text{H}_{15}\text{Br}_3$  requires C, 52.0; H, 2.85%).

12d-Methyl-4b,8b,12b-triphenyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene, 10-Methyl-1,4,7-triphenyltribenzotriquinacene **32**.—Tribromide **31** (530 mg, 1.00 mmol) was dissolved in anhydrous benzene (25  $\text{cm}^3$ ) by slight heating. The solution was stirred and allowed to cool to

room temperature, and a solution of aluminium tribromide (1.07 g, 4.00 mmol) in benzene (5  $\text{cm}^3$ ) was added. The mixture turned red-brown and was stirred for 3 days at room temperature. After addition of water (10  $\text{cm}^3$ ) the mixture was extracted with dichloromethane, and the combined extracts were dried with sodium sulfate. Evaporation of the solvent gave a yellow-brown oil, from which a powder precipitated upon careful addition of ethyl acetate. This material was separated and washed several times with hot ethyl acetate. Recrystallization from xylenes yielded hydrocarbon **32** (203 mg, 40%) as crystals, mp 396 °C;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3026, 2976, 2932, 1494, 1481, 1446, 1033, 748 and 699;  $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  AA'BB' spin system 7.35 (6 H), 7.25 (6 H), 7.20 (6 H, d,  $^3J$  7.8), 7.15 (3 H, d,  $^3J$  6.9), 7.05 (6 H, d,  $^3J$  7.0) and  $-0.28$  (3 H, s);  $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  148.9 and 146.9 (quat. C), 130.2, 128.0, 127.4, 126.2 and 125.5 (tert. C), 77.8 (q, C-12d), 74.1 (q) and 25.7 (s);  $m/z$  522 (79%,  $\text{M}^{+}$ ), 445 (100,  $[\text{M} - \text{C}_6\text{H}_5]^+$ ), 367 (21), 339 (5), 289 (6), 261 (6) and 222.5 (2) (Found: C, 93.4; H, 5.75.  $\text{C}_{41}\text{H}_{30}$  requires C, 94.2; H, 5.8%).

**Cyclodehydrogenation of Compound 32.**—Finely powdered 10-methyl-1,4,7-triphenyltribenzotriquinacene **32** (100 mg, 190  $\mu\text{mol}$ ) was intimately mixed with palladium-on-charcoal (300 mg; 10% Pd; Merck) in a mortar. The mixture was poured to fill a cylindrical steel bomb (160 × 16 mm, inner volume 8  $\text{cm}^3$ ), which was hermetically closed and then carefully introduced into an electric oven preheated to  $500 \pm 20$  °C. After being heated at this temperature for 90 min, the cylinder was allowed to cool, and the reaction product was extracted with chloroform to leave a solid residue (~10 mg), which was analysed by mass and  $^1\text{H}$  NMR spectrometry. The presence of compounds **1** and **14** besides a majority of unidentified products was revealed by their characteristic molecular (base) peaks at  $m/z$  516 and  $m/z$  442 (~1:1) and by the characteristic AA'BB' spectrum of compound **14** at  $\delta$  7.66, 7.16 and 5.08. The mass spectrum also displayed a distinct peak at  $m/z$  368 (suggesting the presence of centrotetrindane **12**) and another one at  $m/z$  592 (indicating a product formed by addition of  $\text{C}_6\text{H}_4$  to compound **1**).

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