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Polycyclic Compounds beyond the Propellanes and Fenestranes: [m.n.o.p.q]Centropenta- and [m.n.o.p.q.r]Centrohexacyclanes

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Abstract: Several new homo- and heterocyclic topologically nonplanar organic compounds (**11**, **14**, **17**–**20**) with centrohexacyclic (K_5 type) molecular frameworks are described. Besides some centrohexaquinanes comprising five-membered rings exclusively ('[5.5.5.5.5.5]centrohexacyclanes'), a number of congeners containing two six or two seven-membered rings have been synthesized for the first time ('[6.5.6.5.5.5]- and [7.5.7.5.5.5]centrohexacyclanes'). Based on [m.n.o.p]fenestranes, a notation is proposed to define unequivocally the mutual orientation of the various rings.

INTRODUCTION

Centrohexacyclic structures are characterized by the mutual annelation of six rings about a common quaternary central atom, which itself may be surrounded by four again quaternary neighbour atoms. For a long time, organic compounds of this scarce, topologically non-planar type have been very difficult to access synthetically due to the spatially extremely close packing of rings.[1,2] In recent years, however, its has been possible to synthesize a number of homo- and heterocyclic centrohexacyclic compounds, such as **3**–**8**[3-5], and to adjoin them to the well-known triether **2**, which was described for the first time in 1981.[6,7]

According to a systematic terminology for centropolycyclic structures,[8] compounds **2**–**8** belong to the families of 'centrohexaquinanes' and 'centrohexaindanes', respectively, since their centrohexacyclic nucleus contains exclusively five-membered rings.[9] In this paper we present, for the first time, some centrohexacyclic organic compounds the polycyclic nuclei of which comprise also rings of other sizes, and we would like to use this opportunity to propose a new more comprehensive definition for highly condensed centropolycyclic compounds, namely, the nomenclature of [m.n.o.p.q.r]centropolycyclanes.

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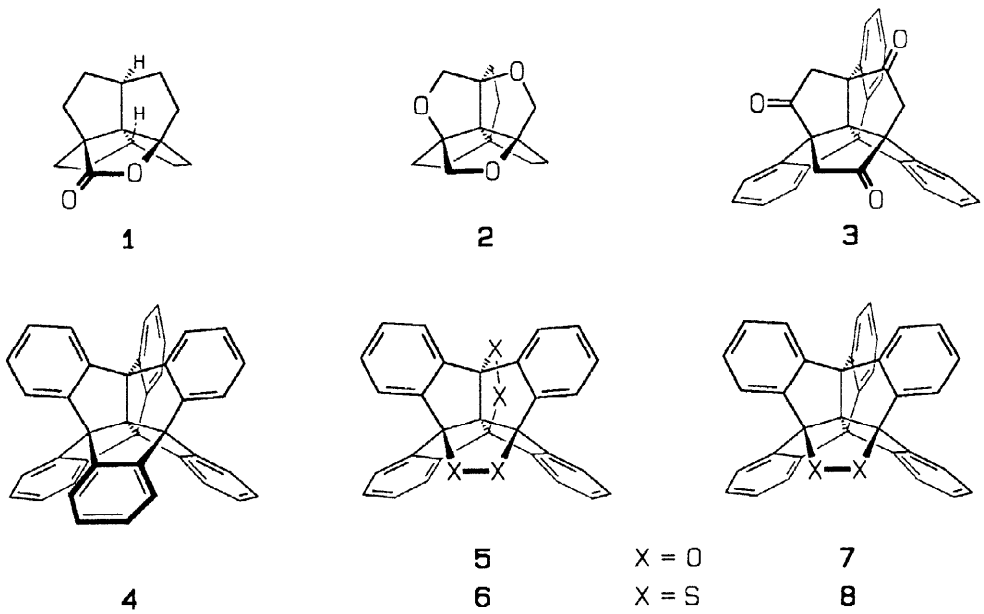
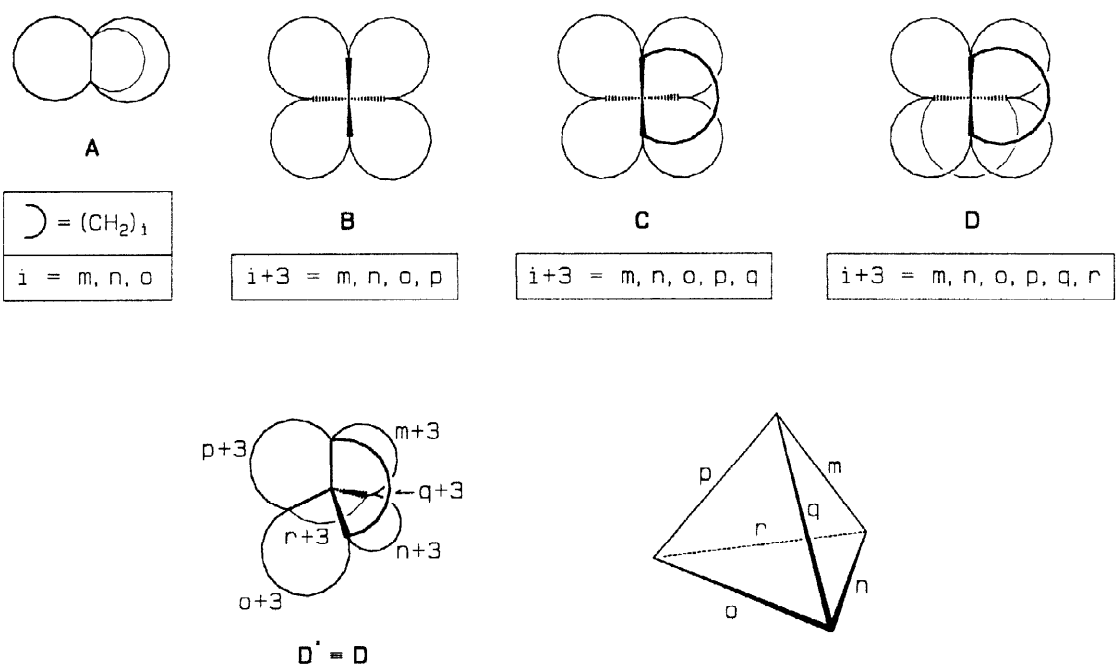


All centrohexacyclic organic structures known to date have been constructed either from [3.3.3]propellanes **A** (i = 3) or from [5.5.5.5]fenestranes **B** (i = 2, Scheme 1). As pointed out earlier, [m.n.o]propellanes[10,11] and [m.n.o.p]fenestranes[12,13] as well as other lower polycycles are comprised in the molecular framework of the centrohexacyclanes[2,8,14,15]. Therefore, it appears obvious to address centropolycyclanes containing *more* than four mutually, centrically fused rings as '[m.n.o.p.q]centropentacyclanes' **C** and '[m.n.o.p.q.r]centrohexacyclanes' **D** (≡ **D'**).



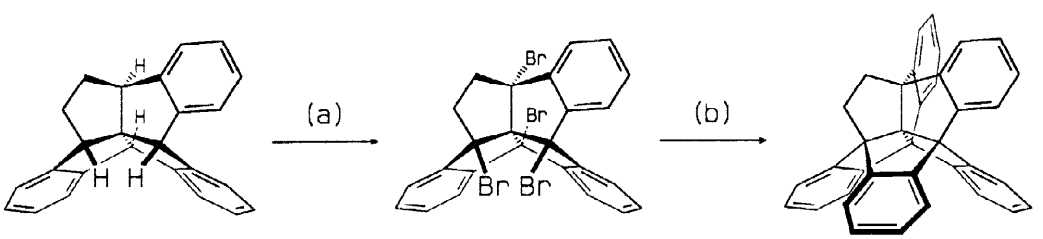
Scheme 1. From [m.n.o]propellanes (**A**) and [m.n.o.p]fenestranes (**B**) to [m.n.o.p.q]centropentacyclanes (**C**) and [m.n.o.p.q.r]centrohexacyclanes (**D**). i may vary for each of the rings. Bottom line: Orientation of the ring fusion (ring sizes: m, n, o, ...) according to the tetrahedral geometry.

Thus, the few centropentaquinanes known to date, viz. lactone **1**[16], centropentaindane **12** and its derivates,[5] as well as some further homocyclic derivates[7b,17] may be termed '[5.5.5.5.5]centropentacyclanes', and the centrohexaquinanes such as **2**–**8** as '[5.5.5.5.5.5]centrohexacyclanes'. Two further examples of the latter type will be presented first, one being a homocyclic [5.5.5.5.5.5]centrohexacyclane, **11**, which is synthesized by the two-fold condensation of benzene of [5.5.5.5]fenestrane **9**,[18] the other being a heterocyclic congener, **14**, which is formed by single bridging of a centropentacyclic hydrocarbon, centropentaindane **12**.[5]

RESULTS

[5.5.5.5.5.5]Centrohexacyclanes

Reaction of [5.5.5.5]fenestrane **9** with four equivalents of bromine leads to the tetrabromide **10**, which, after careful work-up, is obtained as a rather labile product (Scheme 2). Subsequent dissolution of the crude intermediate in benzene followed by treatment with aluminum tribromide gives rise to incorporation of two molecules of benzene across the two faces of the fenestrane framework, generating the centrohexacyclic skeleton of pentabenzocentrohexaquinane **11**. Similar *aufbau* reactions by two-fold or single condensations with benzene have been achieved previously with tetrabromofenestrindane and related bridgehead-brominated centropolyindanes[5,19] but, in contrast to these, tetrabromide **10** contains an alicyclic C_2 bridge which is prone to 1,2-elimination of HBr. In this view, the yield (44 % from **9**) of [5.5.5.5.5.5]centrohexacyclane **11** by the four-fold C–C coupling reaction is remarkable. By far lower efficiency was achieved recently by oxidative degradation of one of the six benzene rings of centrohexaindane (**3**) followed by reduction of the resulting 1,2-diketone.[20]



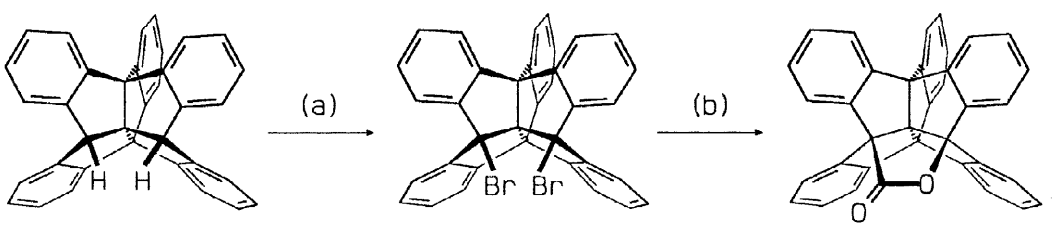
9 **10** **11**

Scheme 2. Conditions: (a) Br_2/CCl_4, hν (addition of Br_2 for 3 h), product not isolated; (b) $AlBr_3/C_6H_6$, 25 °C, 8 d, 44%.

Similar to tribenzo[5.5.5.5.]fenestrane **9**, centropentaindane **12** has been converted to the bridgehead dibromide **13**[5] which allowed us to introduce the sixth, homo- and heterocyclic five-membered ring, such as another indane unit or a 1,2-dioxolane or 1,2-dithiolane ring, leading to various [5.5.5.5.5.5]centrohexacyclanes (**4**, **7** and **8**, respectively).[5] Our attempts to introduce a single carbonyl bridge across the centropentacyclic framework of **13**, that is, to generate [5.5.5.5.5.4]centrohexacyclanes containing an additional four-membered ring, have failed so far. In accordance with similar carbonylation reactions,[21] we treated **13** with dicobalt octacarbonyl in acetonitrile (Scheme 3). Work-up and and separation of the products by chromatography afforded, surprisingly, the centrohexacyclic lactone **14** in low yield along with the corresponding diol.[5] Obviously, only one C–C bond was formed during the carbonylation step while hydrolysis of the remaining bromide during work-up enabled subsequent formation of the lactone owing to the extreme proximity of the two functionalities.

In some parallel to the first [5.5.5.5.5]centropentacyclic lactone **1** described by Keese et al.,[16] compound **14** represents the first [5.5.5.5.5.5]centrohexacyclic lactone.[22]

The identity of lactone **14** follows unequivocally from its ^{1}H and ^{13}C spectra. For example, the molecular C_s symmetry is reflected by four lines in the ^{13}C NMR spectrum in the $65 \lesssim \delta < 100$ range, representing the five carbon atoms of the neopentane core. Interestingly, however, the electron-impact (EI) mass spectrum of **14** does not show the molecular ion peaks, the highest-mass signals corresponding the $[M - CO_2]^{\bullet+}$ peaks (*m/z* 440, 441, etc). Second-most abundant is the doubly charged fragment $[M - CO_2]^{2+}$ (*m/z* 220, 220.5, etc.). This observation is unusual for an aromatic compound bearing that many aromatic rings, but it is conceivable considering the lability of the benzhydrylic bonds which have to be cleaved to expel the very stable CO_2 molecule as the neutral fragment. In contrast to the EI spectrum, the chemical ionization (CI) mass spectrum (using CH_4 as the reactant gas) exhibits the molecular mass of **14** by the $[M + H]^+$ peak of moderate relative intensity. Loss of CO (28 Da) from the $[M + H]^+$ ions, in contrast to loss of CO_2 from $M^{\bullet+}$, gives rise to the primary fragment at *m/z* 457. Whereas in the case of the protonated molecules, favourable protonation at the carbonyl oxygen of the lactone bridge prevents the expulsion of CO_2, the extremely facile decarboxylation of the radical ions $\mathbf{14}^{\bullet+}$ is in line with previous findings on ionized centropentaindanes bearing a heteroatomic bridge (e.g. CO–CO).[5]



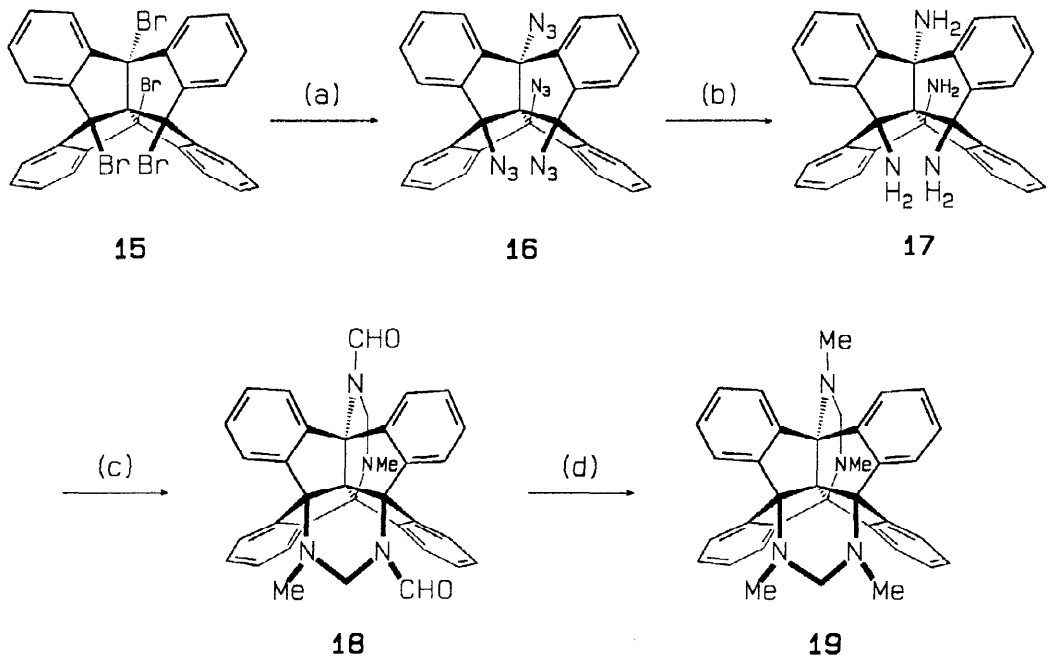
12 **13** **14**

Scheme 3. Conditions: (a) Br_2/CCl_4, Δ, hν, 3 h; crude product (ref. 5); (b) $Co_2(CO)_8$ (excess) in MeCN, 7 d, 40 °C, 25%.

[6.5.6.5.5.5]Centrohexacyclanes

Starting from four-fold bridgehead-substituted fenestrindanes such as tetrabromide **15**,[19] we also synthesized the first (heterocyclic) [m.n.o.p.q.r]centrohexacyclanes bearing rings of *different* sizes. Thus, [6.5.6.5.5.5]centrohexacyclane **19** was obtained in a four-step sequence (Scheme 4). Tetraazidofenestrindane **16** was prepared from **15** by tin(IV)-catalyzed reaction with trimethylsilyl azide[4,23] and converted to tetraaminofenestrindane **17** by reduction with lithium aluminium hydride. Upon attempts to convert **17** to the corresponding tetrakis(dimethylamino)fenestrindane under Eschweiler-Clarke conditions[24] we obtained the bis(formamide) **18**, instead of the sterically congested tertiary amine. Obviously, this [6.5.6.5.5.5]centrohexacyclic compound forms by two-fold C_1-bridging within each of the two pairs of *syn*-oriented amino groups and the remarkable efficiency of this reaction has again to be traced to a proximity effect operating at the mutually fixed bridgehead functionalities of the fenestrane framework.[25] Subsequent reduction of the formamide groups of **18** with lithium aluminium hydride furnished the four-fold methyl-substituted tetraaza[6.5.6.5.5.5]centrohexacyclane **19** in good yield.

The identity of **18** and **19** is again confirmed by mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy. The apparent molecular symmetry of **18** is C_2, giving rise to degeneracy of the NMR resonances of the



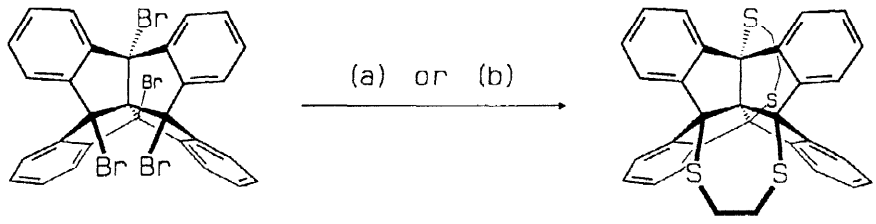
Scheme 4. Conditions: (a) $Me_3SiN_3/SnCl_4/CH_2Cl_2$, 25 °C, 5 h, 94%; (b) $LiAlH_4$/THF, 25 °C, 10 h, then H_2O, 58%; (c) CH_2O (30 %) and HCOOH (95 %) (1 : 1), Δ, 10 h, 35%; (d) $LiAlH_4$/THF, 25 °C, 10 h, then H_2O, 72%.

heterocyclic bridges and also to two-fold equivalence of the elements of the four benzene rings. For example, the ^1H NMR spectrum displays only one single line each for the aldehyde, methylene and methyl groups, and the ^{13}C NMR spectrum exhibits only four lines for the eight quaternary carbon atoms of the benzene rings. In contrast, conversion of the formyl functionalities into methyl increases the symmetry to D_{2d}; consequently, the ^1H NMR spectrum of the bis(aminal) **19** reflects not only the equivalence of the four methyl groups but also that of the four AA'BB' spin systems of the benzo nuclei. Correspondingly, the ^{13}C NMR spectrum shows only three lines for the 24 carbon atoms of the aromatic rings, similar to the spectra of the parent hydrocarbon and of all other fenestrindanes bearing equivalent bridgehead substituents and a conformationally flexible framework.[4,9b]

A [7.5.7.5.5.5]Centrohexacyclane

The first [7.5.7.5.5.5]centrohexacyclane **20** (Scheme 5) was synthesized from tetrabromofenestrindane **15** by reacting it with neat 1,2-dimercaptoethane or, alternatively, by treatment with 1,2-bis(trimethylsilylthio)-ethane in dichloromethane under catalysis with tin(IV) chloride. In this way, we recently converted a number of related bridgehead-brominated centropolyindanes into the corresponding multiple thioethers.[4,5b,26] In the case of **15**, both methods give relatively high yields of **20**. ^1H and ^{13}C NMR spectroscopy corroborate the presence of two 1,4-dithiacycloheptane rings. It is of interest that, in contrast to the [6.5.6.5.5.5]centrohexacyclanes **18** and **19**, which appear conformationally flexible at room temperature, the spectra of the [7.5.7.5.5.5]centrohexacyclane **20** indicate conformational rigidity of the fenestrane framework. In this case, the apparent symmetry is reduced to S_4. This is evident, for example, from the four-fold degeneracy within each set of eight *ortho* and eight *meta* protons, the benzo groups generating four equivalent ABCD spin systems. In line with this, two resonances are found for the quaternary carbon atoms of the indane junctions and four lines reflect the 16 methine carbon atoms of the benzene rings. Not surprisingly, all of the four methylene groups of the

ethylene bridges are equivalent. This should give rise to an AA'BB' spectrum which, however, is reduced to an apparent AB pattern with somewhat broadened signals. Measurements at increased temperatures ($T \leq 160°C$, $CDCl_2CDCl_2$) led to convergent line shift and further broadening but not to coalescence of the methylene



15 20

Scheme 5. Conditions: (a) $HSCH_2CH_2SH$, 160 °C, 2 d, 71%; (b) $SnCl_4/CH_2Cl_2$, $(Me_3SiSCH_2)_2$, 25 °C, 2 h, 75%.

resonances. Therefore, it appears highly probable that the conformation of **20** is 'static', similar to other four-fold bridgehead-substituted fenestrindanes such as **15**, its tetrachloro and, in particular, the related tetrakis-(methylthio) analogue.[4] In all these cases, the steric hindrance within each pair of (large) bridgehead substituents prevents the fast interconversion of the equivalent S_4 conformers. Force-field calculations corroborate the S_4 conformation of the fenestrane framework and suggest, moreover, that the $S-CH_2CH_2-S$ bridges are locked most favourably in a zig-zag orientation. The fact that the steric fit of larger rings at the nucleus of [5.5.5.5]fenestranes is critical, such as in **20**, is further confirmed by the finding that the attempts to perform analogous annelation reactions using higher α,ω-dimercaptoalkanes have been unsuccessful so far.[26a] Further studies may reveal details of the molecular structure of this unusual 'K_5 compound'[2] comprising, in the same time, one [5.5.5.5]- and two [7.5.7.5]fenestranes.

DISCUSSION

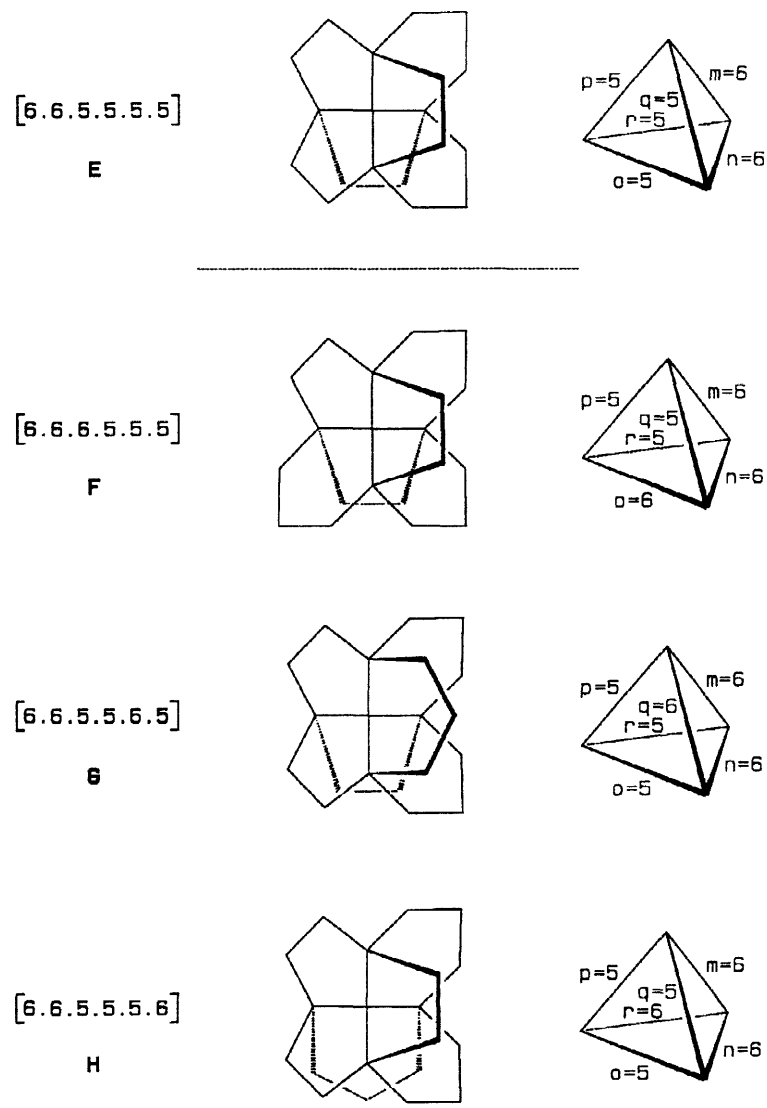
Nomenclature ([m.n.o.p.q.r] Notation) of the Centrohexacyclanes

The synthesis of the first [m.n.o.p.q.r]centrohexacyclanes containing rings of different sizes (**18**–**20**) raises the necessity to define a (general) nomenclature for these complex polycyclic systems. In particular, the mutual orientation of the individual rings has to be defined unequivocally. We propose to assign the prefixes (m, n, o ...) to the rings in the same order as they are defined for [m.n.o]propellanes and [m.n.o.p]fenestranes, that is, by *decreasing ring size using the fenestrane framework as a basis*. This leads to an unequivocal notation for both the [m.n.o.p.q.r]centrohexacyclanes and for their pentacyclic congeners, the [m.n.o.p.q]centropentacyclanes. For convenience, the ring sizes may be assigned according to the six edges of a tetrahedron (cf. Scheme 1). Thus, [6.5.6.5.5.5]centrohexacyclanes **18** and **19** have to be considered derivatives of a [6.5.6.5]-fenestrane bearing two additional five-membered rings whereas, in analogy, [7.5.7.5.5.5]centrohexacyclane **20** represents a doubly pentaanellelated [7.5.7.5]fenestrane.

As a complement to the molecular frameworks of **18** and **19**, we may also consider the (hypothetical) constitutional isomer bearing a [6.6.5.5.5.5] centrohexacyclic structure (Scheme 6, **E**). Apart from very few (unbridged) [6.6.5.5]fenestranes,[27] no higher centropolycyclanes are known to date that contain two (or more) *fuso*-annelated[8] six-membered rings, that is, rings sharing one C–C bond.[28] Also unknown are centrohexa-

cyclanes bearing more than two six-membered rings, as is illustrated in Scheme 6 for the three possible constitutional isomers of the 'centropolyquinane' series with [6.6.6.5.5.5], [6.6.5.5.6.5] and [6.6.5.5.5.6] centrohexacyclic frameworks (**F**, **G** and **H**, respectively). Note that, according to this notation, the first of the additional rings (size q) is added from the upper side of the [m.n.o.p]fenestrane and the second one (size r) from the back. In analogy, the hypothetical centropentacycles are conceivable bearing [6.6.5.5.5] and [6.5.6.5.5] as well as [6.6.6.5.5] and [6.5.6.5.6] annelated rings. Finally, the notation proposed here also offers an unequivocal assignment for the large group of [m.n.o.p.q.r]centrohexacyclanes and [m.n.o.p.q]centropentacyclanes containing rings of multiply different sizes.

As mentioned above, some inorganic and elementorganic [6.6.6.6.6.6]centrohexacyclanes[29] ('centrohexasexanes'[8]) have been described while, besides compounds **18** and **19** presented in this paper, no strictly organic centrohexacyclanes are known bearing six-membered rings in the polycyclic core. It may be assumed, however, that the family of centrohexacyclic compounds will grow further because of the general interest in novel host/guest systems, dendritic and supramolecular structures. Therefore, the simple nomenclature suggested here may be useful for the further development of this field.[30]



Scheme 6.

CONCLUSION

Several new centrohexacyclic organic compounds have been presented based on the [5.5.5.5]framework of fenestrindane. Bridging both of the faces of [5.5.5.5]fenestranes by two-membered units generates two additional five-membered rings and thus [5.5.5.5.5.5]centrohexacyclanes, whereas single bridging would lead to [5.5.5.5.5]centropentacyclanes. Some examples have been presented which show that bridging of fenestrindanes by two heteroatomic three- or even four-membered units is possible leading to two six- or seven-membered heterocyclic rings, fused to the [5.5.5.5]fenestrane framework, and thus to [6.5.6.5.5.5]- and [7.5.7.5.5.5]centrohexacyclanes, respectively. A nomenclature of [m.n.o.p.q.r]centrohexacyclic and, correspondingly, [m.n.o.p.q]centropentacyclic compounds has been proposed to define the relative orientation of rings of different sizes about the tetrahedral core of centropolycyclic molecules beyond the propellanes and fenestranes.

EXPERIMENTAL

General methods

Melting points (uncorrected): Electrothermal melting point apparatus. – IR: Perkin-Elmer 377 and 841. – ^{1}H NMR: Bruker AM 300; $CDCl_3$/TMS, if not stated otherwise. – ^{13}C NMR: Bruker AM 300 (J-modulated spin echo experiments); $CDCl_3$/TMS, if not stated otherwise. ^{1}H-^{1}H COSY measurements: Bruker AM 300. – MS: Finnigan MAT CH5 and Fisons Autospec, EI, 70 eV; samples were introduced by the solids inlet probes. – Exact mass measurements: Fisons Autospec (resolving power $m/\Delta M \approx 8000$). – Thin layer chromatography (TLC): Silica gel (Kieselgel 60) on Al foil (Merck, F 254).

Pentabenzocentrohexaquinane 11 by Bromination/Condensation

(4bα,8bβ,12bα,14aβ)-4b,8b,12b,14a-Tetrabromo-4b,8b,12b,13,14,14a-hexahydrodibenzo[af]benzo[2,3]pentaleno[1,6-cd]pentalene (10). A 2 M solution of bromine (1.28 g, 8.00 mmol) in tetrachloromethane (40 ml) was dropped within 3 h to a solution of tribenzo[5.5.5.5]fenestrane **9** (0.64 g, 2.00 mmol) in 150 ml of the same solvent. The reaction mixture was irradiated with a photolamp (500 W) during addition of the reagent and for another 30 min. Subsequent evaporation of the solvent under reduced pressure leaves the crude tetrabromide, which has not been characterized but can be used directly by re-dissolution.

13H,14H-4b,12b[1',2']:8b,14a[1'',2'']dibenzenodibenzo[a,f]benzo[2,3]pentaleno[1,6-cd]pentalene ('Pentabenzocentrohexaquinane' 11). The residue of **10** was dissolved in anhydrous benzene (100 ml) by stirring and gentle heating to 30 °C. A 0.1 M solution prepared from aluminium tribromide (0.69 g, 2.6 mmol) and benzene (26 ml) was added, while the mixture turns red. Stirring was continued at ambident temperature for 8 d. Thereafter, the mixture was hydrolysed by addition of water (125 ml), the aqueous layer was separated and extracted with dichloromethane. The combined organic solutions were dried with Na_2SO_4 and the solvent was evaporated. The solid residue was purified by filtration through silica gel by using eluent *n*-hexane/$CHCl_3$; subsequent recrystallisation from this solvent mixture gave pure **11** (0.41 g, 44 %) as colourless crystals. Physical and spectral data of the product proved it to be identical with that described earlier.[20]

Centropentaindane Lactone 14

*8b,16b-Oxycarbonyl-8b*H,*16b*H-*4b,12b[1',2']benzenodibenzo[*a,f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]-pentalene (14).* The labile dibromide **13** was prepared from centropentaindane **12** (221 mg, 500 μmol) as

described recently.[5b] The crude product is dissolved unter argon in acetonitrile (50 ml) and dicobaltoctacarbonyl (500 mg, 1.60 mmol; Alfa Ventron) was added. The mixture was stirred at 40 °C for a total period of 7 d, and the same amounts of the reagent were added after 2 and 4 d periods. After evaporation of the solvent in vacuo, the product mixture was separated by chromatography (silica gel/CH_2Cl_2) giving, besides minor amounts of the corresponding diol,[5b] lactone **14** (120 mg, 25 %) as colourless crystals, m.p. > 400 °C. IR (KBr): $\tilde{\nu}$ = 3068 cm^{-1}, 3024, 1764, 1597, 1469, 1305, 1218, 1186, 1095, 986, 967, 949, 760, 737, 622. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.71−7.83 (m, 10 H), 7.28−7.42 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.2 (s), 148.7 (s), 148.4 (s), 146.5 (s), 142.2 (s), 141.8 (s), 130.8 (d), 129.8 (d), 129.1 (d), 129.0 (d), 126.5 (d), 124.9 (d), 124.3 (d), 124.1 (d), 123.7 (d), 98.7 (s, C-8b), 88.9 (s, C-16d), 72.2 (s, C-4b, C-12b), 68.7 (s, C-16b). MS (EI, 70 eV): *m/z* = 440 (100 %, $[M - CO_2]^{\bullet+}$), 363 (9), 220 (35, $[M - CO_2]^{2+}$). MS (CI, CH_4): *m/z* = 485 (33 %, $[M + H]^+$), 457 (32, $[M + H - CO]^+$). (MS found *m/z* 440.1567; $C_{35}H_{20} \equiv [M - CO_2]$ requires 440.1565.)

[6.5.6.5.5.5]Centrohexacyclanes 18 and 19

*(4bα,8bβ,12bα,16bβ)-4b,8b,12b,16b-Tetraazido-4b,8b,12b,16b-tetrahydrodibenzo[a,f]dibenzo[2,3:4,5]-pentaleno[1,6-cd]pentalene (4b,8b,12b,16b-Tetraazidofenestrindane, **16**).* A solution of tetrabromofenestrindane **15** (342 mg, 500 μmol) in anhydrous dichloromethane (50 ml) was stirred under nitrogen while azidotrimethylsilane (2.00 ml, 15.0 mmol, Janssen) and then tin(IV) chloride (100 μl, 860 μmol) were added. Addition of the catalyst produced a transient orange clowding of the solution. Stirring of was continued for 5 h. Then the clear, yellow solution was concentrated to precipitate a fine, crystalline solid. Filtration and washing of the precipitate with a little dichloromethane furnished **16** (251 mg, 94 %) as a colourless powder, which decomposes at ca. 215 °C by explosion. IR (KBr): $\tilde{\nu}$ = 3077 cm^{-1}, 2090, 1472, 1458, 1243, 1171, 1151, 1041, 945, 765, 707, 642, 606. ^1H NMR (300 MHz, $CDCl_3$, 40 °C): δ = 7.65 (br, 4 H), 7.54 (br, 12 H). The signals are diffuse due to the dynamic conformational equilibrium of **16**.[4] ^{13}C NMR (75 MHz, [D_5]pyridine, 70 ° C): δ = 142.3 (s), 131.0 (d), 125.3 (d), 89.0 (s, very weak), 80.6 (s). MS (EI, 70 eV): *m/z* = 504 (4 %, $[M - N_2]^{\bullet+}$), 490 (54), 406 (100), 392 (41), 203 (5).

*(4bα,8bβ,12bα,16bβ)-4b,8b,12b,16b-Tetraamino-4b,8b,12b,16b-tetrahydrodibenzo[a,f]dibenzo[2,3:4,5]-pentaleno[1,6-cd]pentalene (4b,8b,12b,16b-Tetraaminofenestrindane, **17**).* To a solution of tetraazidofenestrindane **16** (106 mg, 200 μmol) in anhydrous tetrahydrofuran (50 ml) was added lithium aluminium hydride (33.4 mg, 880 μmol) and the mixture was stirred at ambident temperature for 10 h. Hydrolysis with water followed by extraction with trichloromethane and ethyl acetate and evaporation of the solvent gave a product mixture, which was subjected to filtration through silica gel and MPLC (silica gel, EtOAc) to give the pure tetraamine **17** (76.0 mg, 58 %) as a light-yellow powder, m.p. 250 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3342 cm^{-1}, 3261, 3066, 2930, 1582, 1274, 1218, 1006, 914, 893, 758, 614. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, ^3J = 7.44 Hz, 4 H), 7.34 (m, 12 H), 2.15 (br s, 8 H, NH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.2 (q), 145.8 (s), 128.60 (d), 128.55 (d), 123.9 (d), 122.6 (d), 81.8 (s, C-16d), 72.8 (s, C-4b/8b/12b/16b). MS (EI, 70 eV): *m/z* = 428 (13 %, $[M]^{\bullet+}$), 412 (2), 411 (5), 395 (16), 394 (47), 378 (100), 291 (10). (MS found *m/z* 428.1993; $C_{29}H_{24}N_4$ requires 428.2001.)

*(4bα,8bβ,12bα,16bβ)-4b,12b;8b,16b-Bis(*N*-formyl-*N*'-methyl-1,3-diazapropano)-4b,8b,12b,16b-tetrahydrodibenzo[a,f]dibenzo[2,3:4,5]pentaleno[1,6-cd]pentalene[4b,12b;8b,16b-Bis(*N*-formyl-*N*'-methyl-1,3-diazapropano)fenestrindane] (**18**).* Tetraminofenestrindane **17** (50.0 mg, 117 μmol) was added to a mixture of aqueous formaldehyde (30 %, 10 ml) and formic acid (90 %, 10 ml) and heated to reflux. After 10 h, another 20 ml of the reagent solution was added and heating was continued for 10 h. The mixture was allowed to cool, diluted

with water and neutralized with aqueous $NaHCO_3$. The mixture was extracted with trichloromethane, the combined extracts were concentrated to dryness and the residue was filtrated through silica gel. Subsequent MPLC (silica gel, *n*-hexane/CH_2Cl_2 4 : 1) gave the bis(formamide) **18** (22.1 mg, 35 %) as a light-yellow solid, m.p. 282 °C. IR (KBr): $\tilde{\nu}$ = 3274 cm^{-1}, 3088, 3031, 1843, 1643, 1292, 1026, 752, 694. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.32 (s, 2 H, CHO), 7.63 (m, 4 H), 7.42 (m, 12 H), 4.06 (s, 4 H, CH_2), 1.89 (s, 6 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.2 (d, CHO), 143.4 (s), 143.2 (s), 143.0 (s), 142.6 (s), 129.1 (d), 128.9 (d), 126.3 (d), 125.8 (d), 125.0 (d), 80.9 (s, C-16d), 75.8 (s), 73.3 (s), 60.6 (t, N-C-N), 37.1 (q, CH_3). MS (EI, 70 eV): *m/z* = 536 (21 %, $[M]^{\bullet+}$), 493 (11), 492 (26), 393 (79), 380 (28), 379 (38), 378 (100), 366 (11), 365 (18), 352 (18), 189 (13), 42 (30). (MS found *m/z* 536.2216; $C_{35}H_{28}N_4O_2$ requires 536.2212)

*(4bα,8bβ,12bα,16bβ)-4b,12b;8b,16b-Bis(*N,N'*-dimethyl-1,3-diazapropano)-4b,8b,12b,16b-tetrahydrodibenzo[a,f]dibenzo[2,3:4,5]pentaleno[1,6-cd]pentalene [4b,12b;8b,16b-Bis(*N,N'*-dimethyl-1,3-diazapropano)-fenestrindane] (**19**).* A solution of the bis(formamide) **18** (100 mg, 186 μmol) in anhydrous tetrahydrofuran (25 ml) was stirred while powdered lithium aluminium hydride (100 mg, 750 μmol) was added. Stirring was continued at ambident temperature for 10 h. The mixture was hydrolysed with water and then extracted with trichloromethane. Evaporation of the solvent followed by filtration through silica gel and purification by MPLC (silica gel, *n*-hexane/CH_2Cl_2 1 : 3) furnished the tetraamine **19** (70.0 mg, 72 %) as a light-yellow solid, m.p. 293 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3412 cm^{-1}, 2938, 1657, 1184, 1066, 767, 629. ^1H NMR (300 MHz, $CDCl_3$): AA'BB' spectrum ($\delta_{AA'}$ = 7.58, $\delta_{BB'}$ = 7.28; 16 H), 3.23 (s, 4 H), 2.10 (s; 12 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.2 (s), 127.1 (d), 125.3 (d), 75.9 (s), 70.3 (t, CH_2), 37.1 (q, CH_3). MS (EI, 70 eV): *m/z* = 508 (35, $[M]^{\bullet+}$), 466 (42), 393 (62), 378 (100), 364 (13), 352 (15), 42 (21). (MS found *m/z* 508.2635; $C_{35}H_{32}N_4$ requires 508.2627.)

[7.5.7.5.5.5]Centrohexacyclane 20

*(4bα,8bβ,12bα,16bβ)-4b,12b;8b,16b-Bis(1,4-dithiabutano)-4b,8b,12b,16b-tetrahydrodibenzo[a,f]dibenzo-[2,3:4,5]pentaleno[1,6-cd]pentalene [4b,12b;8b,16b-Bis(1,4-dithiabutano)fenestrindane] (**20**). (Method A).* A mixture of tetrabromofenestrindane **15**[19] (342 mg, 500 μmol) and ethanedithiol (30 ml) was heated to 160 °C for 2 d. The excess of the reagent was removed in vacuo (ca. 1 mbar) and the highly viscous residue was redissolved in dichloromethane (2 ml). After a short time, a solid precipitated, which was filtered by suction and washed with a dichloromethane. Recrystallisation from THF/*n*-hexane (1 : 1) gave the thioether **20** (195 mg, 71 %) as little, colourless crystals which contained some tetrahydrodfuran.

Method B. A solution of **15** (512 mg, 750 μmol) in dichloromethane (100 ml) was stirred under argon while tin(IV) chloride (350 μl, 3.00 mmol) was added. 1,2-Bis(trimethylsilylthio)ethane (Fluka, 99 %) was then added in the course of 1 h through a rubber septum from a syringe. Stirring was continued for 2 h. The precipitate was isolated by suction and washed several times with water. Recrystallisation from THF/*n*-hexane (1 : 1) gave **20** (300 mg, 75 %) as colourless crystals, m.p. 287 °C. IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 3030, 2962, 2902, 1466, 1270, 1157, 1015, 897, 737, 679, 608. ^1H NMR (300 MHz, $CDCl_2CDCl_2$): ABCD spectrum (δ_A = 7.60, 4 H ; δ_B = 7.44, 4 H; δ_C, δ_D = 7.33, 8 H), 2.80 (d, *J* = 12.3 Hz, 4 H), 2.29 (d, *J* = 12.3 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_2CDCl_2$): δ = 142.5 (s), 139.6 (s), 128.8 (d), 128.3 (d), 125.1 (d), 124.5 (d), 104.6 (s, C-16d), 71.1 (s, C-4b/8b/12b/16b), 35.8 (t, CH_2). MS (EI, 70 eV): *m/z* = 548 (4 %, $[M]^{\bullet+}$), 457 (27), 456 (100, $[M - C_2H_4S_2]^{\bullet+}$), 428 (7), 396 (16), 364 (23, $[M - 2\ C_2H_4S_2]^{\bullet+}$), 363 (20), 228.5 (3), 228 (7), 124 (16). (MS found *m/z* 548.0759; $C_{33}H_{24}S_4$ requires 548.0761.)

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15. In contrast to the propellanes, for which the prefix [m.n.o] defines the lengths of bridges between the bridgeheads, the prefix [m.n.o.p] for fenestranes denotes the ring sites directly. In accordance with this, the notations [m.n.o.p.q] and [m.n.o.p.q.r], respectively, for centropentacyclanes and centrohexacyclanes refer to the ring sizes as well. See, e.g. Greenberg, A.; Liebman, J. L. *Strained Organic Molecules*; Academic Press: New York, 1978.
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