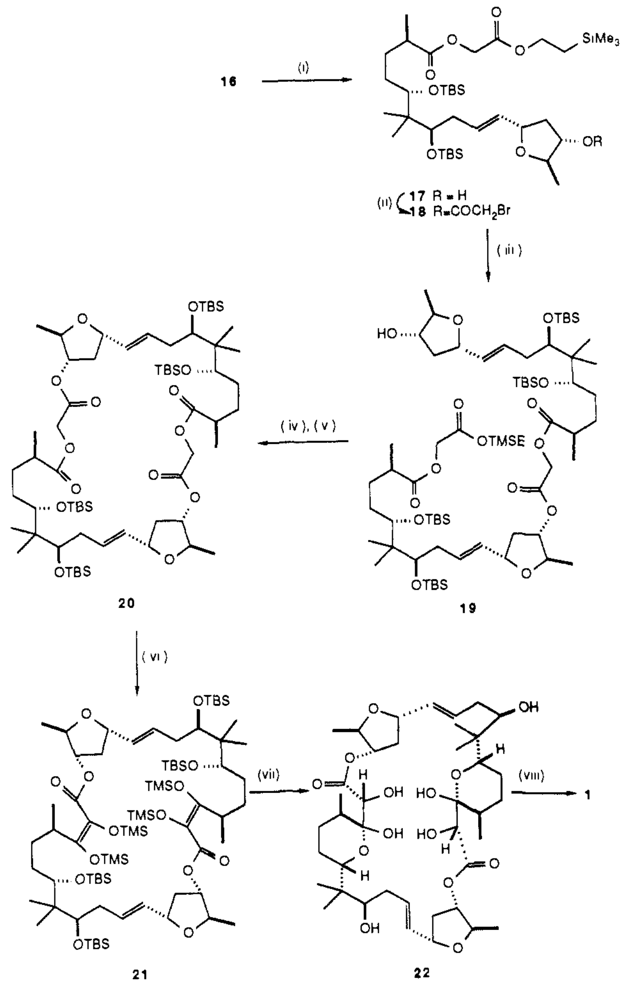
Scheme II[a]



^{a}(i) $BrCH_2CO_2(CH_2)_2SiMe_3$, K_2CO_3, acetone, reflux (93%); (ii) $BrCH_2COCl$, DMAP, Py, CH_2Cl_2, 0 °C (92%); (iii) **16**, K_2CO_3, acetone, reflux (88%); (iv) n-Bu_4NF, THF, 0 °C; (v) 2-chloropyridinium methiodide, Et_3N, CH_2Cl_2 (86%); (vi) LDA, THF, 0 °C, then −78 °C, Me_3SiOTf; (vii) 5% HF, CH_3CN, 3.5 h, 25 °C; (viii) $(MeO)_3B$, MeOH, heat.

this macrocycle is evident from its ^{1}H and ^{13}C NMR spectra and, upon treatment with lithium diisopropylamide followed by trimethylsilyl triflate, a "double-Chan" reaction[13] of **20** afforded **21** in good yield. Simultaneous removal of all silyl protecting groups was accomplished with HF, which also catalyzed intramolecular hemiketalization, to give deboroaplasmomycin **22**, corresponding to material obtained from natural **1** with citric acid. Finally, **22** was treated with anhydrous trimethyl borate[9,18] furnishing aplasmomycin that was identical by comparison of chromatographic properties, infrared and ^{1}H NMR spectra, and optical rotation with the natural substance (Scheme II).

Acknowledgment. We are indebted to Professor Heinz G. Floss, The Ohio State University, and Dr. Yoshiro Okami, Institute of Microbial Chemistry, Tokyo, for samples of natural aplasmomycin and to Professor E. J. Corey, Harvard University, for spectral data of synthetic intermediates. Financial support of this work was provided by the National Institute of Allergy and Infectious Diseases through Grant AI10964.

Supplementary Material Available: Spectral data for **5–7**, **9**, **11**, **14–20**, **22**, **23**, **25–29**, and **31** and synthetic scheme for **6** (8 pages). Ordering information is given on any current masthead page.

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Benzoannelated Centropolyquinanes. 2.[1] *all-cis*-Tetrabenzotetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane, "Fenestrindan"

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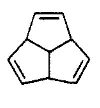
Received July 24, 1986

The carbon skeletons of tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (triquinacene) (**1**)[2] and tetracyclo[5.5.1.0^{4,13}.0^{10,13}]trideca-2,5,8,11-tetraene (**2**)[3] have attracted considerable interest in recent years.[4,5] Both structures offer or promise an access to more highly unsaturated, strained polyquinanes,[6] or, more stricty, *centro*polyquinanes,[7] as well as to related carbanions,[5a] carbocations, and transition-metal complexes.[5e] In particular, centrotetracyclic species like **2** have been investigated by several groups as potential precursors to compounds containing a planar or planarizable carbon atom.[8] In contrast to polyquinenes, benzoannelated polyquinanes have been studied scarcely,[1,8b,c,9] though, in general, strained polycycles gain stability by fusion to aromatic rings.



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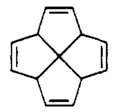

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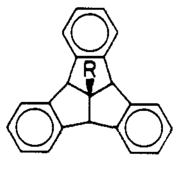

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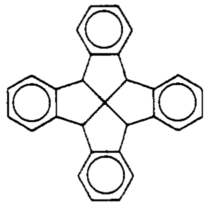

4

In this context, we wish to report on the synthesis and some properties of the tetrabenzo analogoue of **2**, i.e., the title compound

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(1) Part 1: Kuck, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 508. The present work was contributed at the 4th European Symposium on Organic Chemistry, Aix-en-Provence, France, Sept 2–6, 1985.

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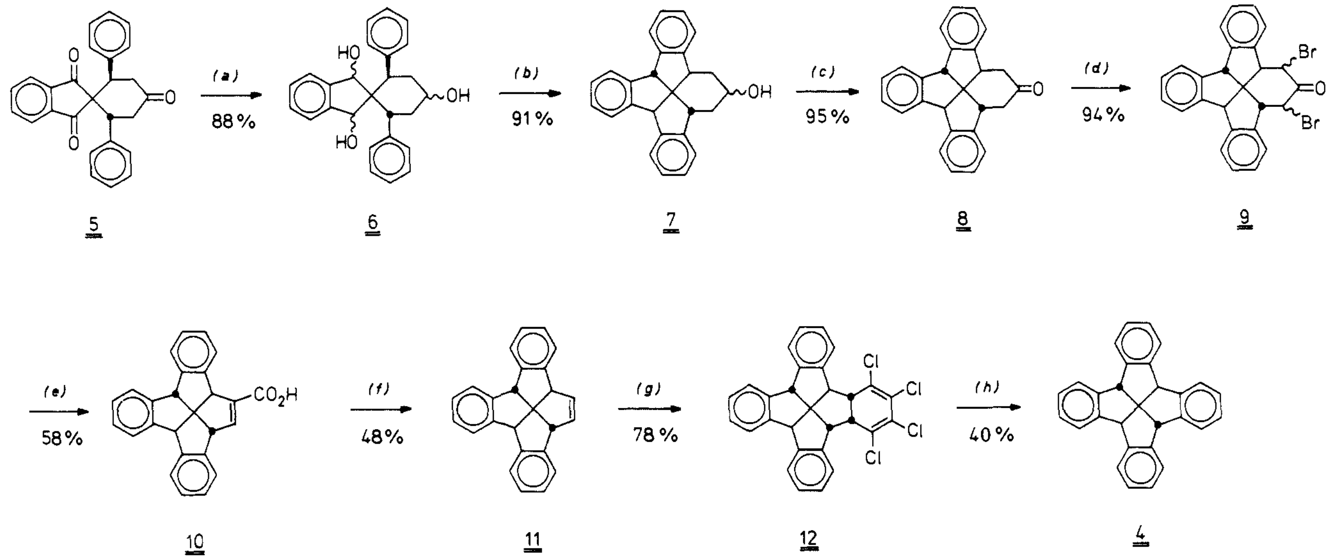
Scheme I[a]



[a] (a) $LiAlH_4$/THF, reflux, 8 h; (b) H_3PO_4/xylene, reflux, 2 h; (c) CrO_3/H_2SO_4/acetone, room-temperature; 12 h; (d) Br_2/AcOH, room temperature, 16 h; (e) KOH/THF/N_2, reflux, 6 h; (f) Cu/quinoline/N_2, 200 °C, 6 h; (g) c-$(CCl)_4SO_2$/benzene (concentrated), 110 °C, 10 h; (h) Na/t-BuOH/THF, reflux, 15 h.

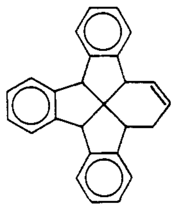
4. Because of the close relation of this fourfold indan hydrocarbon to *all-cis*-[5.5.5.5]fenestrane,[5a-c] we propose for **4** the name "fenestrindan".[10]

We recently reported on a facile synthetic access to benzoannelated centrotriquinanes, e.g., **3** (R = CH_3).[1] The key step of their synthesis is the double cyclodehydration of the corresponding 2,2-disubstituted 1,3-indandiols which can be obtained easily from the related 1,3-indandiones. The same route has now been applied to the synthesis of benzoannelated [6.5.5.5]- and [5.5.5.5]fenestranes, culminating in the following eight-step preparation of fenestrindan (**4**) (Scheme I).

The basis of the synthetic sequence is the double Michael adduct of dibenzal acetone and 1,3-indandione (**5**) described in the literature.[11,12] The trans orientation of the phenyl groups is particularly well suited for the double cyclodehydration of the corresponding spiro triol **6** which is obtained from **5** as a mixture of stereoisomers by using excess $LiAlH_4$ in THF.[13,14] Heating **6** with H_3PO_4/xylene at reflux for 2 h in a water separator affords the [6.5.5.5]fenestrane alcohol **7** in excellent (>91%) yield.[15] Upon prolonged heating (>20 h) only small amounts of the originally expected olefin **13** are formed.[15,16] The fortunate persistence of the cyclohexanol moiety is attributed to an unusually high strain in the doubly fused cyclohexene unit of **13**. Hence the fenestrane ketone **8**[15] is obtained easily by oxidation of **7** in 76% overall yield from **5**. An alternative, yet not optimized access to **8** consists in the conversion of **5** to its 4',4'-ethylene ketal followed by reduction of the corresponding spiro diol and double cyclodehydration concomitant with ketal hydrolysis to give **8** in ~20% overall yield.

Ring contraction of the [6.5.5.5]fenestrane ketone **8** via **9**[15] to acid **10**[15] affords the [5.5.5.5]fenestrane skeleton, and subsequent decarboxylation gives *all-cis*-tribenzo[5.5.5.5]fenestr-11-ene (**11**)[15] in 26% overall yield from ketone **8**. Heating **11** and tetrachlorothiophene *S*,*S*-dioxide[17] affords the cycloadduct **12**[15] which is reduced[18] to the title hydrocarbon in moderate yield. Fenestrindan (**4**) is obtained from EtOH/benzene as colorless platelets of mp 325–230 °C dec.

A number of interesting [6.5.5.5]- and [5.5.5.5]fenestranes are easily prepared from the intermediates described above. Thus, the tribenzofenestranes **14**[15] and **15**[15] and the tetrachlorofenestrindan **16**[15] have been obtained from **8**, **11**, and **12**, respectively, by standard procedures.



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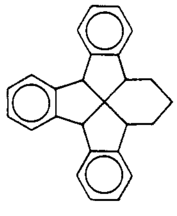

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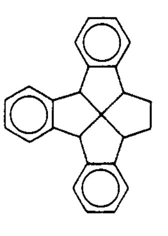

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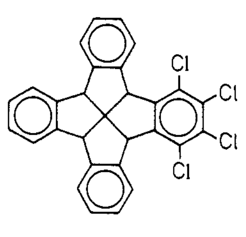

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The C_2 molecular symmetry of **8**, **9**, and **11**, as well as the lack of symmetry in **7**, **10**, and **12**, is nicely confirmed by NMR spectrometry. Some of the former, chiral tetracycles will be subjected to enantiomer separation to obtain optically pure benzofenestranes. In contrast, fenestrindan (**4**) is achiral, its apparent D_{2d} molecular symmetry being manifested by the degeneracy of the four benzhydryl protons and the four benzo AA'BB' spin systems found in the ^1H NMR spectrum as well as by the observation of only five ^{13}C resonances for this $C_{29}H_{20}$ hydrocarbon.[19]

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[10] The parent [5.5.5.5]fenestrane has been called also "staurane",[5d] "tetraquinacane",[5c] and "tetrafusotetraquinane".[7] In our opinion, however, the name "fenestrindan" describes the unique fusion of the eight rings of **4** in the most stringent, unambiguous way.

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[13] At least three diastereomeric triols **6** are formed, which have not been completely purified before cyclodehydration.

[14] All new compounds have been characterized by ^1H NMR, IR, and mass spectrometry and, most of them, by ^{13}C NMR spectrometry. Combustion analysis gave satisfactory results in all cases.

[15] Melting points (°C): **7**, 242 (THF); **8**, 286 (EtOH/THF); **9**, 228 dec; **10**, 295–8 dec; **11**, 192 (EtOH/acetone); **12**, 224 (EtOAc); **13**, 196 (benzene); **14**, 199; **15**, 173–174; **16**, 306–309.

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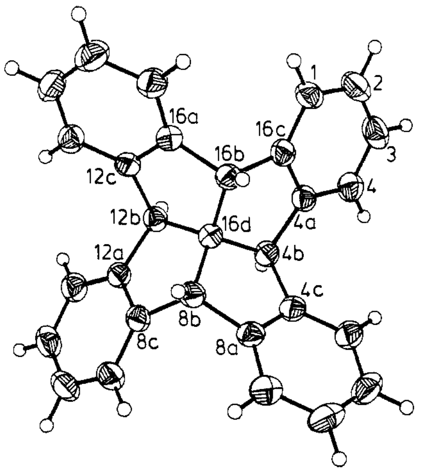

Figure 1. Perspective drawing of the solid-state structure of **4**, viewed along the S_4 axis. Selected bond lengths (pm) and angles (deg): C(4a)–C(4b), 150.6; C(4b)–C(16d), 155.1; C(4a)–C(4b)–C(4c), 117.4; C(4a)–C(4b)–C(16d), 104.2; C(4b)–C(16d)–C(8b), 106.0; C(4b)–C(16d)–C(12b), 116.5.

However, it is interesting to note that the molecular symmetry of **4** is S_4 rather than D_{2d}. An X-ray crystal structure analysis[20] reveals (Figure 1) that the mutual fusion of the two 2,2′-spirobiindan moieties of **4** still allows for the envelope-like bending of each of the four cyclopentene rings. In this way, the central neopentane unit avoids the all-eclipsed conformation which should represent the D_{2d} transition state for interconversion of the two equivalent S_4 conformers. Thus a torsional angle of 20.6° is found for the central C–C bonds (e.g. ∠ H(8b)–C(8b)–C(16d)–C(16b)), and the slightly concave (convex) *o*-xylylene moieties are situated 38 (±1) pm above (below) the central carbon atom. Nevertheless, the dihedral angles between two opposite and respectively two adjacent xylylene moieties are found to remain 90 (±1)° and 120 (±1)°, as anticipated for the D_{2d} conformation. A similar situation should apply to the related tetraene **2**.[3,21]

The UV absorption spectrum of fenestrindan[19] gives no evidence for electronic interactions between the benzo nuclei, the α band closely resembling those of indan and the tribenzocentrotriquinanes.[1] Efforts are under way in this laboratory to investigate the chemistry of fenestrindan and the synthetic potential for bridging the remaining two edges of the central tetrahedron of **4**, producing benzoannelated centropolyquinanes with topologically nonplanar structures.[22]

Acknowledgment. We thank Prof. Dr. A. Müller and Prof. Dr. H.-F. Grützmacher, University of Bielefeld, for their kind support of this work. Thanks are due also to Dr. W.-D. Fessner, University of Freiburg, West Germany, for a helpful discussion.

Supplementary Material Available: ^{1}H NMR (300 MHz) data of compounds **7–13** and positional parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen positions of **4** (6 pages). Ordering information is given on any current masthead page.

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(19) Fenestrindan (**4**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.89 (s, 4 H), 7.27 and 7.53 (AA′BB′, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) 62.17 (d), 71.93 (s), 124.57 (d), 127.63 (d), 144.11 (s); IR (KBr) (cm^{-1}) 3065, 3035, 3018, 2925, 2895 (w), 1478, 1475, 1463, 1454 (s), 763, 760, 754, 730 (s); MS (EI, 70 eV), m/z 368 ($M^{\bullet+}$, 100%), 367 (46), 291 (33), 290 (25), 289 (36), 145 ($[M - C_6H_6]^{2+}$, 31); UV (n-heptane, $c = 2.5 \cdot 10^{-5}$ mol L^{-1}) λ_{max} (nm) 273.5 (ϵ 5000), 267.0 (4130), 261.5 (2380).

(20) Crystals of **4** are triclinic, space group $P\bar{1}$, $a = 1041.4$ (2) pm, $b = 1077.7$ (2) pm, $c = 1099.0$ (2) pm, $\alpha = 115.20$ (2)°, $\beta = 105.67$ (2)°, $\gamma = 104.73$ (2)°, $Z = 2$, $\rho_c = 1.257$ g cm^{-3}. The structure was refined (with hydrogen atoms in calculated positions) to $R = 0.053$ and $R_w = 0.050$ for 2681 independent reflections ($F_o > 3.92\sigma(F_o)$).

(21) A similar torsion of the [5.5.5.5]fenestrane skeleton has been described: Mitschka, R.; Oehldrich, J.; Takahashi, K.; Cook, J. M.; Weiss, U.; Silverton, J. V. *Tetrahedron* **1981**, *37*, 4521.

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Torands: Rigid Toroidal Macrocycles. Calcium Sequestration by a Member of This New Ligand Class

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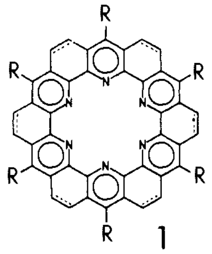
Received July 28, 1986

Discovery of new host families is crucial to the development of tailored molecules capable of molecular recognition and selective catalysis.[1] Heretofore, effective neutral hosts for alkali-metal and alkaline-earth ions have been largely restricted to three main classes: crown ethers,[2] cryptands,[3] and spherands.[4] Model studies of a fully unsaturated nitrogen analogue of 18-crown-6 suggested that fusion of six-membered rings to every position on the periphery of 1,4,7,10,13,16-hexaaza[18]annulene would afford a planar toroidal macrocycle, **1**, having potentially useful metal binding properties.[5] We have now synthesized the first substituent-solubilized ligand of this type, **2**, and we find that this new "torand" complexes calcium.



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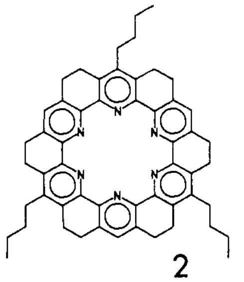

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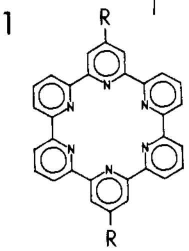
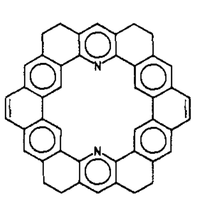


3a R=H

3b $R=C_6H_5$ or $C_6H_4CH_3$



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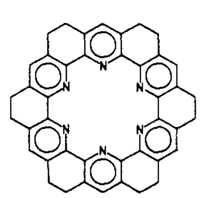

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Formula **1** represents a general ligand structure in which the outer two-carbon bridges may be saturated or unsaturated and the pyridine 4-positions bear up to six substituents (R). Our choice of target system **2** was determined by balancing considerations of solubility and spectroscopic simplicity. In particular, low solubility has hindered studies of "sexipyridines" **3a**[6] and **3b**,[7]

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