Orthocyclophanes. 2.[1] Starands, a New Family of Macrocycles of Spirobicyclic Polyketals with a 2*n*-Crown-*n* Moiety

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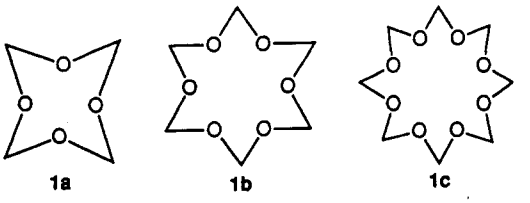
Synthesis and functionalization of higher members of the [1_n]orthocyclophanes, or [1_n]OCPs, have been investigated. Oxidation of the benzylic methylenes in [1_n]OCPs gave the polyoxo derivatives. Exhaustive oxidation of all methylenes in even-numbered [1_n]OCPs gave rearranged isomers of the cyclopolyketal structure instead of the corresponding polyoxo derivatives. We propose the class name "starands" for this new family of crown compounds for their star-shaped crown ether structure. Detailed synthesis and characterization of two starands are described.

Introduction

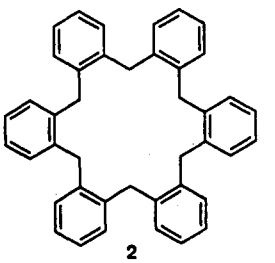
For the past decade, we have been investigating a new branch of orthocyclophane chemistry, the family of orthocyclophanes, or OCPs.[1-4] Since the benzylic methylenes of [1_n]OCPs are subject to chemical reactions, we have been pursuing the modification of [1_n]OCPs and have found that the properties of odd-numbered [1_{2n+1}]OCPs and even-numbered [1_{2n}]OCPs are quite different.

In spite of the extensive investigation of the synthesis and complexation of crown compounds during the past two decades,[5] most coronands (crown ethers) are macrocyclic polyethers whose ligand oxygens are separated from one another by hydrocarbon spacers containing two or more bridging atoms, such as $(CH_2)_2$, $(CH_2)_3$, and *o*- or *m*-phenylene units. Thus, most known crown ethers are composed of repeating ethyleneoxy units, $(CH_2CH_2O)_n$, to give the 3*n*-crown-*n* moiety. There has never been reported a class of coronand containing a 2*n*-crown-*n* moiety, such as **1a–c**, in which the ligand oxygen atoms are separated by one bridging atom.

We reported an unprecedented result in the oxidation of the benzylic methylenes of [1_6]orthocyclophane, or [1_6]-OCP (**2**), which involves the rearrangement of a cyclic polyketone to a cyclic polyketal.[2] Oxidation of the methylenes in the dioxo derivative **16** gave rise to the corresponding pentaoxo derivative, which upon further oxidation did not provide the expected hexaoxo derivative, but rather the star-shaped coronand (2,4)(4,6)(6,8)(8,10)-(10,12)(12,2)-hexa-*o*-phenylene-12-crown-6 (**3**). This striking reaction can be rationalized by assuming that the initially formed hexaone isomerized spontaneously to the less strained polyketal **3**. This result suggested the generation of other homologs of star-shaped coronands from even-numbered [1_n]OCPs.



1a **1b** **1c**



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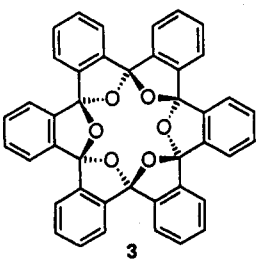

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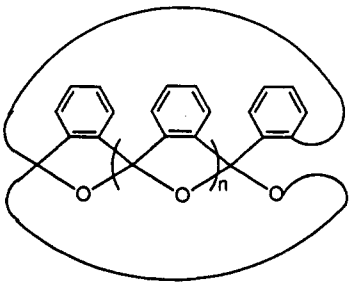
The present paper provides the detailed synthesis and characterization of star-shaped crowns of generic structure **4** as a new family of ionophores. We propose a class name, "starands", for the synthetic host compounds in which the star-shaped 2*n*-crown-*n* moiety is incorporated with [1_n]-OCP to form a cyclic polyketal.



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Results and Discussion

The synthesis of the first starand **3**, [1_6]orthocyclophano-12-crown-6, begins with the coupling of aromatic dibromide **12** with aromatic dialdehyde **14**. The detailed

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(3) Lee, W. Y.; Sim, W.; Choi, K. D. *J. Chem. Soc., Perkin Trans. 1* **1992**, 881.

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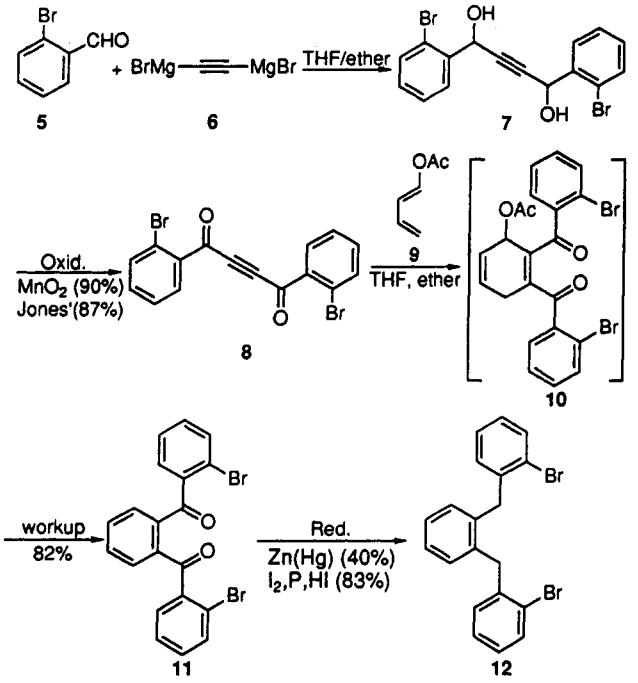
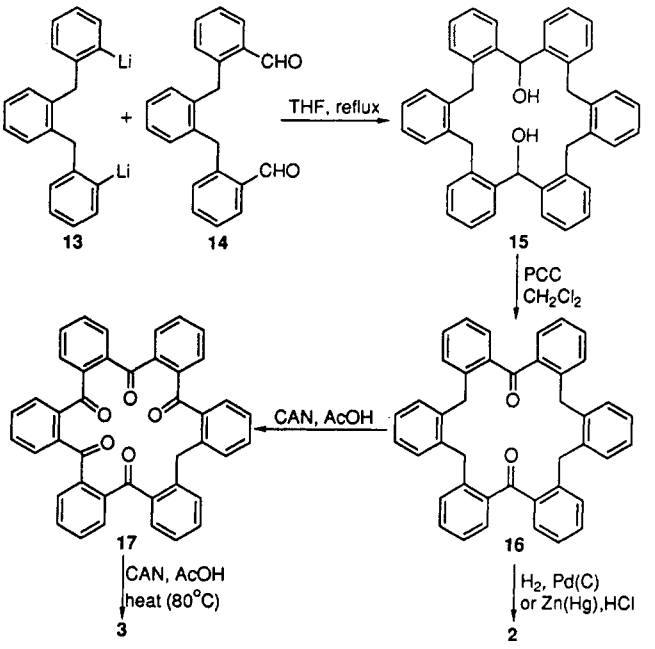
Scheme I



Scheme II



synthesis of the key compound **12** is illustrated in Scheme I. Treatment of 2 mol of 2-bromobenzaldehyde (**5**) with 1 mol of acetylenic di-Grignard reagent **6**[6] gave propargylic diol **7** in good yield (90%). Conversion of **7** into the corresponding acetylenic dione **8** could be carried out by oxidation either with activated manganese dioxide[7] (90%) or with Jones' reagent[8] (87%). The Diels-Alder reaction of dione **8** and 1-acetoxy-1,3-butadiene (**9**)[9] in THF–Et_2O gave 1,2-bis(2-bromobenzoyl)benzene (**11**) in 82% yield. Reduction of **11** with iodine (I_2) and red phosphorus (P) in refluxing hydriodic acid (HI) provided **12** in 83% yield.

The formation of the [1_6]OCP cycle was accomplished by lithiation of **12** to give dilithio reagent **13** followed by condensation with aromatic dialdehyde **14**[10] as shown in Scheme II. In the dimetalation of **12**, metallic magnesium and lithium were found to be ineffective. Dilithiation of **12** at 0 °C in THF with 2 molar equiv of *n*-BuLi followed by reaction of the reagent **13** with dialdehyde **14** in high dilution gave cyclic diol **15**. Diol **15** was oxidized with pyridinium chlorochromate (PCC) without further purification to the corresponding diketone, [1_6]orthocyclophane-1,4-dione (**16**),[11] a crystalline solid, mp > 290 °C dec, in 20–30% yield based on **12**. In the ^{1}H NMR spectrum, the benzylic protons of **16** produced only one singlet at δ 4.02, indicating a flexible, rather than rigid, structure for this compound. The ^{13}C NMR spectrum could not be recorded due to the low solubility of **16**. The high-resolution mass spectrum showed an exact mass of M^+ 568.2368 ($C_{42}H_{32}O_2$ requires M 568.2402). Reduction of 1,4-dione **16** was attempted using various methods, including Pd-catalyzed hydrogenation and Clemmensen reduction. But, we were unable to obtain [1_6]OCP **2**, probably because its insolubility retarded its extraction from the reduction mixture. Reduction of the 1,3-isomer **26** gave the same results (*vide infra*).

The oxidation of dione **16** has been accomplished using a variety of oxidants.[12] However, we were unable to oxidize all of the methylenes of **16** to carbonyls to give the corresponding cyclic hexaketone **29**. The best oxidizing agent for **16** was ceric ammonium nitrate (CAN). Incomplete oxidation of **16** with CAN in acetic acid gave rise to a mixture of the corresponding tri-, tetra-, and pentaketones. After oxidation at room temperature (rt) for 5 days, **17** was the main product revealing its resistance to oxidation. Further oxidation of **17** with CAN at 80 °C for 1 week gave a crystalline product, which gave the mass (M) *m/z* 624 identical to that of cyclic hexaone **29**. However, the IR spectrum of the product did not show a carbonyl frequency, but rather an absorption for an ether linkage. The ^{13}C NMR spectrum of the compound did not reveal ketonic carbon resonance around δ 200 but showed four resonances in the range δ 110–145. These spectral data led us to the star-shaped crown ether structure **3**, for which we propose the name "[1_6]starand".

We cross-checked the formation of **2** and **3** by synthesizing them by the routes shown in Schemes III and IV. The key material **22** was prepared from benzylic diol **18**.[1] Treatment of **18** with dry HBr gas in CH_2Cl_2 gave the corresponding dibromide **19**. Reaction of **19** with Grignard **20**, followed by removal of the THP protecting groups, gave benzylic diol **21**, which upon oxidation with pyridinium dichromate (PDC) in CH_2Cl_2 furnished dialdehyde **22** in 93% yield.

The formation of a [1_6]OCP cycle was accomplished by a procedure shown in Scheme IV. Metalation of dibromide

(6) (a) Walton, D. R. M.; Waugh, F. *J. Organomet. Chem.* **1972**, *37*, 45. (b) Brandsma, L.; Verkruijsse, H. D. Synthesis of Acetylenes, Allenes and Cumulenes; Elsevier: Amsterdam, Oxford, New York, 1981; p 56.

(7) Stork, G.; Tomasz, M. *J. Am. Chem. Soc.* **1964**, *86*, 471.

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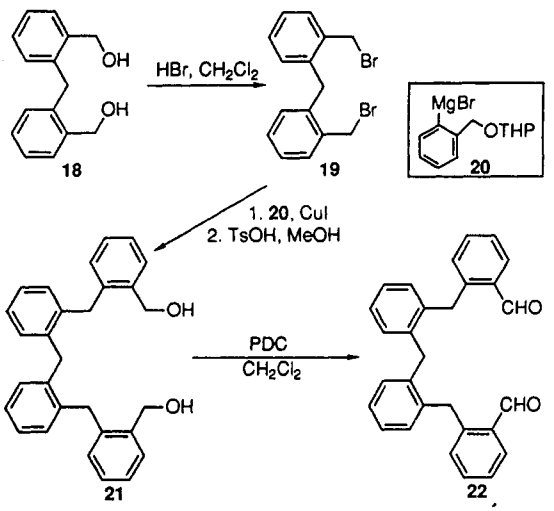
(10) Lee, W. Y.; Park, C. H.; Lee, J. H.; Choi, K. D.; Sim, W. *Bull. Kor. Chem. Soc.* **1989**, *10*, 397.

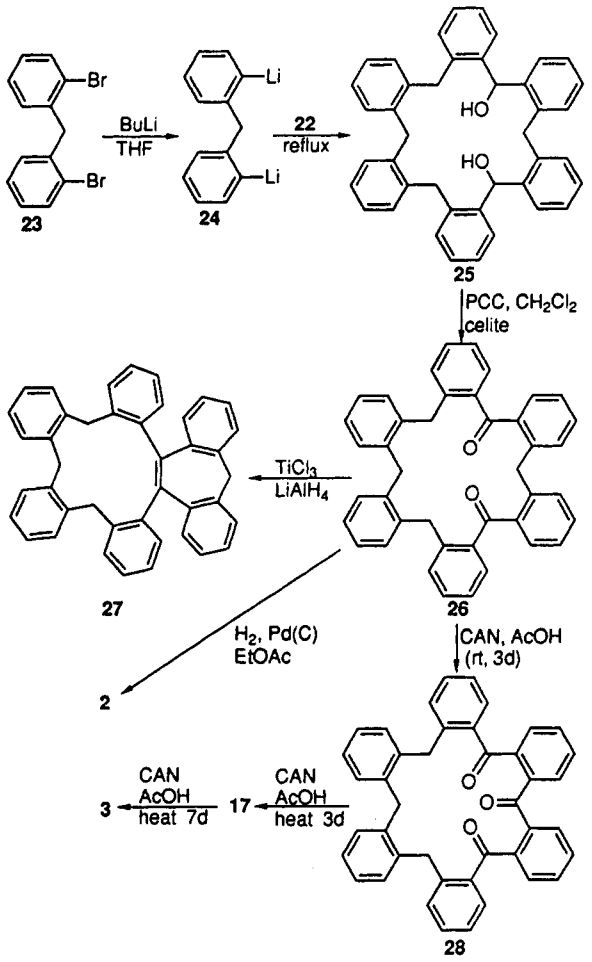
(11) In this paper, we use the terms [1_n]OCP-1,2-dione or [1_n]OCP-1,2,3-trione and so on for the names of the polyoxo derivatives of [1_n]-OCP, in which the numbers denote the positions of benzylic carbons that were oxidized to carbonyls.

(12) Oxidation of diketone **16** with PCC in refluxing toluene gave an oxidation product as a solid which exploded before purification by chromatography.

Scheme III



Scheme IV



23[1] with *n*-BuLi to dilithio reagent **24** followed by reaction with **22** gave cyclic diol **25** as a cyclocondensation product. Oxidation of crude **25** with PCC in CH_2Cl_2 afforded the corresponding cyclic dione, [1$_6$]orthocyclophane-1,3-dione[11] (**26**). In contrast to the insolubility of the highly symmetrical isomeric 1,4-dione **16**, diketone **26** was soluble to some extent in organic solvents. ^{1}H and ^{13}C NMR spectra confirmed the structure. The benzylic protons of **26** exhibited three singlets at δ 4.38, 4.07, and 3.71. In the ^{13}C NMR spectrum, a carbonyl carbon resonance appeared at δ 200.25, aromatic carbons showed 18 signals between δ 140.64 and 125.54, and the benzylic carbons provided three peaks at δ 37.45, 36.03, and 35.78. High resolution mass spectrometry gave the exact mass of M^+ 568.2371 ($C_{42}H_{32}O_2$ requires 568.2402).

The reduction of diketone **26** was attempted in two ways. Reduction with McMurry reagent,[13] $TiCl_3/LiAlH_4$, gave the expected olefinic product, bicyclic biscyclophane **27**, which was consistent with the results obtained in the preceding work[1] where [1$_4$]- and [1$_5$]OCP-1,3-diones were reductively olefinated under the same conditions. Clemmensen reduction also gave the reductive olefination product. The Pd-catalyzed hydrogenation of **26** for 7 days, over wide ranges of H_2 pressure (35–45 psi) and temperature (25–40 °C), was attempted repeatedly to produce normal reduction product **2**. However, we were unable to extract **2** from the reduction mixture, recovering only a trace of the starting material **26**, whereas we could obtain [1$_4$]-, [1$_5$]-,[1] and [1$_7$]OCP[14] by reduction of their dioxo derivatives under the same conditions. This result suggests that the even-numbered [1$_n$]OCPs are less soluble than the odd-numbered [1$_n$]OCPs and that the solubility of [1$_n$]OCPs is largely dependent upon the molecular symmetry; the higher the symmetry of the molecule, the closer the packing. Actually, [1$_4$]OCP is so sparingly soluble that we can not record a ^{13}C NMR spectrum, whereas [1$_5$]OCP and [1$_7$]OCP are reasonably soluble in conventional organic solvents.

Oxidation of **26** was carried out with CAN in acetic acid. When the oxidation was partially complete, the mass spectrum of the product gave rise to *m/z* 582, 596, 610, and 624, indicating a mixture of the tri-, tetra-, penta-, and hexaketones, which could be separated by chromatography. At an early stage of mild oxidation at rt, the main product was a cyclotrione, showing *m/z* 582 as a base peak in the mass spectrum. Since the ^{1}H NMR spectrum showed two singlets at δ 4.43 and 4.17 for benzylic protons in the ratio of 1:2, the cyclotrione of *m/z* 582 might be assigned to [1$_6$]orthocyclophane-1,2,3-trione (**28**). This result reveals that the benzylic carbon between the two carbonyls in **26** is most susceptible to oxidation in spite of the apparent steric crowding. In the last stage of the partial oxidation, the main product was [1$_6$]orthocyclophanepentaone **17**. Exhaustive oxidation of **17** with CAN in acetic acid at 80 °C for a week gave the starand **3**.

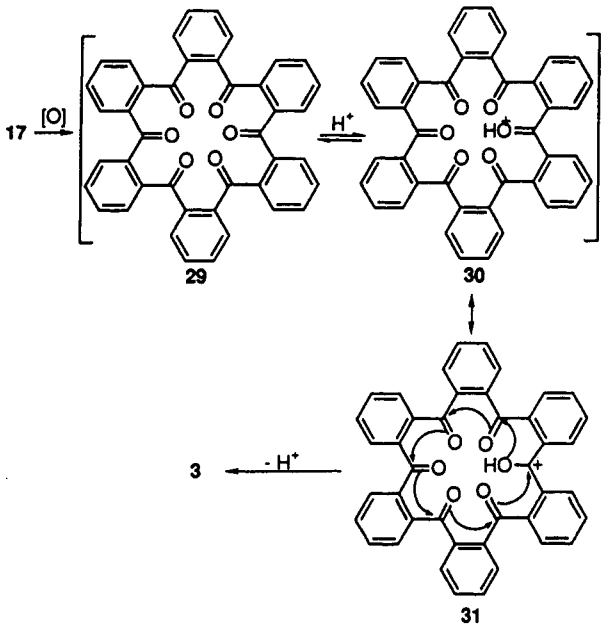
From the experimental facts, the oxidation of dione **26** to **3** proceeds stepwise through the tri-, tetra, and pentaone to the corresponding hexaone **29**, which undergoes rapid rearrangement via the oxonium ions **30** or **31** to generate the more stable, less strained isomer **3** (Scheme V).

The isomerization is rationalized by comparing the structures of polyketal **3** and its ketonic isomer **29**. All atoms in **29** have to be coplanar for the effective conjugation of the sp^2 bonds in the aromatic and carbonyl functions. Inspection of the CPK model indicates that the preferred structure of **29** is an up–down–up conformation of six oxygen atoms to give a spherical cavity inside the molecule, but this conformation is sterically strained. It appears therefore that **29** undergoes spontaneous and rapid isomerization to afford the strain-free isomer **3**, in which sp^2-to-sp^3 rehybridization has taken place in each ketal carbon.

(13) (a) McMurry, J. E.; Kees, K. R. *J. Org. Chem.* **1977**, *42*, 2655. (b) Baumstark, A. L.; Bechara, E. J. H.; Semigran, M. J. *Tetrahedron Lett.* **1976**, 3265.

(14) Lee, W. Y. *et al.* Unpublished results which will be reported in the near future as the third of the series of our research on [1$_n$]OCP, entitled "Orthocyclophanes. 3."

Scheme V



An X-ray analysis confirmed that the structure of **3** is a spirobicyclic polyketal in which six-pointed star **1b** is incorporated with [1_6]OCP **2**.[15] Two crystallographically independent molecules were found at the centers of symmetry within each crystallographically asymmetric unit. However, each of them was known to have an essentially identical conformation containing a rigid, spherical cavity of up–down–up arrangement of the six oxygen atoms. The oxygen atoms were known to deviate about 0.8 Å from the least-squares plane composed of six benzylic carbon atoms. The crystallographic data of **3** are presented in Table I. The ORTEP diagram of one (A form) of the two crystallographically independent molecules of **3** is shown in Figure 1 and the stereoview in Figure 2. Whereas odd-numbered [1_n]OCPs could be converted by exhaustive oxidation to the corresponding polyoxocrowns, such as [1_5]OCP-pentaone and [1_7]OCP-heptaone,[14] the oxidation of [1_6]OCP did not give the corresponding [1_6]OCP-hexaone, but rather generated a rearranged isomer [1_6]starand **3**. This fact suggested the preparation of the other starand homologs from the oxidation of even-numbered [1_n]OCPs.

The synthesis of higher homologs of even-numbered [1_n]OCP was initiated by the synthesis of the [1_8]OCP cycle shown in Scheme VI. Treatment of benzylic diol **21** with HBr in CH_2Cl_2 gave dibromide **32**, and subsequent reaction of **32** with Grignard **20** in the presence of CuI followed by removal of the THP protecting groups gave benzylic diol **33**. Oxidation of **33** with PCC to give diformyl aromatic **34** followed by condensation with 1 molar equiv of dilithio reagent **24** gave cyclic diol **35**. Oxidation of **35** with PCC gave the corresponding cyclic dione, [1_8]-orthocyclophane-1,3-dione (**36**).

Attempted reduction of **36** with reducing agents such as $P_{(red)}/I_2/HI$ or $H_2/Pd(C)$ did not give the parent hydrocarbon [1_8]OCP (**37**), probably because of the insolubility of cycle **37** which prevented its extraction from the reaction mixture. The inability to obtain **37** due to its insolubility was consistent with that of the other even-numbered [1_n]OCPs, such as [1_4]OCP (sparingly soluble) and [1_6]OCP (insoluble), whereas odd-numbered [1_5]OCP[1] and [1_7]OCP[14] are soluble in organic solvents.

Table I. Crystallographic Data[a] of [1_6] Starand 3

formula	$C_{42}H_{24}O_6 \cdot 2CHCl_3$
formula weight	744.04
a, Å	15.813(6)
b, Å	13.108(1)
c, Å	20.257(7)
β, deg	109.35(2)
V, Å^3	3961.6
Z	4
space grp	$P2_1/c$
ρ, g/cm^3	1.25
μ, cm^{-1}	2.7
$R(F_o)$, %	5.2
$R_w(F_o^2)$, %	6.9

[a] T = 298 K, λ = 0.710 73 Å (Mo Kα).

Oxidation of **36** by heating with CAN in AcOH for 1 week afforded [1_8]starand **39**. This result can also be rationalized by the rapid and spontaneous isomerization of octaketone **38** in acid to spirobicyclic octaketal **39**. The ^{1}H NMR spectrum of **39** displayed a multiplet in the range δ 7.42–7.21 for aromatic protons, and the ^{13}C NMR spectrum showed four simple resonances at δ 141.80, 129.69, 122.64 (attributable to aromatic carbon atoms), and 114.77 (attributable to ketal carbon atoms), revealing the high degree of symmetry of starand **39**. The extraordinary rearrangement of polyketone-to-polyketal was reproduced with the [1_8]OCP cycle.

In view of the X-ray analysis of the first starand **3**, there is no doubt about the up-down-up conformation of the new star-crown **39**. The calculated stereo top view (Chem-3D output) of [1_8]starand **39** is shown in Figure 3 and the stereo side view in Figure 4.

Actual features of starands **3** and **39** are shown by space-filling models (Chem-3D out put) in Figure 5 and 6, respectively. Whereas the spherical cavity inside the molecule **3** is too small to encapsulate even a small host (*e.g.*, Li^+), that of **39** is reasonably big to entomb Na^+ ion. The molecular mechanics calculation revealed that the spherical cavity of **39** has a diameter of 2.43 Å, which is much larger than that of its lower homolog **3** (1.02 Å).

Preparation of the lower homolog of starand **3** was also attempted. However, we were unable to obtain [1_4]starand by the oxidation of [1_4]orthocyclophane-1,3-dione.[1] The computer-generated drawing of the lowest energy structure of [1_4]starand shows that the distance of the oxygen atoms from the center of the cavity (1.14 Å) is shorter than the van der Waals radius (1.4 Å) of an oxygen atom. We were also unable to prepare [1_{10}]starand by the oxidation of [1_{10}]orthocyclophane-1,4-dione presumably because of steric strain.

In summary, an unprecedented spontaneous isomerization of cyclopolyketone-to-cyclopolyketal has been observed in the oxidation of even-numbered [1_n]orthocyclophanes. The oxidation of [1_6]- and [1_8]OCP cycles gave two star-shaped crown ethers of spirobicyclic polyketal construction, which are referred to as [1_6]- and [1_8]-starand, respectively. The starands have preorganized, rigid cavities of ligand oxygen atoms and are expected to have characteristic inclusion properties. Further investigation is under way.

(15) The authors have deposited atomic coordinates for **3** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

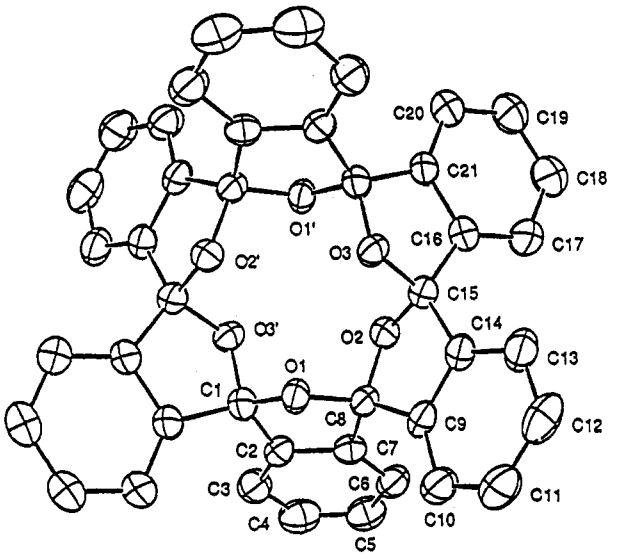


Figure 1. ORTEP Diagram of [1_6]starand **3** (A form). Selected distances (Å) and bond angles (deg): C(1)–C(2), 1.501(4); C(2)–C(3), 1.379(3); C(7)–C(8), 1.498(3); C(9)–C(14), 1.387(4); O(1)–C(1), 1.443(3); O(1)–C(8), 1.430(3); O(1)···O(1′), 3.817(3); O(1)···(2), 2.360(3); O(1)···O(3), 3.049(2); O(1)–C(1)-C(21′), 108.1(2); O(3′)–C(1)–C(2), 108.7(2); O(3′)–C(1)–C(21′), 103.1(2); C(2)–C(1)-C(21′), 124.3(2); C(1)–C(2)–C(3), 130.5(3); C(1)–C(2)–C(7), 108.6(2); C(2)–C(7)–C(6), 121.2(2); C(2)–C(7)–C(8), 108.2(2); C(6)–C(7)–C(8), 130.5(3); C(1)–O(1)–C(8), 108.4(2); O(1)–C(8)–O(2), 111.3-(2); O(1)–C(1)–O(3′), 109.9(2); O(1)–C(1)–C(2), 102.3(2).

Experimental Section

General. All anhydrous reactions were conducted with the rigorous exclusion of air and moisture. Melting points are uncorrected. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were purified by refluxing for a few hours with sodium benzophenone ketyl under nitrogen followed by distillation. Dichloromethane (CH_2Cl_2) was dried by distilling over calcium hydride prior to use. Flash column chromatography was carried out using silica gel 60 (E. M. Merck, 0.040 mm, 230–400-mesh ASTM). All chemical shifts (δ) are reported in parts per million, and J values are in Hz.

General Procedure A. Dilithiation of Aromatic Dibromides 12 and 23. Dilithio reagent (*e.g.*, **13**) was prepared by dropwise addition of 2 molar equiv of *n*-BuLi (*e.g.*, 2.0 mmol) during 10 min to a stirred solution of dibromide (*e.g.*, **12**, 1.0 mmol) in THF under nitrogen followed by stirring 1–2 h to give a yellow-orange solution. Dilithio reagents **13** and **24** were prepared from **12** and **23** at 0 and −30 °C, respectively.

General Procedure B. Cyclocondensation of a Dibromide and a Dialdehyde Followed by Oxidation To Give a Cyclic Diketone. A solution of dialdehyde (*e.g.*, **14**, 1.0 mmol) in THF (50 mL) was added dropwise with stirring at −78 °C to an equimolar amount of dilithio reagent (*e.g.*, **13**, 1.0 mmol), prepared by general procedure A, and stirred for 2 h. The mixture was allowed to warm to room temperature (rt), water (50 mL) was added, and the solvent was removed *in vacuo*. The residual mixture was extracted with CH_2Cl_2, and the extract was washed successively with aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated *in vacuo*. The resultant cyclic diol was oxidized directly without purification. To a solution of the crude diol in CH_2Cl_2 (50 mL) were added Celite (2 g) and pyridinium chlorochromate (PCC) (1.5 g), and the mixture was stirred for 5 h at rt. The reaction mixture was filtered, and the precipitate was washed thoroughly with Et_2O–CH_2Cl_2 (1:1, v/v). The organic layer was evaporated *in vacuo* to give crude cyclic dione (*e.g.*, **16**), which was chromatographed on silica gel eluting with proper solvent, such as CH_2Cl_2 or n-C_6H_{14}/CH_2Cl_2 (1:2, v/v). Recrystallization was carried out by adding an equal volume of n-C_6H_{14} to a solution of the dione in CH_2Cl_2 (10 mL) followed by slow evaporation of the solvent to give crystals.

General Procedure C. Pd-Catalyzed Reduction of a Cyclic Dione to the Parent [1_n]*OCP*. Cyclic dione (*e.g.*, **26**, 300 mg) was hydrogenated at 25–40 °C by stirring with 10% Pd/C in a mixture of EtOH (10 mL), concd. HCl (0.4 mL), and water (1 mL) for 7–10 d under H_2 (*e.g.*, 35–45 psi). The reaction mixture was extracted with CH_2Cl_2, followed by washing the extract with water, drying ($MgSO_4$), and evaporation.

General Procedure D. Oxidation of [1_n]OCP-dione with CAN to Starand. A suspension of cyclic dione (*e.g.*, **16**, 1.0 mmol) and CAN (5 g, 8.6 mmol) in AcOH (50 mL) and water (5 mL) was heated at 80 °C for 1 week, adding more of CAN (total 3 g in small portions) during the reaction to ensure complete oxidation. Water (100 mL) was added, and the reaction mixture was extracted with CH_2Cl_2. The organic layer was washed successively with aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated *in vacuo*. The crude product was chromatographed (SiO_2, CH_2Cl_2–Et_2O), and recrystallized from CH_2Cl_2 or $CHCl_3$, to give the crystalline starand (*e.g.*, **3**).

General Procedure E. Conversion of a Benzylic Diol to the Dibromide. Into a suspension of benzylic diol (*e.g.*, **18**, 50 mmol) in CH_2Cl_2 (80 mL) was passed dry HBr gas at rt until the solution was saturated, whereupon the crystals dissolved immediately to give a clear, orange solution. The reaction flask was stoppered, and the mixture was stirred for 5 h until TLC (SiO_2, CH_2Cl_2) showed only one spot ($R_f \sim 1.0$). The solution was washed successively with aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated *in vacuo*. The crude product was chromatographed (SiO_2, CH_2Cl_2) and recrystallized from n-C_6H_{14}–Et_2O (2:1, v/v) to give the crystalline dibromide (*e.g.*, **19**).

General Procedure F. Coupling of Grignard 20 with a Benzylic Dibromide To Give a Benzylic Diol. To a stirred solution (0 °C) of benzylic dibromide (*e.g.*, **19**, 7.0 mmol) in THF (50 mL) containing CuI (0.4 g) was added dropwise under nitrogen 2 molar equiv of Grignard **20** prepared from 2-bromobenzyl tetrahydropyran-2-yl (THP) ether. After being stirred overnight at rt, the reaction was quenched with aqueous NH_4Cl (50 mL), and the solvent was removed *in vacuo*. Routine workup gave an oily di-THP ether as the biscoupling product. A solution of the crude THP ether in MeOH (60 mL) was refluxed with *p*-TsOH (1 g) for 5 h, the reaction was quenched with aqueous NH_4Cl (20 mL) at rt, and the solvent was removed *in vacuo*. The crude product, barely soluble in organic solvents, was filtered and washed successively with distilled water and diethyl ether to remove water- and ether-soluble impurities to give powdery benzylic diol (*e.g.*, **21**).

General Procedure G. Oxidation of a Benzylic Diol to the Dialdehyde. A mixture of benzylic diol (*e.g.*, **21**, 3.0 mmol), PCC (6 g), and Celite (6 g) in CH_2Cl_2 (100 mL) was stirred for 5 h at rt. The reaction mixture was filtered, and the filtrate was concentrated *in vacuo*. The crude product was chromatographed on silica gel eluting with n-C_6H_{14}/CH_2Cl_2 (1:1, v/v) to give the crystalline dialdehyde (*e.g.*, **22**).

1,4-Bis(2-bromophenyl)-2-butyne-1,4-diol (7). In a 300-mL three-necked round-bottomed flask fitted with a dropping funnel, a reflux condenser, and a gas bubbler was placed EtMgBr prepared from EtBr (11 g, 100 mmol) and Mg turnings (4 g) in THF (200 mL) under nitrogen, carefully avoiding the passing of tiny Mg turnings through the cannula along with the Grignard reagent. The solution was warmed to 50 °C, and dry acetylene was introduced for 20 min through the gas bubbler. The introduction of acetylene was stopped when the temperature decreased to 40 °C. The jelly-like reaction mixture was heated for an additional 2 h at 50 °C while argon was passed into the reaction mixture to remove excess acetylene. To this acetylene di-Grignard **6** was added dropwise at 0 °C a solution of 2-bromobenzaldehyde (**5**) (13.5 g, 73 mmol) in THF (70 mL). The mixture was allowed to warm to rt and then refluxed for 15 h. The dark brown reaction mixture was treated with aqueous NH_4Cl. After routine workup, the crude product was crystallized from CH_2Cl_2/n-C_6H_{14} (2:1, v/v) to give 13.0 g (90%) of propargylic diol **7** as crystals: mp 143–144 °C; IR (KBr) 3230 (OH), 1590, 1490 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) 7.82–7.00 (m, 8 H), 5.87 (d, 2 H), 2.54 (d, 2 H); ^{13}C NMR (DMSO-d_6, 50.29 MHz) 149.06, 147.16, 131.80, 127.58, 114.33, 113.70, 55.62 (ethynyl), 40.09 (COH); EIMS *m/z* (rel int) 398:396:394 (M^+, 0.79:1.7:0.8), 380 (5.0), 378 (10), 351 (7.5), 349 (15), 347 (7.7), 299 (7.7), 271 (28), 269 (29), 185 (100).

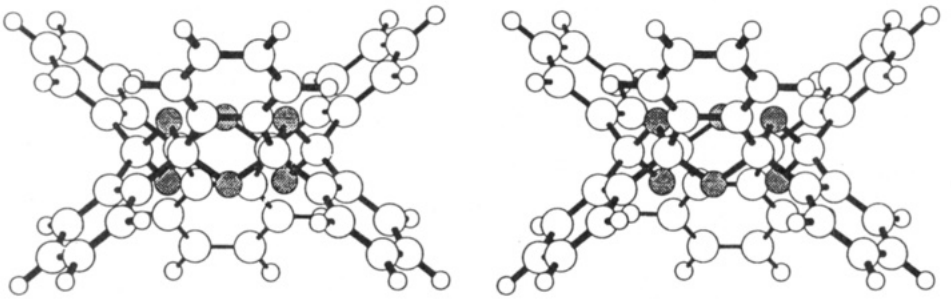
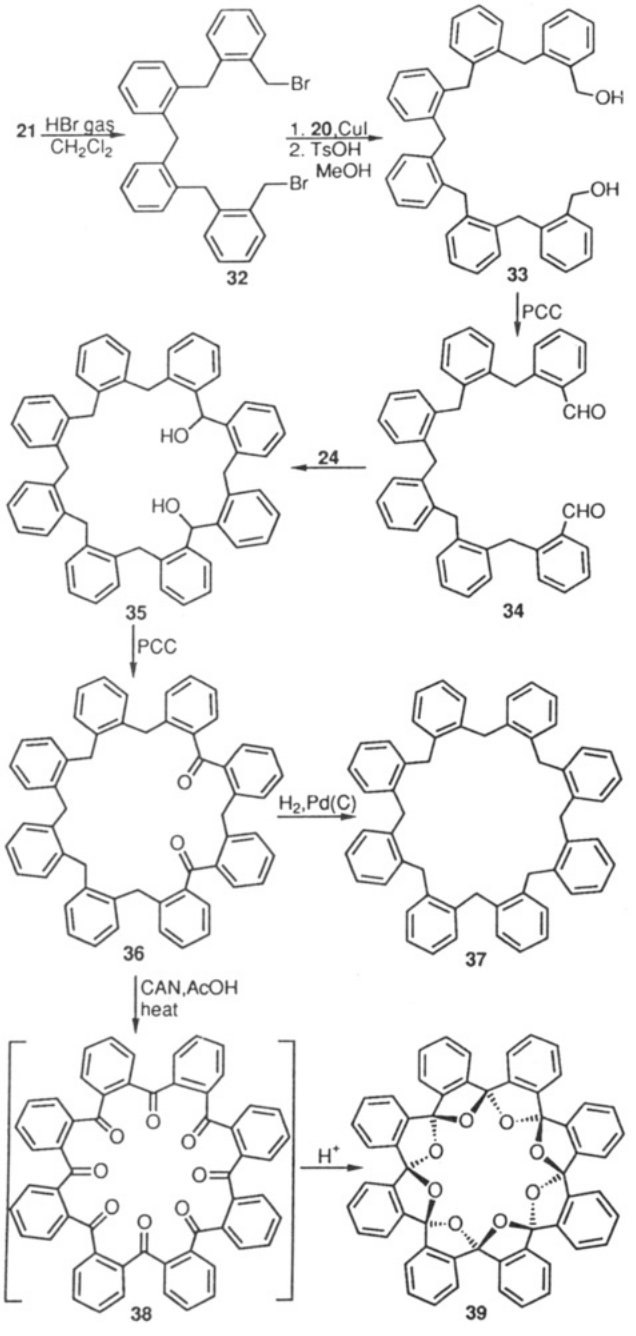


Figure 2. Stereo side view of [1$_6$]starand **3** (A form). Three of the six oxygen atoms are up and the other three are down, showing an up–down–up arrangement. Each oxygen atom deviated 0.8 Å from the least-squares plane composed of six benzylic carbon atoms.

Scheme VI



1,4-Bis(2-bromophenyl)-2-butyne-1,4-dione (8). Oxidation of diol **7** to the corresponding dione **8** was carried out by two methods. **Oxidation of 7 with Jones' Reagent.** To a stirred solution of **7** (2.7 g, 6.8 mmol) in acetone (30 mL) cooled to 0 °C, was added dropwise Jones' reagent (CrO_3–H_2SO_4)[8] (10 mL), and the mixture was stirred for 3 h at 0 °C. To this mixture was added $NaHSO_3$ (5 g) in small portions with stirring, and the solvent was removed *in vacuo*. After routine workup, the crude product was chromatographed on silica gel eluting with CH_2Cl_2/*n*-C_6H_{14} (1:1, v/v) and recrystallized from CCl_4/*n*-C_6H_{14} (1:1, v/v) to give 2.34 g (87%) of crystalline dione **8**: mp 133.5–134 °C; IR (KBr) 3010, 1660, and 1580 cm^{-1}; ^{1}H NMR ($CDCl_3$, 80 MHz) 8.15–8.03 (m, 2 H), 7.79–7.67 (m, 2 H), 7.52–7.26 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 175.78 (*C*=O), 135.68, 134.93, 134.07, 128.09, 121.83, and 87.04 (ethynyl); EIMS *m/z* (rel int) 394:392:390 (M^+, 30:59:30), 336 (60), 313 (20), 283 (7.7), 185 (99), 183 (100). **Oxidation of 7 with Activated Manganese Dioxide.** To a suspension of activated MnO_2[7] (5 g) in CH_2Cl_2 (30 mL) was added a solution of **7** (0.52 g, 1.3 mmol) in CH_2Cl_2 (100 mL), and the mixture was stirred for 8 h at rt. The precipitate was filtered through anhydrous $MgSO_4$ on a Büchner funnel followed by washing the precipitate on the funnel several times with CH_2Cl_2. The organic layer was concentrated, and the crude product was chromatographed (SiO_2, CH_2Cl_2) to give 0.46 g (90%) of crystalline **8**. When this oxidation was scaled up, the yield dropped to 10–20%.

1,2-Bis(2-bromobenzoyl)benzene (11). A solution of dione **8** (11 g, 28 mmol) and 1-acetoxy-1,3-butadiene (**9**) (3.3 g, 29.5 mmol) in dry benzene (400 mL) was refluxed under nitrogen for 24 h. After removal of the solvent from the reaction mixture *in vacuo*, the crude product was chromatographed on silica gel eluting with *n*-C_6H_{14}/CH_2Cl_2 (1:1, v/v) to give 10.2 g (82%) of crystalline **11**: mp 109–110 °C; IR (KBr) 1680 and 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 7.60–7.23 (m, 12 H); ^{13}C NMR ($CDCl_3$, 75.468 MHz) δ 195.56 (*C*=O), 139.23, 138.43, 133.95, 132.25, 131.50, 131.27, 130.69, 127.01, and 120.86; EIMS *m/z* (rel int) 446, 444, and 442 (M^+, 0.5:1.0:0.6), 365 (97), 364 (100), 363 (99), 335 (21), 287 (97), 255 (56), 183 (97), and 152 (75).

1,2-Bis(2-bromobenzyl)benzene (12). Reduction of diketone **11** to dibromide **12** was conducted in two ways. **Reduction of 11 with P(red)–I_2 in HI.** A mixture of red P_4 (15 g, 480 mmol), I_2 (3 g, 12 mmol), **11** (3.8 g, 8.6 mmol), and HI (47%, 70 mL) was heated with stirring at 140 °C for 24 h. The reaction mixture was allowed to cool to rt, and the supernatant solution was decanted. After routine workup, the crude product was chromatographed on silica gel eluting with CH_2Cl_2/*n*-C_6H_{14} (1:2, v/v) and recrystallized from *n*-hexane to give 2.95 g (83%) of crystalline dibromide **12**: mp 133–134 °C; IR (KBr) 1600 and 1560 cm^{-1}; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 7.60–6.85 (m, 12 H), 4.03 (s, 4 H); ^{13}C NMR ($CDCl_3$, 75.468 MHz) δ 139.39, 137.65, 132.63, 130.57, 129.88, 127.78, 127.32, 126.78, 125.06, and 39.09; EIMS *m/z* (rel int) 418, 416, and 414 (M^+, 11:21:11), 337 (2.3), 335 (2.3), 179 (100), and 165 (26); HRMS (EI) found M^+, 413.9634, calcd for $C_{20}H_{16}Br_2$ 413.9620. **Clemmensen Reduction of 11** gave **12** in 40% yield.

2,23-Dioxoheptacyclo[36.4.0.0^{3,8}.0^{10,15}.0^{17,22}.0^{24,29}.0^{31,36}]-dotetraconta-1(38),3(8),4,6,10(15),11,13,17(22),18,20,24(29),-25,27,31(36),32,34,39,41-octadecaene; [1$_6$]Orthocyclophane-1,4-dione (16). Cyclocondensation of dibromide **12** (0.31 g, 0.75 mmol) with 1,2-bis(2-formylbenzyl)benzene (**14**)[12] (0.23 g, 0.73 mmol), from general procedures A and B, afforded crystalline **16** in 20–30% yield based on **12**: mp > 290 °C dec; IR (KBr) 1660, 1600, 1560, and 1445 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.34–6.90 (m, 24 H), and 4.02 (s, 8 H); EIMS *m/z* (rel int) 568 (M^+, 100), 550 (15), 353 (47), 265 (20), 194 (10.2), and 179 (14); HRMS

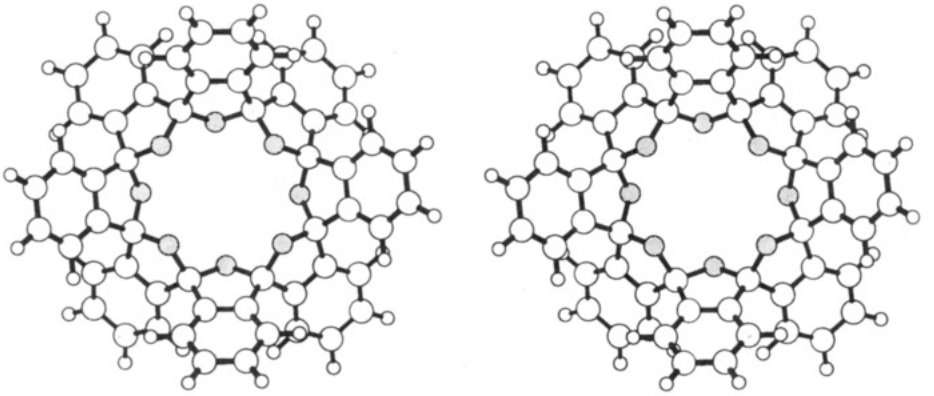


Figure 3. Stereo top view of [1_8]starand **39**. A rigid, spherical cavity is formed inside the macrocycle by the up–down–up arrangement of eight oxygen atoms. When viewed from the top, the oxygen atoms form a 8-pointed star-shaped moiety.

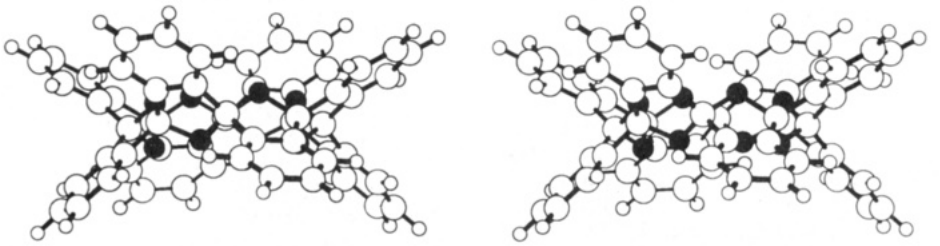


Figure 4. Stereo side view of [1_8]starand **39.** Four oxygen atoms are located above and the other four are below the least-squares plane composed of six benzylic carbon atoms, revealing the up–down–up arrangement of eight oxygen atoms.

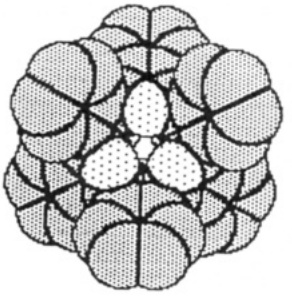


Figure 5. Space-filling model of [1_6]starand **3**. Six oxygen atoms form a spherical cavity with a diameter 1.02 Å, and six benzene rings are arranged up–and–down to give a 6-winged propeller.

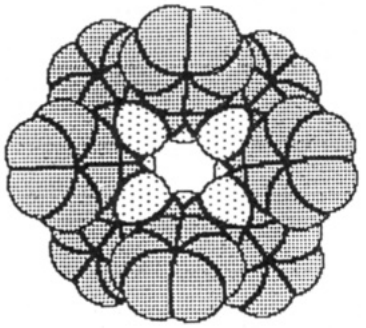


Figure 6. Space-filling model of [1_8]starand **39**. Eight oxygen atoms form a spherical cavity with a diameter 2.43 Å, and eight benzene rings are arranged up–and–down to give a 8-winged propeller.

(EI) found M^+ 568.2368, calcd for $C_{42}H_{32}O_2$ M 568.2402. The ^{13}C NMR could not be recorded because of the low solubility of the compound.

Reduction of 16 to Heptacyclo[36.4.0.0^{3,8}.0^{1,15}.0^{17,22}.0^{24,29}.0^{31,36}]-dotetraconta-1(38),3(8),4,6,10(15),11,13,17(22),18,20,24(29),-25,27,31(36),32,34,39,41-octadecaene (2). The hydrocarbon **2** could not be obtained by the reduction of general procedure C. The failure may be responsible to the insolubility of the reactant **16** or to that of product **2**. The preparation of **2** was also attempted using the more soluble isomer **26** (*vide infra*).

43,44,45,46,47,48-Hexaoxatridecacyclo[34.6.1.1^{1,8}.1^{8,15}.1^{15,22}.1^{22,29}.1^{29,36}.0^{2,7}.0^{9,14}.0^{16,21}.0^{23,28}.0^{30,35}.0^{37,42}]dotetraconta-2(7),3,5,9(14),10,12,16(21),17,19,23(28),24,26,30(35),31,-33,37(42),38,40-octadecaene; [1_6]Starand (3). Dione **16** (200 mg, 0.35 mmol) was oxidized with CAN (5 g) for 8 d according to general procedure D to give 20 mg (9%) of **3** as monoclinic crystals: mp > 350 °C; IR (KBr) 3020, 1065, 1040, 1010, and 710 cm^{-1}; ^1H NMR (CD_2Cl_2, 200 MHz) δ 7.52–7.27 (m, 24 H); ^{13}C NMR (CD_2Cl_2, 50.29 MHz) δ 142.51, 128.99, 123.11, 113.18; EIMS *m/z* (rel int) 624 (M^+, 100), 504 (16.8), 372 (13.7), 236 (16.6); HRMS (EI) found M^+ 624.1666, calcd for $C_{42}H_{24}O_6$ M 624.1573.

Oxidation of **16** to **3** did not proceed in high yield because of the insolubility of **16** in AcOH. The preferred alternative is the oxidation of more soluble isomer **26** with CAN to give **3** in higher yield (*vide infra*).

2,9,16,23,30-Pentaoxoheptacyclo[36.4.0.0^{3,8}.0^{10,15}.0^{17,22}.0^{24,29}.0^{31,36}]dotetraconta-1(38),3(8),4,6,10(15),11,13,17(22),18,-20,24(29),25,27,31(36),32,34,39,41-octadecaene; [1_6]Orthocyclophanepentaone (17). Compound **17** was separated from an incomplete oxidation product obtained by oxidation of **16** for 5 d with CAN in AcOH at rt or by heating the mixture at 80 °C for 2 d. Routine workup and chromatographic separation gave crystalline **17** in 10% yield: mp > 290 °C dec; IR (KBr) 1677 and 1565 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) 7.77–6.69 (m, 24 H), 3.29 (broad s, 2 H); EIMS *m/z* (rel int) 610 (M^+, 85.9), 593 (44.1), 564 (97.5), 397 (30.2), 236 (100), 180 (26.6). ^{13}C NMR could not be obtained because of the insolubility of **17**. The preferred alternative of preparation of **17** is the oxidation of more soluble isomer **26** with CAN in hot AcOH (*vide infra*).

Oxidation of 17 to 3. Oxidation of **17** (50 mg, 0.082 mmol) with CAN at 80 °C for 7 d according to general procedure D provided 38 mg (74%) of [1_6]starand **3.**

Bis[(2-bromomethyl)phenyl]methane (19). Treatment of diol **18**[1] (12 g, 52.6 mmol) with HBr according to general procedure E gave 17.5 g (94%) of crystalline **19**: mp 83–84 °C; IR (KBr) 1600, 610 and 570 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 7.45–6.68 (m, 8 H), 4.89 (s, 4 H), 4.28 (s, 2 H); ^{13}C NMR ($CDCl_3$, 20.15 MHz) δ 138.68, 136.01, 130.65, 130.30, 128.19, 127.15, 34.62, 31.76; EIMS *m/z* (rel int) 356, 354, and 352 (M^+, 2.43:5.61:2.88), 275 (77.7),

273 (47.0), 193 (100), 178 (67.0); HRMS (EI) found M^+ 351.9412, calcd for $C_{15}H_{14}Br_2$ M 351.9462.

Bis[2-[(hydroxymethyl)benzyl]phenyl]methane (21). Biscoupling of dibromide **19** (2.5 g, 7.06 mmol) and Grignard **20** (20 mmol) according to general procedure F provided 2.4 g (83%) of diol **21** as a powdery solid: mp 127–128 °C; IR (KBr) 3350, 1600, 1050, and 740 cm^{-1}; ^1H NMR (acetone-d_6, 200 MHz) δ 7.49–6.83 (m, 16 H), 4.51 (d, J = 4.8 Hz, 4 H), 3.92 (s, 6 H), and 2.95 (m, 2 H); ^{13}C NMR (acetone-d_6, 50.29 MHz) δ 140.99, 139.71, 139.57, 138.45, 130.42, 130.33, 129.94, 128.10, 127.82, 127.23 and 126.9, 62.59 (CH_2OH), 36.70 and 35.75 (ArCH_2Ar); EIMS m/z (rel int) 372 ($M^+ - 2\ H_2O$, 41), 281 (31), 192 (26), 179 (100); HRMS (EI) found $M^+ - 2H_2O$ 372.1882, calcd for $C_{29}H_{24}$ M $- 2H_2O$ 372.1878.

Bis[2-(2-formylbenzyl)phenyl]methane (22). Oxidation of diol **21** (1.3 g, 3.2 mmol) with PCC (6 g) according to general procedure G afforded 1.2 g (93%) of crystalline **22**: mp 121–122 °C; IR (KBr) 2850, 2760, 1690, and 1595 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 10.67 (s, 2 H), 7.68–6.86 (m, 16 H), 4.31 (s, 4 H), and 3.91 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 192.26 (*C*HO), 142.30, 138.33, 138.05, 134.04, 133.98., 133.75, 132.14, 130.84, 129.79, 129.71, 126.78, 26.72, 36.35, and 35.25; EIMS m/z (rel int) 404 (M^+, 0.34), 387 (23.6), 386 (84.9), 267 (31.4), 195 (100), and 179 (62.5); HRMS (EI) found M^+ 404.1823, calcd for $C_{29}H_{24}O_2$ M 404.1776.

2,16-Dioxoheptacyclo[36.4.0.0^{3,8}.0^{10,15}.0^{17,22}.0^{24,29}.0^{31,36}]-dotetraconta-1(38),3(8),4,6,10(15),11,13,17(22),18,20,24(29),-25,27,31(36),32,34,39,41-octadecaene; [1$_6$]Orthocyclophane-1,3-dione (26). Dilithiation of dibromide **23** (0.98 g, 3.0 mmol) followed by cyclocondensation with dialdehyde **22** (1.01 g, 2.5 mmol) by use of general procedures A and B gave 0.69 g (48.6%) of crystalline dione **26**: mp 288–289 °C; IR (KBr) 1655, 1595, 1050, and 740 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.36–6.71 (m, 24 H), 4.38 (s, 2 H), 4.07 (s, 4 H), and 3.71 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 200.25 (*C*=O), 140.64, 140.16, 139.52, 138.82, 138.65, 138.31, 131.21, 131.11, 130.86, 130.77, 130.65, 130.51, 130.32, 129.56, 126.32, 126.09, 125.81, 125.54, 37.45, 36.03, and 35.78; EIMS m/z (rel int) 568 (M^+, 100), 550 (24.1), 347 (22.4), 281 (19.5), 265 (23.1), and 179 (17.5); HRMS (EI) found M^+ 568.2371, calcd for $C_{42}H_{32}O_2$, M 568.2402.

Nonacyclo[27.13.0.0^{2,7}.0^{9,14}.0^{16,21}.0^{23,28}.0^{30,35}.0^{37,42}]ditetraconta-1(29),2(7),3,5,9(14),10,12,16(21),17,19,23(28),24,26,30(35),31,33,-37(42),38,40-nonadecaene (27). McMurry Olefination[1,13] of Diketone 26. A mixture of $LiAlH_4$ (76 mg, 2.0 mmol) and $TiCl_3$ (0.77 g, 5.0 mmol) in dry THF (60 mL) was refluxed under nitrogen for 30 min. To the resultant mixture was added dione **26** (470 mg, 0.83 mmol), and the mixture was refluxed for 1 d. After routine workup, the crude product was chromatographed (SiO_2, CH_2Cl_2) and recrystallized from Et_2O–CH_2Cl_2 (1:2 v/v) to give 0.41 g (92%) of bicyclic cyclophane **27**: mp 285 °C dec; IR (KBr) 3060, 2940, 1595, 1445, 1160, 1050, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.71–6.35 (m, 24 H), 4.79 (d, J_{AB} = 17.1 Hz, 2 H, ArC*H*H, quasi equatorial), 3.20 (d, J_{AB} 17.1 Hz, 2 H, ArCH*H*, quasi axial), 4.27 (d, J_{AB} = 12.7 Hz, 1 H, ArC*H*H, quasi equatorial), 3.96 (d, J_{AB} = 12.7 Hz, 1 H, ArCH*H*, quasi axial), 3.30 (d, J_{AB} = 14.6 Hz, 1 H, ArC*H*H, quasi equatorial), and 3.20 (d, J_{AB} = 14.6 Hz, 1 H, ArCH*H*, quasi axial); EIMS m/z (rel int) 536 (M^+, 100), 431 (5.3), 339 (4.2), and 179 (8.8); HRMS (EI) found M^+ 536.2510, calcd for $C_{42}H_{32}O_2$ M 536.2504. ^{13}C NMR could not be obtained due to the insolubility of the compound.

Reduction of 26 to 2. We were unable to obtain [1$_6$]OCP **2** by the reduction of **26** according to general procedure C but recovered a trace of starting material **26**. This result is consistent with those of the reduction of **16** (*vide supra*).

Oxidation of 26 with Ceric Ammonium Nitrate (CAN). Oxidation of **26** according to general procedure D was dependent upon the reaction time and temperature. When the oxidation was partially completed at low temperature, a mixture of various oxidation products was obtained, which could be separated by chromatography. The major product in the early oxidation stage after oxidation for 3 d at rt was [1$_6$]orthocyclophane-1,2,3-trione **28**, and the major product after oxidation for 3 d under reflux was [1$_6$]orthocyclophanepentaone (**17**). Exhaustive oxidation of **17** under refluxing temperature for 1 week gave the corresponding hexaketone, which rearranged spontaneously to the isomeric cyclopolyketal **3**.

2,9,16-Trioxoheptacyclo[36.4.0.0^{3,8}.0^{10,15}.0^{17,22}.0^{24,29}.0^{31,36}]-dotetraconta-1(38),3(8),4,6,10(15),11,13,17(22),18,20,24(29),-25,27,31(36),32,34,39,41-octadecaene; [1$_6$]Orthocyclophane-1,2,3-trione (28). Crystalline **28** was separated as the main product from the early oxidation stage of **26** with CAN in AcOH for 3 d at rt: mp 295 °C dec; IR (KBr) 1665, 1595, and 1485 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.42–7.06 (m, 24 H), 4.43 (s, 2 H), 4.17 (s, 4 H); EIMS m/z (rel int) 582 (M^+, 100), 564 (29), 339 (11), and 281 (28).

Although ^{13}C NMR could not be obtained because of insolubility of the trione, the 2:1 ratio of the two benzylic proton resonances can be evidence for the 1,2,3-trione since the 1,2,4-trione must display three resonances in the 1:1:1 ratio.

Oxidation of 26 to Pentaone 17. Crystalline **17** was separated in 30% yield as the main product from partial oxidation of **26** with CAN in AcOH for 5 d at rt or by heating at reflux for 3 d (*vide supra*).

Oxidation of 26 to Starand 3. Oxidation of dione **26** (100 mg, 0.18 mmol) with CAN at 80 °C for 1 week according to general procedure D gave 30 mg (28 %) of **3** as monoclinic crystals.

X-ray structural Analysis of 3. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ (No. 14), with a = 15.813(6) Å, b = 13.108(1) Å, c = 20.257(7) Å, β = 109.35(2)°, V = 3961.6 Å^3, d_{calcd} = 1.25 g/cm^3, and Z = 4. The data were collected on an Enraf-Nonius CAD4 diffractometer. Of the 5142 unique data collected with Mo Kα radiation (l = 0.710 73 Å), the 4212 with $F_o > 1.0$ s (F) were used in the least-squares refinement of yield R = 5.20%, Rw = 6.9% after an absorption correction was applied. Two crystallographically independent molecules were found at the center of symmetry within each crystallographic symmetric unit. Outside the molecule two solvent molecules were located with the geometry consistent with that of chloroform.

The X-ray analysis confirmed that the compound **3** has a cyclic hexaketal structure in which six oxygen atoms are arranged up-and-down to give a rigid, spherical cavity with a diameter 1.02 Å. When viewed from the top, the ORTEP diagram and stereoview revealed that the molecule has a star-shaped moiety of six oxygen atoms that are incorporated with [1$_6$]orthocyclophane.

Bis[2-(2-bromomethylbenzyl)phenyl]methane (32). Benzylic diol **21** (3.61 g, 8.9 mmol) was converted by general procedure E to 4.44 g (94.5%) of crystalline dibromide **32**: mp 110–111 °C; IR (KBr) 3040, 2880, 1495, 1450, 715, and 605 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 7.28–6.99 (m, 16 H), 4.34 (s, 4 H), 4.00 (s, 4 H), 3.92 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.29 MHz) 139.06, 138.44, 138.02, 135.78, 130.47, 130.16, 129.73, 129.63, 129.08, 126.87, 126.82, 126.69, 36.32, 35.43, 31.89; EIMS m/z (rel int) 534 (M^+, 7.2), 373 (8.6), 269 (28.7), 193 (100), 179 (90.2).

Bis[2-[2-[2-(hydroxymethyl)benzyl]benzyl]phenyl]-methane (33). Reaction of dibromide **32** (9.00 g, 16.9 mmol) and Grignard **20** (50 mmol) by general procedure F gave 9.70 g (97.6%) of powdery diol **33**: mp 103–104 °C; IR (KBr) 3350, 3060, 2900, 1600, 1450, 1050, and 695 cm^{-1}; ^1H NMR (acetone-d_6, 80 MHz) 7.52–6.84 (m, 24 H), 4.46 (s, 4 H), 3.85 (s, 4 H), 3.80 (s, 4 H), 3.77 (s, 2 H); ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 50.29 MHz) δ 138.89, 137.63, 137.51, 137.42, 137.38, 136.43, 128.55, 128.28, 126.49, 126.20, 125.54, 125.32, 60.94, 38.99, 35.10, 34.17; EIMS m/z (rel int) 552 ($M^+ - 2H_2O$, 58.9), 267 (38.1), and 179 (100); HRMS (EI) found M^+ 552.2814, calcd for $C_{43}H_{40}O_2$ M 588.3028.

Bis[2-[2-(2-formylbenzyl)benzyl]phenyl]methane (34). Oxidation of diol **33** (9.10 g, 15.5 mmol) with PCC according to general procedure G gave 8.4 g (92.9%) of crystalline **34**: mp 114–115 °C; IR (KBr) 1790, 1600, 1490, 1450, and 745 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 9.98 (s, 2 H), 7.86–6.77 (m, 24 H), 4.19 (s, 4 H), 3.77 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 192.16, 142.31, 138.43, 138.22, 138.12, 138.08, 134.00, 133.75, 131.81, 130.92, 129.81, 129.58, 129.39, 126.79, 126.66, 126.56, 36.26, 35.14; EIMS m/z (rel int) 566 ($M^+ - H_2O$, 100), 476 (7.8), 267 (22.7), 179 (95.9); HRMS (EI) found M^+ 566.2608, calcd for $C_{43}H_{36}O_2$ M 584.2715.

2,16-Dioxononacyclo[50.4.0.0^{3,8}.0^{10,15}.0^{17,22}.0^{24,29}.0^{31,36}.0^{38,43}.0^{45,50}]-hexapentaconta-1(52),3(8),4,6,10(15),11,13,17(22),18,20,24-(29),25,27,31(36),32,34,38(43),39,41,45(50),46,48,53,55-tetracosaene; [1$_8$]Orthocyclophane-1,3-dione (36). Cyclocondensation of dibromide **23** (1.60 g, 4.91 mmol) and **34** (1.90 g, 3.25 mmol) according to general procedures A an B provided 0.62 g (25.5%)

of crystalline dione **36**: mp 263–265 °C; IR (KBr) 1655, 1595, 1480, 1445, and 645 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.35–6.70 (m, 32 H), 4.24 (s, 2 H,), 4.06 (s, 4 H), 3.75 (s, 4 H), 3.52 (s, 2 H); ^{13}C NMR (CD_2Cl_2, 50.29 MHz) δ 199.79, 141.29, 141.08, 139.69, 139.24, 139.10, 139.02, 138.91, 131.37, 131.25, 131.15, 130.62, 130.22, 129.79, 129.72, 129.66, 126.50, 126.44, 126.40, 125.93, 125.88, 36.80, 36.31, and 36.19; EIMS *m/z* (rel int) 748 (M^+, 100), 341 (23.5), and 262 (66.2); HRMS (EI) found M^+ 748.3502, calcd for $C_{56}H_{44}O_2$ M 748.3341.

Reduction of 36. We were unable to obtain hydrocarbon **37** by Pd-catalyzed reduction of dione **36** according to the general procedure C.

57,58,59,60,61,62,63,64-Octaoxa[48.6.1.1^{1,8}.1^{8,15}.1^{15,22}.1^{22,29}.1^{29,36}.1^{36,43}.1^{43,50}.0^{2,7}.0^{9,14}.0^{16,21}.0^{23,28}.0^{30,35}.0^{37,42}.0^{44,49}.0^{51,56}]hexapentaconta-2(7),3,5,9(14),10,12,16(21),17,19,23(28),24,26,30(35),31,33,37(42),38,40,44(49),45,47,51(56),52,54-tetracosaene; [1$_8$]-Starand (39). Oxidation of dione **36** (300 mg, 0.40 mmol) with CAN (10 g, 17 mmol) by general procedure D provided 90 mg (27.0%) of **39** as monoclinic crystals: mp > 260 °C dec; IR (KBr) 3015, 1470, 1280, 1065, 1050, 1015, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.42–7.21 (m, 32 H); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 141.80, 129.69, 122.64, 114.77; EIMS *m/z* (rel int) 832 (M^+, 15.3), 504 (4.93), 372 (78.7), 268 (87.6), 239 (99.4), 208 (76.9), and 152 (100).

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Supplementary Material Available: Additional spectral data and ^1H and ^{13}C NMR spectra (40 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.