Oxa Bowls: Synthesis and C−H···O Mediated Solid State Structure of Pentaoxa-[5]-peristylane

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We have conceptualized [*n*]-oxa-[*n*]-peristylanes as a new family of "oxa bowls" having a crownlike shape and potential C_{nv} symmetry. Recognizing their equivalence to the corresponding [*n*]-formyl-[*n*]-cycloalkanes, we have conceived of a general synthetic strategy in which "intramolecular cascade acetalizations" constitute the pivotal step. As our first synthetic effort, we describe the synthesis of pentaoxa-[5]-peristylane **3b** from the readily available Diels−Alder adduct **10** of 5,5-dimethoxy-tetrachlorocyclopentadiene and maleic anhydride. The norbornyl framework of **10** serves as the rigid structural matrix to build the stereochemical features and latent aldehyde functionalities as in **9** through a series of functional group adjustments. Ozonation of **9** furnished **3b** in a one-step transformation in which five tetrahydrofuran rings were generated. While **3b** exhibited C_{5v} symmetry in solution, its symmetry in the solid state was observed to be C_s by X-ray crystallography. In the solid state, **3b** is endowed with a multicolumnar architecture, whose distinctive features include C−H···O interactions involving the less acidic cyclopentane hydrogens. Indeed, all the 10 CH moieties and 5 oxygen atoms (through both the lone pairs) of **3b** ($C_{10}H_{10}O_5$) are involved in short C−H···O contacts (strong and soft) and its crystal structure indicates marked proclivity toward maximal hydrogen bonding.

Design and synthesis of polycyclic entities, with unusual shape, symmetry, and chemically distinct surfaces, constitute an interesting area of organic chemistry research.[1] Such molecules are expected to display many interesting properties such as selective avidity for metal ions, face-selective chemical reactivity (they may find a role in ion transport phenomena), surfactant chemistry, and enzyme mimicry. The basic structural requirement of such bipolarofacial molecular entities is for one of the faces of the molecule to be hydrophobic while the other is hydrophilic with interspersed recognition sites. Hence, it was visualized that the heteroanalogues of polycyclic hydrocarbons, having high symmetry and either cagelike or other specific architecture, could be interesting target structures in which the heteroatoms could be strategically placed.[2] In this context, we have conceived of a new family of [*n*]-hetero-[*n*]-peristylanes as heterocyclic analogues of [*n*]-peristylanes. [*n*]-Peristylanes **1a**−**4a** are a class of aesthetically pleasing and topologically novel molecular entities in which the carbon atoms of an inner [*n*]-membered ring clasp the alternate corners of an outer [2*n*]-membered ring. Such a fascinating union generates a range of bowl-shaped molecules, with [$n + 1$] number of rings and potential C_{nv} symmetry, whose walls are exclusively composed of five-membered rings.[3] When all the methylene groups on the rim of the bowl are replaced by a heteroatom, the resulting [*n*]-hetero-[*n*]-peristylanes **1b,c**−**4b,c** (*n*-heterobowls) are expected to not only be more stable than their carba-analogues, due to the elimination of HC−CH_2 torsional strain but also have the potential to exhibit interesting structural characteristics, possibly bind to metal ions and small molecules, and facilitate chemical transportation, due to their chemically distinct surfaces (hydrophobic base and hydrophilic rim) (see Chart 1).

We have embarked on a program directed toward the synthesis of [*n*]-hetero-[*n*]-peristylanes **1b,c**−**4b,c** and identified [*n*]-oxa-[*n*]-peristylanes **1b**−**4b** as the initial objectives. Our general synthetic strategy toward [*n*]-oxa-[*n*]-peristylanes **1b**−**4b** evolved through the recognition that they can be regarded as the cyclic acetals of the corresponding *all-cis*-[*n*]-formyl-[*n*]-cycloalkanes **5**−**8**, respectively, Scheme 1. Hence, the approach that emanated for the construction of oxa−peristylane frameworks was to generate the *all-cis*-[*n*]-formyl-[*n*]-cycloalkanes **5**−**8** and induce them into nucleophile-triggered intramolecular acetalization cascade, as shown for **7** to **3b** in Scheme 1. Following this strategy, we have accomplished the synthesis of several oxa bowls[4,5,6] and oxa cages[2i] and

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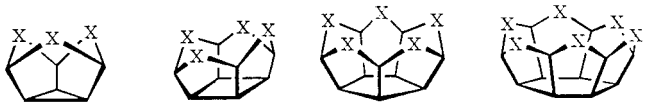
Chart 1



1a. X= CH_2 **2a,b,c** **3a,b,c** **4a,b,c**
b. X=O
c. X=N, S, etc.

herein report the synthesis and solid state structure of pentaoxa-[5]-peristylane **3b**.[4]

From a practical standpoint, it was felt that unraveling the *all-cis*-cyclopentane pentacarbaldehyde moiety **7** in a single step and subjecting it to cascade intramolecular acetalization offered the best chance to prepare the pentaoxa-[5]-peristylane **3b**. To access the *all-cis*-1,2,3,4,5-cyclopentane-pentacarbaldehyde **7**, it was sought to exploit the rigid, stereochemically well-defined norbornane framework with appropriate substituents that could serve as surrogates for the aldehyde functionalities. A retrosynthetic theme shown in Scheme 2 was thus delineated, and *endo,endo*-5,6-divinyl-*anti*-7-formyl bicyclo-[2.2.1]heptene **9** was identified as the equivalent of **7**, in which the C1−C2 and C3−C4 bonds and the C5, C6, and C7 substituents are all cis to each other (see dotted lines) on a five-membered ring (heavy line) embedded within the norbornyl framework. Ozonolysis of **9** was envisaged to unravel the five-membered ring as well as the requisite five aldehyde functionalities to furnish **7** or its equivalent, which on nucleophile-triggered intramolecular cascade cyclization could deliver **3b**, Scheme 2. For the successful execution of this strategy, the readily available Diels−Alder adduct **10**[7] was identified as the starting material.

As a prelude to the synthesis of **3b**, it was considered appropriate to carry out a model study aimed toward *seco*-pentaoxa-[5]-peristylane **11**. For this purpose, *endo,-endo*-diol **12**, which is also readily available from **10**, was identified as the precursor. It was anticipated that oxidative cleavage of the norbornene double bond in **12** will lead, through intramolecular acetalization, to the *seco*-pentaoxa-[5]-peristylane **11**, which could be further elaborated to **3b** through oxidation−cyclization maneuvers, Scheme 3.

Diels−Alder adduct **10**[7] of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and maleic anhydride on reductive dechlorination, in the presence of Na/liquid NH_3, acid-catalyzed methanolysis, and careful ketal hydrolysis afforded the highly crystalline ketone **13**, Scheme 4.[8] The C7 carbonyl group in the norbornenone **13** was next homologated to the aldehyde moiety.

Wittig olefination on **13** with methoxymethyltriphenylphosphorane furnished the enol-ether **14**, and further acid hydrolysis afforded the aldehydes **15a** and **15b** as a mixture of diastereomers (^{1}H NMR) in 80% yield, Scheme 4. The two diastereomers **15a** and **15b** could be separated by careful column chromatography, and the stereochemistry of *syn*-**15a** and *anti*-**15b** was secured through incisive analyses of their ^{1}H and ^{13}C NMR spectral data. In particular, the deshielding effect of the C7 aldehyde group on the C5 and C6-*exo*-hydrogens, in the case of the *syn*-isomer **15a,** assisted in the structural assignment. The aldehyde moiety in **15** (used as mixture of **15a** and **15b**) was protected as the dimethyl acetals **16a** and **16b**. Protection of the aldehyde functionality was also carried out independently for the purpose of characterization, and **15a** and **15b** furnished **16a** and **16b**, respectively, Scheme 4.

The acetal diester **16a,b** was subjected to $LiAlH_4$ reduction to furnish *endo,endo*-norbornene diol **17a,b** in 70−80% yield, Scheme 4. Ozonolysis of the norbornene double bond in the diol **17a,b** furnished a mixture of trioxa-cage compound **18** and *seco*-pentaoxa-[5]-peristylane **11** in a ratio of 2:1 in 40% yield as crystalline solids, Scheme 4.[5c] The structure and C_s symmetry of **11** followed from the ^{1}H NMR and six-line ^{13}C NMR spectral data. The likely mechanism for the formation of **18** and **11** from **17a** and **17b**, respectively, is depicted in Scheme 5.

The trioxa-cage compound **18** on exposure to Amberlyst-15 could be converted to the corresponding aldehyde **19** and **11** in a ratio of 5:1, Scheme 6. It was observed that the aldehyde **19** is in equilibrium with **11**. On separation and exposure to acid catalysis, **19** was efficiently transformed to **11** in 78% yield through a possible mechanism shown in Scheme 6.

In the backdrop of the experience gained during the synthesis of **11**, we proceeded to implement the theme directed toward **3b**, Scheme 2. The readily available Diels−Alder adduct **10** on reduction with $LiAlH_4$ and reductive dechlorination in Na/liquid NH_3 furnished the unsaturated diol **20**,[8] which is the starting point of our projected synthesis, Scheme 7. The diol **20** was selectively oxidized with a hypervalent iodine reagent (IBX)[9] to furnish lactol **21** as a single isomer in 96% yield, Scheme 7. The hemiacetal **21** was subjected to Wittig olefination, and under the reaction conditions used, it reacted in the hydroxy aldehyde form to stereoselectively furnish the *endo, endo*-vinyl carbinol **22** as the major product in 56% yield, Scheme 7.

Swern oxidation[10] of the *endo*-carbinol **22** afforded the corresponding vinyl aldehyde **23** in excellent yield, which was further subjected to Wittig olefination with methylenetriphenylphosphorane to furnish the desired divinyl ketals **24a,b** as a mixture of *endo,endo*-**24a** and *endo,-exo*-**24b** isomers in a 85:15 ratio as shown by the ^{1}H NMR spectrum, Scheme 7. The mixture of two epimers **24a** and **24b** could be resolved and separated by column chromatography over $AgNO_3$-impregnated silica gel, and each isomer was fully characterized. In the case of **24a**, its eight-line ^{13}C NMR spectrum revealed its symmetrical structure.

Deprotection of the ketal moiety in **24a** was achieved through careful transacetalization in the presence of Amberlyst-15 to furnish the norbornenyl ketone **25** in

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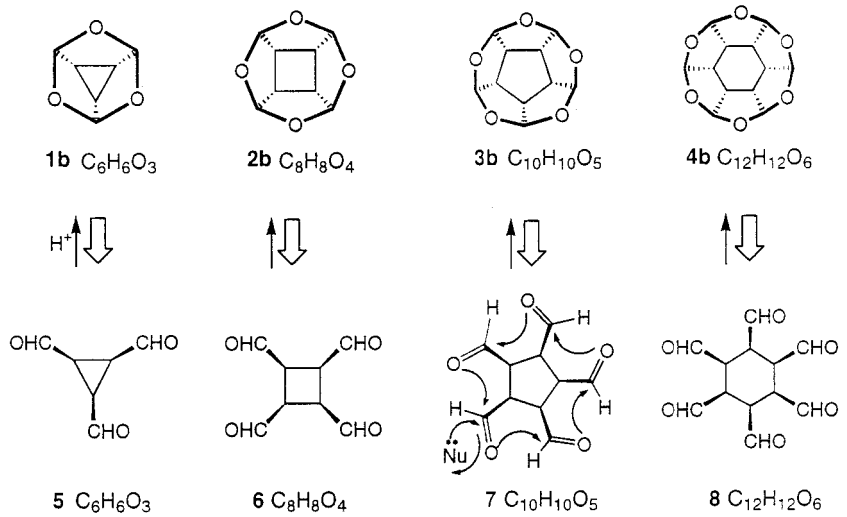
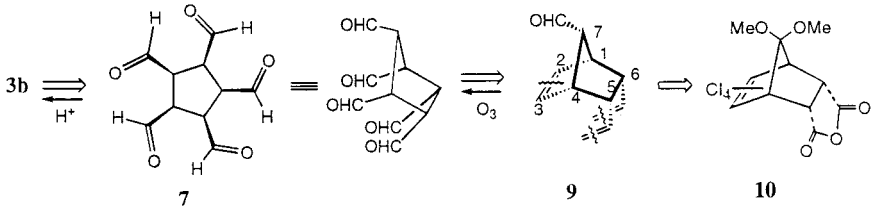
(9) Corey, E. J.; Palani, A. *Tetrahedron Lett*. **1995**, *36*, 7945.

(10) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651.

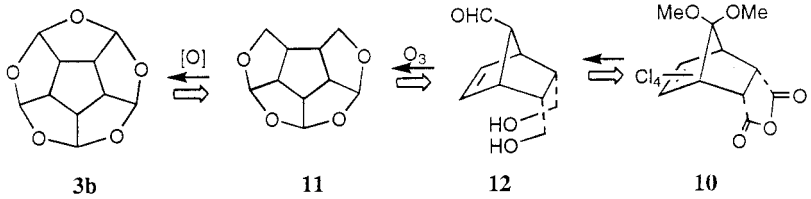
Scheme 1



Scheme 2



Scheme 3



90% yield. Wittig olefination on **25** using methoxymethylphosphorane led to the formation of methyl enol-ether **26** as the major product, Scheme 7. Hydrolysis of **26** in aqueous perchloric acid afforded a mixture of diastereomeric *syn*- and *anti*-aldehydes **9a,b** in a 3:1 ratio (^{1}H NMR) in quantitative yield. To our satisfaction, aldehyde **9** turned out to be the equivalent of cyclopentane pentacarbaldehyde **7**, as projected in Scheme 2.

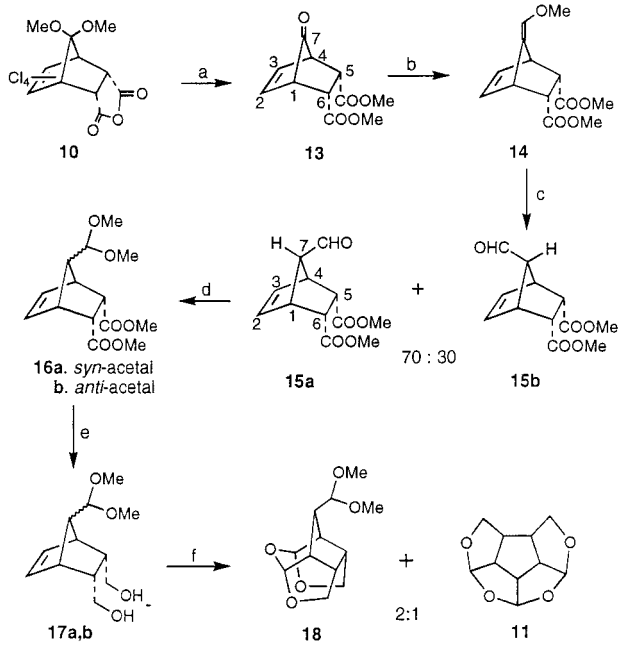
Recognizing that **9a** and **9b** could readily equilibrate under acid catalysis, we decided to proceed with the mixture of the two diastereomers to the next step. When **9a,b** was subjected to ozonolysis, followed by workup with dimethyl sulfide, a mixture of tetraoxa-aldehyde **27** and the desired pentaoxa-[5]-peristylane **3b** was obtained in a ratio of 2:1 in 39% yield, Scheme 7.[4a] The tetraoxa-aldehyde **27**, possibly derived from the isomer **9b** on exposure to Amberlyst-15 catalyst, was further transformed into the target compound **3b**, Scheme 7.

The intermediate **7** or its equivalent generated during ozonolysis of **9** underwent facile cascade cyclizations as contemplated to furnish the parent pentaoxa-[5]-peristylane **3b**, mp > 230 °C dec. The two-line ^{1}H NMR spectrum with signals in a 1:1 ratio and the two-line ^{13}C NMR spectrum were in accordance with the C_{5v} symmetry and structural formulation of pentaoxa-[5]-peristylane **3b**. The mass spectrum of **3b** exhibited the molecular ion peak at *m*/*z* 211 ($M^+ + 1$), and the structure was fully secured through its X-ray crystal structure determination. Interestingly, the X-ray crystal structure of **3b** revealed that it does not possess the anticipated C_{5v} symmetry in the solid state but displays C_s symmetry instead and the molecules are tightly packed with a high crystal density of 1.73 g cm^{-3}.[4b] This deviation from the anticipated symmetry and high crystal density led us to examine the crystal packing of **3b** in a detailed manner.

Crystal Structure of Pentaoxa-[5]-peristylane 3b. Slow evaporation of a solution of **3b** in dichloromethane−hexane provided needle-shaped crystals that belonged to the space group *Pnma* with four molecules present in the unit cell. The crystal data are reported in detail in the Experimental Section. The molecules are tightly packed with high crystal density, and **3b** does not possess C_{5v} symmetry in the solid state (cf. C_{5v} in solution as revealed by ^{1}H and ^{13}C NMR spectra) but displays C_s symmetry instead in the crystal, with the crystallographic mirror plane passing through O1, C1−H1, and C4−H4, Figure 1. In agreement with the C_s symmetry of **3b**, the following intramolecular distances (Å) are observed between oxygen atoms: O1···O2 = 2.337; O2···O3 = 2.337; O3···O3* = 2.304; O1···O3 = 3.389; O2···O3* = 3.874; O2···O2* = 4.144.

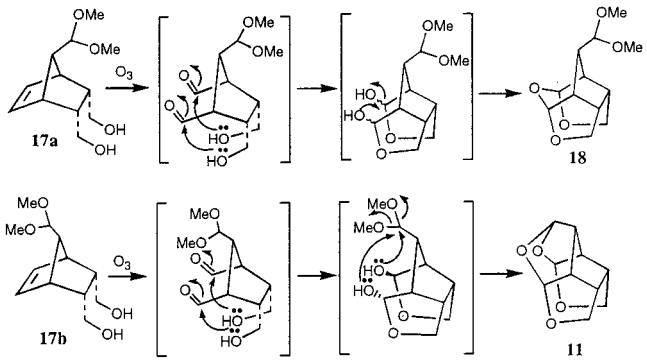
In the solid state of pentaoxa-[5]-peristylane **3b**, the organization of the molecules in the *ab*-plane exhibits hexagonal network, with six molecules surrounding the

Scheme 4[a]

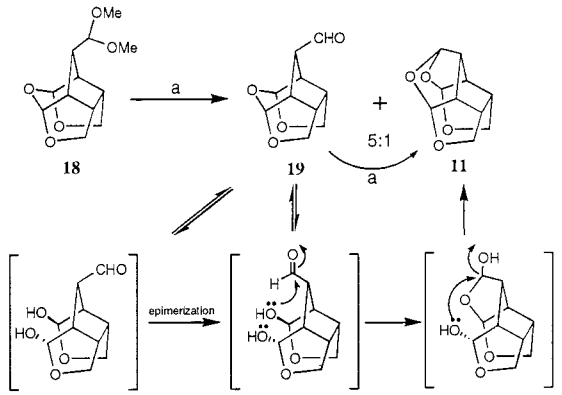


[a] Reagents and Conditions. (a) i, Na/liquid NH_3, THF, 30%; ii, CH_3OH, concd H_2SO_4, 86%; iii, 5% H_2SO_4, THF reflux, 2 h, 70%; (b) $CH_3OCH_2PPh_3Cl$, NaO^{t}Am, THF, 55%; (c) 35% $HClO_4$, DCM, rt, 2−3 h, 80%; (d) PTSA, MeOH−C_6H_6, reflux, 3−4 h, 92%; (e) $LiAlH_4$, THF, rt, 4 h, 70−80%; (f) O_3, DCM, −78 °C; DMS, −78 °C, 40%.

Scheme 5



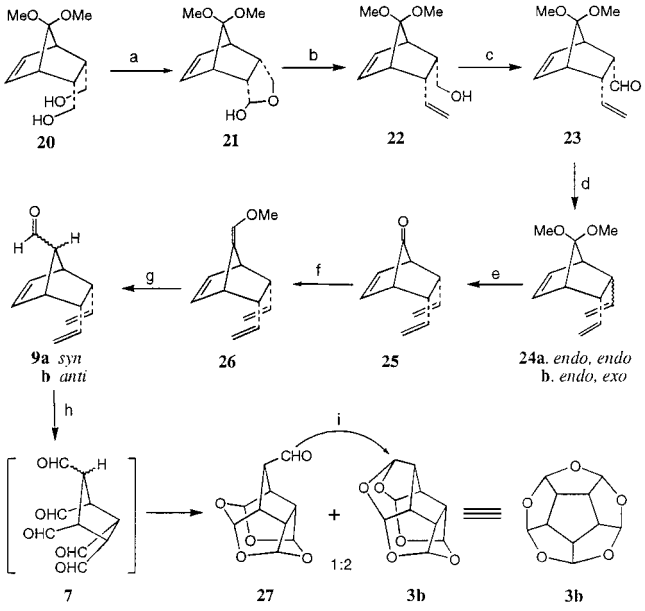
Scheme 6[a]



[a] Reagents and Condition. (a) Amberlyst-15, moist acetone, 78%.

one at the center and interconnecting through the C−H···O hydrogen bonds, Figure 2. Along the *a*-axis, the molecules are arranged in an alternate concave−convex

Scheme 7[a]



[a] Reagents and Conditions. (a) IBX, DMSO:Acetone, rt, 2 h, 96%; (b) $CH_3PPh_3^+Br^-$, ^{t}AmONa, THF, rt, 30 min, 56%; (c) $(COCl)_2$, DMSO, Et_3N, DCM, −60 °C, 90%; (d) CH_3PPh_3Br, NaO^{t}Am, THF, 30 min, 70%; (e) Amberlyst-15, acetone, reflux, 6 h, 90%; (f) $CH_3OCH_2PPh_3Cl$, NaO^{t}Am, THF, 30 min, 50%; (g) 35% $HClO_4$, DCM, 5 h, quantitative yield; (h) O_3, DCM, −78 °C; DMS, 39%; (i) Amberlyst-15, DCM.

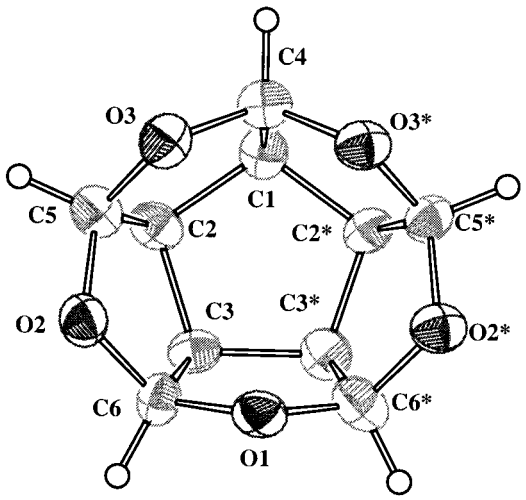


Figure 1. ORTEP diagram of **3b**.

manner resulting in a bowl inversion pattern. When viewed along the *c*-axis, the oxa bowls stack on top of each other, in a top to bottom fashion, forming infinite columns in channel-like architecture. The arrangement of these columns can be visualized in three distinct patterns. The columns along the *a*-axis grow in opposite directions. However, when viewed through *c*-axis, the columns are arranged in two wavelike patterns; one with the columns growing in the same direction and the other with the columns growing in opposite directions, Figure 3. This columnar arrangement is solely dictated by C−H···O hydrogen bonds. Further incisive analysis of the crystal packing reveals that a network of C−H···O hydrogen bonds, essentially along the three crystallographic axes, is responsible for giving a form and shape to the entire supramolecular assembly (first three

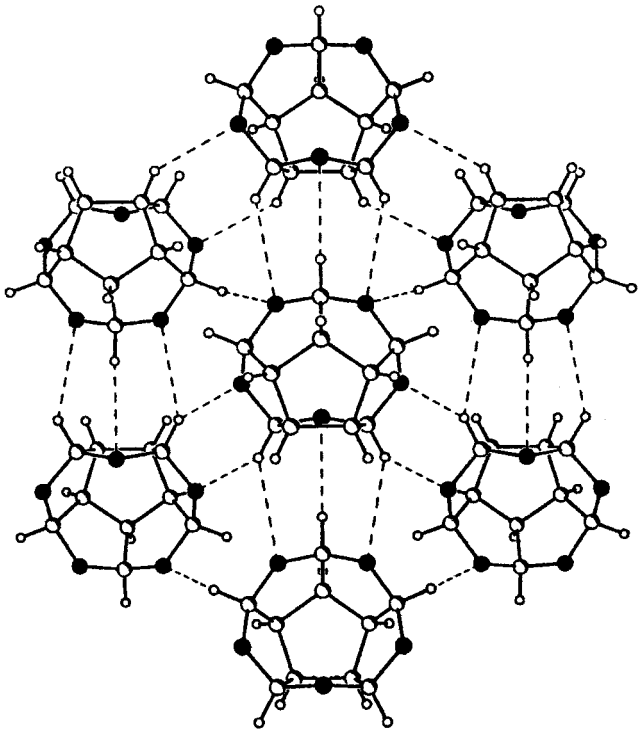


Figure 2. Network of C−H···O hydrogen bonding in the *ab*-plane.

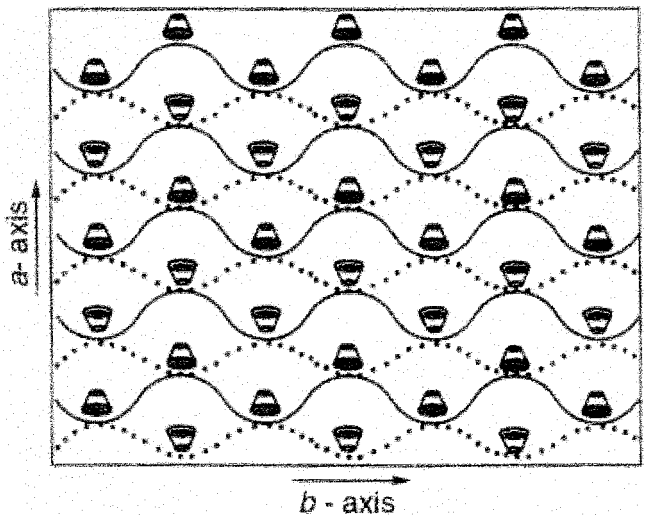


Figure 3. Wavelike pattern of columns: —, unidirectional and ···, alternating directionality.

entries in Table 1). Each molecule in this assembly has short contacts with 10 of its symmetry-related neighboring molecules through 20 C−H···O interactions (14 strong and 6 soft, see Table 1).[11] In addition, the crystal structure of **3b** also reveals the presence of several bifurcated C−H···O hydrogen bonds, Figure 2

A significant and novel aspect of the C−H···O hydrogen bonding present in **3b** is the involvement of the least acidic cycloalkane hydrogens of the cyclopentane ring, forming the base of the oxa bowl. Indeed, the C2−H2···O2 (d = 2.56 Å, θ = 150.4°) hydrogen bonds

Table 1. Intermolecular C−H···O Interactions in the Crystal of 3b

C−H···O[a] participating atoms	H···O dist d (Å)	C···O dist D (Å)	C−H···O angle θ (deg)	no. of C−H···O contacts[c] (direction)
C2−H2···O2[b] O2···H2−C2[b]	2.56(2)	3.426(2)	150.4	4 (*c*-axis)
C5−H5···O3[b] O3···H5−C5[b]	2.66(2)	3.439(2)	135.3	4 (*b*-axis)
C4−H4···O1[b] O1···H4−C4[b]	2.66(2)	3.558(3)	150.6	2 (*a*-axis)
C6−H6···O3[b] O3···H6−C6[b]	2.76(2)	3.556(2)	134.5	4 (*a*-axis)
C3−H3···O2[b] O2···H3−C3[b]	2.81(2)	3.671(2)	146.4	4 (*b*-axis)
C1−H1···O1[b] O1···H1−C1[b]	2.92(2)	3.195(3)	97.5	2 (*c*-axis)

[a] Two lone pairs on each oxygen atom involved in C−H···O interaction. [b] Atoms of the neighboring molecules. [c] No. of contacts based on the mirror plane symmetry in **3b** (direction), and the interactions with the neighboring molecules.

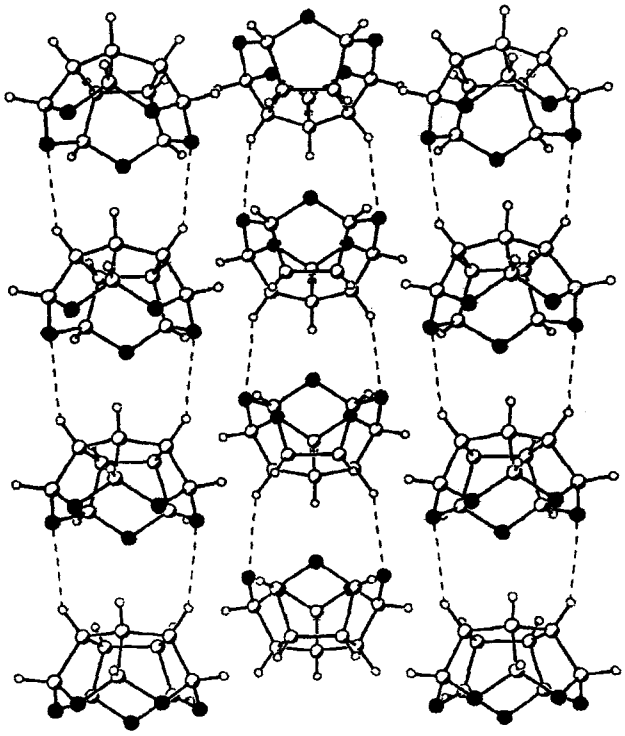


Figure 4. Infinite columnar C−H···O hydrogen bonding along *c*-axis: d = 2.56 Å, D = 3.426 Å, θ = 150.4°.

turn out to be the strongest (see Table 1) and are responsible for sustaining the infinite "top to bottom" columnar motif (the motif is a hydrogen-bonded set in which only one type of hydrogen bond is present and not one hydrogen atom)[12] along the shortest crystallographic *c*-axis, Figure 4. This hydrophobic end to hydrophilic end piling of the "bowls" is quite unique and aesthetically pleasing. The oxa-bowl columns in turn are held in place through an intricate network of C−H···O contacts. The columns growing in the same direction along the *c*-axis are held together through infinite spiral hydrogen-bonding C5−H5···O3 (d = 2.66 Å, θ = 135.3°) in clockwise and anticlockwise directions along the *b*-axis, Figure 5.

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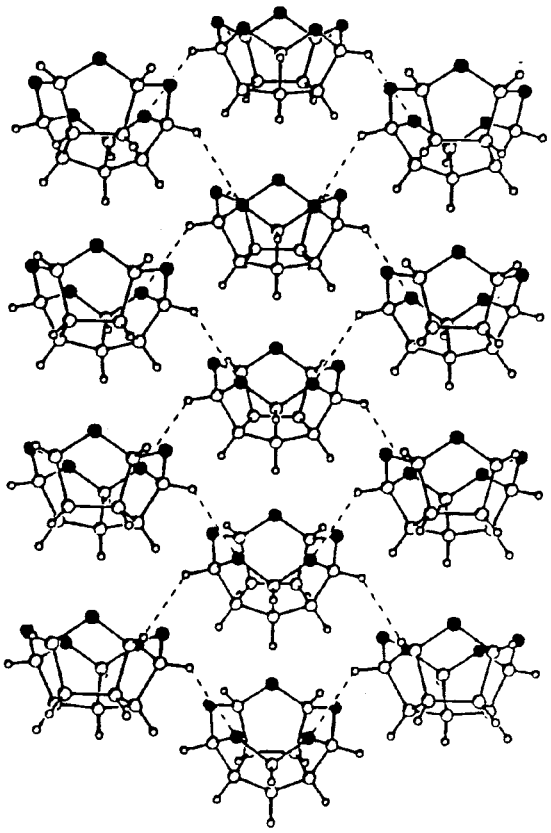

Figure 5. Infinite spiral C−H···O hydrogen bonding along the *b*-axis and hydrogen bonding along the *b*-axis: $d = 2.66$ Å, $D = 3.439$ Å, $\theta = 135.3°$.

Since these hydrogen bonds connect molecules not only in the same layer but also in the next layer, the attainment of the spiral pattern is facilitated. The two strands of the oxa-bowl columns constituting the two wavelike patterns are interconnected, with each molecule of one strand forming three hydrogen bonds, C4−H4···O1 ($d =$ 2.66 Å, $\theta = 150.6°$) and C6−H6···O3 ($d = 2.76$ Å, $\theta =$ 134.5°), with its counterpart in the other strand along the *a*-axis, Figure 2.

The other close contacts that could be observed in this supramolecular assembly are C3−H3 with O2 and C1−H1 with O1 (see Table 1). The softness of these interactions (C−H···O distances of 2.81 and 2.92 Å, respectively) could be ascribed to their concurrent involvement in a bifurcated manner (C1−H1···O3, $d = 3.04$ Å, $\theta = 153.3°$ and C6−H6···O2, $d = 2.79$ Å, $\theta = 144.0°$), Figure 2.

It was also of interest to assess the strength of the observed C−H···O interactions by IR spectroscopy. Generally, the C−H···O interactions weaken the C−H bond and thus shift the C−H stretching vibration to a lower frequency. The difference between the free C−H stretching frequency determined for a solution and the hydrogen-bonded C−H stretching frequency in the solid state gives a qualitative indication of the strength of the C−H···O interaction.[13] Therefore, IR spectra were recorded for the crystals ($\upsilon_{C-H} = 2973$, 2957 cm^{-1}) and a dilute solution of **3b** in $CDCl_3$ ($\upsilon_{C-H} = 2988$, 2967 cm^{-1}). The shift in the expected direction gave a clear indication of the presence of C−H···O interactions. However, the very small shift in frequency (10−15 cm^{-1}) precluded any definitive conclusion regarding the strength of the C−H···O interactions. Nonetheless, in the solid state, the oxa bowl pentaoxa-[5]-peristylane **3b** with a hydrophobic base (bottom) and hydrophilic rim (top) possesses a novel supramolecular architecture in which all the 10 CH units and 5 oxygen atoms (through both the lone pairs) of the molecule are involved in a network of unique C−H···O interactions[11] and this constitutes a remarkable example of the "...principle of maximum hydrogen bonding".[14]

Synthetic access to pentaoxa-[5]-peristylane **3b** spurred us to investigate its binding ability. The symmetrical and crownlike disposition of the oxygen atoms in the oxa-peristylanes **1b**−**4b** (2*n*-crown-*n*) makes them attractive targets for metal−ion complexation. We have studied the energetic and the structural consequences of metal complexation by taking Li^+ as a model.[15] The unusual flexibility observed for **3b** is reduced on complexation, and only one minimum energy structure corresponding to one of the oxygen atoms pushed in could be located. The Li^+ complex of **3b** has three oxygens coordinated to Li^+, and the symmetry is reduced to C_s. With this understanding, we investigated the metal-ion binding potential of oxa bowl **3b** through NMR studies using Li and Na perchlorate salts.[16] Unfortunately, there was no significant change in the proton and ^{13}C resonances in the NMR spectra of **3b** solutions. Similarly, alkali metal picrate extraction[16] protocol also provided no evidence of metal complexation. The response of **3b** to metal binding is indeed unexpected and surprising.

In summary, synthesis of the oxa bowl pentaoxa-[5]-peristylane **3b** is reported by following the strategy of intramolecular cascade acetalization in *all-cis*-[*n*]-formyl-[*n*]-cycloalkanes. In the solid state, **3b** displays C_s symmetry as opposed to the expected C_{5v} in solution. The multicolumnar architecture of pentaoxa-[5]-peristylane in the solid state involving the least acidic cyclopentane hydrogens as well as acetal hydrogen atoms is delineated.

Experimental Section

General. Melting points are uncorrected. IR spectra were recorded on JASCO FT-IR 5300 spectrometer with solid samples as KBr wafers and liquid samples as thin films between NaCl plates. ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Bruker AC 200, and the NMR samples were made in $CDCl_3$ solvent. Elemental analyses were performed on a Perkin-Elmer 240C-CHN analyzer. Column chromatography was performed using Acme's silica gel (100−200 mesh), and ethyl acetate−hexane was used as eluent. All reactions were monitored employing a TLC technique using an appropriate solvent system for development. THF was distilled prior to use from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride.

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Dimethyl-7-methoxymethylenebicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate (14). To a suspension of (methoxymethyl)-triphenylphosphonium chloride (14 g, 41.071 mmol) in dry THF (30 mL) was added freshly sublimed sodium *t*-amyloxide (1.7 g, 15.402 mmol) in dry THF (10 mL) under N_2 atmosphere, and the mixture was stirred for 5 min at room temperature. To the resulting dark red ylide was added ketone **13**[8] (2.3 g, 10.268 mmol) in 10 mL of dry THF, and the reaction mixture was stirred further for 30 min and then quenched with water (15 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with water and brine and dried over sodium sulfate. The solvent was evaporated, and the residue was charged on a silica gel column. Elution with 6% EtOAc−hexane furnished **14** (1.4 g, 55%), which was crystallized from dichloromethane−hexane: mp 86−87 °C; IR (KBr) 2997, 1728, 1195 cm^{-1}; ^1H NMR δ 6.42−6.32 (m, 2H), 5.47 (s, 1H), 3.84 (br. s, 1H), 3.62 (s, 6H), 3.51 (s, 3H), 3.37−3.32 (m, 3H); ^{13}C NMR δ 172.2 (2C), 135.4, 134.8, 130.8, 128.3, 59.6, 51.5 (2C), 49.2, 47.9, 46.6, 44.2; MS *m*/*z* 253 ($M^+ + 1$). Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 62.01; H, 6.41.

Dimethyl 7-formylbicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate (15). To a solution of **14** (1.4 g, 5.556 mmol) in 10 mL of dichloromethane, a few drops of 35% $HClO_4$ were added at 0 °C, and the mixture was stirred for 2−3 h at room temperature. The reaction mixture was quenched with sodium bicarbonate solution, and the organic layer was washed with water and brine and dried over sodium sulfate. The solvent was removed, and the crude residue was purified by silica gel column chromatography. Elution with 10% EtOAc−hexane furnished the *syn*-aldehyde **15a** (0.78 g, 59%), and *anti*-aldehyde **15b** (0.28 g, 21%) was obtained. **15a**: IR (neat) 1743, 1199, 1062 cm^{-1}; ^1H NMR δ 9.59 (s, 1H), 6.34 (s, 2H), 3.63 (s, 6H), 3.45 (s, 2H), 3.29 (d, 2H, $J = 1.6$ Hz), 2.53 (d, 1H, $J = 1.6$ Hz); ^{13}C NMR δ 199.6, 172.0 (2C), 135.2 (2C), 68.7, 51.7(2C), 45.9 (2C), 45.5 (2C); MS *m*/*z* 239 ($M^+ + 1$). Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.55; H, 5.95. **15b** (unstable): IR (neat) 1739, 1197, 1170 cm^{-1}; ^1H NMR δ 9.60 (s, 1H), 6.31 (s, 2H), 3.64 (s, 6H), 3.53 (br. s, 2H), 3.39 (s, 2H), 2.38 (s,1H); ^{13}C NMR δ 202.6, 171.5 (2C), 133.3 (2C), 69.7, 51.7 (2C), 48.0 (2C), 47.6 (2C).

Dimethyl-7-dimethoxymethylbicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate (16). To a solution of **15a,b** (1 g, 4.202 mmol) in dry benzene/methanol (4:1), catalytic *p*-toluenesulfonic acid was added, and the mixture was refluxed using Dean−Stark apparatus under N_2 atmosphere for 3 h. After the removal of the solvent, the residue was dissolved in ethyl acetate, washed with water, saturated bicarbonate solution, and brine, and dried over sodium sulfate. The product was chromatographed on a silica gel column to furnish **16a,b** (1.1 g, 92%). As the separation was found to be difficult at this stage, for characterization purposes, **15a** and **15b** were independently converted to **16a** and **16b**, respectively, as described above. **16a**: IR (neat) 1745, 1197, 1064 cm^{-1}; ^1H NMR δ 6.32 (t, 2H, $J = 1.7$ Hz), 4.15 (d, 1H, $J = 8.7$ Hz), 3.62 (s, 6H), 3.31(s, 8H), 3.06 (br. s, 2H), 1.97 (d, 1H, $J = 8.7$ Hz); ^{13}C NMR δ 172.5 (2C), 136.1 (2C), 101.8, 60.5, 52.8 (2C), 51.6 (2C), 46.7 (2C), 46.1 (2C); MS *m*/*z* 284 (M^+), 253 ($M^+ -$ OMe). Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 59.19; H, 7.11. **16b**: IR (neat) 1745, 1195, 1053 cm^{-1}; ^1H NMR δ 6.21 (s, 2H), 4.25 (d, 1H, $J = 8$ Hz), 3.61 (s, 6H), 3.33 (s, 2H), 3.30 (s, 6H), 3.16 (s, 2H), 1.97 (d, 1H, $J = 8$ Hz); ^{13}C NMR δ 172.2, 132.6, 102.9, 62.7, 53.7, 51.5, 48.4, 47.6. Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 59.18; H, 7.12.

7-Dimethoxymethyl-3-hydroxymethylbicyclo[2.2.1]hept-5-en-2-ylmethanol (17). To a solution of diester **16a,b** (1 g, 3.521 mmol) in dry THF (10 mL) was added $LiAlH_4$ (270 mg, 7.042 mmol) under N_2. The reaction mixture was stirred at room temperature for 4 h and quenched with EtOAc and saturated Na_2SO_4. The granular precipitate that formed was filtered and washed with EtOAc. The filtrate and the washings were combined, washed with brine, and then dried over Na_2SO_4. Removal of solvent and filtration through a silica gel column afforded **17a,b** (0.562 g, 70%) as revealed by the ^1H and ^{13}C NMR spectra of the mixture. However, for characterization purposes, pure **17a** was prepared from **16a** as described above. **17a**: IR (neat) 3383, 1448, 1039 cm^{-1}; ^1H NMR δ 6.08 (br. s, 2H), 4.33 (d, 1H, $J = 9$ Hz), 4.00 (br. s, 2H, −O*H*), 3.66−3.41 (m, 4H), 3.31 (s, 6H), 2.71 (br. s, 2H), 2.55 (d, 2H, $J = 6.3$ Hz), 1.83 (d, 1H, $J = 9$ Hz); ^{13}C NMR δ 135.8 (2C), 102.0, 63.0 (2C), 61.1, 52.9 (2C), 46.9 (2C), 42.8 (2C); MS *m*/*z* 211 ($M^+ -$ OH). Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.11; H, 8.86.

2-Dimethoxymethyl-6,8,10-trioxatetracyclo[7.3.0.0^{3,7}.0^{4,12}]-dodecane (18) and Perhydro-2,3,4,5-tetraoxacyclopenta-[*cd*]pentaleno[2,1,6-*gha*]pentalene (11). Through a solution of the diol **17a,b** (100 mg, 0.439 mmol) in dichloromethane (20 mL), ozone was bubbled at −78 °C, and the resulting ozonide was quenched with dimethyl sulfide (0.1 mL). The reaction mixture was brought to room temperature and stirred for 2 h. Concentration under vacuum and chromatography on a neutral alumina column (elution with 10% EtOAc−chloroform) furnished first the trioxa acetal **18** followed by the tetraoxa compound **11** (42 mg, 40%), which were crystallized from dichloromethane−hexane. **18**: mp 130−131 °C; IR (KBr) 2953, 1049 cm^{-1}; ^1H NMR δ 5.50 (d, 2H, $J = 5.7$ Hz), 4.22−4.18 (m, 3H), 3.93−3.88 (m, 2H), 3.40 (s, 6H), 2.85 − 2.68 (m, 4H), 2.29 (d, 1H, $J = 8$ Hz); ^{13}C NMR δ 104.5 (3C), 69.6 (2C), 53.4 (2C), 48.2 (2C), 41.0 (2C), 39.7; MS *m*/*z* 211($M^+ -$ OMe). Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.55; H, 7.52. **11**: mp 170 °C; IR (KBr) 2966, 1086, 949 cm^{-1}; ^1H NMR δ 5.86 (d, 2H, $J = 5.4$ Hz), 5.72 (d, 1H, 5.6 Hz), 4.31 (dd, 2H, $J = 9.1$, 4.6 Hz), 4.03 (t, 2H, $J = 7$ Hz), 3.54−3.46 (m, 2H), 3.32−3.24 (m, 1H), 3.10−3.01 (m, 2H);^{13}C NMR(DEPT) δ 112.3 (2C, CH), 111.5 (CH), 70.6 (2C, CH_2), 59.4 (2C, CH), 53.0 (CH), 47.5 (2C, CH); MS *m*/*z* 197($M^+ + 1$). Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16. Found: C, 61.25; H, 6.18.

10,10-Dimethoxy-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-en-3-ol (21).[9] A mixture of dimethyl sulfoxide (5.5 mL), acetone (20 mL), and *o*-iodoxybenzoic acid (3.14 g, 11.215 mmol) was stirred for 1 h, and the resulting solution was added to the diol **20**[8] (2 g, 9.346 mmol). After being stirred for 1 h at room temperature, the reaction mixture was diluted with water (20 mL) and filtered. The filtrate was extracted with dichloromethane, dried over Na_2SO_4, and concentrated. The residue was purified through silica gel column chromatography (elution with 50% EtOAc−hexane) to afford the lactol **21** (1.9 g, 96%) as a colorless oily liquid: IR (neat) 3414, 1653, 1437, 1043 cm^{-1}; ^1H NMR δ 6.21−6.10 (m, 2H), 5.01 (s, 1H), 3.99 (t, 1H, $J = 8$ Hz), 3.47 (dd, 1H, $J = 9$, 2 Hz), 3.19 (s, 3H), 3.11 (s, 3H), 3.10−3.04 (m, 2H), 2.99−2.95 (m, 1H), 2.92−2.90 (m, 1H); ^{13}C NMR δ 132.2, 131.6, 121.7, 99.9, 68.6, 53.0, 52.1, 49.7, 48.4, 47.3, 43.5; MS *m*/*z* 212 (M^+). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.30; H, 7.58.

7,7-Dimethoxy-3-vinylbicyclo[2.2.1]hept-5-en-2-yl methanol (22). To a suspension of methyltriphenylphosphonium bromide (9.5 g, 26.611 mmol) in dry THF (20 mL) was added freshly sublimed sodium *t*-amyloxide (1.5 g, 13.636 mmol) in THF (5 mL), and the mixture was stirred for 5 min at room temperature. To the canary yellow ylide was added the lactol **21** (1.9 g, 8.962 mmol) in THF (10 mL), and the reaction mixture was stirred for 20 min and then quenched with water (10 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine and dried. The resulting residue was charged on a silica gel column. Elution with 15% EtOAc−hexane furnished **22** (1.05 g, 56%): IR (neat) 3406, 3070, 1635, 1064 cm^{-1}; ^1H NMR δ 6.18−6.16 (m, 2H), 5.50−5.28 (m, 1H), 5.18−4.88 (m, 2H), 3.38−3.17 (m, 2H), 3.20 (s, 3H), 3.10 (s, 3H), 2.99−2.91 (m, 1H), 2.85−2.78 (m, 1H), 2.70−2.52 (m, 1H), 2.20−2.08 (m, 2H); ^{13}C NMR δ 138.3, 132.9, 132.8, 118.5, 117.0, 62.5, 51.8, 51.0, 49.8, 47.5, 44.5 (2C); MS *m*/*z* 210(M^+). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.68. Found: C, 68.60; H, 8.67.

7,7-Dimethoxy-6-vinylbicyclo[2.2.1]hept-2-ene-5-carbaldehyde (23). To oxalyl chloride (0.82 mL, 9.524 mmol) in dichloromethane (2 mL) was added dimethyl sulfoxide (1.7 mL, 23.810 mmol) in dichloromethane (2 mL) at −60 °C under N_2. After 15 min, alcohol **22** (1 g, 4.762 mmol) in dichloromethane (5 mL) was added. Triethylamine (5.5 mL, 39.604 mmol) was

added after another 15 min, and the reaction was warmed to 0 °C and quenched with water (10 mL). Extraction with dichloromethane and purification through a silica gel column (elution with 5% EtOAc−hexane) afforded aldehyde **23** as a yellow oil (0.66 g, 90%): IR (neat) 2733, 1716, 1269 cm^{-1}; ^1H NMR δ 9.40 (d, 1H, J = 2 Hz), 6.30 (dd, 1H, J = 5.6, 2.8 Hz), 6.16 (dd, 1H, J = 6.4, 3.2 Hz), 5.50−4.99 (series of m, 3H), 3.41 (dt, 1H, J = 9.6, 6 Hz), 3.24−3.17 (m, 2H), 3.19 (s, 3H), 3.11 (s, 3H), 2.90−2.87 (m, 1H); ^{13}C NMR δ 204.1, 137.3, 133.7, 132.5, 118.0, 117.7, 55.5, 52.0, 50.6, 49.9, 47.0, 46.4; MS m/z 208(M^+). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.25; H, 7.77.

7,7-Dimethoxy-5,6-divinylbicyclo[2.2.1]hept-2-ene (24). Wittig olefination of the aldehyde (0.66 g, 3.173 mmol) was carried out as described above for **22**. After the usual workup, the residue was charged on a silica gel column. Elution with hexane furnished the divinyl compound **24** (0.46 g, 70%) which was found to be a mixture of *endo,endo*- and *endo,exo*- isomers **24a** and **b** in a ratio of ∼85:15 (^1H NMR). Column chromatography using 15% $AgNO_3$-impregnated silica gel and elution with 5−10% EtOAc−hexane furnished the *endo,exo*-isomer **24b** and *endo,endo*-isomer **24a** as oily liquids. **24a**: IR (neat) 2829, 1635, 1277 cm^{-1}; ^1H NMR δ 6.22−6.20 (m, 2H), 5.50−5.30 (m, 2H), 5.07−4.90 (m, 4H), 3.24 (s, 3H), 3.14 (s, 3H), 3.14−3.09 (m, 2H), 2.87 (br. s, 2H); ^{13}C NMR δ 139.2, 133. 0, 118.2, 115.5, 51.8, 50.7, 49.8, 46.9. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.72; H, 8.83. **24b**: IR (neat) 3074, 1635, 910 cm^{-1}; ^1H NMR δ 6.30−6.00 (m, 2H), 5.62−5.48 (m, 2H), 5.04−4.87 (m, 4H), 3.22 (s, 3H), 3.15 (s, 3H), 2.86 (br. s, 1H), 2.68−2.60 (m, 2H), 1.86−1.78 (m, 1H); ^{13}C NMR δ 140.9, 140.5, 135.3, 131.1, 119.0, 114.6, 114.3, 51.7, 51.5, 51.0, 50.4, 49.7, 47.0.

5,6-Divinylbicyclo[2.2.1]hept-2-en-7-one (25). A solution of **24a** (350 mg, 1.699 mmol) in moist acetone (7 mL) was refluxed with Amberlyst-15 resin for 6 h. The resin was filtered off, and the solvent was removed. The residue was purified by column chromatography on silica gel to furnish **25** (0.25 g, 90%) as a colorless liquid: IR (neat) 1774, 1637, 916 cm^{-1}; ^1H NMR δ 6.59−6.57 (m, 2H), 5.50−5.30 (m, 2H), 5.14−5.01 (m, 4H), 3.10−2.99 (m, 4H); ^{13}C NMR δ 203.3, 136. 8, 131.9, 117.0, 53.0, 44.8. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.56. Found: C, 82.51; H, 7.59.

7-Methoxymethylene-5,6-divinylbicyclo[2.2.1]hept-2-ene (26). To a suspension of (methoxymethyl)triphenylphosphonium chloride (1.6 g, 4.678 mmol) in dry THF (5 mL), freshly sublimed sodium *t*-amyloxide (0.26 g, 2.364 mmol) in THF (3 mL) was added, and the mixture was stirred for 5 min at room temperature. To the blood red ylide was added ketone **25** (0.25 g, 1.563 mmol) in THF (5 mL), and stirring was continued for 30 min. Reaction was quenched with water (10 mL) and extracted with ether. The combined organic layer was washed and dried. The solvent was evaporated, and the residue was charged on a silica gel column. Elution with *n*-pentane furnished **26** (0.15 g, 50%) as a colorless liquid: IR (neat) 3074, 1635, 1118 cm^{-1}; ^1H NMR δ 6.34 (br. s, 2H), 5.47 (s, 1H), 5.50−5.30 (m, 2H), 5.10−4.90 (m, 4H), 3.56−3.51 (m, 1H), 3.52 (s, 3H), 3.10−2.97 (m, 3H); ^{13}C NMR δ 139.7, 139.5, 135.9, 135.4, 134.3, 127.2, 115.6, 115.5, 59.5, 50.5, 49.2, 49.1, 46.7. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.00; H, 8.61.

5,6-Divinylbicyclo[2.2.1]hept-2-ene-7-carbaldehyde (9). To a solution of **26** (0.15 g, 0.798 mmol) in dichloromethane (5 mL), a few drops of 35% aqueous $HClO_4$ were added at 0 °C, and the mixture was stirred at room temperature for 5 h. The reaction was quenched with sodium bicarbonate solution and diluted with dichloromethane. The organic layer was washed with brine and then dried over Na_2SO_4. Evaporation of the solvent afforded aldehydes **9a,b** (0.14 g, quantitative yield) as a *syn*−*anti* (3:1) mixture (NMR) of diastereomers: IR (neat) 2854, 1718, 914 cm^{-1}; ^1H NMR (from mixture) δ 9.67 (s, 1H), 6.27 (s, 2H), 5.50−5.30 (m, 2H), 5.09−4.93 (m, 4H), 3.17 (br. s, 2H), 2.90−2.84 (m, 2H), 2.45 (br. s, 1H) (major-syn); ^{13}C NMR (mixture) δ 201.1, 138.8, 135.8, 116.1, 69.6, 48.1, 46.6 (signals for the major *syn*-isomer); δ 204.8, 138.4, 133.8, 116.1, 71.4, 50.1, 49.1 (signals for the minor anti-isomer).

2,4,6,8,15-Pentaoxahexacyclo[7.5.1.0^{3,13}.0^{5,12}.0^{7,11}.0^{10,14}]-pentadecane (3b) and 8,10,12,13-Tetraoxapentacyclo-[5.5.1.0^{2,6}.0^{3,11}.0^{4,9}]tridecane-5-carbaldehyde (27). Through a solution of the *syn*- and *anti*-aldehydes **9a,b** (40 mg, 0.230 mmol) in dichloromethane at −78 °C, ozone was bubbled, and the resulting ozonide was quenched with dimethyl sulfide (0.1 mL). The reaction mixture was stirred at room temperature for 5 h. Concentration under vacuum and silica gel chromatography (elution with 60% EtOAc−hexane) furnished the tetraoxa aldehyde **27**. Further elution of the column with EtOAc furnished the pentaoxa compound **3b** as a colorless solid in 39% yield. **27**: IR (KBr) 1730, 1265, 1053 cm^{-1}; ^1H NMR δ 9.77 (s, 1H), 5.88 (d, 2H, J = 4.6 Hz), 5.62 (d, 2H, J = 6 Hz), 3.46−3.42 (m, 2H), 3.24 (s, 1H), 3.18−3.15 (m, 2H); ^{13}C NMR δ 199.0, 109.8 (2C), 103.0 (2C), 55.7, 51.9 (2C), 45.6 (2C); MS m/z 210 (M^+). Anal. Calcd for $C_{10}H_{10}O_5$: C, 57.14; H, 4.80. Found: C, 57.21; H, 4.82. **3b**: mp 230 °C (charred); IR (KBr) 2974, 1383, 1095 cm^{-1}; ^1H NMR δ 5.93 (br. s, 5H), 3.66 (br. s, 5H); ^{13}C NMR(DEPT) δ 113.6 (5C, CH), 58.2 (5C, CH); MS m/z 211(M^++1). Anal. Calcd for $C_{10}H_{10}O_5$: C, 57.14; H, 4.80. Found: C, 57.18; H, 4.82.

Crystal Data for Pentaoxa-[5]-peristylane 3b. $C_{10}H_{10}O_5$, M = 210.19, crystallizes from dichloromethane−hexane as colorless needles with crystal dimensions 0.50 × 0.30 × 0.25 mm^3. The molecule crystallizes in an orthorhombic space group *Pnma*, with unit cell parameters a = 13.356(2), b = 10.962(2), and c = 5.516(2) Å. V = 807.6(2) $Å^3$, Z = 4, D_c = 1.729 g cm^{-3}, $F(000)$ = 440.00, T = 25.0 °C, and $2\theta_{max}$ = 60.0°. The X-ray data were collected on a Rigaku AFC7S diffractometer by the $\omega-2\theta$ scan mode using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). A total of 1405 unique reflections were collected, and 860 of them are considered observed ($I > 3\sigma(I)$). The data were corrected for Lorentz and polarization effects, and an empirical correction based on azimuthal scans of several reflections was applied (μ = 1.4 cm^{-1}, transmission factors ranging from 0.99 to 1.00). The structure was determined by direct methods and refined by full matrix least-squares techniques against F^2 to the final R = 0.036 and R_w = 0.038, no. of parameters is 96. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

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Supporting Information Available: Tables of X-ray crystal data, atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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