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A Novel Architecture in Solid State with Extensive Network of C-H...O Interactions. X-Ray Crystal Structure of the 'Oxa-Bowl' Pentaoxa[5]peristylane

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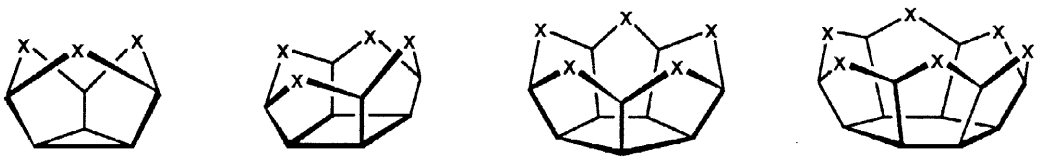
Abstract: In the crystal, the "oxa-bowl" **3** ($C_{10}H_{10}O_5$) possesses a fascinating columnar architecture built around numerous C-H...O interactions, in which all the ten CH units and five oxygen atoms (through both the lone pairs) are involved.

Design of new molecular entities and probing their molecular and supramolecular characteristics is one of the mainline activities in contemporary Organic Chemistry research. In this context, we have conceived[1] of a new family of aesthetically appealing and topologically novel molecules, the 'hetero-bowls' **1-4** [$C_{2n}H_{2n}X_n$, n-hetero-n-peristylanes], which are constituted through the union of an inner n-membered carbocyclic ring with the alternate corners of an outer 2n-membered heterocyclic ring to generate an array of bowl shaped molecules



1 (X= O, N, S...) **2** **3** **4**

with potential C_{nv} symmetry and inherent avidity towards metal ion binding and related supramolecular interactions. Recently, a synthesis of novel 'oxa-bowl' **3** (X=O), following a short, convergent strategy, has been accomplished by us.[1a] We find that the crystal structure of **3** ($C_{10}H_{10}O_5$) possesses a novel supramolecular architecture in which all the ten CH moieties and five oxygen atoms (through both the lone pairs) are involved in a network of unique C-H...O interactions[2] and this constitutes an example of the "...*principle of maximum hydrogen bonding*".[3]

Slow evaporation of a solution of **3** in dichloromethane-hexane provided needle shaped crystals and X-ray analysis[4] showed that the space group is Pnma with four molecules present in the unit cell. The molecules are tightly packed with high crystal density 1.73 g/cm^3 and **3** does not possess the anticipated C_{5v}-symmetry in the solid state (*cf.* C_{5v} in solution as revealed by ^{1}H and ^{13}C NMR)[1a] but displays C_s symmetry [5] in the crystal with the crystallographic mirror plane passing through O1, C1-H1 and C4-H4 , Fig.1.

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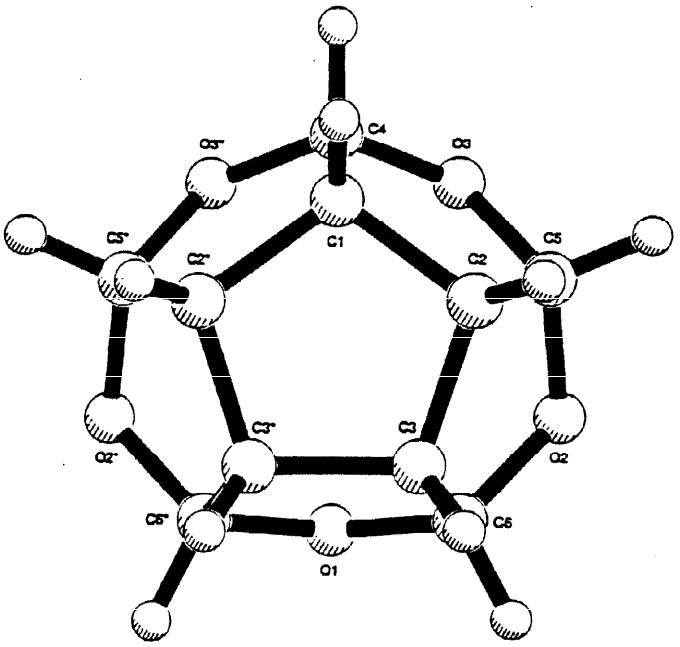

Fig.1 ORTEP diagram of **3**.

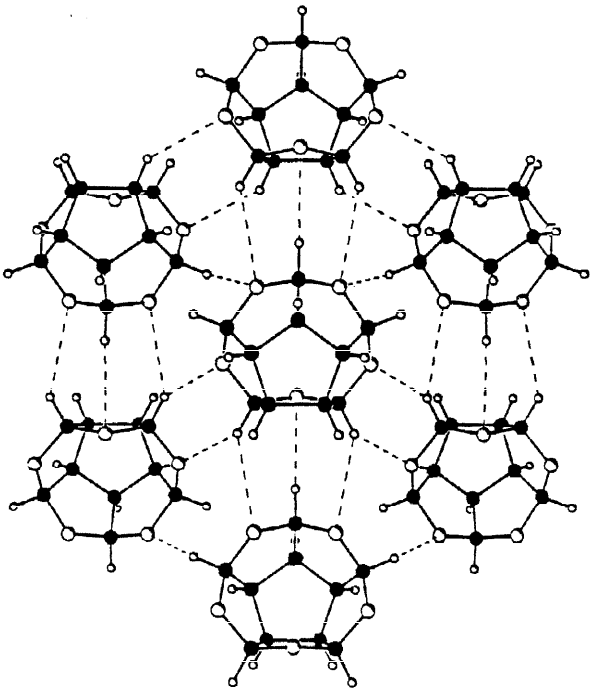

Fig.2 Network of C-H...O interactions in *ab*-plane

In the crystal of **3**, the organization of the molecules in the *ab*-plane, exhibits hexagonal network interconnecting through C-H...O hydrogen bonds, Fig. 2. Along *a*-axis, the molecules are arranged in alternate concave-convex manner resulting in bowl inversion pattern. When viewed along the *c*-axis, the oxa-bowls stack on top of each other, in top to bottom fashion, forming infinite columns. The arrangement of these columns can be visualized in three distinct patterns. The columns along *a*-axis grow in opposite directions. However, when viewed through *c*-axis, the columns are arranged in two wave-like patterns; one with the columns growing in the same direction and the other with the columns growing in the opposite directions, Fig. 3. Each molecule in this assembly has short contacts with ten of its symmetry related neighboring molecules through twenty C-H...O interactions. While ten of these are within the accepted limits

Table: Intermolecular C-H...O interactions in **3**

C-H...O[a]	d (Å) [b]	D(Å) [b]	θ(°) [b]	contacts[c]
C_2-H_2...O_2	2.56(2)	3.426(2)	150.4	4
C_5-H_5...O_3	2.66(2)	3.439(2)	135.3	4
C_4-H_4...O_1	2.66(2)	3.558(3)	150.6	2
C_6-H_6...O_3	2.76(2)	3.556(2)	134.5	4
C_3-H_3...O_2	2.81(2)	3.671(3)	146.4	4
C_1-H_1...O_1	2.92(2)	3.195(3)	97.5	2

[a] Both the lone pairs on each oxygen are involved [b] d=H...O distance, D=C...O , θ=C-H...O angle [c] symmetry based

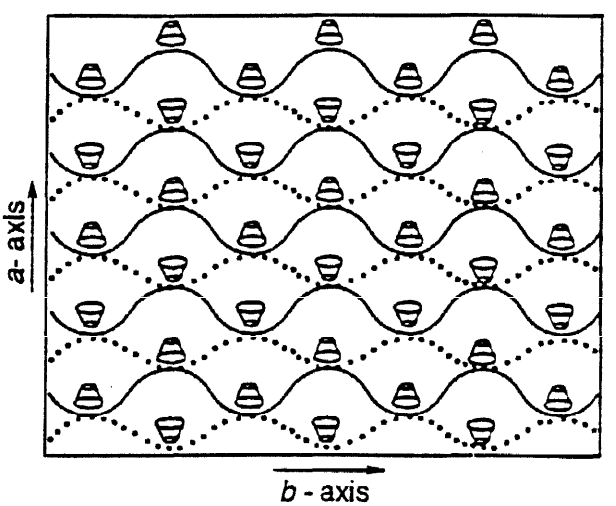

Fig.3 Wave-like pattern of columns
——— : unidirectional
------- : alternating directionality

of C-H...O hydrogen bonds[2], first three entries in the Table, the other ten are soft contacts, last three entries in the Table. In addition, the crystal structure of **3** also reveals the presence of several bifurcated C-H...O hydrogen bonds, Fig. 2.

A novel aspect of the C-H...O hydrogen bonding present in **3** is the involvement of the least acidic cycloalkane hydrogens of the cyclopentane ring, forming the base of the oxa-bowl. Indeed, the C_2-H_2...O_2 [d=2.56 Å] hydrogen bonds turn out to be the most significant (see Table) and are responsible for sustaining the infinite 'top to bottom' columnar motif along the shortest crystallographic *c*-axis, Fig. 4. This hydrophobic-end to hydrophilic- end piling of '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 c-axis are held together through infinite spiral hydrogen bonding C_5-H_5...O_3, [d=2.66 Å], in clockwise and anticlockwise directions along *b*-axis, Fig. 5. The two strands of the 'oxa-bowl' columns constituting the two wave-like patterns are interconnected, with each molecule of one strand forming three hydrogen bonds, C_4-H_4...O_1, [d=2.66 Å] and C_6-H_6...O_3, [d=2.76 Å] with its counter part in the other strand along *a*-axis, Fig. 2.

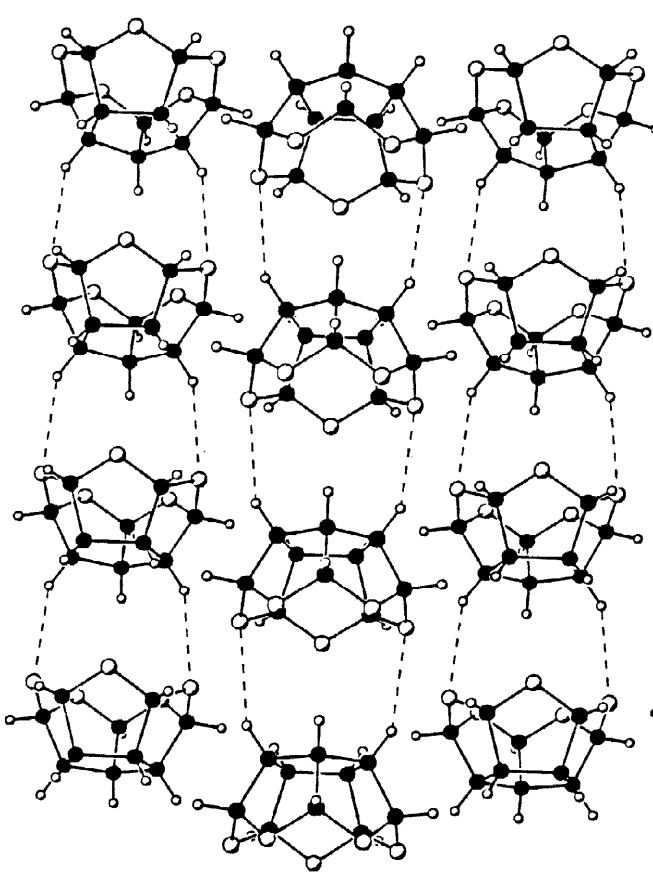

Fig.4 Infinite columnar C-H...O bonding

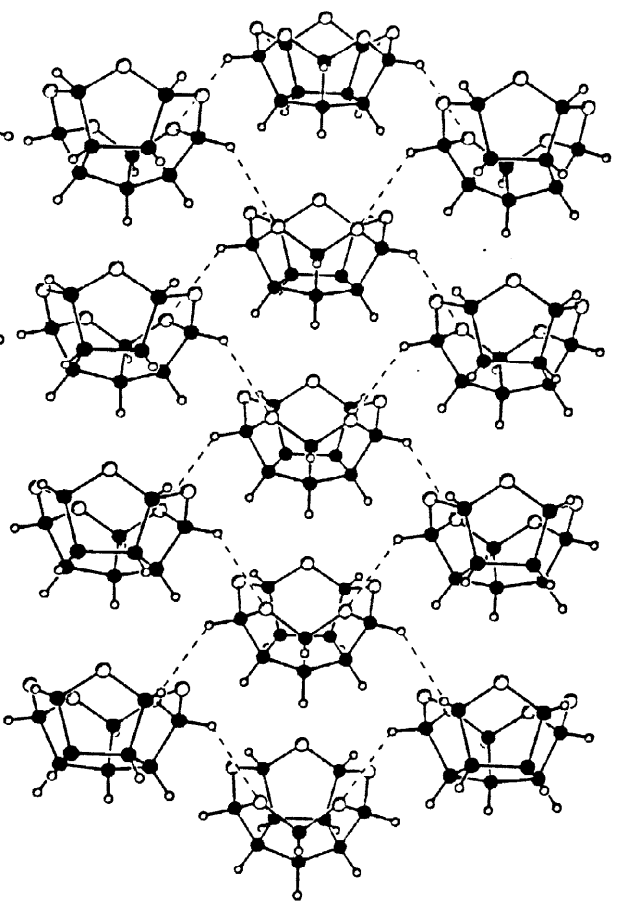

Fig.5 Infinite spiral C-H...O bonding

The other close contacts that could be observed in this supramolecular assembly are C_3-H_3 with O_2 and C_1-H_1 with O_1, (see Table). 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 [C_1-H_1...O_3, d=3.04Å θ=153.3° and C_6-H_6...O_2, d=2.79Å θ=144.0°], Fig. 2.

In summary, we have demonstrated that in solid state, pentaoxa[5]peristylane **3** is endowed with a multi-columnar, supramolecular architecture, whose distinctive features include the first time observation of C-H...O interaction involving least acidic cyclopentane hydrogen atoms. It is noteworthy that all the hydrogen bonding sites, the ten CH moieties and five oxygen atoms (through both the lone pairs) are involved in short C-H...O contacts (strong and soft)[2] and the crystal structure of **3** constitutes a paradigm for the attainment of maximal hydrogen bonding.

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[4] **Crystal data**: $C_{10}H_{10}O_5$, M=210.19, crystallizes from dichloromethane-hexane as colorless needles with crystal dimensions 0.50 x 0.30 x 0.25 mm. 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, $2\theta_{max}$=60.0°. The X-ray data were collected on a Rigaku AFC7S diffractometer by the ω-2θ scan mode using graphite monochromated M_o-K_α radiation (λ=0.7107Å). 1405 unique reflections were collected and 860 of them are considered observed [I>3σ(I)]. The data were corrected for Lorentz and polarization effects and an empirical correction based on azimuthal scans of several reflections were applied (μ=1.4cm^{-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 Rω=0.038, no. of parameters 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.

[5] In agreement with the *Cs* symmetry of **3**, the following intramolecular distances (Å) between oxygen atoms are observed: O1...O2=O2...O3=2.337; O3...O3*=2.304; O1...O3=3.389; O2...O3*=3.874; O2...O2*=4.144.