Pergamon

Tetrahedron Letters 40 (1999) 2417–2420

TETRAHEDRON
LETTERS

Crystal Structure of Tetraoxa[4]peristylane: Novel C-H...O Mediated Architecture in the Solid State

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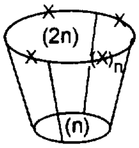
Received 23 November 1998; accepted 11 January 1999

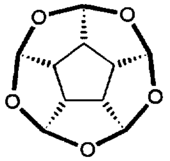
Abstract: In the crystal, the molecules of 'oxa-bowl' **3** are interconnected in rim-up, rim-down fashion through an extensive network of C(sp^3)-H...O hydrogen bonds involving even a non acidic cyclobutane ring hydrogen, leading to a multi-columnar arrangement of bowls and a 3D interpenetrating C-H...O net.

Keywords: *X- ray crystal structure; C-H... O hydrogen bonds; ozonolysis*

We have conceived of [n]-hetero-[n]-peristylanes (n-hetero-bowls **1**) as a novel class of molecular entities, which besides having aesthetically pleasing architecture are also likely to exhibit selective avidity for metal ions and small molecules.[1] Structurally, these [n]-hetero-bowls **1** are constituted through a union between a n-membered carbocyclic base and a 2n-membered heterocyclic rim with n-hetero atoms and having an overall C_{nv} symmetry. As a part of wider interest in these [n]-hetero-bowls, we have initially directed out attention towards oxa-bowls and



1 X = O, N etc.



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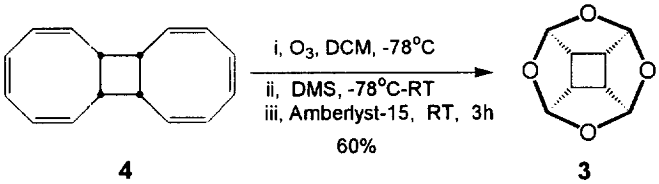
accomplished a synthesis of pentaoxa-[5]-peristylane **2**.[1a] In the crystal, molecules of **2** exhibit an interesting, columnar, bowl-to-bowl packing pattern, sustained by an extensive network of C-H...O interactions.[2] These observations spurred us to seek another member of the oxa-bowl family and study its solid state structure. In this context, we have prepared[3] tetraoxa-[4]-peristylane **3**[4] from the cyclooctatetraene dimer **4** as shown in the Scheme and determined its X-ray crystal structure. The variation in size and symmetry in going from **2** to **3**, caused subtle but significant alteration in the packing motif, despite the presence of similar functionalities. Herein, we report that in the solid state **3** has a novel, interpenetrating architecture, governed by intermolecular C(sp^3)-H...O interactions.



4 **3**

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PII: S0040-4039(99)00118-5

X-ray data[5] revealed that the needle shaped crystals of **3** belonged to the space group Pbca with two crystallographically independent molecules in the asymmetric unit (designated hereafter as A and B) oriented perpendicular to each other, which are tightly packed as seen from the high value for its crystal density (1.65g/cm^3). Details of the molecular geometry of the independent molecules (bond lengths, bond angles and torsion angles) showed that the molecular symmetry is almost C_{4v} although there are slight deviations. Fig.1 portrays the ORTEP perspective of the molecules A and B. The packing pattern reveals a large number of close intermolecular contacts among the symmetry related molecules of A and B as well as between molecules A and B that are within the range of van der Waals interactions and C-H...O hydrogen bonding. The significant intermolecular C-H...O hydrogen bonds that are within the presently acceptable limits (with H...O< 2.70Å and angle C-H...O > 120°)[7] are recorded in the Table. The resulting supramolecular architecture, composed of an extensive network of C-H...O hydrogen bonds is displayed in Fig.2, viewed along the b-axis.

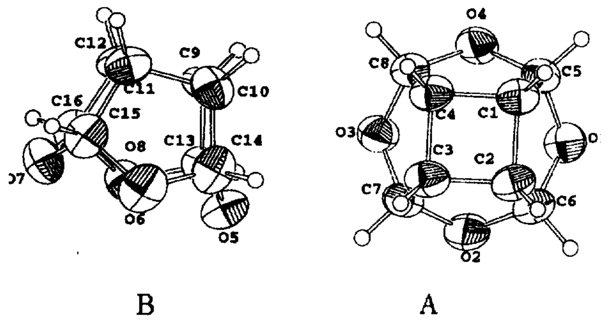

Fig. 1 ORTEP diagram of 3

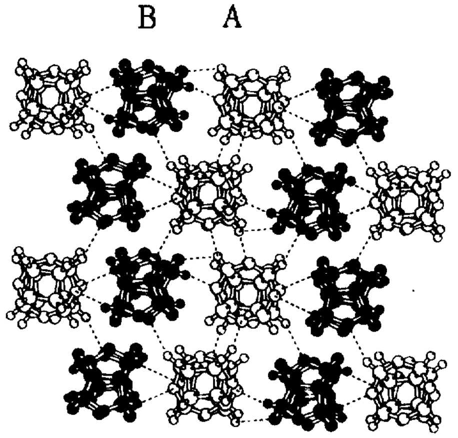

Fig. 2 Network of C-H...O interactions in *ac*-plane

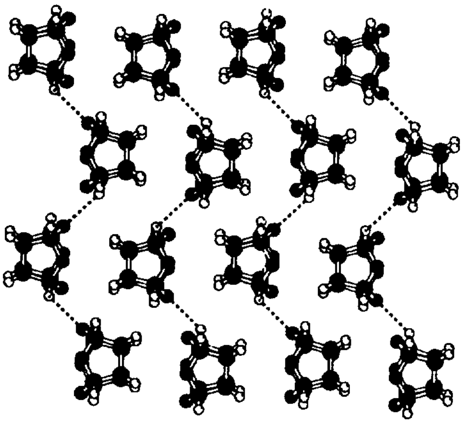

Fig.3 Wave-like hydrogen bonding among molecules A essentially along *a*- axis

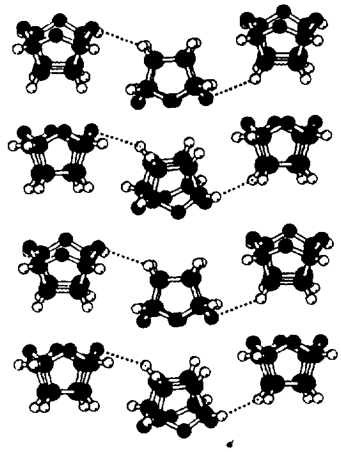

Fig.4 Wave-like hydrogen bonding of molecules B essentially along *b*-axis

When viewed down *b*-axis, the bowls A are arranged in alternate rim-up, rim-down fashion in the *ac*-plane, Fig.2. These bowls are interconnected by C_5-H_5...O_2 (d=2.560Å, θ=129.1°) hydrogen bonding along *a*-axis involving the acetal hydrogen and acetal oxygen. Since there is a glide plane perpendicular to *a*-axis, this pattern repeats along *b*-axis resulting in columns growing in opposite directions and defining an infinite wave-like pattern of hydrogen bonding essentially along *a*-axis, Fig.3.

Table: Intermolecular C-H...O interactions[7] in crystal **3** (molecules A and B)[a]

C-H...O	Type	d(H...O)Å	D(C...O)Å	θ(C-H...O)°
C8-H8...O8	A-B	2.388	3.305	155.5
C5-H5...O2	A-A	2.560	3.268	129.1
C13-H13...O3	B-A	2.587	3.250	125.0
C5-H5...O7	A-B	2.637	3.248	120.7
C11-H11...O8	B-B	2.643	3.403	134.5
C15-H15...O1	B-A	2.674	3.351	126.5

[a] There are four additional C-H...O interactions in the range of d= 2.7- 2.8Å, but only those <2.7 Å are mentioned here.

The bowls B are also arranged in alternate rim-up, rim-down fashion along *b*-axis and are juxtaposed in the voids in between the wave-like hydrogen bonded strands of molecules A. Along *b*-axis, the bowls B are interconnected by C_{11}-H_{11}...O_8 (d=2.643Å, θ=134.5°) hydrogen bonding involving the less acidic hydrogen of the cyclobutane ring and the acetal oxygen. Again, this hydrogen bond connectivity attains wave-like pattern essentially along *b*-axis. This pattern formed by B molecules repeats along *a*-axis and hence resulting in columns growing in opposite directions, Fig.4. These wave-like hydrogen bonding motif and the columns running in opposite directions formed by molecules B are perpendicular to those formed by molecules A resulting in a compact packing (Fig.5) with columns growing in different directions (see Fig.3 & Fig.4).

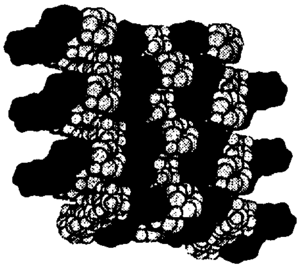

Fig. 5 Space filling diagram (light: molecules A; dark: molecules B) of the interpenetrating supramolecular architecture of 3

The interpenetrating C-H...O waves along *b*-axis (formed between B molecules) and *a*-axis (formed between A molecules), with bowls arranged in alternate concave-convex fashion, are interconnected through many strong C-H...O hydrogen bonds (see Table) between bowls A and B forming a 3D net. The shortest hydrogen bond observed in the network is C_8-H_8...O_8 (d=2.388Å, θ=155.5°) between acetal hydrogen of molecule A and oxygen atom of molecule B and is essentially along *a*-axis. Thus, the oxygen atom O_8 forms hydrogen bonds along *a*- and *b*-axes through both of its lone pairs. Further analysis showed that there are a few bifurcated hydrogen bonds between molecules A and B, mainly the acetal hydrogen H_5 of molecule A forms the bifurcated hydrogen bond with O_2 of molecule A and O_7 of molecule B (d=2.637Å, θ=120.7°) and these are essentially along *a*- & *c*-axes, respectively. The other two hydrogen bonds observed within the accepted range are C_{13}-H_{13}...O_3 and C_{15}-H_{15}...O_1 (see Table) involving acetal hydrogens of molecule B and oxygen atoms of molecule A forming an interesting pattern essentially along *b*-axis. The two independent motifs formed by molecules A and molecules B are held together mainly through the above mentioned four A-B connectivities.

It is to be noted that in the solid state **3**, as well as related 'oxa-bowl', the pentaoxa-[5]-peristylane **2** exhibit some similar features, like, alternate concave-convex orientation of bowls, columnar arrangement and the participation of least acidic hydrogen atoms in the C-H...O bond formation but differ in a subtle manner. For example there is no direct hydrogen bond connectivity between the bowls in a column in **3** and there are two distinct columnar motifs which constitute an interpenetrating 3D net.

Acknowledgements: We are most grateful to Professor G. Schroder for generously sparing the COT-dimer used in this study. We would like to thank Dr.K.Sekar of Bio-informatics Centre of I.I.Sc., Bangalore for help. The crystal data was collected at the National Single Crystal X-ray Facility, University of Hyderabad. One of us (RV) thanks CSIR for the award of a research fellowship.

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4. Selected data for **3**: ^{1}H NMR ($CDCl_3$, 200MHz): δ 6.01(br s, 4H), 3.25(br s, 4H); ^{13}CNMR ($CDCl_3$, 50MHz): 111.44(4C), 43.72(4C); LRMS: m/z 169(M^++1).
5. Crystal data for **3**: $C_8H_8O_4$, M = 168.14, colourless crystals, orthorhombic, space group *P*bca, a = 10.911(2), b = 10.960(6) and c = 22.616(2)Å, V = 2704.6(2)$Å^3$, Z=16, D_c=1.652 Mg m^{-3}, T = 293K, F(000)=704, μ(Mo-K_α)=0.067mm^{-1}, crystal dimensions 0.18 x 0.20 x 0.32 mm^3. Data were collected on Enraf-Nonius MACH-3 diffractometer, graphite-monochromated Mo-K_α radiation (λ=0.7107Å), by ω scan method in the range $1.80 \leq \theta \leq 29.94°$, 3927 unique reflections [R_{int}=0.00], of which 2451 had $F_o > 4\sigma(F_o)$, were used in all calculations. At final convergence $R_1[I>2\sigma(I)]$= 0.0646, wR_2=0.1620 for 217 parameters and 0 restraint, GOF=1.06, $\Delta\rho_{max}$ = 0.400e$Å^{-3}$, $\Delta\rho_{min}$= -0.595e$Å^{-3}$. The data were reduced using XTAL (ver 3.4), solved by direct methods, refined by full-matrix least-squares on F^2 with the non-H atoms anisotropic and H atoms were placed in calculated positions and were allowed to ride on their parent atoms.[6]
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