Oxa-bowls: formation of exceptionally stable diozonides with novel, C–H···O hydrogen bond directed, solid state architecture

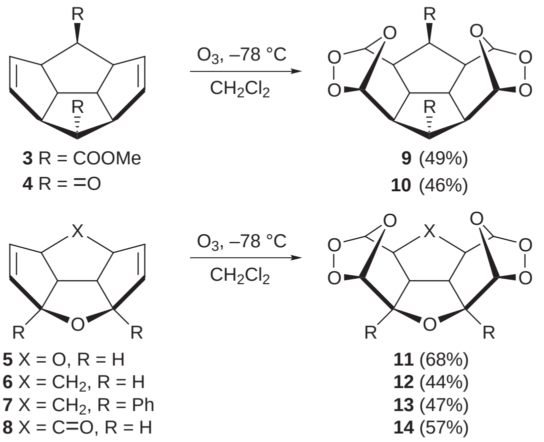
Goverdhan Mehta*† and R. Uma

Molecular Design and Synthesis Laboratory of JNCASR, School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

Several tetraquinane-based diolefins on ozonization furnish unusually stable diozonides of 'bowl-like' topology and their solid state structure reveals interesting architecture woven through a network of unique C–H···O interactions.

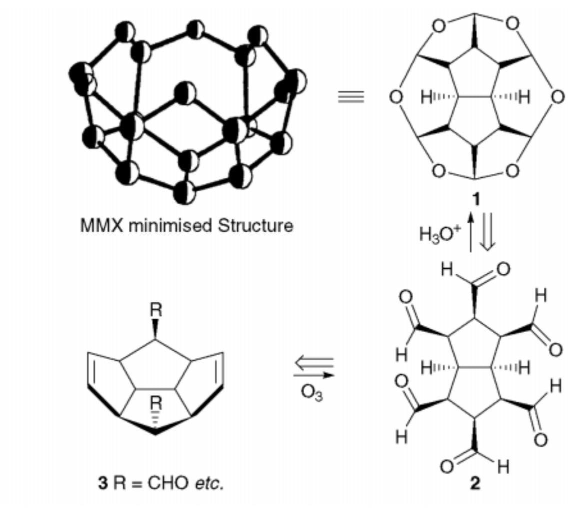
We have been engaged in the synthesis of a range of novel, high symmetry, 'bowl-shaped' molecular entities, composed of a carbocyclic base and hetero-atom speckled rim.[1] In the context of these endeavours, we became interested in an octacyclic, hexaoxa-bowl **1**, $C_{14}H_{14}O_6$, of C_{2v} symmetry, which we planned to access from the hexaaldehyde **2**, through a cascade of intramolecular acetalization protocols.[1] Compound **2**, in turn, was proposed to be prepared from the C_{2v} tetraquinane **3** *via* ozonolysis or equivalent oxidative cleavage of the disubstituted double bonds (Scheme 1). During our studies of **1**, we observed that several derivatives of **3** on ozonization furnish remarkably stable diozonides in a highly stereoselective manner. Two of these tetraquinane derived diozonides readily furnished single crystals and their X-ray crystallographic analysis shows a fascinating packing pattern and supramolecular arrangement, sustained by a network of C–H···O hydrogen bonds.[2] To the best of our knowledge, only one stable diozonide [derived from hexamethyl (Dewar) benzene] is known[3a] so far, although several stable mono-ozonides have been reported recently.[3c,d] The crystal structure[3a,b] of the diozonide from hexamethyl (Dewar) benzene has also been determined, but the authors did not observe any significant intermolecular contacts.

Tetraquinanes **3**, **4** and their oxa-analogues **5**–**8** reported earlier by us,[4] on ozonolysis in CH_2Cl_2 at −78 °C directly furnished the corresponding diozonides **9**–**14** after the removal of the solvent and could be readily crystallized (Scheme 2). All the diozonides were stable at room temperature (for months) and showed little decomposition on either moderate heating or on exposure to Me_2S and triphenylphosphine under standard conditions (stirring in CH_2Cl_2 solution). The gross structures of **9**–**14** were fully revealed through the incisive analysis of their ^1H and ^{13}C NMR data.[5] However, the bowl-like *syn,syn*-stereochemistry present in **9**–**14**, with the two oxa-bridges protruding inwards could not be delineated unambiguously, although the MMX calculations showed this arrangement to be the most stable.‡ Therefore, recourse was taken to X-ray crystallography and two of the diozonides **9** and **14** furnished single crystals suitable for structure determination.



Scheme 2

The diozonide **9** crystallized in space group *C*2/*c* and an ORTEP perspective (Fig. 1)§ revealed the stereochemistry as *syn,syn* with the O1 and O1a oxa-bridges tilting significantly inwards (O1 and O1a distance being 2.62 Å), and this orientation is facilitated by intramolecular C–H···O hydrogen bonds[2] between the bridgehead H1 and H1a atoms and the O4a



Scheme 1

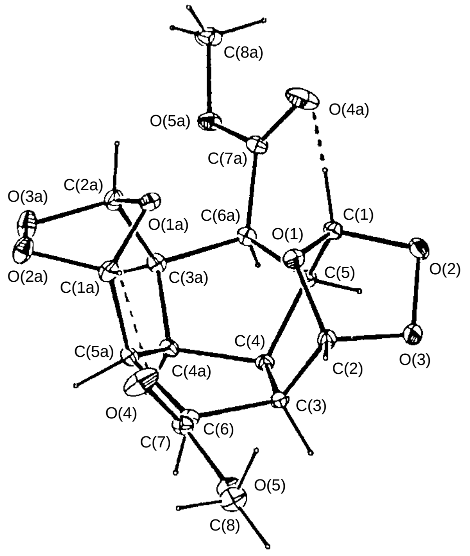


Fig. 1 ORTEP plot of **9**

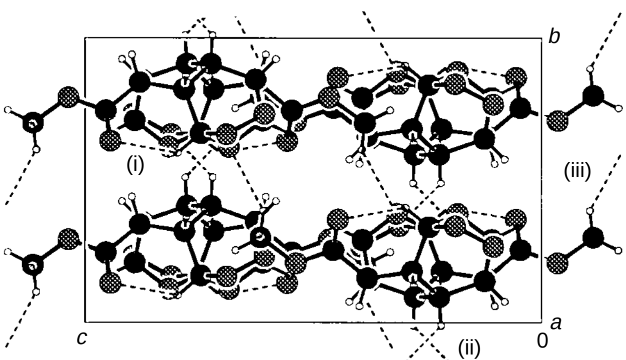


Fig. 2 Crystal packing in **9**, view down *a* axis. Selected C–H···O interactions: [H···O (Å), C(H)···O (Å), CH···O (°)]: (i) (intra, C1–H1···O4) 2.21, 2.93, 129.5; (ii) (inter, C4–H4···O2) 2.58, 3.34, 134.4; (iii) (inter, C8–H8C···O1) 2.60, 3.18, 119.5.

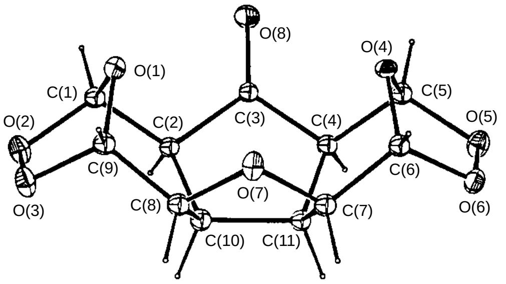


Fig. 3 ORTEP plot of **14**

and O4 carbonyl groups of the ester moieties (H···O distance 2.21 Å, C···O 2.93 Å and C–H···O angle of 129.5°) (Fig. 1). The packing pattern shows that the bowl-like molecules of **9** are stacked one over the other along the *b* axis in a columnar arrangement (Fig. 2). In the *ab* plane there are arrays of unidirectional bowls, each engaged in four C–H···O hydrogen bonds (two below and two above) to nearest neighbours through H4, H4a (ring junction protons on the diquinane moiety) and O2a, O2 oxygens of the peroxo bridge (H···O distance 2.58 Å, C···O 3.34 Å and C–H···O angle of 134.4°) along the *b* axis. The adjacent *ab* planes consist of bowls growing in opposite directions and are held by weak C–H···O contacts between the Hc protons of the ester methyls and O1 oxa-bridges of the inversion related bowls (Fig. 2).

The oxa-bowl **14** crystallizes in space group $Pca2_1$ and the molecules are tightly packed as indicated by its high density (1.681 Mg m^{-3}). An ORTEP diagram (Fig. 3)§ once again revealed the *syn,syn* stereochemistry but the two oxa-bridges are now far apart (O1 to O4 distance is 4.22 Å), perhaps due to repulsion within the congested concave surface with O7. The bowls are held by C–H···O hydrogen bonds (H···O distance 2.36 Å, C···O 3.28 Å and C–H···O angle of 155.1°) between H10 (ring junction proton on the diquinane moiety) and O7 ether oxygen, along the *c* axis, defining a ribbon-like pattern (Fig. 4). There is a bowl inversion pattern along the *a* axis and these bowls are held through a C1–H1···O5 contact. Along the *b* axis the bowls are held by C–H···O hydrogen bonds between the H7 (α to the ether oxygen) and the O8 carbonyl oxygen (H···O distance 2.57 Å, C···O 3.49 Å and C–H···O angle of 156.6°) to generate another ribbon-like pattern (Fig. 4). It is noteworthy that in the structures of both **9** and **14**, the least acidic diquinane ring junction protons are involved in the C–H···O hydrogen bonds and this is perhaps a consequence of the bowl-like topology present in these molecules.

In summary, we have described the characterization of several 'bowl-like' diozonides of exceptional stability and their X-ray structure reveals a novel architecture sustained through a network of C–H···O hydrogen bonds.

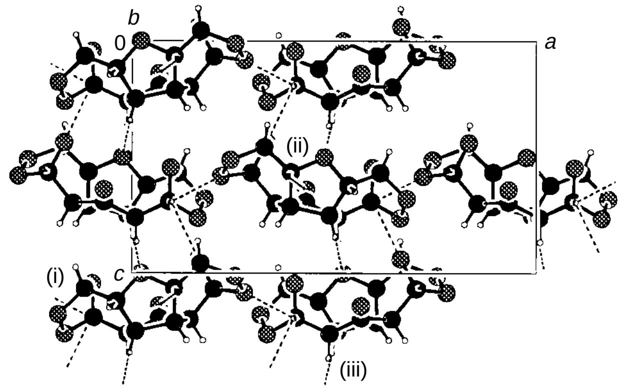


Fig. 4 Crystal packing in **14**, view down *b* axis. Selected C–H···O interactions: [H···O (Å), C(H)···O (Å), CH···O (°)]: (i) (inter, C1–H1···O5) 2.42, 3.05, 121.4; (ii) (inter, C7–H7···O8) 2.57, 3.49, 156.6; (iii) (inter, C10–H10···O7) 2.36, 3.28, 155.1.

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Notes and References

† E-mail: gm@orgchem.iisc.ernet.in

‡ The diozonides **9**–**14** can in principle occur in three diastereoisomeric forms, *viz. syn,syn* (with the two oxa-bridges directed within the diquinane moiety), *anti,anti* (with the two peroxy-bridges directed within the diquinane moiety) and *syn,anti* (with one oxa- and one peroxy-bridge directed within the diquinane moiety).

§ *X-Ray data* for **9**: $C_{16}H_{18}O_{10}$, M = 370.30, colourless crystals from CH_2Cl_2, monoclinic, space group $C2/c$, a = 11.534(6), b = 9.174(9) and c = 14.825(19) Å, β = 101.12(8)°, V = 1539(3) Å^3, Z = 4, D_c = 1.598 Mg m^{-3}, T = 293 K, $F(000)$ = 776, μ(Mo-Kα) = 0.135 mm^{-1}, crystal dimensions 0.23 × 0.11 × 0.15 mm. Data were collected on Enraf–Nonius MACH-3 diffractometer, graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), by the ω scan method in the range $2 \leqslant \theta \leqslant 25°$, 1351 unique reflections [R_{int} = 0.0379], of which 1211 had $F_o > 4\sigma(F_o)$, were used in all calculations. At final convergence R_1 [$I > 2\sigma(I)$] = 0.0447, wR_2 = 0.1197 for 119 parameters, GOF = 1.074, $\Delta\rho_{max}$ = 0.297 e Å^{-3}, $\Delta\rho_{min}$ = −0.251 e 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 isotropic.[6] For **14**: $C_{11}H_{10}O_8$, M = 270.19, colourless crystals from ethyl acetate–hexane, orthorombic, space group $Pca2_1$ (no. 29), a = 15.547(3), b = 7.584(1) and c = 9.052(10) Å, V = 1067.3(13) Å^3, Z = 4, D_c = 1.681 Mg m^{-3}, T = 293 K, $F(000)$ = 560, μ(Mo-Kα) = 0.147 mm^{-1}, crystal dimensions 0.20 × 0.11 × 0.13 mm. Data were collected as above in the range $2 \leqslant \theta \leqslant 30°$, 1648 unique reflections [R_{int} = 0.0], of which 741 had $F_o > 4\sigma(F_o)$, were used in all calculations. At final convergence R_1[$I > 2\sigma(I)$] = 0.0672, wR_2 = 0.1724 for 117 parameters, GOF = 1.046, $\Delta\rho_{max}$ = 0.294 e Å^{-3}, $\Delta\rho_{min}$ = −0.283 e Å^{-3}. The structure was solved as above with all O atoms anisotropic, C and H atoms isotropic.[6] CCDC 182/918.

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