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

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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 hexaldehyde 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 known3 to date, although several stable mono-ozonides have been reported recently.3c,d The crystal structure3a,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_{2}Cl_{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_{2}S and triphenylphosphine under standard conditions (stirring in CH_{2}Cl_{2} solution). The gross structures of 9–14 were fully revealed through the incisive analysis of their 1H and 13C 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.

The diozonide 9 crystallized in space group C2/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§ between the bridgehead H1 and H1a atoms and the O4a...
X-ray structure reveals a novel architecture sustained through a several ‘bowl-like’ diozonides of exceptional stability and their ring junction protons are involved in the C–H···O hydrogen that in the structures of both generate another ribbon-like pattern (Fig. 4). It is noteworthy (the bowls are held by C–H···O hydrogen bonds between the H7 molecules are tightly packed as indicated by its high density Å, C···O 3.34 Å and C–H···O angle of 134.4°) along the O2a, O2 oxygens of the peroxo bridge (H···O distance 2.58 Å, H4, H4a (ring junction protons on the diquinane moiety) and bonds (two below and two above) to nearest neighbours through directional bowls, each engaged in four C–H···O hydrogen stacked one over the other along the O1 axis. Selected C–H···O interactions: \[(\text{inter, } \text{C}1–\text{H}1···\text{O}5) 2.60, 3.18, 119.5.\]

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Notes and References

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‡ The diozonides 9–14 can in principle occur in three diastereoisomeric forms, viz. syn,syn (with the two peroxy-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: \[\text{C}_9\text{H}_{18}\text{O}_{10}, M = 370.30, \text{colourless crystals from } \text{CH}_2\text{Cl}_2, \text{monoclinic, space group } \text{C}2/c, a = 11.534(6), b = 9.174(9) \text{Å, } c = 14.825(19) \text{Å, } \beta = 101.128(9)^\circ, V = 1539(3) \text{Å}^3, Z = 4, D_t = 1.598 \text{Mg m}^{-3}, T = 293 \text{K}, F(000) = 776, \mu(\text{Mo-K}\alpha) = 0.113 \text{mm}^{-1}, \text{crystal dimensions } 0.23 \times 0.119 \times 0.71073 \text{Å}, \text{by the } \omega \text{ scan method in the range } 2 \theta \leq 25^\circ, 1351 \text{ unique reflections } \{R_{\text{int}} = 0.0379\}, \text{of which 1211 had } F_o > 4\sigma(F_o), \text{were used in all calculations. At final convergence } R_1 \{ | I > 2\sigma(I) \} = 0.0447, wR_2 = 0.1197 \text{ for 119 parameters, } GOF = 1.074, \Delta \rho_{\text{max}} = 0.297 e \text{ Å}^{-3}, \Delta \rho_{\text{min}} = -0.251 e \text{ Å}^{-3}. \text{The data were reduced using XTAL (ver. 3.4), solved by direct methods, refined by full-matrix least-squares on } F^2 \text{ with the non-H atoms anisotropic, and H atoms isotropic.} \text{For 14: } \text{C}_9\text{H}_{18}\text{O}_{10}, M = 270.19, \text{colourless crystals from ethyl acetate–hexane, orthorhombic, space group } \text{P}2_12_12_1, a = 11.534(6), b = 7.584(1) \text{Å and } c = 9.052(10) \text{Å, } V = 1067.3(13) \text{Å}^3, Z = 4, D_t = 1.681 \text{Mg m}^{-3}, T = 293 \text{K}, F(000) = 560, \mu(\text{Mo-K}\alpha) = 0.147 \text{mm}^{-1}, \text{crystal dimensions } 0.20 \times 0.11 \times 0.13 \text{mm. Data were collected as above in the range } 2 \theta \leq 36^\circ, 1684 \text{ unique reflections } \{R_{\text{int}} = 0.03\}, \text{of which 741 had } F_o > 4\sigma(F_o), \text{were used in all calculations. At final convergence } R_1 \{ | I > 2\sigma(I) \} = 0.0672, wR_2 = 0.1724 \text{ for } 117 \text{ parameters, } GOF = 1.046, \Delta \rho_{\text{max}} = 0.294 e \text{ Å}^{-3}, \Delta \rho_{\text{min}} = -0.283 e \text{ Å}^{-3}. \text{The structure was solved as above with all O atoms anisotropic, C and H atoms isotropic.} \text{CCDC 1822918.}

5 All compounds were fully characterized on the basis of their spectral and analytical data.
6 G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.

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