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Packing in three cyclooctitol acetates

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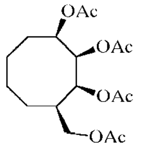
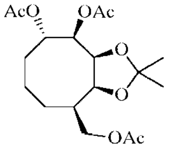
Three cyclooctitol derivatives, in the form of a tetraacetate, (1*S**,2*R**,3*S**,4*S**)-2,3,4-triacetoxycyclooctan-1-ylmethyl acetate, $C_{17}H_{26}O_8$, and two regioisomeric acetonide triacetates, (3a*S**,4*R**,8*S**,9*S**,9a*S**)-8,9-diacetoxy-2,2-dimethylcyclooctano[*d*][1,3]dioxan-4-ymethyl acetate and (3a*S*,4*R*,7*S*,9*R*,9a*S*)-7,9-diacetoxy-2,2-dimethylcyclooctano[*d*][1,3]dioxan-4-ylmethyl acetate, both $C_{18}H_{28}O_8$, have been studied. The conformation of the cyclooctane ring in the three compounds is quite close to the boat–chair form of the parent hydrocarbon. Packing is effected through weak C—H···O and van der Waals contacts.

Comment

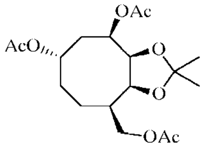
Details of the synthesis of the three cyclooctitol derivatives (I)–(III) have been reported previously (Mehta & Pallavi, 2002). The synthetic scheme provided, through moderate regio- and stereocontrol, a convenient access to cyclooctitols – an emerging class of medium ring glycomimics which have been projected to provide better adaptability at the active site of a glycosidase enzyme than cyclohexitols and cyclopentitols (Wang *et al.*, 2000; Paquette & Zhang, 2006). Though interesting in their own right, studies into the solid-state supramolecular assemblies of cyclooctitols or their derivatives have been rarely reported in the literature (Salamci *et al.*, 2006; Kawazoe *et al.*, 2001; Andriuzzi *et al.*, 2005; Wang *et al.*, 2001). We report here details of the conformations of the eight-membered carbocyclic rings in the crystal structures of the three cyclooctitol derivatives (I)–(III) and examine how these molecules pack in the solid state. Preliminary details of the structures of (II) and (III) in CIF form were a minor part of the Mehta & Pallavi (2002) publication.



(I)



(II)



(III)

In the monocyclic cyclooctane tetraacetate (I) (Fig. 1), the puckering parameters (Cremer & Pople, 1975) of the cyclooctane ring [q_2 = 1.0294 (18) Å, q_3 = 0.5718 (19) Å, q_4 = −0.3209 (19) Å, φ_2 = 5.05 (10)°, φ_3 = 180.00 (19)° and Q_T = 1.2206 (19) Å] are in conformity with those of the boat–chair (BC) form (Evans & Boeyens, 1988; Allen *et al.*, 1996), which is the predominant conformer of the cyclooctane molecule as revealed through gas-phase electron diffraction analysis at 300 K and an NMR study in solution at 161.5 K (Rocha *et al.*, 1998). The crystal packing of (I) is realized mainly through van der Waals interactions. The shortest intermolecular contact is between the poorly resolved methyl atom H13*A* and an adjacent inversion-related carbonyl O atom (O6; Table 1), giving rise to potential dimers [graph-set motif $R^2_2(8)$; Bernstein *et al.*, 1995], as shown in Fig. 2(*a*). As methyl H atoms are not noted for their acidity and the H-atom positions are not well defined in this room-temperature structure determination, this may be an adventitious contact. Such a motif, though very similar to the archetypical carboxylic acid dimer synthon (Fig. 2*b*), is not commonly encountered. A Cambridge Structural Database (CSD; Version 5.28 of November 2006; Allen, 2002) search for the centrosymmetric $R^2_2(8)$ C—H···O motif (as shown in Fig. 2*a*) in organic molecules whose crystal structures were refined to $R < 0.1$, with low-temperature data and correctly oriented methyl H atoms, only generated eight hits.

Owing to its fusion with the 1,3-dioxolane ring, the eight-membered ring in the bicyclic cyclooctitol triacetate (II) (Fig. 3) distorts slightly from the expected BC conformation,

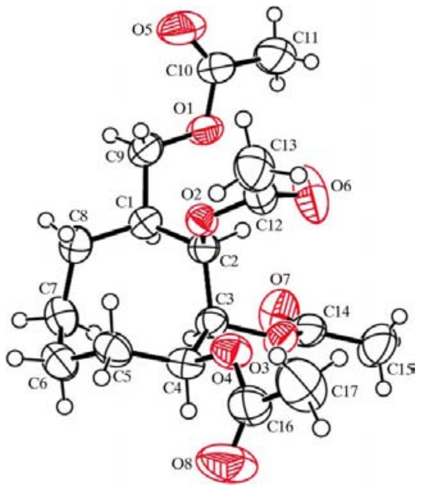
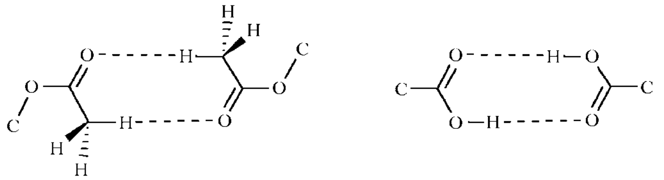


Figure 1
A view of the tetraacetate (I), showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.



(*a*) (*b*)

Figure 2
(*a*) The centrosymmetric C—H···O motif employed in the CSD search and seen in (I), and (*b*) its similarity to the carboxylic acid dimer synthon.

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as revealed by its puckering parameters [q_2 = 0.8958 (17) Å, q_3 = 0.6673 (17) Å, q_4 = −0.3004 (17) Å, φ_2 = 258.18 (11)°, φ_3 = 123.87 (14)° and Q_T = 1.1567 (17) Å]. The puckering parameters of the five-membered 1,3-dioxolane ring [q_2 = 0.3380 (15) Å and φ_2 = 158.2 (3)°] best describe a half-chair (*T*) conformation, twisted at the C12—O2 bond (Cremer & Pople, 1975). As with (I), the crystal packing of (II) involves mainly van der Waals interactions; the shortest contact is between methylene atom H6*B* (on C6) and carbonyl atom O8 of an adjacent glide-related molecule (Table 2), and gives rise to chains extending along *c* as shown in Fig. 4.

In the bicyclic cyclooctitol triacetate (III) (Fig. 5), a regioisomer of (II), the eight-membered ring is slightly distorted – as with (II), through its fusion with the 1,3-dioxolane ring – from the expected BC conformation [puckering parameters: q_2 = 0.845 (2) Å, q_3 = 0.657 (2) Å, q_4 = −0.321 (2) Å, φ_2 = 81.50 (16)°, φ_3 = 306.9 (2)° and Q_T = 1.118 (2) Å]. As in (II), the puckering parameters of the five-membered 1,3-dioxolane ring in (III) [q_2 = 0.330 (2) Å and φ_2 = 348.8 (4)°] best describe a half-chair (*T*) conformation, twisted at the C12—O2 bond. As with (I), the packing is realized mainly through van der Waals interactions; the shortest intermolecular contact is between the poorly resolved methyl atom H16*A* and the adjacent inversion-related carbonyl atom O6 (Table 3) at (1 − *x*, −*y*, −*z*), which would give rise to dimers with graph-set motif $R_2^2(24)$ involving the transannular acetate groups at atoms C1 and C4.

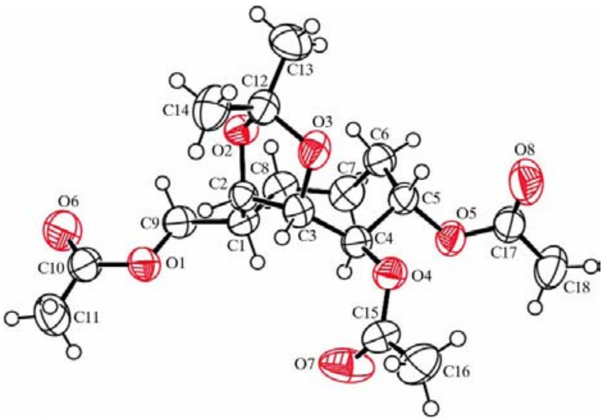

Figure 3
A view of the triacetate (II), showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

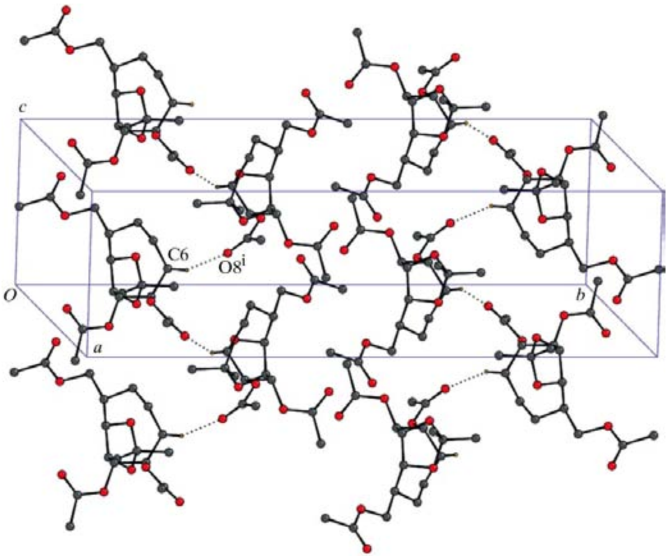

Figure 4
The molecular packing of (II). H atoms not involved in hydrogen bonding have been omitted for clarity. Dotted lines indicate short H···O separations (see Table 2).

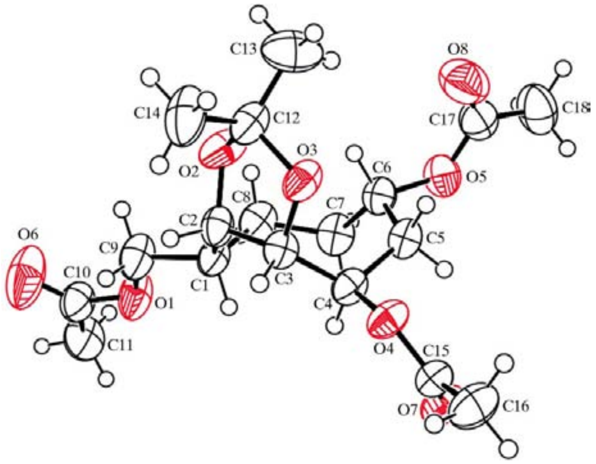

Figure 5
A view of the triacetate (III), showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

To summarize, the present study reports on the conformations and packing of three cyclooctitol acetates. Two types of packing interactions are observed, *viz*. centrosymmetric dimers and glide-related chains.

Experimental

The cyclooctitol derivatives (I)–(III) were prepared as previously reported (Mehta & Pallavi, 2002). Crystals of (I)–(III) suitable for single-crystal X-ray diffraction analyses were grown from their dilute solutions in a 1:2 dichloromethane–petroleum ether mixture by slow solvent evaporation.

Compound (I)

Crystal data

$C_{17}H_{26}O_8$
M_r = 358.38
Triclinic, $P\bar{1}$
a = 9.1632 (9) Å
b = 9.2131 (9) Å
c = 11.5904 (11) Å
α = 94.709 (2)°
β = 92.486 (2)°
γ = 102.912 (2)°
V = 948.60 (16) Å^3
Z = 2
Mo *K*α radiation
μ = 0.10 mm^{-1}
T = 291 (2) K
0.35 × 0.31 × 0.28 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.936, T_{max} = 0.973
9524 measured reflections
3500 independent reflections
2880 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

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Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.136$
$S = 1.06$
3500 reflections
230 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 1
Short intermolecular contact geometry (Å, °) for (I).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
C13—H13$A$$\cdots$O6$^{\rm i}$	0.96	2.53	3.439 (3)	158

Symmetry code: (i) $-x+1, -y, -z+2$.

Compound (II)

Crystal data

$C_{18}H_{28}O_8$
$M_r = 372.40$
Orthorhombic, $Pccn$
$a = 19.206$ (12) Å
$b = 26.611$ (17) Å
$c = 7.748$ (5) Å
$V = 3960$ (4) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 291$ (2) K
0.49 × 0.40 × 0.39 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.905$, $T_{\max} = 0.963$
24680 measured reflections
3822 independent reflections
2811 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.111$
$S = 1.04$
3822 reflections
241 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}

Table 2
Short intermolecular contact geometry (Å, °) for (II).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
C6—H6$B$$\cdots$O8$^{\rm i}$	0.97	2.54	3.438 (3)	154

Symmetry code: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Compound (III)

Crystal data

$C_{18}H_{28}O_8$
$M_r = 372.40$
Triclinic, $P\overline{1}$
$a = 7.7179$ (16) Å
$b = 11.486$ (2) Å
$c = 11.720$ (2) Å
$\alpha = 76.515$ (4)°
$\beta = 74.547$ (4)°
$\gamma = 85.394$ (4)°
$V = 973.6$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 291$ (2) K
0.33 × 0.27 × 0.26 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.925$, $T_{\max} = 0.975$
10725 measured reflections
4173 independent reflections
2082 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.080$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.132$
$S = 0.89$
4173 reflections
240 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Table 3
Short intermolecular contact geometry (Å, °) for (III).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
C16—H16$A$$\cdots$O6$^{\rm i}$	0.96	2.53	3.399 (3)	151

Symmetry code: (i) $-x+1, -y, -z$.

All H atoms were initially located in a difference Fourier map. The methine (CH) and methylene (CH_2) H atoms were then placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H distances of 0.97 and 0.98 Å, and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C). The methyl H atoms were not well defined in difference maps and were constrained to an ideal geometry, with a C—H distance of 0.96 Å and $U_{\rm iso}$(H) values of $1.5U_{\rm eq}$(C). During refinement, each methyl group was allowed to rotate freely about its C—C bond.

For all three compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3073). Services for accessing these data are described at the back of the journal.

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