Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Two new heterocyclic [3.3.3.$0^{1,5}$]-propellanoid compounds: 2,8-dioxatricyclo[3.3.3.$0^{1,5}$]undecane-3,7-dione and a related dimer

Jonglin F. Tsao, Sana R. Faruqi, Hugh W. Thompson and Roger A. Lalancette*

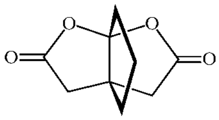
Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ 07102, USA
Correspondence e-mail: rogerlal@andromeda.rutgers.edu

Received 14 October 2002
Accepted 3 December 2002
Online 11 January 2003

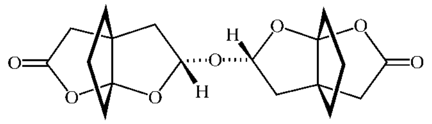
2,8-Dioxatricyclo[3.3.3.$0^{1,5}$]undecane-3,7-dione, $C_9H_{10}O_4$, (I), is the dilactone acylal of cyclopentanone-2,2-diacetic acid. Both molecules in the asymmetric unit have conformational chirality and differ principally in the flexing of the carbon ring, which produces a resolvable conformational disorder in one of the molecules. Three intermolecular C—H···O close contacts exist. 7,7′-Oxybis(2,8-dioxatricyclo[3.3.3.$0^{1,5}$]undecan-3-one), $C_{18}H_{22}O_7$, (II), a racemate, lies on a C_2 axis and is a non-*meso* furanosyl furanoside dimer derived from the monoacid monoaldehyde corresponding to (I). One intermolecular C—H···O close contact exists. Diminished intramolecular void space in these small propellanoids generates unusually high crystal density in both species, particularly (I).

Comment

The propellanoids are an important class of fused polycyclic compounds in which three rings all share the same pair of adjacent tetrahedral atoms. A number of propellanoid natural products offer tempting and extraordinarily challenging synthetic targets (Corey & Cheng, 1989). Syntheses of propellanoids, despite being widely ignored in historical accounts, actually date back at least into the mid-1930s, with reports of both carbocyclic (Fieser & Dunn, 1936) and heterocyclic examples (Diels & Friedrichsen, 1934; Fieser & Hershberg, 1936; Alder & Backendorf, 1938) arising from studies involving the Diels–Alder reaction. Syntheses specifically aimed at propellanoids *per se* first appeared in the mid-1960s (Snatzke & Zanati, 1965; Nerdel *et al.*, 1965; Altman *et al.*, 1966; Thompson, 1966, 1968), and the name 'propellanoid' and their recognition as a distinct class originated during this period (Altman *et al.*, 1966). Since that time, numerous propellanoids have been reported, and our own investigations have produced several heterocyclic examples (Thompson, 1967; Zwege *et al.*, 1999; Tsao *et al.*, 2002), among them the two new compounds, (I) and (II), whose solid-state structures we now report.



(I)



(II)

Fig. 1 shows the asymmetric unit for (I), which is the dilactone acylal of cyclopentanone-2,2-diacetic acid. In the subsequent discussion, primed numbering is used for the second of the two molecules in the asymmetric unit. Although the molecule contains a potential plane of symmetry, both (I) and (I′) have conformational chirality, due to flexing of the various rings. The lactone rings depart only slightly from planarity, with atoms O3 and O7 displaced by 0.125 (4) and −0.013 (5) Å from, and atoms O3′ and O7′ tilted 0.015 (5) and 0.074 (4) Å out of, their respective ring planes. The carbon ring in both (I) and (I′) adopts an envelope conformation. The dihedral angle between C9′—C10′—C11′ and C9′—C1′—C5′—C11′ is 37.0 (3)°, and this displaces atom C10′ from the plane of the remaining C atoms of its ring by 0.524 (7) Å.

In component (I), this folded conformation for the carbon ring displays a disorder, corresponding to a flexing motion for atom C10, which is resolvable into two components. The predominant species in this 59 (2):41 (2) disorder (Fig. 1) has atom C10 lying over the C6—C7—O8 ring, 0.44 (2) Å out of the C9—C1—C5—C11 plane, with a dihedral angle of 30.4 (6)° between the latter plane and C9—C10—C11. In the 41% component, atom C10*A* lies over the other lactone ring (O2—C3—C4), −0.300 (16) Å out of the C9—C1—C5—C11 plane, with a dihedral angle of 22.3 (14)° between the latter plane and C9—C10*A*—C11. We have no information as to whether this disorder is a dynamic wagging or is static.

From studies of ring-chain tautomerism, it is known that γ-lactones are generally more stable than their δ homologs, so

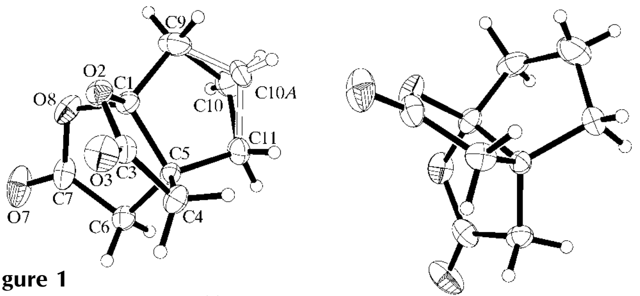


Figure 1
The asymmetric unit of (I) and its numbering. The numbering scheme for the second molecule in the asymmetric unit has primed atom labels. Solid bonds show the major component in one ring and open bonds the minor component [0.59 (2):0.41 (2)]. Displacement ellipsoids are set at the 15% probability level and H atoms are shown as small spheres of arbitrary radii.

DOI: 10.1107/S0108270102022369

that acylglutaric acid cases similar to (I) tend to close spontaneously (Soffer *et al.*, 1950; Valente *et al.*, 1998), while in the six-membered counterparts, this equilibrium must often be driven to closure (Thompson, 1967).

Three significant intermolecular C—H···O close contacts were found in the packing of (I), namely between atoms O3 and H6′*B* (2.47 Å), between atoms O7 and H4′*A* (2.55 Å), and between atoms O3′ and H6*B* (2.58 Å). These distances all lie within the 2.7 Å range often employed for non-bonded C—H···O packing interactions (Steiner, 1997). Based on compiled data for a large number of C—H···O contacts, Steiner & Desiraju (1998) found significant statistical directionality even as far out as 3.0 Å, and concluded that these are legitimately viewed as 'weak hydrogen bonds', with a greater contribution to packing forces than simple van der Waals attractions.

Compound (II) is a furanosyl furanoside dimer derived from the monoacid monoaldehyde corresponding to (I). Fig. 2 shows its full structure, which consists of two asymmetric units related by a twofold axis through atom O7. Compound (II) is therefore non-*meso*, but is racemic overall. The atom-numbering scheme is identical for the two halves of the full molecule. As in (I), the lactone ring is the most planar and the carbon ring the least planar of the three, with the acetal ring significantly flexed as well. Within the asymmetric unit, the stereochemistry of the furanosyl acetal ring involves extension of atom O7 in the direction of the lactone ring and of atom H7 toward the carbon ring. Of all the diastereomers possible, compound (II), having stereochemically and chirally identical subunits, seems to have been formed in high predominance in this process, although another apparent isomer was found (gas chromatography/MS) in the mixture. The selectivity involved may have been due to displacement of equilibria by selective precipitation. One intermolecular C—H···O close contact was found within 2.7 Å, between atoms O2 and H11*B* (2.59 Å).

The essential characteristic core of two attached quaternary sites in propellanoids represents a region of high atom and ring density. Small members of this class consequently have less void space and potentially higher crystal density than other comparable aliphatic compounds, as is the case for both (I) and (II), whose crystal densities are 1.413 and 1.382 Mg m^{-3}, respectively. A similar but even higher crystal density (1.452 Mg m^{-3}) is seen in the *transoid* analog of (I) (Tsao *et al.*, 2002). This density potential may not be realised in cases where the packing is dominated by hydrogen-bonding forces, which can actually prevent the closest possible (van der Waals) packing. Thus, the C_{13} propellanoid keto lactam described by Zwege *et al.* (1999), the packing of which is determined by hydrogen bonding in both its reported crystalline modifications, has crystal densities of 1.229 and 1.275 Mg m^{-3}. These values are entirely normal for aliphatic species, but markedly lower than those found for (I) and (II), in which hydrogen bonding is absent.

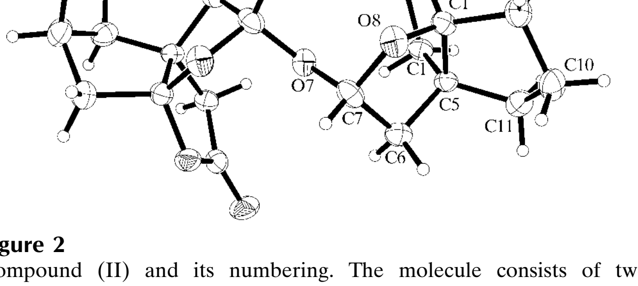


Figure 2
Compound (II) and its numbering. The molecule consists of two asymmetric units related by a twofold axis through atom O7. Displacement ellipsoids are set at the 20% probability level and H atoms are shown as small spheres of arbitrary radii.

Experimental

Compound (I) was synthesized from indane by a series of steps that included lithium–ammonia reduction and selective epoxidation (Giovanni & Wegmüller, 1958), acid-catalyzed rearrangement, and oxidative alkene cleavage (Carlsen *et al.*, 1981). Compound (II) is a by-product, arising from incomplete oxidation. Neither (I) nor (II) has been reported previously, although their dioxatricyclic ring system is known (Mehta *et al.*, 1987).

The $CHCl_3$ IR spectrum of (I) displays a single intense C═O peak at 1797 cm^{-1}. ^{1}H NMR (δ, p.p.m.): 2.80 (2H, *d*, J = 19.17 Hz), 2.77 (2H, *d*, J = 19.16 Hz), 2.23 (2H, *t*, J = 7.12 Hz), 1.99 (2H, *t*, J = 6.57 Hz), 1.86 (2H, quintet, J = 6.57 and 7.12 Hz). ^{13}C NMR (δ, p.p.m.): 173.42, 122.53, 49.61, 42.73. 40.04, 36.81, 23.68. Major EI/MS peaks appear at *m*/*e* 182 (M^+, 0.7%), 154 (9.0), 110 (91.9), 82 (81.6), 67 (100), 55 (76.1) and 39 (53.6). Crystals of (I) (m.p. 379 K) suitable for X-ray analysis were obtained from CH_2Cl_2.

The KBr IR spectrum of (II) displays a single C═O peak at 1786 cm^{-1}. ^{1}H NMR (δ, p.p.m.): 5.62 (2H, *d*, J = 4.58 Hz), 2.80 (2H, *d*, J = 18.92 Hz), 2.66 (2H, *d*, J = 18.62 Hz), 2.20 (2H, *m*), 2.14 (2H, *d*, J = 13.43 Hz), 2.02–1.94 (4H, *m*, including 1.86, 2H, *dd*, J = 13.43 and 4.58 Hz), 1.86 (4H, *m*), 1.70 (4H, *m*). ^{13}C NMR (δ, p.p.m.): 176.74, 127.61, 103.29, 53.26, 45.86. 44.98, 40.45, 37.02, 24.64. Major EI/MS peaks appear at *m*/*e* 278 (1.2%), 167 (100), 149 (16.4), 139 (10.8), 125 (20.6), 110 (15.0), 95 (10.1), 67 (9.3) and 55 (12.7). Crystals of (II) (m.p. 465 K) suitable for X-ray analysis were obtained from methyl *tert*-butyl ether/CH_2Cl_2.

Compound (I)

Crystal data

$C_9H_{10}O_4$
M_r = 182.17
Monoclinic, $P2_1/c$
a = 12.697 (3) Å
b = 12.240 (5) Å
c = 11.509 (4) Å
β = 106.79 (2)°
V = 1712.4 (10) Å^3
Z = 8
D_x = 1.413 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 reflections
θ = 3.8–8.8°
μ = 0.11 mm^{-1}
T = 296 (2) K
Square tablet, yellow
0.48 × 0.36 × 0.24 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: analytical (*SHELXTL*; Sheldrick, 1997)
$T_{\min}$ = 0.94, $T_{\max}$ = 0.96
3839 measured reflections
3008 independent reflections
1898 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 25°
$h = -15 \rightarrow 14$
$k = -14 \rightarrow 1$
$l = -1 \rightarrow 13$
3 standard reflections every 97 reflections intensity variation: <1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.158$
$S = 1.04$
3008 reflections
243 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2 + 0.6938P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.022 (2)

Compound (II)

Crystal data

$C_{18}H_{22}O_7$
$M_r = 350.36$
Orthorhombic, *Fdd*2
$a = 11.571$ (5) Å
$b = 27.069$ (10) Å
$c = 10.754$ (5) Å
$V = 3368$ (2) Å^3
$Z = 8$
$D_x = 1.382$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 2.7$–$6.2°$
$\mu = 0.11$ mm^{-1}
$T = 296$ (2) K
Parallelepiped, colorless
0.44 × 0.38 × 0.12 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997)
$T_{\min} = 0.96$, $T_{\max} = 0.99$
1578 measured reflections
789 independent reflections
463 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 25°$
$h = -13 \rightarrow 13$
$k = -32 \rightarrow 32$
$l = -12 \rightarrow 12$
3 standard reflections every 97 reflections intensity variation: <1.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.082$
$S = 1.00$
789 reflections
114 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.11$ e Å^{-3}
$\Delta\rho_{\min} = -0.13$ e Å^{-3}

All the H atoms of (I) and (II) were found in electron-density difference maps, but were placed in calculated positions (C—H distances of 0.97 Å for methylene H atoms and 0.98 Å for methine H atoms) and allowed to refine as riding models on their respective C atoms, with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$. Atom C10 of (I) exhibited significant disordering [ratio 0.59 (2):0.41 (2)].

For both compounds, data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1401). Additional figures are also available. Services for accessing these data are described at the back of the journal.

References

Alder, K. & Backendorf, K. H. (1938). *Chem. Ber.* **71**, 2199–2209.

Altman, J., Babad, E., Itzchaki, J. & Ginsburg, D. (1966). *Tetrahedron*, *Suppl.* 8, Part 1, pp. 279–304.

Carlsen, P. H. J., Katsuki, T., Martin, V. S. & Sharpless, K. B. (1981). *J. Org. Chem.* **46**, 3936–3938.

Corey, E. J. & Cheng, X.-M. (1989). *The Logic of Chemical Synthesis*, pp. 225, 374, 375, 399, 403, 404. New York: John Wiley & Sons.

Diels, O. & Friedrichsen, W. (1934). *Liebigs Ann. Chem.* **513**, 145–155.

Fieser, L. F. & Dunn, J. T. (1936). *J. Am. Chem. Soc.* **58**, 1054–1055.

Fieser, L. F. & Hershberg, E. B. (1936). *J. Am. Chem. Soc.* **58**, 2314–2318.

Giovanni, E. & Wegmüller, H. (1958). *Helv. Chim. Acta*, **41**, 933–938.

Mehta, G., Rao, H. S. P. & Reddy, K. R. (1987). *J. Chem. Soc. Chem. Commun.* pp. 78–80.

Nerdel, F., Janowsky, K. & Frank, D. (1965). *Tetrahedron Lett.* pp. 2979–2981.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Snatzke, G. & Zanati, G. (1965). *Liebigs Ann. Chem.* **684**, 62–78.

Soffer, M. D., Stewart, R. A., Cavagnol, J. C., Gellerson, H. E. & Bowler, E. A. (1950). *J. Am. Chem. Soc.* **72**, 3704–3709.

Steiner, T. (1997). *J. Chem. Soc. Chem. Commun.* pp. 727–734.

Steiner, T. & Desiraju, G. R. (1998). *J. Chem. Soc. Chem. Commun.* pp. 891–892.

Thompson, H. W. (1966). *Tetrahedron Lett.* pp. 6489–6494.

Thompson, H. W. (1967). *J. Org. Chem.* **32**, 1222–1224.

Thompson, H. W. (1968). *J. Org. Chem.* **33**, 621–625.

Tsao, J. F., Thompson, H. W. & Lalancette, R. A. (2002). *Struct. Chem.* **13**, 455–458.

Valente, E. J., Fuller, J. F. & Ball, J. D. (1998). *Acta Cryst.* B**54**, 162–173.

Zwege, D., Thompson, H. W., Brunskill, A. P. J. & Lalancette, R. A. (1999). *Acta Cryst.* C**55**, 1370–1373.