

Supramolecular aggregation of two hydroxycarboxylic acid derivatives

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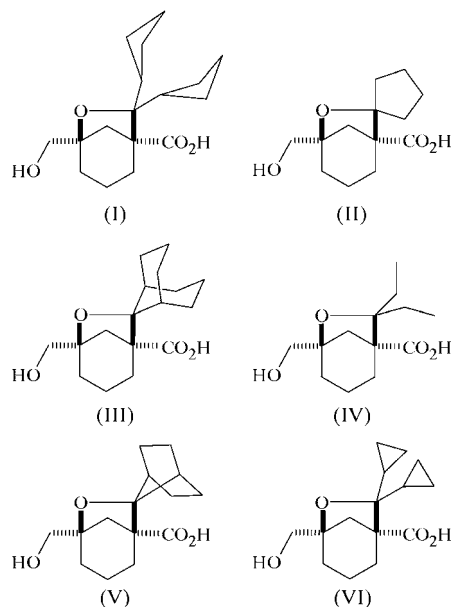
The crystal structures of 7,7-dicyclobutyl-5-hydroxymethyl-6-oxabicyclo[3.2.1]octane-1-carboxylic acid, C₁₇H₂₆O₄, (I), and 1-(hydroxymethyl)-7-oxaspiro[bicyclo[3.2.1]octane-6,1'-cyclopentane]-5-carboxylic acid, C₁₃H₂₀O₄, (II), determined at 170 K, show that the conformation of the hydroxymethyl group (*anti* or *gauche*) affects the dimensionality (one- or two-dimensional) of the supramolecular structures *via* O—H...O hydrogen bonds. In (I), the carboxyl and hydroxymethyl groups interact with themselves, forming a one-dimensional step-ladder, while in (II), a two-dimensional structure is made up of carboxylic acid centrosymmetric R₂²(8) dimers connected by hydroxyl-to-ether contacts.

Comment

We have reported that compounds possessing axially oriented hydroxyl/carboxylic acid functions might create, by incorporation of water molecules, three-dimensional tubular structures in the crystalline state. Compounds (I) and (II) were considered to be promising candidates, since their respective homologues, (III) and (IV), have been shown to adopt hydrated tubular structures in the solid state (Carrasco *et al.*, 2001). The crystal structures of compounds (I) and (II), reported in this paper, reveal a lack of hydration water molecules, although they were crystallized in a water-saturated atmosphere. To date, compound (IV) is the only one of this series which crystallizes in the anhydrous and hydrated forms in the absence or presence of a water atmosphere, respectively.

The molecular structures of compounds (I) and (II) are displayed in Figs. 1 and 2, respectively. In (I), the cyclobutane rings are puckered (Table 1), with dihedral angles of 26.1 (2) (C13/C10/C11 and C11/C12/C13 planes) and 31.7 (1)° (C15/C14/C17 and C15/C16/C17 planes). In both compounds, the oxolane ring presents a distorted ⁴T₅ half-chair toward an E₅ envelope conformation, according to the puckering parameters (Cremer & Pople, 1975) and the notation of Giaco-

vazzo *et al.* (1992) for the C1–O1–C9–C5–C6 sequence [$\varphi_2 = -50.1$ (2) and -51.7 (1)°]. The cyclohexane presents a distorted ¹C₄ towards ¹E conformation [C6–C1–C2–C3–C4–C5; $\varphi = 0.4$ (3) and 1.8 (3)°, and $\theta = 27.0$ (3) and 23.8 (1)°].



The molecules of (II) exhibit positional disorder of the cyclopentane ring and of the carboxylic acid group (Fig. 2). The cyclopentane ring adopts two conformations, namely ⁵T₄ and ⁵E for molecules A [$\varphi_2 = 133.3$ (6)°], and between ⁵T₁ and E₁ for molecules B [$\varphi_2 = 173.9$ (11)°], for the C9–C10–C11A or C11B–C12–C13 sequences. In the carboxylic acid group, the C–O distances and O–C–C angle are significantly different from those in (I) (Tables 1 and 3), although they are in good agreement with the values previously reported for the disordered group (Carrasco *et al.*, 2001).

The O—H...O hydrogen-bonding motifs may be described as double-strand ladders in (I) and as sheets in (II) (Figs. 3 and 4), which are closely related to the *anti* and *gauche* conformations of the hydroxyl group with respect to the oxolane bridge (Tables 1 and 3). As observed previously (Carrasco *et al.*, 2001), the *anti* conformation gives one-dimensional assemblies, while a *gauche* conformation gives either one- or two-dimensional assemblies.

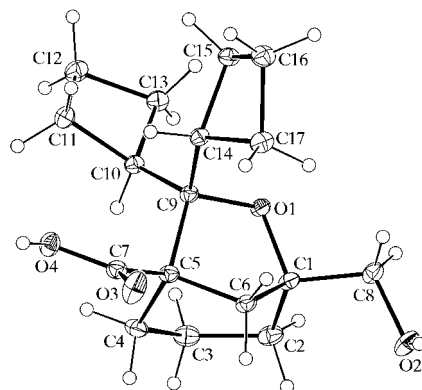


Figure 1

The molecular structure of (I), shown with 30% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

The supramolecular structure in (I) also differs from that in (II), in the absence of the centrosymmetric $R_2^2(8)$ motif (Tables 2 and 4). In (I), the carboxylic acid group acts as both a donor to the hydroxyl group, forming strands, and as an acceptor, joining two strands into a step-ladder structure

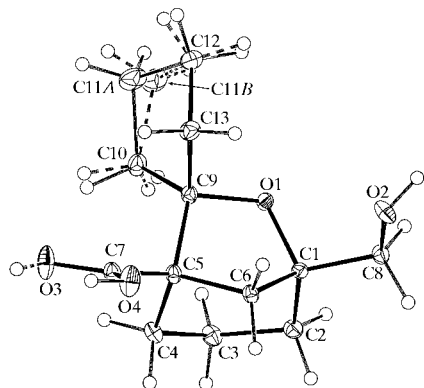


Figure 2
The molecular structure of (II), shown with 30% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii. The disorder model in the cyclopentane ring and in the carboxylic acid group is represented by dashed lines.

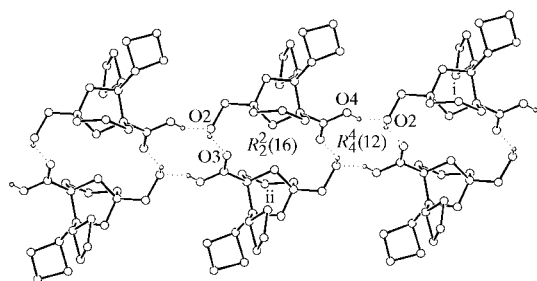


Figure 3
The one-dimensional hydrogen-bonded step-ladders in (I), formed by hydroxyl-to-hydroxyl/carbonyl bonds (dotted lines). H atoms not involved in the hydrogen bonds have been omitted for clarity. [Symmetry codes: (i) $x - 1, 1 + y, z$; (ii) $1 - x, -y, -z$.]

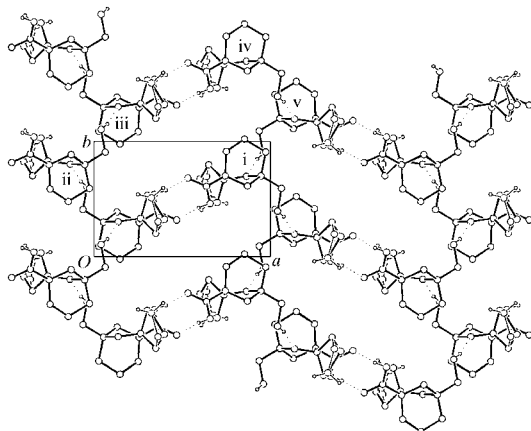


Figure 4
The two-dimensional hydrogen-bonded layer in (II), formed by molecules joined *via* a combination of acid-to-acid and hydroxyl-to-ether hydrogen bonds (dotted lines). H atoms not involved in the hydrogen bonds and the minor component of the disordered carboxylic acid group have been omitted for clarity. [Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, 1 + y, z$; (iv) $1 - x, 2 - y, -z$; (v) $1 + x, \frac{3}{2} - y, -\frac{1}{2} + z$.]

(Nguyen *et al.*, 2001) of alternating $R_2^2(16)$ and $R_4^4(12)$ motifs. Each strand (Fig. 3) contains only one enantiomer, related only by translation, whereas the step-ladder is formed by one strand of one handedness and one strand of opposite handedness, giving rise to an achiral ladder. A similar supramolecular structure is present in the anhydrous form of compound (IV) and in the homologues (V) and (VI) (Carrasco *et al.*, 2001), which have two fewer C atoms. No other weak interactions, except van der Waals interactions, are observed between ladders (Fig. 5).

In compound (II), the H-atom disorder does not affect the supramolecular structure, since the carboxylic acid group interacts strongly with itself, forming the acid-to-acid hydrogen-bonding $R_2^2(8)$ motif (Leiserowitz, 1976; Etter, 1990; Bernstein *et al.*, 1995). This dimeric association, linked by hydroxyl-to-ether hydrogen bonds, results in sheets (Fig. 4) that are further joined *via* C—H...O interactions into a three-dimensional network (see Table 4 and the dashed lines in Fig. 6). The formation of the $R_2^2(8)$ motif is prevented in the related analogues with two-dimensional structures (Carrasco *et al.*, 2001).

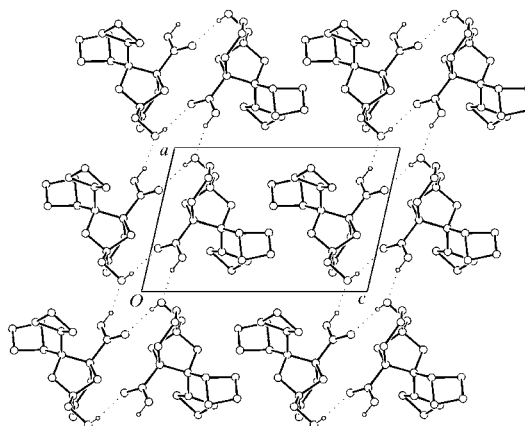


Figure 5
A packing diagram for (I), illustrating the disposition of two ladders running along $[110]$. H atoms not involved in hydrogen bonds have been omitted for clarity.

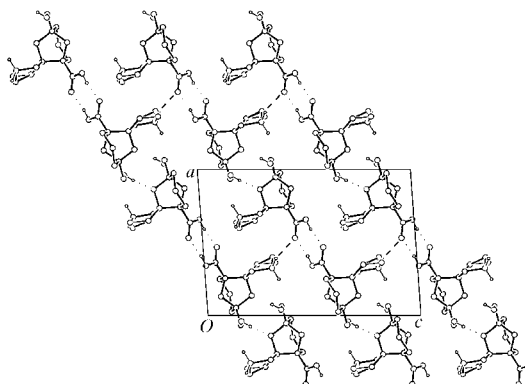


Figure 6
A packing diagram for (II), illustrating the disposition of the sheets. C—H...O interactions (dashed lines) link the sheets into a three-dimensional network. H atoms not involved in hydrogen bonds and the minor component of the disordered carboxylic acid group have been omitted for clarity.

Comparison with the previously reported hydroxy-acid analogues confirms that the relative positions of the hydroxyl and carboxylic acid groups, together with the molecular size, can lead to a range of hydrogen-bonded supramolecular structures with various dimensionalities. The reliability of the axially oriented hydroxyl/carboxylic acid functions in giving anhydrous layers reduces the design of the last remaining dimension to the incorporation of water molecules.

Experimental

Compounds (I) and (II) were synthesized by condensing the dilithium salt of 3-methylenecyclohexanecarboxylic acid with, respectively, dicyclobutylmethanone (Erickson *et al.*, 1966) and cyclopentanone, following the synthetic sequence reported for the other members of this family of compounds (Carrasco *et al.*, 2001). Analysis for compound (I): m.p. 448–449 K; ^1H NMR (300 MHz, MeOD): δ 3.67 (*d*, $J = 11.5$ Hz, 1H), 3.62 (*d*, $J = 11.5$ Hz, 1H), 3.23 (*m*, 1H), 2.61 (*m*, 1H), 2.47 (*d*, $J = 11.8$ Hz, 1H), 2.27 (*m*, 3H), 2.12 (*m*, 2H), 1.99 (*m*, 3H), 1.74 (*m*, 8H), 1.58 (*m*, 2H), 1.40 (*d*, $J = 11.8$ Hz, 1H); ^{13}C NMR (75.4 MHz, MeOD): δ 17.7, 18.1, 19.5, 26.2, 26.7, 27.4, 31.9, 32.8, 40.4, 41.1, 44.6, 47.6, 56.9, 67.3, 82.4, 86.4, 176.2; IR (KBr, ν_{max} , cm^{-1}): 3398, 2950, 2363, 1701, 1651, 1540, 1458, 1251, 1167, 1123, 995. Analysis for compound (II): m.p. 426–427 K; ^1H NMR (300 MHz, MeOD): δ 3.48 (*d*, $J = 11.7$ Hz, 1H), 3.42 (*d*, $J = 11.7$ Hz, 1H), 2.50 (*d*, $J = 11.4$ Hz, 1H), 2.20 (*m*, 2H), 1.95 (*m*, 2H), 1.73 (*m*, 5H), 1.59 (*d*, $J = 11.4$ Hz, 1H), 1.50 (*m*, 4H), 1.40 (*dd*, $J_1 = 12.4$, $J_2 = 5.8$ Hz, 1H); ^{13}C NMR (75.4 MHz, MeOD): δ 19.7, 24.1, 24.5, 31.7, 31.8, 32.0, 39.2, 40.6, 55.6, 66.4, 82.3, 94.1, 176.0; IR (KBr, ν_{max} , cm^{-1}): 3749, 3380, 2956, 2870, 2361, 2337, 1703, 1456, 1339, 1257, 1157, 1046, 1002. Single crystals of (I) and (II) suitable for X-ray analysis were grown at room temperature from a damp carbon tetrachloride–2,2,4-trimethylpentane mixture (3:1).

Compound (I)

Crystal data

$\text{C}_{17}\text{H}_{26}\text{O}_4$	$Z = 2$
$M_r = 294.38$	$D_x = 1.270 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.757$ (3) Å	Cell parameters from 3531 reflections
$b = 8.807$ (3) Å	$\theta = 1.8\text{--}27.5^\circ$
$c = 11.769$ (6) Å	$\mu = 0.09 \text{ mm}^{-1}$
$\alpha = 84.073$ (11)°	$T = 170$ (2) K
$\beta = 75.766$ (13)°	Prism, colourless
$\gamma = 61.044$ (9)°	$0.45 \times 0.10 \times 0.10 \text{ mm}$
$V = 769.7$ (5) Å ³	

Data collection

Nonius KappaCCD area-detector diffractometer	$\theta_{\text{max}} = 27.5^\circ$
φ and ω scans	$h = 0 \rightarrow 11$
3531 measured reflections	$k = -9 \rightarrow 11$
3531 independent reflections	$l = -14 \rightarrow 15$
3087 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1125P)^2 + 0.2845P]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.176$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$
3531 reflections	$\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$
191 parameters	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.155 (15)

Table 1

Selected geometric parameters (Å, °) for (I).

O3–C7	1.209 (2)	O4–C7	1.318 (2)
O3–C7–C5	123.5 (2)	O4–C7–C5	113.1 (1)
O1–C1–C8–O2	−179.8 (1)	O1–C9–C14–C15	59.9 (2)
O1–C9–C10–C11	−156.9 (1)	O1–C9–C14–C17	−49.1 (2)
O1–C9–C10–C13	−47.6 (2)	C17–C14–C15–C16	−22.2 (1)
C13–C10–C11–C12	18.3 (1)	C14–C15–C16–C17	22.4 (1)
C10–C11–C12–C13	−18.4 (1)	C15–C16–C17–C14	−22.4 (1)
C11–C12–C13–C10	18.4 (1)	C15–C14–C17–C16	22.2 (1)
C11–C10–C13–C12	−18.3 (1)		

Table 2

Hydrogen-bond geometry (Å, °) for (I).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O2–H2 \cdots O3 ⁱ	0.84	1.96	2.718 (2)	149
O4–H4 \cdots O2 ⁱⁱ	0.84	1.78	2.585 (2)	159

Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $x - 1, y + 1, z$.

Compound (II)

Crystal data

$\text{C}_{13}\text{H}_{20}\text{O}_4$	$D_x = 1.325 \text{ Mg m}^{-3}$
$M_r = 240.29$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2589 reflections
$a = 10.850$ (3) Å	$\theta = 1.9\text{--}27.0^\circ$
$b = 7.050$ (2) Å	$\mu = 0.10 \text{ mm}^{-1}$
$c = 15.790$ (5) Å	$T = 170$ (2) K
$\beta = 94.207$ (10)°	Sphere, colourless
$V = 1204.6$ (6) Å ³	$0.50 \times 0.50 \times 0.45 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	$\theta_{\text{max}} = 27.0^\circ$
φ and ω scans	$h = 0 \rightarrow 13$
2589 measured reflections	$k = 0 \rightarrow 8$
2589 independent reflections	$l = -20 \rightarrow 20$
2377 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.111P)^2 + 0.2862P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.154$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
2589 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
169 parameters	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.20 (2)

Table 3

Selected geometric parameters (Å, °) for (II).

O3–C7	1.257 (2)	O4–C7	1.275 (2)
O3–C7–C5	118.7 (1)	O4–C7–C5	118.4 (1)
O1–C1–C8–O2	72.76 (12)	C11A–C12–C13–C9	44.3 (4)
O1–C9–C10–C11A	−95.2 (4)	C10–C9–C13–C12	−39.2 (1)
O1–C9–C10–C11B	−77.2 (5)	C13–C9–C10–C11B	36.9 (5)
C13–C9–C10–C11A	18.8 (5)	C9–C10–C11B–C12	−20.1 (8)
C9–C10–C11A–C12	8.4 (7)	C10–C11B–C12–C13	−4.3 (8)
C10–C11A–C12–C13	−32.3 (6)	C11B–C12–C13–C9	27.0 (5)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2...O1 ⁱ	0.84	1.96	2.790 (1)	170
O3—H3...O4 ⁱⁱ	0.84	1.83	2.636 (2)	162
O4—H4...O3 ⁱⁱ	0.84	1.80	2.636 (2)	171
C12—H12D...O3 ⁱⁱⁱ	0.99	2.60	3.561 (2)	163

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

All H atoms were located in difference Fourier maps and subsequently allowed to refine as riding, with C—H = 0.99 (CH₂) or 1.00 Å (CH) and O—H = 0.84 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$. The molecules of (II) exhibit positional disorder in the carboxylic acid H atom [pp(H4) = 0.59 (3) and pp(H3) = 0.41 (3)] and in the cyclopentane ring [pp(C11A) = 0.58 (2) and pp(C11B) = 0.42 (2)]. The bond distances around the disordered atoms C11A/B in the cyclopentane ring were restrained using the DFIX command based on the average $\text{Csp}^3\text{—Csp}^3$ value (Allen *et al.*, 1987). Attempted free refinement led to unrealistic geometrical parameters.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; structure solution: *SIR97* (Altomare *et al.*, 1999); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal3.6* (Hall *et al.*, 1999) and *PLATON* (Spek, 2003); publication software: *SHELXL97*, *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1124). Services for accessing these data are described at the back of the journal.

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