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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: NA1231). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Carboxy- and 2,7-Dicarboxy-4,5-benzotropone: Hydrogen-Bonding Patterns of a β-Keto Acid and a Related β-Keto 1,5-Diacid

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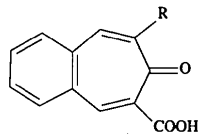
Abstract

The two title compounds exhibit strikingly different hydrogen-bonding modes. The monoacid $C_{12}H_8O_3$, (I) (alternative systematic name: 7-oxo-7*H*-benzocycloheptene-6-carboxylic acid), adopts a nearly planar conformation with the carboxyl internally hydrogen-bonded to the ketone; the molecules pack in stacks at an interplanar distance of 3.397 (4) Å with six lateral C═O···H—C close contacts. In the diacid $C_{13}H_8O_5$, (II) (alternative systematic name: 7-oxo-7*H*-benzocycloheptene-6,8-dicarboxylic acid), the ketone carbonyl, which is not involved in hydrogen bonding, lies out of the general molecular plane, while the carboxylic acids are paired by hydrogen bonding with those of neighboring molecules, forming flat zigzag chains. Both (I) and (II) adopt slightly asymmetric conformations.

Comment

The crystalline states of acetic and formic acids involve chains (catemers) created by repeating intermolecular O—H···O═C hydrogen bonds (Jones & Templeton, 1958; Nahringbauer, 1978). This pattern is otherwise unusual among carboxylic acids, which typically form hydrogen-bonding dimers (Leiserowitz, 1976). Our interest in the X-ray structures of simple keto carboxylic acids concerns such hydrogen-bonding motifs, of which four are known. The most common has acid dimers, in which the ketone is not involved. Less frequently, intermolecular carboxyl-to-ketone hydrogen bonds repeat along one cell axis to yield a catemer. A third, rare arrangement is an internal hydrogen bond, and one instance is known of acid-to-ketone dimerization. We have previously referenced and discussed numerous examples (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1996).

The geometry of β-keto acids appears attractive for internal hydrogen bonding (Toffoli, Khodadad & Rodier, 1988), consistent with the six-centered internal H-atom transfer underlying their thermal decarboxylation (Logue, Pollack & Vitullo, 1975). However, crystallographically, this hydrogen-bonding mode has been found only in γ-keto acids (and one ε-keto acid), requiring larger hydrogen-bonding rings. Internal six-membered hydrogen-bonding does occur in several α,β-unsaturated acids where a β′-oxo function is part of a vinylogous amide or ester and thus more negative than in ketones, but evidence for it in simple crystalline β-keto acids has been lacking. In our study of these patterns, we have examined the title compounds, 2-carboxy-4,5-benzotropone, (I), and 2,7-dicarboxy-4,5-benzotropone, (II), which include the first case of a true β-keto acid with internal hydrogen bonding.



(I) = H
(II) = COOH

Fig. 1 presents a view of molecule (I) with its atomic numbering. The internal angles in a planar heptagon average 128.57°; these angles in (I) are

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all indeed abnormally wide relative to normal sp^2 angles, varying from 123.8 (3)° at the ketone (C2—C1—C7) to 134.6 (3)° for C2—C3—C4. However, like benzotropone itself (Ibata, Shimanouchi, Sasada & Hato, 1975), (I) is not quite planar and this imparts a chirality to the asymmetric unit. The average deviation from the mean-square plane for all non-H atoms is 0.06 Å, but this deviation is concentrated in the region of the hydrogen-bonding ring. Torsion angles not involving C1 or O1 deviate from planarity by no more than 3.1°, but several torsion angles including these atoms lie in the range 3.8–7.0° from planarity. The ketone C=O bond is unusually long, 1.254 (3) Å, consistent with the strong $C^{\delta+}O^{\delta-}$ polarization associated with α,β-unsaturation plus the aromaticity of the tropone structure (see below).

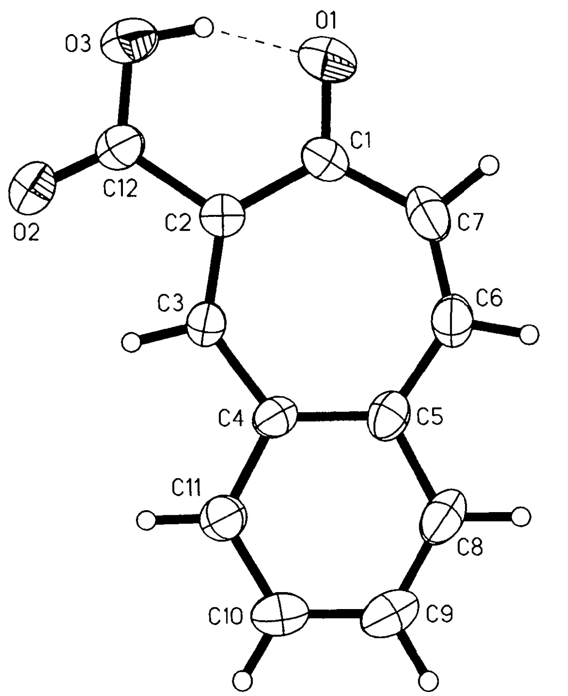

Fig. 1. A view of keto monoacid (I) with its numbering scheme. Ellipsoids are at the 40% probability level.

As can be seen in Fig. 1, the carboxyl is internally hydrogen bonded to the ketone, one of only two instances of this we have encountered so far in our own work (Coté, Lalancette & Thompson, 1996). This arrangement requires an antiplanar (*s-trans*) carboxyl conformation, less stable than the synplanar by energies estimated variously at 2–4 kcal mol^{-1} (Leiserowitz, 1976) and 1.5–5.5 kcal mol^{-1} (Gandour, 1981) (1 kcal = 4.184 kJ). As expected for non-dimeric cases, the carboxyl C—O bond lengths and C—C—O angles in (I) are highly ordered.

With one exception, the internal angles of the hydrogen-bonding ring all lie within normal ranges. We have reported (Thompson, Lalancette & Vanderhoff, 1992) that catemeric and dimeric cases favor O—H···O angles in the range 155–180°, with none known below 141°. In (I) this angle is 156 (5)°, achieved principally by narrowing the C=O···H angle to 101 (2)°. The preferred C=O···H angle in surveyed catemeric (Thompson, Lalancette & Vanderhoff, 1992) and acid–dimer cases (Lifson, Hagler & Dauber, 1979) is 114–156°, significantly wider than that found here. Successful internal hydrogen-bond formation is known in several β-oxo carboxylic acids which are not strictly ketones. In these cases O—H···O angles of 153–157° are achieved at the expense of C=O···H angles of *ca* 98° (Toffoli, Khodadad & Rodier, 1988). In general, appropriate hydrogen-bonding angles are clearly much easier to achieve with seven-membered rings in γ-keto acids, for which, indeed, some six cases are known (Coté, Lalancette & Thompson, 1996).

Fig. 2 illustrates the packing of (I). The cell contains a screw-related pair of molecules of each conformational handedness (chirality differentiated by shading), which stack in the **b** direction. The cell is extremely shallow in this dimension [3.843 (1) Å] but, because of tilting, the interplanar separation is actually only 3.397 (4) Å. The interplanar distance in graphite is 3.354 Å (Nelson & Riley, 1945), in benzene, 3.8 Å (Cox, 1932) and in phenanthrene, 3.55 Å (Trotter, 1963). Laterally, each molecule is linked to four glide-related molecules of opposite chirality by six close contacts, also shown.

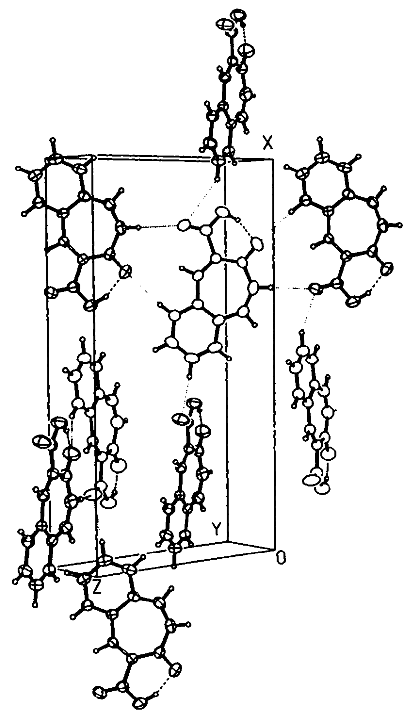

Fig. 2. A packing diagram for (I) with the chirality of each molecule shown by patterning of its bonds and atoms. Extracellular molecules are included to illustrate one complete set of lateral close contacts. Ellipsoids are at the 40% probability level.

These all involve carbonyl O atoms and carbon-bound H atoms, and range from 2.412 (5) to 2.501 (4) Å in length. They probably represent significant polar attractions contributing to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).

Fig. 3 presents a view of (II), with its numbering scheme, showing that neither carboxyl is internally hydrogen bonded. In spite of its molecular symmetry, (II) adopts a chiral conformation, most easily seen in the disposition of the acid carbonyl groups. The dihedral angle between C2,C12,O2,O3 and the ketone group C2,C1,C7,O1 is 53.1 (2)° while the corresponding dihedral angle for the other carboxyl is 38.0 (2)°. The packing-induced dissymetry includes visibly differing external angles of 118.7 (3) and 121.5 (3)° around the ketone carbonyl. The molecule is also significantly nonplanar: the ketone and one of the carboxyl O atoms are tilted out of the plane defined by the aromatic portion, with a dihedral angle of 40.2 (1)° between the ketone group, O1—C1—C2—C7, and the remainder of the two-ring system. The ketone C═O bond length is 1.227 (4) Å, in the normal range for a ketone with one α,β-unsaturation. This shortening relative to (I) presumably reflects lessened C═O polarization associated with the loss of resonance-enabling planarity in (II) relative to (I). Although averaging of carboxyl C—O bond lengths and C—C—O angles by disorder occurs in some dimeric acids (Dieterich, Paul & Curtin, 1974; Borthwick, 1980), it is not significant here.

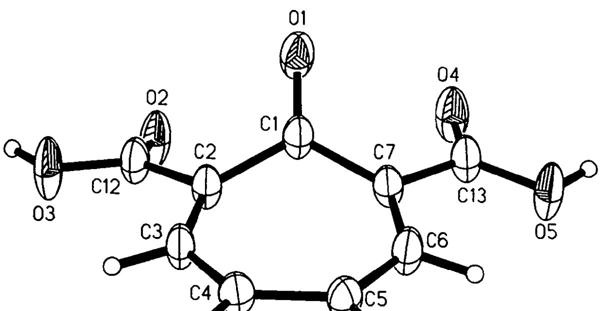

Fig. 3. Keto diacid (II) with its numbering scheme. The molecule adopts a chiral conformation with the ketone and one carboxyl oxygen lying significantly out of the general molecular plane. Ellipsoids are at the 30% probability level.

In the packing arrangement for (II), shown in Fig. 4, no hydrogen-bonding role is played by the ketone. Each carboxyl forms non-centrosymmetric dimeric H bonds with a neighboring molecule of opposite conformational chirality, creating flat sawtooth chains resembling rick-rack ribbon. These ribbons stack in the **a** direction with an interlayer separation in the order of 3.5 Å, but owing to the tilt of the glide-related molecules with respect to each other, adjacently stacked ribbons are not parallel, having a dihedral angle of 10.6 (2)° between their benzene rings.

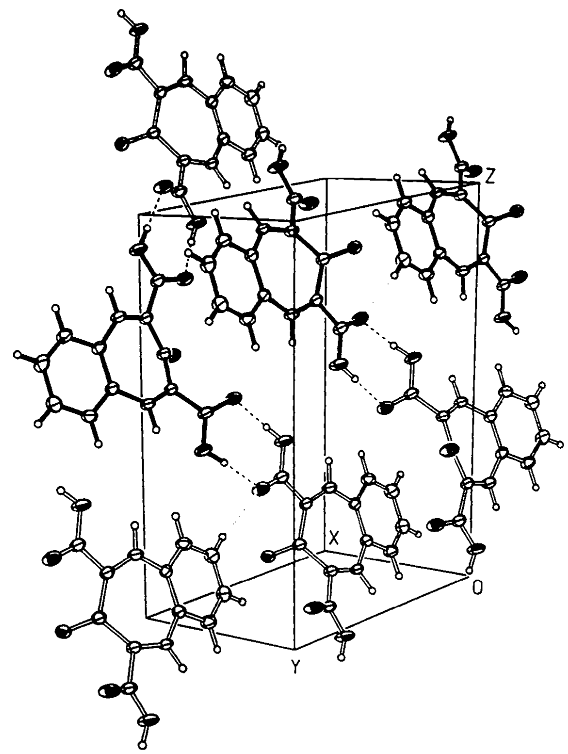

Fig. 4. A packing diagram for (II) with extracellular molecules included to illustrate the separate hydrogen-bonding ribbons. Intermolecular contacts between O4 and H9*A* (at *x*, *y* − 1, *z*; 2.38 Å) and between O2*A* and H10*A* (at *x*, *y* − 1, *z*; 2.60 Å) are shown. The handedness of the molecules is differentiated by the shading of the bonds. Ellipsoids are at the 30% probability level.

Although (I) is the first demonstrated case of an internally hydrogen-bonded β-keto acid, the C═O group of tropones is not typical even of conjugated ketones. While benzotropone appears to be more weakly aromatic than tropone (Pauson, 1955), the weak aromaticity of its seven-membered ring requires that the carbonyl be more polarized than normal in the $C^{\delta+}O^{\delta-}$ sense. This is reflected in the assignment of the infrared C═O stretch of benzotropones at 1590–1607 cm^{-1} (Götz, Heilbronner, Katritzsky & Jones, 1961; Cook & Forbes, 1968) (*cf.* 1665 cm^{-1} for benzalacetone) and should favor ketone hydrogen bonding, as in (I).

The solid-state (KBr) infrared spectra of (I) and (II) each contain several bands of medium strength in the 1500–1600 cm^{-1} region, but we were unable to make positive ketone C═O assignments from them. Each spectrum has a single sharp, intense absorption in the normal C═O stretch region which is evidently due only to the carboxyl C═O. This peak, at 1722 cm^{-1} for (I), is consistent with a structure whose carboxyl C═O is not hydrogen bonded, while the absorption for (II) at 1703 cm^{-1} is typical for a carboxyl C═O involved in hydrogen-bonded dimerization (Coté, Lalancette & Thompson, 1996; Vanderhoff, Lalancette & Thompson, 1990). In $CHCl_3$ solution, this C═O band for (I) remains nearly unchanged, at 1726 cm^{-1}, while that for (II) shifts markedly to 1737 cm^{-1}, indicating substantial internal hydrogen bonding, probably for both carboxyl groups.

Experimental

Claisen–Schmidt condensation of dimethyl 3-oxoglutarate with *o*-phthalaldehyde led to (II) (Thiele & Schneider, 1909; Föhlisch, 1972), crystallized from 70:30 toluene/ethanol at room temperature. Even below its m.p. at 486 K, (II) loses CO_2 to yield (I), m.p. 445 K, which was crystallized from the same solvent.

Compound (I)

Crystal data

$C_{12}H_8O_3$
$M_r = 200.19$
Orthorhombic
$Pca2_1$
$a = 20.154$ (5) Å
$b = 3.843$ (1) Å
$c = 11.787$ (3) Å
$V = 912.9$ (4) $Å^3$
$Z = 4$
$D_x = 1.456$ Mg m^{-3}
$D_m = 1.44$ (1) Mg m^{-3}
D_m measured by flotation in cyclohexane/CCl_4

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 21 reflections
$\theta = 5.78$–12.72°
$\mu = 0.105$ mm^{-1}
$T = 293$ (2) K
Parallelepiped
0.74 × 0.28 × 0.20 mm
Pale yellow

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: face-indexed numerical
$T_{min} = 0.967$, $T_{max} = 0.979$
1694 measured reflections
1607 independent reflections
1237 observed reflections [$F > 4\sigma(F)$]

$R_{int} = 0.0380$
$\theta_{max} = 25.00°$
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 4$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 97 reflections intensity decay: 1.85%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0531$
$wR(F^2) = 0.1185$
$S = 1.096$
1607 reflections
141 parameters
Carboxyl H3 coordinates and *U* refined, all other H atoms riding [C—H 0.96 Å]

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.053 (9)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

$w = 1/[\sigma^2(F_o^2) + (0.0736P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.036$
$\Delta\rho_{max} = 0.233$ e $Å^{-3}$
$\Delta\rho_{min} = -0.228$ e $Å^{-3}$

Absolute configuration: Flack (1983)
Flack parameter = 1 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for (I)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
O1	0.71531 (12)	0.4030 (7)	0.4793 (2)	0.0699 (8)
O2	0.66639 (11)	0.9470 (9)	0.7588 (3)	0.0750 (9)
O3	0.63227 (12)	0.6798 (8)	0.6064 (2)	0.0677 (8)
C1	0.7631 (2)	0.5122 (8)	0.5375 (2)	0.0433 (7)
C2	0.75070 (15)	0.6936 (7)	0.6441 (2)	0.0393 (7)
C3	0.79608 (14)	0.7990 (8)	0.7205 (2)	0.0396 (7)
C4	0.86762 (13)	0.7828 (7)	0.7272 (3)	0.0391 (7)
C5	0.91048 (14)	0.6481 (8)	0.6429 (2)	0.0428 (7)
C6	0.8891 (2)	0.5012 (9)	0.5380 (3)	0.0512 (8)
C7	0.8288 (2)	0.4398 (9)	0.4935 (3)	0.0553 (9)
C8	0.97930 (15)	0.6619 (9)	0.6628 (3)	0.0546 (9)
C9	1.0051 (2)	0.7960 (10)	0.7607 (3)	0.0601 (9)
C10	0.9636 (2)	0.9234 (9)	0.8429 (3)	0.0560 (9)
C11	0.89569 (15)	0.9184 (8)	0.8267 (3)	0.0469 (8)
C12	0.6796 (2)	0.7828 (9)	0.6752 (3)	0.0492 (8)

Table 2. *Selected geometric parameters (Å, °) for (I)*

O1—C1	1.254 (3)	C4—C5	1.415 (4)
O2—C12	1.200 (4)	C4—C11	1.402 (5)
O3—C12	1.313 (4)	C5—C6	1.426 (4)
C1—C2	1.458 (4)	C5—C8	1.408 (4)
C1—C7	1.450 (4)	C6—C7	1.344 (4)
C2—C3	1.346 (4)	C8—C9	1.366 (5)
C2—C12	1.518 (4)	C9—C10	1.370 (5)
C3—C4	1.445 (4)	C10—C11	1.383 (4)
C1—O1—H3	101 (2)	C3—C2—C12	114.3 (3)
C12—O3—H3	106 (3)	C1—C2—C12	118.5 (3)
O1—C1—C7	116.2 (3)	O2—C12—O3	120.3 (3)
O1—C1—C2	120.0 (3)	O2—C12—C2	121.8 (3)
C7—C1—C2	123.8 (3)	O3—C12—C2	117.9 (3)

Table 3. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1	0.94 (6)	1.60 (6)	2.485 (4)	156 (5)

Compound (II)

Crystal data

$C_{13}H_8O_5$
$M_r = 244.19$
Monoclinic
$P2_1/n$
$a = 7.191$ (7) Å
$b = 9.912$ (5) Å
$c = 14.430$ (9) Å
$\beta = 95.53$ (5)°
$V = 1023.7$ (13) $Å^3$
$Z = 4$
$D_x = 1.584$ Mg m^{-3}
$D_m = 1.58$ (1) Mg m^{-3}
D_m measured by flotation in cyclohexane/CCl_4

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 17 reflections
$\theta = 5.9$–15.1°
$\mu = 0.124$ mm^{-1}
$T = 296$ (1) K
Clear prism
0.50 × 0.40 × 0.35 mm
Yellow

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans

904 observed reflections [$F > 4\sigma(F)$]

Absorption correction: ψ scans (26 reflections) (*XPREP*, *SHELXTL/PC*; Sheldrick, 1990*b*)	$R_{int} = 0.0649$
$T_{min} = 0.760$, $T_{max} = 0.873$	$\theta_{max} = 22.5°$
2820 measured reflections	$h = -7 \rightarrow 0$
1341 independent reflections	$k = -10 \rightarrow 10$
	$l = -15 \rightarrow 15$
	3 standard reflections monitored every 97 reflections intensity decay: 2.98%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.346$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.0544$	$\Delta\rho_{min} = -0.235$ e Å^{-3}
$wR(F^2) = 0.1252$	Extinction correction: *SHELXL*93 (Sheldrick, 1993)
$S = 1.103$	Extinction coefficient: 0.043 (8)
1341 reflections	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
165 parameters	
H atoms riding (O—H 0.92, C—H 0.96 Å)	
$w = 1/[\sigma^2(F_o^2) + (0.0799P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max} = -0.001$	

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.0524 (4)	0.8080 (2)	0.6364 (2)	0.0537 (8)
O2	−0.3091 (4)	0.7599 (2)	0.5390 (2)	0.0574 (9)
O3	−0.3159 (4)	0.9248 (2)	0.43469 (15)	0.0600 (9)
O4	0.0283 (4)	0.7540 (2)	0.8199 (2)	0.0571 (9)
O5	0.1006 (4)	0.9336 (2)	0.90869 (15)	0.0576 (9)
C1	−0.0334 (5)	0.9092 (3)	0.6565 (2)	0.0385 (9)
C2	−0.1663 (5)	0.9721 (3)	0.5839 (2)	0.0366 (9)
C3	−0.1891 (5)	1.1038 (3)	0.5672 (2)	0.0379 (9)
C4	−0.1169 (5)	1.2226 (3)	0.6173 (2)	0.0357 (9)
C5	−0.0343 (5)	1.2226 (3)	0.7100 (2)	0.0361 (9)
C6	0.0000 (5)	1.1049 (3)	0.7686 (2)	0.0422 (10)
C7	−0.0014 (5)	0.9721 (3)	0.7495 (2)	0.0356 (9)
C8	0.0151 (5)	1.3472 (3)	0.7518 (2)	0.0453 (10)
C9	−0.0091 (5)	1.4664 (4)	0.7031 (2)	0.0515 (11)
C10	−0.0859 (5)	1.4660 (3)	0.6124 (2)	0.0478 (10)
C11	−0.1412 (5)	1.3454 (3)	0.5700 (2)	0.0444 (10)
C12	−0.2680 (5)	0.8744 (4)	0.5173 (2)	0.0435 (10)
C13	0.0460 (5)	0.8772 (4)	0.8284 (2)	0.0431 (10)

Table 5. *Selected geometric parameters (Å, °) for (II)*

O1—C1	1.227 (4)	C4—C5	1.410 (5)
O2—C12	1.222 (4)	C4—C11	1.399 (4)
O3—C12	1.308 (4)	C5—C6	1.448 (4)
O4—C13	1.232 (4)	C5—C8	1.404 (4)
O5—C13	1.312 (4)	C6—C7	1.344 (4)
C1—C2	1.485 (5)	C7—C13	1.491 (5)
C1—C7	1.478 (4)	C8—C9	1.377 (5)
C2—C3	1.335 (4)	C9—C10	1.371 (5)
C2—C12	1.504 (5)	C10—C11	1.384 (5)
C3—C4	1.451 (4)		
O1—C1—C7	121.5 (3)	O3—C12—C2	113.9 (3)
O1—C1—C2	118.7 (3)	O4—C13—O5	122.0 (3)
O2—C12—O3	122.7 (3)	O4—C13—C7	122.4 (3)
O2—C12—C2	123.3 (3)	O5—C13—C7	115.6 (3)
O1—C1—C2—C3	−1383 (4)	C3—C2—C12—O3	22.3 (5)
O1—C1—C2—C12	34.6 (5)	C1—C2—C12—O3	−1513 (3)
O1—C1—C7—C6	142.5 (4)	C6—C7—C13—O4	171.7 (4)
O1—C1—C7—C13	−33.3 (5)	C1—C7—C13—O4	−12.1 (5)
C3—C2—C12—O2	−1550 (4)	C6—C7—C13—O5	−5.6 (5)
C1—C2—C12—O2	31.4 (5)	C1—C7—C13—O5	170.6 (3)

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O4^{i}	0.92	1.69	2.604 (3)	175
O5—H5···O2^{ii}	0.92	1.80	2.721 (3)	178

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.

For both compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990*a*); program(s) used to refine structures: *SHELXTL/PC* (Sheldrick, 1990*b*); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1171). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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