Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Phenyl- and mesitylglyoxylic acids: catemeric hydrogen bonding in two α-keto acids

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Received 4 April 2000
Accepted 5 June 2000

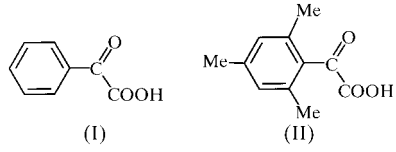
α-Oxobenzeneacetic (phenylglyoxylic) acid, $C_8H_6O_3$, adopts a *transoid* dicarbonyl conformation in the solid state, with the carboxyl group rotated 44.4 (1)° from the nearly planar benzoyl moiety. The heterochiral acid-to-ketone catemers [O···O = 2.686 (3) and H···O = 1.78 (4) Å] have a second, longer, intermolecular O—H···O contact to a carboxyl sp^3 O atom [O···O = 3.274 (2) and H···O = 2.72 (4) Å], with each flat ribbon-like chain lying in the *bc* plane and extending in the *c* direction. In α-oxo-2,4,6-trimethylbenzeneacetic (mesitylglyoxylic) acid, $C_{11}H_{12}O_3$, the ketone is rotated 49.1 (7)° from planarity with the aryl ring and the carboxyl group is rotated a further 31.2 (7)° from the ketone plane. The solid consists of chiral conformers of a single handedness, aggregating in hydrogen-bonding chains whose units are related by a 3_1 screw axis, producing hydrogen-bonding helices that extend in the *c* direction. The hydrogen bonding is of the acid-to-acid type [O···O = 2.709 (6) and H···O = 1.87 (5) Å] and does not formally involve the ketone; however, the ketone O atom in the acceptor molecule has a close polar contact with the same donor carboxyl group [O···O = 3.005 (6) and H···O = 2.50 (5) Å]. This secondary hydrogen bond is probably a major factor in stabilizing the observed *cisoid* dicarbonyl conformation. Several intermolecular C—H···O close contacts were found for the latter compound.

Comment

Our interest in the crystal structures of keto carboxylic acids lies in understanding the molecular characteristics that control their five known hydrogen-bonding modes (Lalancette *et al.*, 1999). The commonest of these, acid dimerization, lacks ketone involvement, but carboxyl-to-ketone chains (catemers) constitute a sizable minority of cases. The remaining types are all relatively rare.

Although oxocarboxylic acids can hydrogen bond internally, the geometric constraints required to stabilize this in the crystal are substantial. Our studies show that intramolecular carboxyl hydrogen bonding in keto acids is usually only possible for seven-membered hydrogen-bonding rings with greatly restricted freedom of rotation (Coté *et al.*, 1996). Internal six-membered hydrogen bonding, which is elegant but is nearly unknown in keto acids (Thompson *et al.*, 1996), becomes easier when the acceptors are carbonyls significantly more basic than a ketone, *e.g.* amides, vinylogous amides, esters, *etc*. Potential opportunities for five-membered intramolecular hydrogen bonding are offered by variants such as peroxyacids and α-keto acids. Although evidence exists in favor of some such arrangements in solution (Schellenberger & Oehme, 1966) and they are cited mechanistically, examples of their existence in the crystalline state are notably absent.

The X-ray literature for α-keto (pyruvic and glyoxylic) acids is not large. Apart from enolized cases (Okabe & Inubushi, 1997; Sheldrick & Trowitzsch, 1983), only four previous crystal structures have appeared, and all are carboxyl dimers without ketone involvement: Cambridge Structural Database (CSD; Cambridge Structural Database, 1999) reference codes CNAPGA10 (Cantrell *et al.*, 1982), COTPAC (Lis & Matuszewski, 1984), DBZPYR (Hamelin & Jeannin, 1980) and PRUVAC (Harata *et al.*, 1977). We present here the crystal structures of phenylglyoxylic acid, (I), and mesitylglyoxylic acid, (II), the hydrogen bonding in both of which involves catemeric arrangements not reported heretofore in α-keto acids. The hydrogen-bonding aggregation of (II), in particular, is unusual among carboxylic acids in general and rare in keto acids.



(I) (II)

Fig. 1 shows the asymmetric unit of (I) with the atom-numbering scheme. The ketone and its ring are nearly coplanar, with a C6—C1—C7—O1 torsion angle of −4.2 (4)°. The carboxyl is rotated so that the O1—C7—C8—O2 torsion angle is 134.3 (3)°. Such *transoid* dicarbonyl arrangements are common in 1,2-dicarbonyl compounds, and the corresponding torsion angles for the other known α-keto acid crystal structures are 144.2 (4) (Cantrell *et al.*, 1982), 169.0 (9) (Lis & Matuszewski, 1984), 179.3 (Hamelin & Jeannin, 1980) and 176.5° (Harata *et al.*, 1977).

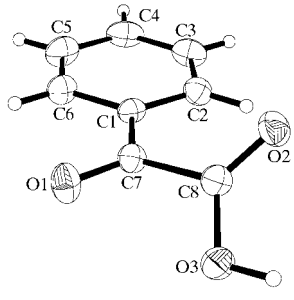


Figure 1
A view of the asymmetric unit of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as spheres of arbitrary radii.

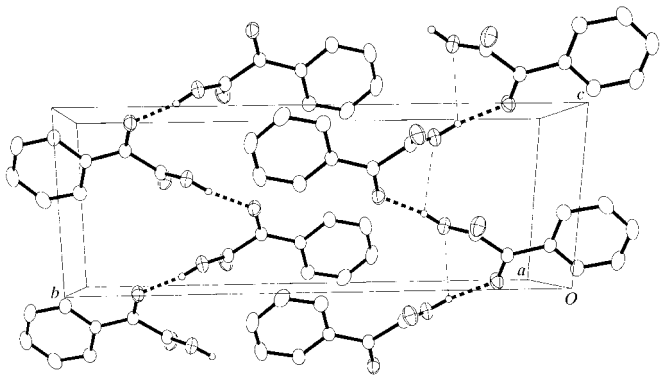


Figure 2
A partial packing diagram for (I) with extracellular molecules, showing the two single-strand catemers in the cell created by acid-to-ketone hydrogen bonds proceeding along a chain of molecules glide-related in **c**. For one of the chains, both the primary (H3···O1^{i}; heavy dashed lines) and the longer secondary (H3···O3^{i}; light dashed lines) hydrogen bonds are shown [symmetry code: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$]. Displacement ellipsoids are drawn at the 20% probability level.

Fig. 2 illustrates the packing in the cell of (I), with acid-to-ketone catemers composed of glide-related molecules of alternating conformational chirality; hydrogen-bond data are given in Table 2. The intrachain units in catemers may be categorized as homochiral (screw- or translationally related) or heterochiral (glide-related), and for keto-acid catemers overall, the order of prevalence observed thus far is screw > translation > glide. Such heterochiral catemers are typically much more flattened and ribbon-like than helices. In (I), the hydrogen-bonding chains proceed in the *c* direction and lie quite flat, parallel to the *bc* plane, with the aromatic rings splayed out alternately to either side of the hydrogen-bonding 'spine'. When these chains are viewed along **a**, a zigzag profile is seen, and the centrosymmetrically related pairs of chains passing counterdirectionally through the cell appear to intermesh. However, these chains actually lie in parallel planes separated by 3.731 Å (half the *a* cell length). In addition to the normal hydrogen bond [H3···O1^{i}; symmetry code: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$], a second, longer, intermolecular O—H···O contact was found involving O3 (see Table 2). This may contribute materially to maintaining the observed *transoid* dicarbonyl conformation.

The geometry of catemers cannot support the carboxyl-disordering mechanisms available in dimerically hydrogen-bonded acids (Leiserowitz, 1976). Hence, in (I), these C—O bond lengths are 1.196 (3) and 1.312 (4) Å, with angles of 123.4 (3) and 110.9 (3)°. Our own survey of 56 keto-acid structures that are not acid dimers gives average values of 1.20 (1) and 1.32 (2) Å, and 124.5 (14) and 112.7 (17)° for these lengths and angles, consonant with typical values of 1.21 and 1.31 Å, and 123 and 112° cited for highly ordered dimeric carboxyls (Borthwick, 1980).

Fig. 3 shows the asymmetric unit of (II) with the atom-numbering scheme. Steric interference with the *ortho* methyl groups forces the ketone significantly out of the aryl plane, producing an O1—C7—C1—C2 torsion angle of −49.0 (8)° (Anca *et al.*, 1967; Florencio & Smith, 1970; Benghiat & Leiserowitz, 1972). Moreover, the carboxyl does not lie fully coplanar with the ketone, as described by the O2—C8—C7—O1 torsion angle of −31.4 (8)°. The dicarbonyl arrangement is not *transoid* as in (I) and the other α-keto acids referenced, but *cisoid*.

For the reasons cited for (I), the carboxyl group of (II) is highly ordered, with C—O bond lengths of 1.221 (6) and 1.303 (6) Å, and C—C—O angles of 121.7 (5) and 113.0 (5)°. However, significant 'hexagonal' rotational disorder is displayed by the H atoms of the *para* methyl group [occupancy ratio 75:25(8)] and one of the *ortho* methyls [occupancy ratio 77:23(8)]. The other *ortho* methyl, toward which the carboxyl is tilted, shows no discernable disorder.

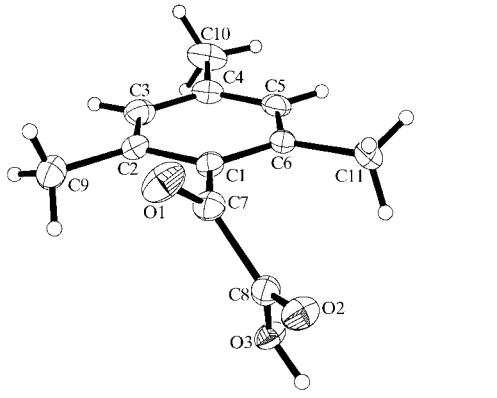


Figure 3
A view of the asymmetric unit of (II) with the atom-numbering scheme. Only the major site occupants are shown for the rotational disorder at C9 (77:23) and C10 (75:25). Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as spheres of arbitrary radii.

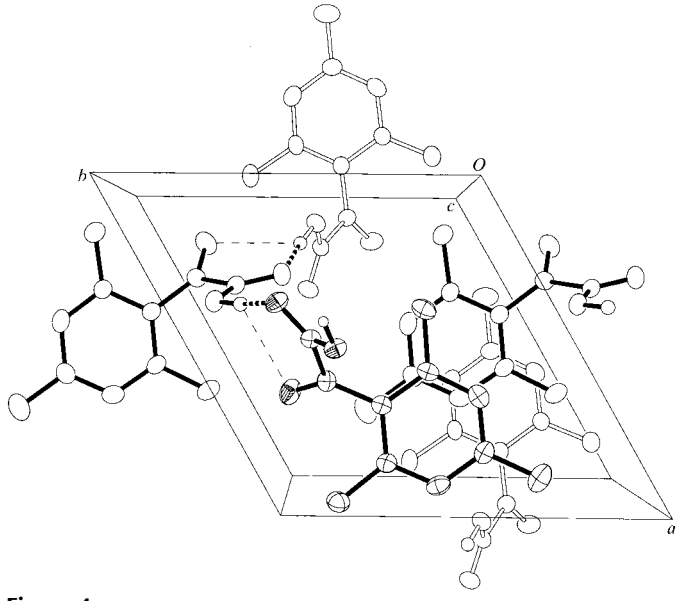


Figure 4
A partial packing diagram for (II) with extracellular molecules, showing the single-strand helix created by acid-to-acid hydrogen bonds proceeding along a chain of molecules screw-related in **c**, with differential shading used to distinguish molecules at progressive depths along the line of sight (cell dimension *c*); heavy dashed lines indicate acid-to-acid hydrogen bonds and light dashed lines indicate secondary hydrogen bonds. Only the major site occupants are shown. Displacement ellipsoids are drawn at the 20% probability level.

Fig. 4 illustrates the packing in the cell and the acid-to-acid hydrogen bonds connecting screw-related molecules to yield a single-strand hydrogen-bonding helix passing through the cell in the *c* direction. Additional molecules are included to show the interleaving of the aromatic rings from adjacent chains. The hydrogen bonding is of the relatively rare acid-to-acid type, seen heretofore in only three keto acid cases: CSD reference codes JEFCOM (Nishizawa *et al.*, 1989), MEMYCA (Haneishi *et al.*, 1974) and NIFGUE (Lalancette *et al.*, 1998). However, beyond this normal hydrogen bonding (see Table 4), the distance separating H3 from the ketone [O1^{ii}; symmetry code: (ii) $-x+y, 1-x, z-\frac{1}{3}$] of the same acceptor molecule is only 2.50 (5) Å. This falls well within the range normally accepted for polar close contacts (Steiner, 1997), and here certainly represents a major polar attraction, probably accounting for the *cisoid* dicarbonyl conformation: in effect, it is a secondary hydrogen bond (see Table 4). Several intermolecular close contacts of the normal C—H···O type were found, involving O1 and O3 and falling within the range of distances and angles (Steiner, 1997; Steiner & Desiraju, 1998) characteristic of polar attractions that contribute materially to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).

The axis of the hydrogen-bonding helix in (II) coincides with one of the 3_1 axes lying within the cell (*i.e.* not passing through the origin), while the aromatic rings 'stack' in a spiral around a second 3_1 axis. Adjacent aromatic rings lying about this axis are not parallel, but lie in planes with a dihedral angle of 5.1° between them. The simplest descriptor for the 'inter-ring distance' is the separation of C5 atoms in adjacent molecules on this 3_1 screw axis; this distance is 3.540 (1) Å, almost exactly one third (33.47%) of the *c*-axis cell length.

Although crystallization in space group $P3_1$ is in itself quite unusual ($P3_1$ and $P3_2$ together represent *ca* 0.14% of all compounds in the CSD), an equally remarkable aspect of the packing of (II) is the presence of only one chiral conformer. Incorporation of a single chiral conformer into crystals precipitating from a solution of an inherently achiral material is rare but far from unknown (Jacques *et al.*, 1981; Desiraju, 1989). Among keto acids, five instances are known of this phenomenon: CSD reference codes CUHCUD (Kawai *et al.*, 1985), JISVAI (Abell *et al.*, 1991), KICRIX (Halfpenny, 1990) and ZEMJIK (McGuire *et al.*, 1995), plus the case of 4-oxocyclohexaneacetic acid (Barcon *et al.*, 1999). It has been shown in a similar case that the particular enantiomer crystallizing from such a solution can depend merely on which one chances to crystallize first, and that rapid stirring seeds the solution and may largely or entirely prevent the enantiomeric species from crystallizing (Kondepudi *et al.*, 1990). In the present instance, since the Flack parameter was not adequate for us to assign a specific handedness to (II) with any confidence, the enantiomer actually illustrated is arbitrary.

The solid-state (KBr) infrared spectrum of (I) displays C═O stretching absorptions at 1741 and 1659 cm^{-1}, consistent with known shifts due to removal of hydrogen bonding from carboxyl C═O and addition of hydrogen bonding to aryl ketones, respectively. In $CHCl_3$ solution, these bands appear at 1733 and 1687 cm^{-1}, accompanied by a separate, sharper, peak of medium intensity at 1776 cm^{-1}, which has been attributed to an internally hydrogen-bonded species (Schellenberger & Oehme, 1966). In CCl_4, four bands are seen at 1780, 1724, 1695 and 1672 cm^{-1}; with successive dilution the band at 1724 cm^{-1} diminishes in intensity relative to the others, without any marked concomitant increase in the one at 1780 cm^{-1}. The spectrum of (II) in KBr has absorptions at 1718 and 1691 cm^{-1}, which shift in $CHCl_3$ solution and partly coalesce to a broad structure, with a maximum at 1703 cm^{-1} and a major shoulder at *ca* 1728 cm^{-1}. As with (I), a separate, sharper, peak of medium intensity appears at 1780 cm^{-1}, presumably due to an internally hydrogen-bonded species.

Experimental

Compound (I) was used as purchased from Acros Organics/Fisher Scientific, Pittsburgh, Pennsylvania, USA (m.p. 342 K). Compound (II) was prepared by saponification of the product resulting from the Friedel–Crafts acylation of mesitylene with ethyl oxalyl chloride. Crystallization from CH_2Cl_2–hexane gave pale-yellow crystals (Dauben & Rogan, 1956; m.p. 392 K). The yellow color in both (I) and (II) is probably inherent, due to the 1,2-dicarbonyl function; simple *cisoid* and *transoid* α-diketone models for both (I) and (II) have a weak $n\rightarrow\pi^*$ absorption in the range 420–466 nm (Woo & Chang, 1945; Leonard & Mader, 1950).

Compound (I)

Crystal data

$C_8H_6O_3$
M_r = 150.13
Monoclinic, $P2_1/c$
a = 7.462 (2) Å
b = 16.513 (5) Å
c = 6.483 (3) Å
β = 115.32 (2)°
V = 722.1 (4) Å^3
Z = 4
D_x = 1.381 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15 reflections
θ = 3.2–12.3°
μ = 0.107 mm^{-1}
T = 293 (2) K
Parallelepiped, colorless
0.64 × 0.50 × 0.30 mm

Data collection

Siemens $P4$ diffractometer
2θ–θ scans
1562 measured reflections
1271 independent reflections
740 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25°
$h = -8 \rightarrow 8$
$k = -1 \rightarrow 19$
$l = -1 \rightarrow 7$
3 standard reflections every 97 reflections
intensity variation: <1.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.153
S = 1.05
1271 reflections
105 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0743P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C7	1.217 (3)	O3—C8	1.312 (4)
O2—C8	1.196 (3)		
O2—C8—C7	123.4 (3)	O3—C8—C7	110.9 (3)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^{i}	0.92 (4)	1.78 (4)	2.686 (3)	168 (4)
O3—H3···O3^{i}	0.92 (4)	2.72 (4)	3.274 (2)	120 (3)

Symmetry code: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

Compound (II)

Crystal data

$C_{11}H_{12}O_3$
M_r = 192.21
Trigonal, $P3_1$
a = 9.1210 (10) Å
c = 10.5760 (10) Å
V = 761.97 (14) Å^3
Z = 3
D_x = 1.257 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17 reflections
θ = 5.6–12.0°
μ = 0.091 mm^{-1}
T = 248 (2) K
Block, colorless
0.30 × 0.28 × 0.26 mm

Data collection

Siemens $P4$ diffractometer
2θ–θ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997)
T_{min} = 0.967, T_{max} = 0.977
2050 measured reflections
1772 independent reflections
574 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 25°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 12$
3 standard reflections
every 97 reflections
intensity variation: <3.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.127
S = 1.02
886 reflections
141 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Refinement of (I) with Friedel data led to an inconclusive Flack (1983) value of 0.3 (3); therefore, for the final refinement, the Friedel data were merged. All H atoms for both (I) and (II) were found in electron-density difference maps but were placed in calculated positions and allowed to refine as riding models. For (I), the displacement parameters of the phenyl-ring H atoms were refined as a group and had a group U_{iso} of 0.085 (5) Å^2. For (II), the *para* methyl H atoms and one of the two *ortho*-group methyl H atoms were treated as disordered, with two different sets of three H atoms each [occupancy ratio 77:23(8) for C9 and 75:25(8) for C10], with a group U_{iso} of 0.09 (2) Å^2 for both sets. A group U_{iso} of 0.063 (9) Å^2 was found for the H atoms of the C11 methyl. The isotropic displacement parameters of the two phenyl H atoms were allowed to refine individually.

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C7	1.213 (6)	O3—C8	1.303 (6)
O2—C8	1.221 (6)		
O2—C8—C7	121.7 (5)	O3—C8—C7	113.0 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^{ii}	0.88 (5)	2.50 (5)	3.005 (6)	117 (3)
O3—H3···O2^{ii}	0.88 (5)	1.87 (5)	2.709 (6)	159 (4)

Symmetry code: (ii) $-x+y, 1-x, z-\frac{1}{3}$.

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*.

The authors would like to dedicate this paper to a valued colleague, Emeritus Professor Benjamin Carroll on the occasion of his 90th birthday.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1604). Services for accessing these data are described at the back of the journal.

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