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1′-Acetylferrocene-1-carboxylic acid: an instance of hydrogen bonding in the rare dimeric acid-to-ketone mode

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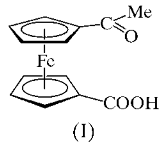
The title compound, [Fe($C_6H_5O_2$)(C_7H_7O)], adopts a conformation involving partial staggering of its rings and aggregates in the solid as acid-to-ketone hydrogen-bonding dimers [O···O = 2.720 (4) Å and O—H···O = 164°] having centrosymmetrically related components. Close intermolecular C—H···O contacts were found to both carboxyl O atoms.

Comment

Placing ketone and carboxylic acid groups within the same molecule brings together a single hydrogen-bond donor and two potential acceptors. The result, in the absence of other hydrogen-bonding groups, is five known modes of hydrogen bonding. Our continuing study of keto-acid crystal structures has so far explored these modes and the factors that control them for some 70 compounds. Two of the modes do not involve the ketone, and correspond to the common pairing and much rarer chain modes of simple acids (Leiserowitz, 1976; Lalancette *et al.*, 1998). Of the three known acid-to-ketone modes, chains (catemers) constitute a sizable overall minority of cases, while intramolecular hydrogen bonds are only very occasionally observed (Coté *et al.*, 1996). Instances of acid-to-ketone dimerization, however, are so rare (with only four literature examples) that until our examination of the presently reported compound, this hydrogen-bonding mode had remained the only one we ourselves had never observed. Compound (I) belongs, at least formally, to the category of δ-keto acids, one generally rich in hydrogen-bonding types, embracing catemers of the screw, translation and glide types, as well as dimers and hydrated patterns.

Fig. 1 presents a view of the asymmetric unit of (I) with its numbering. The energy difference between the staggered and eclipsed rotational conformations in ferrocene itself is about 2 kcal mol^{-1} (Butler & Harrod, 1989), with an energy barrier of only 2–5 kcal mol^{-1} (Schlögl, 1967). The barrier is *ca* 3 kcal mol^{-1} for decamethylferrocene (Aime *et al.*, 1992), and is generally so low for simple substituted ferrocenes that conformations in crystals are expected to be determined mainly by associational forces (Cotton & Wilkinson, 1966). Indeed, examples of both eclipsed and staggered conformations (and ones in between) are found in crystal structures, although the former are more common (Kerber, 1995).



(I)

Where perfect staggering of the two rings in ferrocene requires a rotational offset of 36°, the conformation adopted by (I) involves only 20.7 (5)° of axial twist, placing the two substituents roughly halfway between an eclipsed and a 'synclinal' arrangement. The two rings are not quite parallel, having a dihedral angle of 1.5 (3)°. The substituents lie nearly coplanar with their respective rings; the dihedral angle for the carboxyl *versus* its ring is 2.3 (3)°, while that for the acetyl group is 6.2 (3)°, with the two carbonyl dipoles aligned in the same direction.

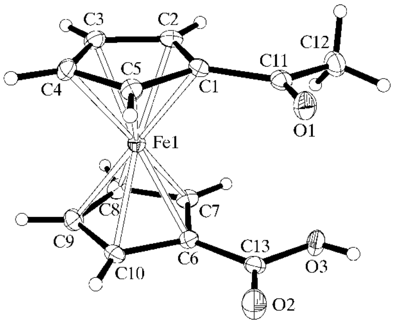


Figure 1
A view of the asymmetric unit of (I) with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level.

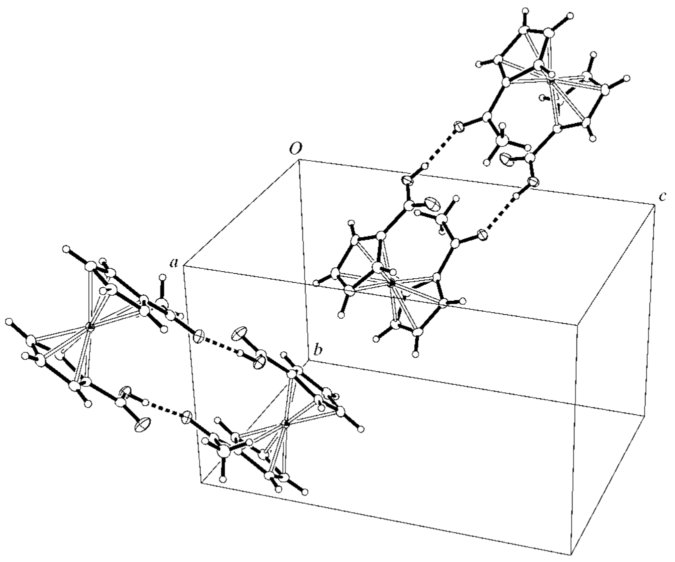


Figure 2
A packing diagram showing the acid-to-ketone dimerization across the *b* and *c* edges of the chosen cell. Displacement ellipsoids are shown at the 20% probability level.

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Averaging of the C—O bond lengths and C—C—O angles by disorder is often observed in carboxyl acids, but only in the acid-to-acid dimerization mode (Leiserowitz, 1976), which permits the averaging processes. In (I), these C—O bond lengths are 1.214 (4)/1.334 (5) Å, with angles of 123.7 (4)/112.9 (3)° (Table 1). Our own survey of 56 keto-acid structures which are not acid dimers gives average values of 1.200 (10)/1.32 (2) Å and 124.5 (14)/112.7 (17)°, respectively, for these lengths and angles, in accord with typical values of 1.21/1.31 Å and 123/112° cited for highly ordered dimeric carboxyls (Borthwick, 1980). The methyl group displays no detectable rotational disorder.

Fig. 2 shows the centrosymmetric pairing of asymmetric units *via* mutual acid-to-ketone hydrogen bonds [O···O = 2.720 (4) Å and O—H···O = 164°]. In the packing of the chosen cell, all the dimerization occurs at the boundaries, across the *b* and *c* edges. In the X-ray literature, such acid-to-ketone dimerization is the least often reported among keto-acid hydrogen-bonding modes, and (I) joins a very small number of other examples, *viz*. Cambridge Structural Database (CSD; Cambridge Structural Database, 1999) refcodes BOZTUF (Peeters *et al.*, 1983), FAZGAO (Nuhrich *et al.*, 1986), JIKDEM (Abell *et al.*, 1991) and TEVGIK (Kosela *et al.*, 1995).

We have characterized the geometry of hydrogen bonding to carbonyls using a combination of the H···O═C angle and H···O═C—C torsion angle. These describe the approach of the acid H atom to the O atom in terms of its deviation from, respectively, C═O axiality (ideal = 120°) and planarity with the carbonyl (ideal = 0°). In (I), the values for these two angles are 129 and −10°, respectively.

Close intermolecular C—H···O contacts were found for O2 (2.52 Å to a methyl hydrogen, H12*A*, in the dimeric partner and 2.46 Å to H10 in a *c* translation of the dimeric partner), as well as for O3 (2.56 Å to H2 in a *c* translation of a glide-related molecule). These contacts all lie within the 2.7 Å range we usually employ for non-bonded H···O packing interactions (Steiner, 1997). Using compiled data for a large number of C—H···O contacts, Steiner & Desiraju (1998) have found significant statistical directionality even as far out as 3.0 Å, and conclude that these are legitimately viewed as 'weak hydrogen bonds', with a greater contribution to packing forces than simple van der Waals attractions.

The solid-state (KBr) IR spectrum of (I) has a C═O stretching absorption at 1720 cm^{-1} (acid), plus a poorly resolved pair of peaks at 1637 and 1633 cm^{-1} (ketone), consistent with known shifts produced when hydrogen bonding is removed from carboxyl C═O and added to a ketone. In $CHCl_3$ solution, these bands appear at 1712 and 1671 cm^{-1}.

Experimental

When the procedure of Yamakawa *et al.* (1963) failed to yield any useful product, compound (I) was prepared *via* acetylation of *N,N*-diphenylcarbamylferrocene according to the procedure of Little & Eisenthal (1960). Flash chromatography followed by sublimation and crystallization from diethyl ether gave crystals (m.p. 431 K) suitable for X-ray analysis.

Crystal data

$[Fe(C_6H_5O_2)(C_7H_7O)]$	D_x = 1.623 Mg m^{-3}
M_r = 272.08	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 26 reflections
a = 9.331 (5) Å	θ = 2.7–8.4°
b = 8.769 (5) Å	μ = 1.35 mm^{-1}
c = 13.616 (8) Å	T = 296 (2) K
β = 92.290 (16)°	Flat plate, red–orange
V = 1113.2 (11) Å^3	0.42 × 0.30 × 0.06 mm
Z = 4	

Data collection

Siemens *P*4 diffractometer	R_{int} = 0.034
$2\theta/\theta$ scans	θ_{max} = 25.0°
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997)	$h = -11 \rightarrow 1$
T_{min} = 0.68, T_{max} = 0.92	$k = -10 \rightarrow 1$
2676 measured reflections	$l = -16 \rightarrow 16$
1957 independent reflections	3 standard reflections
1441 reflections with $I > 2\sigma(I)$	every 97 reflections intensity variation: <2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0340P)^2 + 0.3257P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.042	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.095	$(\Delta/\sigma)_{max} < 0.001$
S = 1.03	$\Delta\rho_{max}$ = 0.30 e Å^{-3}
1957 reflections	$\Delta\rho_{min}$ = −0.31 e Å^{-3}
155 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O2—C13	1.214 (4)	O3—C13	1.334 (5)
O2—C13—C6	123.7 (4)	O3—C13—C6	112.9 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^{i}	0.82	1.92	2.720 (4)	164

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

All the H atoms in (I) were found in electron-density difference maps but were placed in calculated positions (0.96 Å for methyl H atoms, 0.98 Å for ferrocene H atoms, and 0.82 Å for the carboxyl H atom) and allowed to refine as riding models on their respective C and O atoms. Their displacement parameters were fixed at 120% of those of their attached C atoms and 150% of the attached O atom.

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: FR1360). Services for accessing these data are described at the back of the journal.

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