

Disordered *syn-anti* hydrogen-bonded chains in 3-(ferrocenylcarbonyl)-propionic acid

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Received 21 February 2003

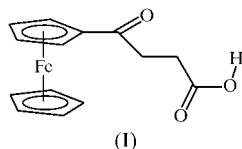
Accepted 18 March 2003

Online 10 April 2003

The title compound, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_9\text{H}_9\text{O}_3)]$, has Fe-centroid distances of 1.6551 (11) and 1.6445 (11) Å to the cyclopentadienyl rings. The carboxyl group forms hydrogen bonds in the extremely rare *syn-anti* chain motif, with O...O distances of 2.667 (3) and 2.655 (3) Å. The carboxyl group and the hydrogen-bonded chains are disordered.

Comment

In the process of preparing 2-propenyl 4-ferrocenyl-4-oxobutanoate, reported earlier by our group (Giralés *et al.*, 2001), the title compound, (I), was used as a starting material. It is a common, commercially available, ferrocene, but its crystal structure has not been reported previously, only that of a complex of its carboxylate with a zirconocene (Ma *et al.*, 1989). Thus, we undertook to determine its structure at low temperature.



The molecule of (I) is depicted in Fig. 1, which shows the normal eclipsed conformation of the cyclopentadienyl (Cp) rings. The Fe-centroid distance to the unsubstituted ring [1.6551 (11) Å] is slightly longer than that to the substituted ring [1.6445 (11) Å], and the centroid-Fe-centroid angle is linear [179.95 (7)°]. The unsubstituted Cp ring forms a weak intramolecular C—H...O hydrogen bond (Steiner & Desiraju, 1998) with the carboxyl group (Table 2). This hydrogen bond was also present in 2-propenyl 4-ferrocenyl-4-oxobutanoate (Giralés *et al.*, 2001), but involved an ester carbonyl O atom, was somewhat shorter [3.289 (2) Å] and slightly less linear (159°).

The carboxyl group is disordered, with equal C—O distances midway between those expected for ordered carboxyl groups (Borthwick, 1980). The carboxyl H atoms must also be disordered over two half-populated positions, and both sites were clearly visible in difference maps. The half H atom on O3 lies in the *synplanar* position usually observed in carboxylic acids, while that on O2 lies in the rare *antiplanar* position normally found only in intramolecular hydrogen bonds (Leiserowitz, 1976). The *synplanar* conformation is more stable by 8–17 kJ mol⁻¹ (Miyazawa & Pitzer, 1959; Lide, 1964; Karpfen, 1984; Marcoccia *et al.*, 1990). The *antiplanar* conformation was apparently unknown in intermolecular hydrogen bonds before about 1980 (Fujinaga & James, 1980). We have previously encountered it in hydrogen bonds to water molecules from carboxyl groups on crown ethers and their metal ion complexes (Dutton *et al.*, 1990, 1993). In those cases, the water molecule was encapsulated by the crown, which had insufficient flexibility to allow a *syn-H* atom on the carboxyl group to donate to the water molecule. This could only happen with the *antiplanar* conformation, so those cases were somewhat analogous to intramolecular hydrogen bonds.

Hydrogen bonding involving the carboxyl groups is illustrated in Fig. 2. Both partially occupied carboxyl H-atom positions lie near inversion centers, *viz.* that on O2 near 0, $\frac{1}{2}$, 0, and that on O3 near 0, $\frac{1}{2}$, $\frac{1}{2}$. Thus, the carboxyl groups form disordered hydrogen-bonded chains running in the [001]

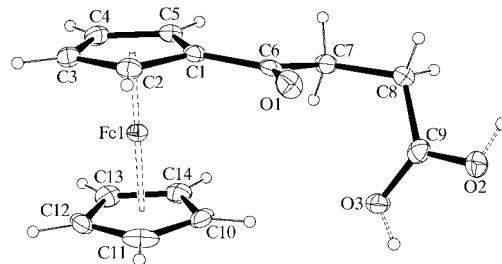


Figure 1

View of the title compound, showing the atom-numbering scheme and ellipsoids at the 50% probability level. Dashed bonds in the carboxyl group are to half-populated H-atom sites.

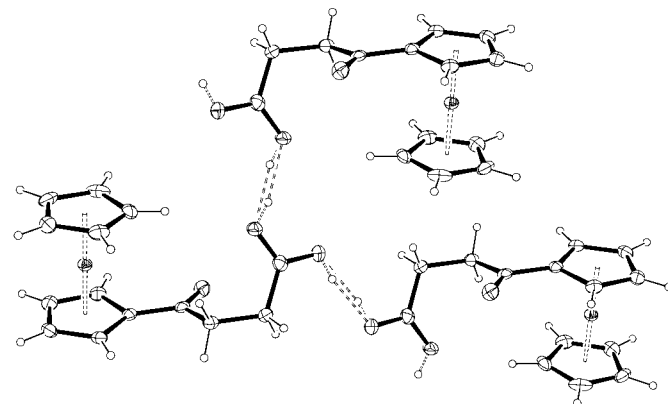


Figure 2

A portion of the disordered hydrogen-bonded chain in (I).

direction, and these chains are of the rare *syn-anti* type, similar to that observed in the isostructural compounds 4-bromocubane-1-carboxylic acid and its iodo analog (Kuduvu *et al.*, 1999). Ordered *syn-anti* chains are also present in other cubane carboxylic acids (Ermer & Lex, 1987) and seem to be the dominant pattern in that class of compounds, despite occurring for an estimated 0.15% of all organic carboxylic acids (Kuduvu *et al.*, 1999). The existence of the antiplanar conformation in the carboxyl group of the cubane acids was attributed to its allowance of C—H···O hydrogen bonding involving the acidic cubane H atoms, an idea which is supported by the structure of formic acid—HF (Wiechert *et al.*, 1997), which is able to form C—H···O hydrogen bonds in conjunction with *anti-anti* carboxyl chains. The role of C—H···O hydrogen bonding in allowing the less stable *anti* carboxyl group conformation in (I) is less clear. In addition to the intramolecular interaction mentioned above, (I) has a shorter but less linear intermolecular hydrogen bond involving atom C13 and ketone atom O1 (Table 2). However, it is not obvious why (I) could not form the ubiquitous *syn-syn* carboxyl dimers or *syn-syn* chains and still be able to form both the observed intra- and intermolecular C—H···O hydrogen bonds.

The cell dimensions at 292 K, measured using a CAD-4 diffractometer with Cu $K\alpha$ radiation (25 reflections, $14 < \theta < 27^\circ$), are $a = 5.7331$ (4), $b = 27.099$ (3), $c = 7.7730$ (6) Å and $\beta = 100.622$ (5)°.

Experimental

The title compound was synthesized and purified following the procedure of Suzuki *et al.* (1993). It was then further purified using column chromatography (hexanes/diethyl ether, 9:1). Crystals used for X-ray analysis were grown from a hexanes/diethyl ether (9:1) solution.

Crystal data

[Fe(C ₅ H ₅)(C ₉ H ₉ O ₃)]	$D_x = 1.631 \text{ Mg m}^{-3}$
$M_r = 286.10$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2661 reflections
$a = 5.673$ (2) Å	$\theta = 2.5\text{--}27.5^\circ$
$b = 26.892$ (6) Å	$\mu = 1.29 \text{ mm}^{-1}$
$c = 7.764$ (2) Å	$T = 120 \text{ K}$
$\beta = 100.433$ (10)°	Prism, orange
$V = 1164.9$ (6) Å ³	$0.20 \times 0.13 \times 0.07 \text{ mm}$
$Z = 4$	

Table 1

Selected geometric parameters (Å, °).

Fe1—C1	2.032 (2)	Fe1—C12	2.043 (2)
Fe1—C2	2.043 (2)	Fe1—C13	2.049 (2)
Fe1—C3	2.058 (2)	Fe1—C14	2.045 (2)
Fe1—C4	2.051 (2)	O1—C6	1.224 (3)
Fe1—C5	2.036 (2)	O2—C9	1.274 (3)
Fe1—C10	2.045 (2)	O3—C9	1.271 (3)
Fe1—C11	2.046 (2)		
O3—C9—O2	120.5 (2)	O2—C9—C8	120.6 (2)
O3—C9—C8	118.8 (2)		
C2—C1—C6—O1	−11.9 (3)	C7—C8—C9—O2	−155.7 (2)
C6—C7—C8—C9	62.3 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O2 ⁱ	0.84	1.84	2.667 (3)	169
O3—H3O···O3 ⁱⁱ	0.84	1.83	2.655 (3)	166
C10—H10···O3	0.95	2.51	3.443 (3)	168
C13—H13···O1 ⁱⁱⁱ	0.95	2.54	3.326 (3)	140

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

Data collection

Nonius KappaCCD diffractometer	13 367 measured reflections
(fitted with an Oxford Cryo-systems Cryostream cooler)	2673 independent reflections
ω scans with κ offsets	2059 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (HKL SCALEPACK; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.025$
$T_{\text{min}} = 0.804, T_{\text{max}} = 0.914$	$\theta_{\text{max}} = 27.5^\circ$
	$h = -7 \rightarrow 7$
	$k = -34 \rightarrow 34$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0150P)^2 + 1.1438P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.073$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
2673 reflections	$\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$
166 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0019 (5)

H atoms were placed in calculated positions [C—H = 0.95–0.99 Å and O—H = 0.84 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O})$], and thereafter treated as riding. A torsional parameter was refined for each OH group. The carboxyl groups are disordered, with the H atoms half-populated and lying near inversion centers.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2002).

The purchase of the diffractometer was made possible by grant No. LEQSF(1999–2000)-ESH-TR-13, administered by the Louisiana Board of Regents. We thank Professor Leslie Leiserowitz for helpful suggestions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1207). Services for accessing these data are described at the back of the journal.

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