

Ferrocene compounds: methyl 1'-aminoferrocene-1-carboxylate

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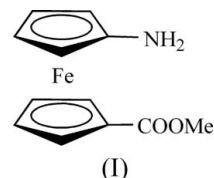
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The title compound, $[\text{Fe}(\text{C}_5\text{H}_6\text{N})(\text{C}_7\text{H}_7\text{O}_2)]$, features one strong intermolecular hydrogen bond of the type $\text{N}-\text{H}\cdots\text{O}=\text{C}$ [$\text{N}\cdots\text{O} = 3.028$ (2) Å] between the amine group and the carbonyl group of a neighbouring molecule, and *vice versa*, to form a centrosymmetric dimer. Furthermore, the carbonyl group acts as a double H-atom acceptor in the formation of a second, weaker, hydrogen bond of the type $\text{C}-\text{H}\cdots\text{O}=\text{C}$ [$\text{C}\cdots\text{O} = 3.283$ (2) Å] with the methyl group of the ester group of a second neighbouring molecule at $(x, -y - \frac{1}{2}, z - \frac{1}{2})$. The methyl group also acts as a weak hydrogen-bond donor, symmetry-related to the latter described $\text{C}-\text{H}\cdots\text{O}=\text{C}$ interaction, to a third molecule at $(x, -y - \frac{1}{2}, z + \frac{1}{2})$ to form a two-dimensional network. The cyclopentadienyl rings of the ferrocene unit are parallel to each other within 0.33 (3)° and show an almost eclipsed 1,1'-conformation, with a relative twist angle of 9.32 (12)°. The ester group is twisted slightly [11.33 (8)°] relative to the cyclopentadienyl plane due to the above-mentioned intermolecular hydrogen bonds of the carbonyl group. The N atom shows pyramidal coordination geometry, with the sum of the $X-\text{N}-\text{Y}$ angles being 340 (3)°.

Comment

The artificial amino acid 1-aminoferrocene-1'-carboxylic acid (Fca) (Heinze & Schlenker, 2004; Barišić *et al.*, 2002; Butler & Quayle, 1998) plays an important role in the fields of organometallic oligomers (Khan *et al.*, 2006; Heinze & Siebler, 2007) and bioorganometallic chemistry as a building block for artificial peptides, and therefore as an organometallic β -turn mimetic in ferrocene conjugates of amino acids and peptides (van Staveren & Metzler-Nolte, 2004; Kirin *et al.*, 2006). The latter application is based on the favourable inter-ring distance of ferrocene of about 3.3 Å, close to the $\text{N}\cdots\text{O}$ distance in β -sheets of peptides. Thus, many Fca derivatives and related compounds have been investigated on the basis of their ability to form hydrogen bonds and in order to study the respective bonding patterns (Okamura *et al.*, 1998; Pavlović *et al.*, 2002, 2003; Heinze & Schlenker, 2004; Chowdhury *et al.*, 2006; Barišić *et al.*, 2006; Heinze & Siebler, 2007).

The synthetic procedure for obtaining and spectroscopic data of the title compound, (I), have been described previously by Butler & Quayle (1998) and Barišić *et al.* (2002), but any attempts at structural characterization were without success due to twinning problems. It was proposed that (I) crystallizes as a hydrogen-bonded dimer (Butler & Quayle, 1998), which is now confirmed by the crystal structure analysis presented here (Fig. 1). In contrast with previous attempts, no twinning problem was observed for the crystal studied here.



The asymmetric unit of (I) consists of one independent molecule. The mean $\text{Fe}-\text{C}$ bond distance is 2.0509 (15) Å. The mean $\text{C}-\text{C}$ bond distance for the cyclopentadienyl rings is 1.4250 (9) Å. The Cp rings are parallel to each other within 0.33 (3)°. The distances of Fe to $\text{Cg}1$ (the centroid of Cp1, atoms C1–C5) and $\text{Cg}2$ (the centroid of Cp2, atoms C6–C10) are 1.6608 (7) and 1.6481 (7) Å, respectively. The orientation of the Cp rings deviates from the eclipsed 1,1'-conformation by a maximum of 9.32 (12)°, as defined by the torsion angles $\text{C}(\text{any C atom in Cp1})-\text{Cg}1-\text{Cg}2-\text{C}(\text{any C atom in Cp2})$, where 0° describes the fully eclipsed and 36° the fully staggered conformation. The dihedral angle between the mean plane of $\text{C}6-\text{COOMe}$ and the Cp2 mean plane is 11.33 (8)°, defined by non-H atoms. This is probably due to the intermolecular hydrogen bonds (see below). Atoms H1 and H2 of the amine group could be located reliably and refined with restrained $\text{N}-\text{H}$ bond lengths (Table 1). The sum of the $X-\text{N}-\text{Y}$ angles [340 (3)°] quantifies the pyramidal geometry of the amine group. The bond between atoms C6 and C11 shows some π character, due to extension of the Cp π system to the $\text{C}=\text{O}$ group. The same characteristics can be found for the $\text{N}1-\text{C}1$ bond, where the distance is between a single and a double bond (Allen *et al.*, 1987). Similar geometric parameters

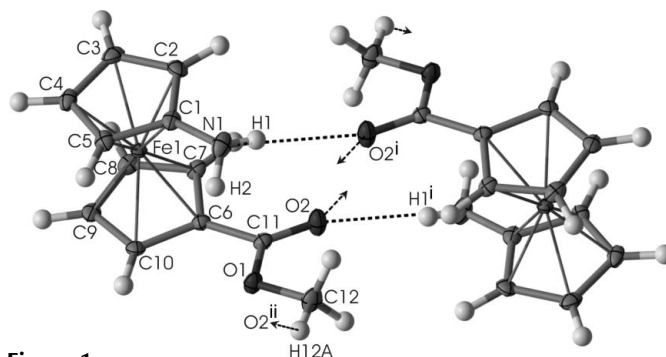
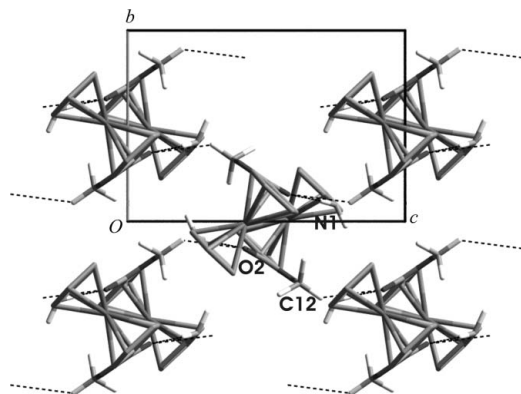


Figure 1

A view of the dimer of (I), connected *via* pairs of intermolecular $\text{N}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds (dashed lines), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed arrows indicate $\text{C}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds to neighbouring molecules. [Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $x, -y - \frac{1}{2}, z + \frac{1}{2}$.]


Figure 2

A partial packing diagram of the dimers of (I), viewed parallel to the *a* axis. Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

for partial double bonds were also found for related compounds, *viz.* Fc-NH₂ (Heinze & Schlenker, 2004), Fc-COOME (Beck *et al.*, 2001) and MeOOC-NH-Fc-COOME (Pavlović *et al.*, 2002).

As mentioned above and proposed by Butler & Quayle (1998), (I) forms a centrosymmetric dimer with a neighbouring molecule at $(-x, -y, -z + 1)$, connected *via* a pair of N—H...O=C hydrogen bonds between the amine and carbonyl groups (Fig. 1 and Table 2). The O atom of the ester group of (I) acts as a double H-atom acceptor in the formation of another hydrogen bond of the type C12—H12A...O2=C11 with a second at neighbour $(x, -y - \frac{1}{2}, z - \frac{1}{2})$. Furthermore, the methyl group interacts, symmetry-related to the latter described hydrogen bond, with a third molecule at $(x, -y - \frac{1}{2}, z + \frac{1}{2})$ in the latter described fashion. In conclusion, each dimer is connected to four other dimers, which leads to the formation of a two-dimensional network parallel to the *bc* plane along the 2₁ screw axis (*b* axis) and the *c*-glide plane (Table 2 and Fig. 2).

Experimental

Boc-NH-Fc-COOME (2.19 g, 6.1 mmol) was dissolved in dichloromethane (20 ml) and trifluoroacetic acid (20 ml) was added at 273 K. The resulting red solution was warmed to room temperature and stirred for 2 h. The solvent was removed *in vacuo*, and the residue was dissolved in water (200 ml) and washed with diethyl ether (3 × 50 ml). The water layer was made alkaline (pH 8) by the addition of 5% aqueous NaOH solution and extracted with ethyl acetate (3 × 100 ml) until the water layer was nearly colourless. The organic layer was dried over MgSO₄ and the solvent removed *in vacuo* (yield 89%, 1.40 g, 5.4 mmol). The product, (I) (20 mg), was dissolved in ethyl acetate (3 ml) and hexane (1 ml) was added. Crystallization at 277 K yielded the title compound, (I), as orange plates.

Crystal data

[Fe(C ₅ H ₆ N)(C ₇ H ₇ O ₂)]	$V = 1069.66 (3) \text{ \AA}^3$
$M_r = 259.08$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 13.72031 (18) \text{ \AA}$	$\mu = 1.39 \text{ mm}^{-1}$
$b = 7.34436 (10) \text{ \AA}$	$T = 173 \text{ K}$
$c = 11.04962 (14) \text{ \AA}$	$0.30 \times 0.20 \times 0.08 \text{ mm}$
$\beta = 106.1201 (7)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	25686 measured reflections
Absorption correction: multi-scan (MULABS; Spek, 2009)	2763 independent reflections
$T_{\min} = 0.680, T_{\max} = 0.897$	2425 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.077$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.071$	$\Delta\rho_{\max} = 0.33 \text{ e \AA}^{-3}$
$S = 1.07$	$\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$
2763 reflections	
153 parameters	
2 restraints	

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

C6—C11	1.469 (2)	O1—C12	1.4501 (18)
C11—O2	1.2133 (17)	N1—C1	1.396 (2)
C11—O1	1.3390 (17)	N1—H2	0.869 (16)
O2—C11—O1	123.03 (13)	C1—N1—H1	112.4 (17)
O2—C11—C6	124.03 (13)	C1—N1—H2	115.1 (16)
O1—C11—C6	112.94 (12)	H1—N1—H2	113 (2)
C11—O1—C12	115.59 (12)		

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1...O2 ⁱ	0.831 (16)	2.21 (2)	3.028 (2)	167 (2)
C12—H12A...O2 ⁱⁱ	0.98	2.49	3.283 (2)	138

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

The positions of all H atoms, except those of the amine group (H1 and H2), were generated with appropriate geometric constraints and allowed to ride on their respective parent C atoms, with C—H = 1.00 Å (0.98 Å for methyl C—H) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ [1.5 $U_{\text{eq}}(\text{C})$ for methyl H atoms]. The H atoms of the amine group were found in a difference Fourier map and refined with bond lengths restrained to 0.87 (2) Å.

Data collection: APEX2 (Bruker, 2006); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: Mercury (Version 2.3; Macrae *et al.*, 2006); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3033). Services for accessing these data are described at the back of the journal.

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