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Methyl 3-ferrocenylpropanoate

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Ferrocene compounds, part XXXII.

The title compound, [Fe(C_5H_5)($C_9H_{11}O_2$)], was prepared and characterized by spectroscopic methods and crystal structure determination. The average values of the bond distances between the C atoms in the cyclopentadienyl rings are 1.422 (3) Å in the substituted and 1.404 (4) Å in the unsubstituted ring. The Fe—C bond distances range from 2.036 (2) to 2.061 (2) Å and the bond angles in both rings range from 107.1 (2) to 108.9 (2)°. The cyclopentadienyl rings are almost parallel and deviate only slightly from the eclipsed conformation. The molecules are connected into dimers by very weak C—H···O intermolecular hydrogen bonds.

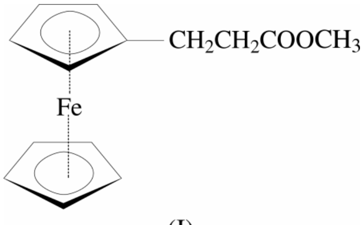
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.099
Data-to-parameter ratio = 20.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The study of ferrocene compounds has led to important developments in the fields of catalysis and biocatalysis (Patti & Nicolosi, 2000), polymers (Gonsalves & Chen, 1995) and bioorganometallic chemistry (Severin *et al.*, 1998; Metzler-Nolte, 2001). Various functional groups on the cyclopentadienyl (Cp) rings influence the electronic properties of ferrocene derivatives and this leads to different applications of these complexes (Oberhoff *et al.*, 1996). The present study of methyl 3-ferrocenylpropanoate, (I), forms part of wider research on differently substituted ferrocene compounds, their synthesis, stereochemistry and structural analysis (Zorić *et al.*, 1999; Lapić & Rapić, 2000; Barišić *et al.*, 2002; Cetina *et al.*, 2002; Pavlović *et al.*, 2002).



(I)

The molecular structure of (I) is shown in Fig. 1. The distances between the C atoms in the Cp rings are greater in the substituted ring (C1–C5) than in the unsubstituted ring (C6–C10), with average values of 1.422 (3) and 1.404 (4) Å, respectively (Table 1). The Fe—C bond distances range from 2.036 (2) to 2.061 (2) Å. The longest Fe—C distance is Fe—C1, as was generally observed in monosubstituted ferrocene derivatives with the isolated π-electron system (Allen & Kennard, 1993). The values of the bond angles in the Cp rings range from 107.1 (2) to 108.9 (2)° (Table 1). The bond distances in the ferrocenyl skeleton and the methylcarboxylate group are in agreement with those found in other ferrocenes having a methylcarboxylate group on one of the rings (Luo *et*

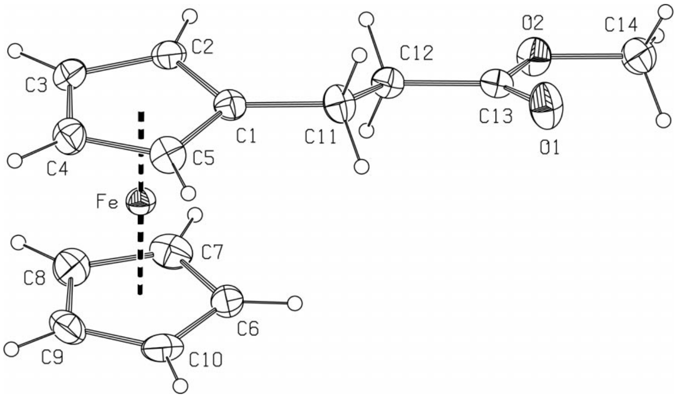


Figure 1
View of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 20% probability level.

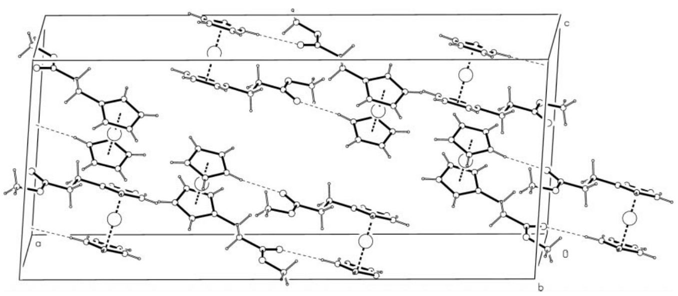


Figure 2
Crystal-packing diagram of (I).

al., 1990; Podlaha *et al.*, 1996; Hobi *et al.*, 1997; Beck *et al.*, 2001; Costa *et al.*, 2001). The geometry of the title compound is also in a good agreement with the structure of 3-ferrocenylpropanoic acid (Cetina *et al.*, 2002). In these two structures, a difference in the orientation of the Cp rings was observed; in the title compound they deviate only slightly from the eclipsed conformation. The values of the corresponding pseudo-torsion angles defined by joining two eclipsing Cp C atoms through the ring centroids ($C-Cp_1-Cp_2-C$; Cp_1 and Cp_1 are the Cp ring centroids) are in the range 1.9 (2)–2.6 (2)°. In the structure of 3-ferrocenylpropanoic acid, the Cp rings are twisted from the eclipsed conformation by 8.3 (2)° (average value). The Cp rings are almost parallel [dihedral angle 1.3 (1)°] and the largest observed deviation of the C atoms from their mean planes is 0.001 (3) Å. Furthermore, the Fe atom is almost equidistant from the centroids of the Cp rings [$Fe-Cp_1$ = 1.651 (1) Å and $Fe-Cp_2$ = 1.655 (1) Å] and the angle defined by the ring centroids and the Fe atom deviates very slightly from 180° [$Cp_1-Fe-Cp_2$ = 178.9 (1)°].

Atom C1 of the ferrocenyl skeleton and atom C13 of the methoxycarbonyl group are antiperiplanar, as are atom C14 of the methyl group and atom C12 of the ferrocenylethyl skeleton. The values of the corresponding torsion angles C1—C11—C12—C13 and C14—O2—C13—C12 are −178.7 (2) and −178.8 (2)°, respectively. The plane defined by the atoms C12, C13, O1 and O2 is more twisted with respect to the substituted Cp ring [dihedral angle 19.4 (1)°], compared to the situation in 3-ferrocenylpropanoic acid, where they are nearly coplanar. The same plane is also parallel with the shortest crystallographic axis *b* [dihedral angle 0.5 (1)°].

The molecules are connected by a very weak intermolecular hydrogen bond $C6-H6\cdots O1^{i}$ [symmetry code: (i) $-x, +y, \frac{1}{2}-z$], forming dimers (Fig. 2). The $D\cdots A$ and $H\cdots A$ distances are 3.433 (3) and 2.51 Å, respectively, and the $D-H\cdots A$ angle is 170°. A survey of the Cambridge Structural Database (Allen & Kennard, 1993) lists three structures of ferrocene derivatives with the same type of C(Cp)—H···O(=C) hydrogen-bonded dimers (Kałuski *et al.*, 1979; Abrán *et al.*, 1999; Ansorge *et al.*, 2000).

Experimental

The title compound (Roberts *et al.*, 1967) was prepared by refluxing a methanolic solution of 3-ferrocenylpropanoic acid (Hauser & Lindsay, 1957; Cetina *et al.*, 2002) in the presence of BF_3 in diethyl ether. After purification on silica-gel plates (Merck, Kieselgel 60 HF_{254}), using CH_2Cl_2 as eluent, an 87% yield of orange crystals was obtained [m.p. 310–311 K; literature m.p. 309–310 K (Roberts *et al.*, 1967)]. The single crystal used for analysis was obtained by slow evaporation from a cyclohexane solution at room temperature. IR (CH_2Cl_2, ν): 3099 *w* (C—H) ferrocene; 2924 *w* (C—H) aliphatic; 1732 (*s*, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 4.07 (*d*, 9H, ferrocene), 3.67 (*s*, 3H, OCH_3), 2.65 (*t*, 2H, CH_2CO), 2.54 (*t*, 2H, $FcCH_2$). ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 173.72 (C=O), 87.23, 68.32, 67.70 (substituted ferrocene ring), 67.18, 60.16 (unsubstituted ferrocene ring), 51.37 (OCH_3), 35.22 ($FcCH_2$), 24.58 (CH_2). The melting point was determined using a Buechi apparatus, The IR spectrum was recorded on a Bomen MB100 Mid FT–IR spectrophotometer and the ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer, with tetramethylsilane as the internal standard.

Crystal data

$[Fe(C_5H_5)(C_9H_{11}O_2)]$
M_r = 272.12
Monoclinic, $C2/c$
a = 29.425 (9) Å
b = 6.1454 (9) Å
c = 13.739 (2) Å
β = 96.38 (1)°
V = 2469.0 (9) Å^3
Z = 8

D_x = 1.464 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 28 reflections
θ = 6.2–13.3°
μ = 1.21 mm^{-1}
T = 295 (2) K
Prism, orange
0.90 × 0.75 × 0.60 mm

Data collection

Philips PW1100 diffractometer updated by Stoe
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.306, T_{max} = 0.502
3235 measured reflections
3235 independent reflections
2526 reflections with $I > 2\sigma(I)$

R_{int} = 0.016
θ_{max} = 28.9°
$h = -40 \rightarrow 39$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 18$
4 standard reflections
frequency: 120 min
intensity decay: 2.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.099
S = 1.07
3235 reflections
155 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.5699P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0027 (4)

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Table 1
Selected geometric parameters (Å, °).

C—C(Cp)(av.)subst.	1.421 (3)	O2—C14	1.441 (2)
C—C(Cp)(av.)unsubst.	1.404 (4)	C1—C11	1.505 (3)
O1—C13	1.197 (2)	C11—C12	1.510 (3)
O2—C13	1.338 (2)	C12—C13	1.500 (3)
C13—O2—C14	116.83 (17)	C6—C7—C8	107.7 (2)
C2—C1—C5	107.09 (18)	C9—C8—C7	107.7 (2)
C2—C1—C11	127.90 (19)	C10—C9—C8	108.3 (2)
C5—C1—C11	124.97 (18)	C9—C10—C6	108.6 (2)
C1—C2—C3	108.3 (2)	C1—C11—C12	113.53 (16)
C4—C3—C2	107.94 (19)	C13—C12—C11	114.07 (16)
C3—C4—C5	107.83 (19)	O1—C13—O2	123.16 (19)
C1—C5—C4	108.87 (19)	O1—C13—C12	126.48 (18)
C10—C6—C7	107.8 (2)	O2—C13—C12	110.35 (16)

All H atoms were included in calculated positions as riding atoms, with *SHELXL*97 (Sheldrick, 1997) defaults.

Data collection: *STADI*4 (Stoe & Cie, 1995); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *SHELXL*97.

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