

Ferrocene compounds. XXXVIII.¹ Dimethyl ferrocene-1,1'-dicarboxylate

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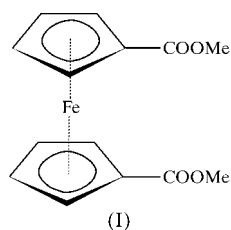
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In the title compound, $[\text{Fe}(\text{C}_7\text{H}_7\text{O}_2)_2]$, the cyclopentadienyl rings and the two attached methoxycarbonyl groups, in an *anti* arrangement, form an extended π -conjugated system. The Fe—C distances range from 2.035 (3) to 2.061 (3) Å and the average value of the C—C bond lengths in the two cyclopentadienyl rings is 1.419 (5) Å. The rings are almost parallel to one another [$1.0 (2)^\circ$] and are mutually twisted from an eclipsed conformation by only $1.8 (3)^\circ$ (average value). The methoxycarbonyl groups are twisted out of the plane of the cyclopentadienyl rings by $6.5 (4)$ and $15.7 (4)^\circ$, respectively. The molecules are joined into dimers by intermolecular C—H \cdots O hydrogen bonds that form ten-membered rings. The same types of hydrogen bonds form eight-membered rings and infinite chains along the *b* axis.

Comment

The present study forms part of our wider research on homo- and heteroannularly disubstituted ferrocene compounds, with regard to their synthesis, stereochemistry and structural analysis (Zorić *et al.*, 1999; Lapić & Rapić, 2000; Cetina *et al.*, 2002, 2003; Pavlović *et al.*, 2002). The applications of these



complexes rely on their electronic properties, which depend on various functional groups substituted on the cyclopentadienyl rings (Oberhoff *et al.*, 1996). The study of these

¹Part XXXVII: Kovač *et al.* (2003).

metallocenes has led to important developments in the field of homogeneous catalysis, including carbonylation, hydrogenation and polymerization (Gonsalves & Chen, 1995; Severin *et al.*, 1998; Patti & Nicolosi, 2000; Metzler-Nolte, 2001).

In the title compound, (I), the cyclopentadienyl rings bear two methoxycarbonyl groups in an *anti* arrangement (Fig. 1). The almost parallel cyclopentadienyl (Cp) rings [the dihedral angle is $1.0 (2)^\circ$] adopt an almost totally eclipsed conformation. The values of the corresponding pseudo-torsion angles defined by joining two eclipsed Cp C atoms through the ring centroids, *viz.* C—Cg1—Cg2—C (Cg1 and Cg2 are the centroids of the C1—C5 and C6—C10 rings, respectively), range from $1.3 (3)$ to $2.6 (3)^\circ$. The Fe atom is almost equidistant from the centroids [Fe—Cg1 = $1.654 (1)$ Å and Fe—Cg2 =

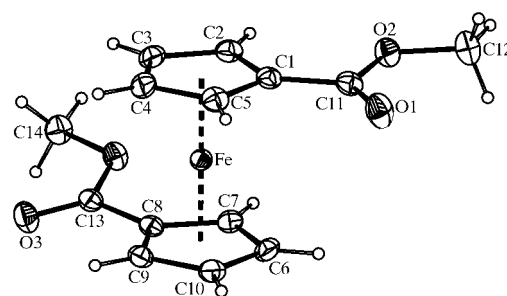


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are shown at the 20% probability level.

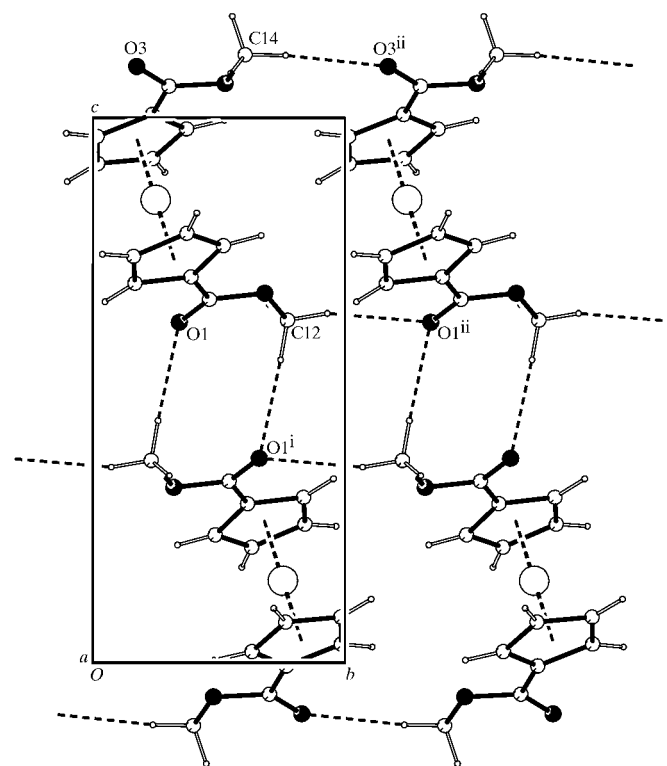


Figure 2
Crystal packing diagram of (I), viewed along [100]. Hydrogen bonds are indicated by dashed lines. [Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$.]

1.652 (1) Å], and the Cg1–Fe–Cg2 angle deviates very slightly from 180° [179.6 (1)°].

The C–C bond distances in the Cp rings are in the range 1.402 (6)–1.436 (5) Å for the C1–C5 ring and 1.408 (5)–1.429 (5) Å for the C6–C10 ring, with an average value of 1.419 (5) Å for both rings. The values of the bond angles in the Cp rings are in the range 106.9 (3)–109.3 (3)°. The structural parameters are consistent with those of similar structures that have a methoxycarbonyl group on one of the Cp rings (Luo *et al.*, 1990; Podlaha *et al.*, 1996; Hobi *et al.*, 1997; Beck *et al.*, 2001; Costa *et al.*, 2001) and with the structure of methyl 3-ferrocenylpropanoate (Cetina *et al.*, 2002). Selected geometric parameters for (I) are listed in Table 1.

The methoxycarbonyl groups and Cp rings form an extended π -conjugated system. The C_{ring}–C_{carboxyl} single bonds are shorter than the standard ‘unconjugated’ Csp²–Csp² bond (1.478 Å) and agree with the ‘conjugated’ bond distance of 1.455 Å (Allen *et al.*, 1987). The coplanar arrangement of a carbonyl group attached to the ring should allow the maximum interaction of two π systems. In (I), the substituted groups are slightly twisted out of the plane of the Cp rings to which they are attached. The twisting is more pronounced for the C13/O3/O4 group with respect to the C6–C10 ring than for the C11/O1/O2 group with respect to the C1–C5 ring [15.7 (4) and 6.5 (4)°, respectively]. The π conjugation also influences the Fe–C distances [range 2.035 (3)–2.061 (3) Å]. A survey of the Cambridge Structural Database (Allen, 2002) reveals that in structures with efficient overlap of two π systems, the shortest Fe–C distance is generally Fe–C_{subst} [Fe–C1 = 2.038 (3) Å; C_{subst} is the substituted C atom of the Cp ring]. However, the shortest distance can also involve the nearest atom to C_{subst}, such as atom C7 of the C6–C10 ring in (I) [Fe–C7 = 2.035 (3) Å].

The molecules form dimers through very weak intermolecular C12–H12A···O1ⁱ hydrogen bonds, thus forming a ten-membered ring [Table 2 and Fig. 2; symmetry code: (i) $-x, 1 - y, 1 - z$]. To our knowledge, two methoxycarbonyl groups attached to the Cp rings form such R₂²(10) rings in only two ferrocene structures (Luo *et al.*, 1990; Podlaha *et al.*, 1996). The dimers are connected by intermolecular C12–H12B···O1ⁱⁱ hydrogen bonds, which form R₄²(8) rings, and C14–H14B···O3ⁱⁱⁱ hydrogen bonds, which form infinite chains along the *b* axis [symmetry code: (ii) $x, 1 + y, z$]. The geometric centers of both rings coincide with a crystallographic center of inversion.

Experimental

The title compound (Woodward *et al.*, 1952; Sonoda & Moritani, 1971) was prepared by refluxing a methanol solution of 1,1'-ferrocenedicarboxylic acid in the presence of BF₃·Et₂O. After purification on silica-gel plates (Merck, Kieselgel 60 HF₂₅₄) using CH₂Cl₂ as eluant, (I) was obtained as orange crystals [yield 97%, m.p. 388–390 K; literature m.p. 386–387 K (Sonoda & Moritani, 1971)]. The single crystal of (I) used for X-ray analysis was obtained by slow evaporation from a cyclohexane solution at room temperature. IR (CH₂Cl₂, cm⁻¹): ν 3090 (*w*, C–H, ferrocene), 1716 (*s*, C=O); ¹H NMR (CDCl₃, p.p.m.): δ 4.80 (*s*), 4.43 (*s*), 4.34 (*s*), 4.25 (*d*, 8H,

ferrocene), 3.84 (*s*, 6H, COOCH₃); ¹³C NMR (CDCl₃, p.p.m.): δ 172.74, 172.72 (C=O), 71.59, 70.35 (ferrocene substituted ring), 51.73, 51.37 (OCH₃).

Crystal data

[Fe(C ₇ H ₇ O ₂) ₂]	<i>D</i> _x = 1.589 Mg m ⁻³
<i>M</i> _r = 302.10	Mo K α radiation
Monoclinic, C2/c	Cell parameters from 2802 reflections
<i>a</i> = 32.7581 (10) Å	θ = 2.6–26.7°
<i>b</i> = 5.9616 (2) Å	μ = 1.20 mm ⁻¹
<i>c</i> = 13.3424 (5) Å	<i>T</i> = 293 (2) K
β = 104.2847 (13)°	Irregular, orange
<i>V</i> = 2525.08 (15) Å ³	0.30 × 0.20 × 0.10 mm
<i>Z</i> = 8	

Data collection

Nonius KappaCCD area-detector diffractometer	2640 independent reflections
φ and ω scans	2039 reflections with <i>I</i> > 2 σ (<i>I</i>)
Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)	<i>R</i> _{int} = 0.066
<i>T</i> _{min} = 0.697, <i>T</i> _{max} = 0.887	θ _{max} = 26.7°
13 701 measured reflections	<i>h</i> = –39 → 40
	<i>k</i> = –6 → 7
	<i>l</i> = –16 → 16

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.083P)^2 + 3.7923P]$
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)] = 0.046	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.141	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.03	$\Delta\rho$ _{max} = 0.87 e Å ⁻³
2640 reflections	$\Delta\rho$ _{min} = –0.48 e Å ⁻³
174 parameters	
H-atom parameters constrained	

All H atoms were included in calculated positions as riding atoms, with C–H distances of 0.93 (C_{Cp}–H) or 0.96 Å (C_{Me}–H).

Table 1
Selected geometric parameters (Å, °).

O1–C11	1.202 (4)	O4–C13	1.339 (4)
O2–C11	1.335 (5)	O4–C14	1.447 (4)
O2–C12	1.449 (5)	C1–C11	1.458 (5)
O3–C13	1.203 (4)	C8–C13	1.464 (5)
C11–O2–C12	115.7 (3)	O1–C11–O2	122.7 (3)
C13–O4–C14	115.6 (3)	O1–C11–C1	124.8 (3)
C5–C1–C11	124.0 (3)	O2–C11–C1	112.5 (3)
C2–C1–C11	128.1 (3)	O3–C13–O4	123.1 (3)
C9–C8–C13	124.0 (3)	O3–C13–C8	124.7 (3)
C7–C8–C13	128.3 (3)	O4–C13–C8	112.2 (3)
C12–O2–C11–C1	173.1 (3)	C14–O4–C13–C8	178.4 (3)
C2–C1–C11–O2	6.8 (5)	C7–C8–C13–O3	166.2 (4)

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C12–H12A···O1 ⁱ	0.96	2.47	3.401 (6)	162
C12–H12B···O1 ⁱⁱ	0.96	2.54	3.447 (5)	157
C14–H14B···O3 ⁱⁱⁱ	0.96	2.50	3.442 (5)	166

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

The reflection data were collected on the Nonius KappaCCD diffractometer at the Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia. We acknowledge with thanks the financial contribution of the Ministry of Education, Science and Sport of the Republic of Slovenia through grant Nos. X-2000 and PS-511-103, which made the purchase of the apparatus possible.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1249). Services for accessing these data are described at the back of the journal.

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