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Ferrocene compounds. XXXIX.[1] 1-Ferrocenylisochromane

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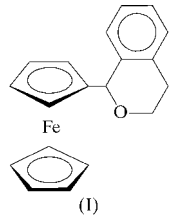
In the title compound, $[Fe(C_5H_5)(C_{14}H_{13}O)]$, the plane of the heterocyclic ring is almost perpendicular to the plane of the substituted cyclopentadienyl ring, and the heterocyclic ring adopts a half-chair conformation. The conformation of the nearly parallel cyclopentadienyl (Cp) rings [the dihedral angle between their planes is 2.7 (1)°] is almost halfway between eclipsed and staggered, and the rings are mutually twisted by about 19.4 (2)° (mean value). The mean lengths of the C—C bonds in the substituted and unsubstituted cyclopentadienyl ring are 1.420 (2) and 1.406 (3) Å, respectively, and the Fe—C distances range from 2.029 (2) to 2.051 (2) Å. The phenyl and unsubstituted cyclopentadienyl rings are involved in C—H···π interactions, with intermolecular H···centroid distances of 2.85 and 3.14 Å for C—H···π(Ph), and 2.88 Å for C—H···π(Cp). In two of these interactions, the C—H bond points towards one of the ring bonds rather than towards the ring centroid. In the crystal structure, the C—H···π interactions connect the molecules into a three-dimensional framework.

Comment

Optically active ferrocene derivatives are widely employed as chiral ligands in asymmetric reactions, and there is continuing interest in the development of efficient procedures for the preparation of these derivatives in enantiopure forms (Gonsalves & Chen, 1995; Bolm *et al.*, 1998; Pioda & Togni, 1998; Perea *et al.*, 1999). Ferrocene derivatives exhibiting centro- and planar chirality are very convenient substrates for biotransformations (Köllner *et al.*, 1998; Richards & Locke, 1998; Schwink & Knochel, 1998; Patti & Nicolosi, 1999; Đaković *et al.*, 2003). In the course of our research on enzyme-catalyzed resolution of centrochiral ferrocene compounds, racemic 2-(α-hydroxyferrocenyl)benzenethanol and 1-ferrocenylisochromane, (I), were prepared by reduction of methyl 2-(ferrocenoyl)benzeneacetate (Đaković, 2000).



(I)

The molecular structure of (I) is the first reported structure to contain an isochromanyl group attached to the ferrocenyl moiety (Fig. 1). Moreover, the Cambridge Structural Database (Allen, 2002) lists only three structures containing an isochromanyl group at all (Yamato *et al.*, 1984; Unterhalt *et al.*, 1994; Eikawa *et al.*, 1999). The heterocyclic six-membered ring

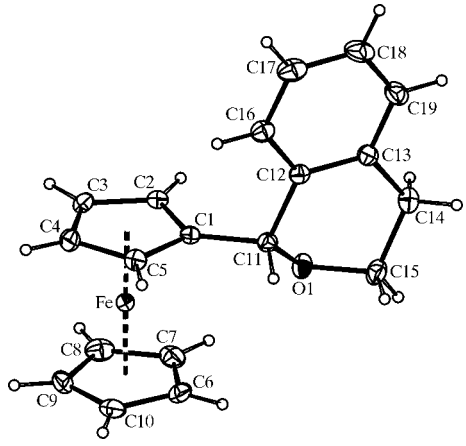


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 20% probability level.

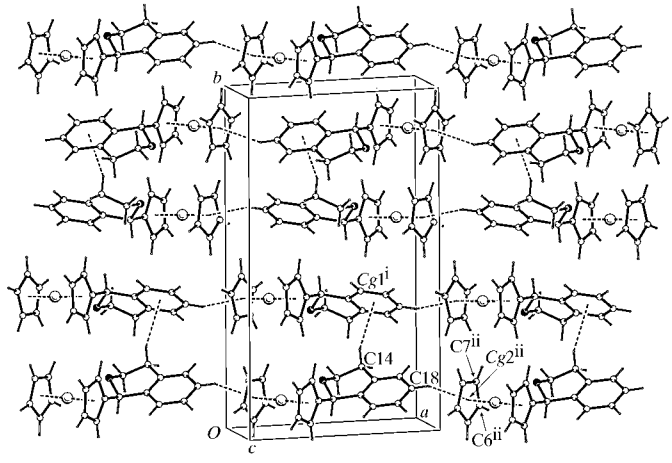


Figure 2
Part of the crystal structure of (I), showing the formation of (010) sheets built from C14—H14*A*···*Cg*1^{i} and C18—H18···*Cg*2^{ii} interactions (*Cg*1 and *Cg*2 are the centroids of rings C12/C13/C16–C19 and C6–C10, respectively). C—H···π interactions are indicated by dashed lines. [Symmetry codes: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $1+x, y, 1+z$.]

[1] Part XXXVIII: Cetina *et al.* (2003).

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adopts a distorted half-chair conformation, in which atoms O1 and C15 are 0.426 (1) and −0.348 (2) Å from the plane of the other ring atoms (C11–C14); the C11—C12—C13—C14 torsion angle is 2.4 (2)°. The bond lengths in the heterocyclic and fused phenyl rings (Table 1) mostly agree with the equivalent bond lengths in the structures of 1,1′-oxybis(isochromane) (Eikawa *et al.*, 1999) and (*S*)-1-(phenyl)ethylammonium (*S*)-isochromane-1-carboxylate (Unterhalt *et al.*, 1994). The exception is the C12—C13 bond, which is shorter (∼0.04 Å) in the latter structure. Heterocyclic ring atoms O1, C11 and C15 and cyclopentadienyl (Cp) ring atom C1 lie in the same plane, the C15—O1—C11—C1 torsion angle being 178.95 (14)°. The dihedral angle between the mean plane of these four atoms and the C1–C5 Cp ring is 47.8 (1)°. Furthermore, the plane of the heterocyclic ring is almost perpendicular to the plane of the C1–C5 ring and is parallel to the plane of the fused phenyl ring. The corresponding dihedral angles are 87.3 (1) and 4.0 (1)°.

The exocyclic C2—C1—C11 bond angle is larger than the C5—C1—C11 angle (Table 1). The Cp rings are planar and almost parallel to each other [the dihedral angle between their planes is 2.7 (1)°], and the Fe—C distances are in the range 2.034 (2)–2.051 (2) Å for the substituted (C1–C5) and 2.029 (2)–2.049 (2) Å for the unsubstituted (C6–C10) ring, the average values being 2.042 (2) and 2.038 (2) Å, respectively. The C—C bonds are slightly longer in the substituted ring than in the unsubstituted ring [1.410 (3)–1.429 (2) *versus* 1.397 (3)–1.414 (3) Å], and the bond angles in both rings range from 107.52 (15) to 108.33 (18)°.

The geometry of the ferrocenyl moiety agrees well with the structures of ferrocene (Seiler & Dunitz, 1979) and of the ferrocene derivatives we have reported previously (Cetina *et al.*, 2002, 2003). The main conformational difference was observed in the orientation of the Cp rings. In (I), the rings are twisted from an eclipsed conformation by 19.4 (2)° (mean value). The values of the corresponding C—*Cg*3—*Cg*2—C pseudo-torsion angles (*Cg*3 and *Cg*2 are the centroids of the C1–C5 and C6–C10 rings, respectively), defined by joining two eclipsing Cp C atoms through the ring centroids, range from 19.0 (2) to 19.7 (2)°. The conformation is almost exactly halfway between eclipsed and staggered, as demonstrated by the C1—*Cg*3—*Cg*2—C9 torsion angle of 163.4 (1)°. This angle would be 180° for a staggered conformation and 144° for a fully eclipsed conformation. The centroids of the Cp rings are almost equidistant from the Fe atom; the Fe—*Cg*3 and Fe—*Cg*2 distances are 1.647 (1) and 1.650 (1) Å, respectively, while the *Cg*3—Fe—*Cg*2 angle is 178.2 (1)°.

There are a number of C—H···π interactions (Table 2 and Fig. 2). Atom H14*A* of the heterocyclic ring is positioned almost perpendicularly above the phenyl-ring centroid (*Cg*1) of the adjacent molecule. The six relevant H···C distances fall in the narrow range 3.06–3.28 Å, and the H···Cg^{i} distance is significantly shorter than any of the H···C distances [symmetry code: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$; Table 2]. The C—H···$\pi$ interaction between phenyl atom H18 and the unsubstituted Cp ring exhibits a completely different geometry. The H18···$C7^{ii}$ distance is shorter than the H···Cg^{ii} distance [symmetry code: (ii) $1+x, y, 1+z$]. The second shortest H···C contact is that to atom C6, and the C—H bond points towards the C6—C7 bond of the Cp ring rather than towards the ring centroid (*Cg*2). Similarly, the longest interaction, C5—H5···$Cg1^{iii}$ [symmetry code: (iii) $1-x, -y, 2-z$], points towards the C12—C13 bond. Both the H5···$C12^{iii}$ and the H5···$C13^{iii}$ contacts are shorter than the H···Cg^{iii} distance. The molecules linked by these C—H···π interactions build a three-dimensional framework (Fig. 3).

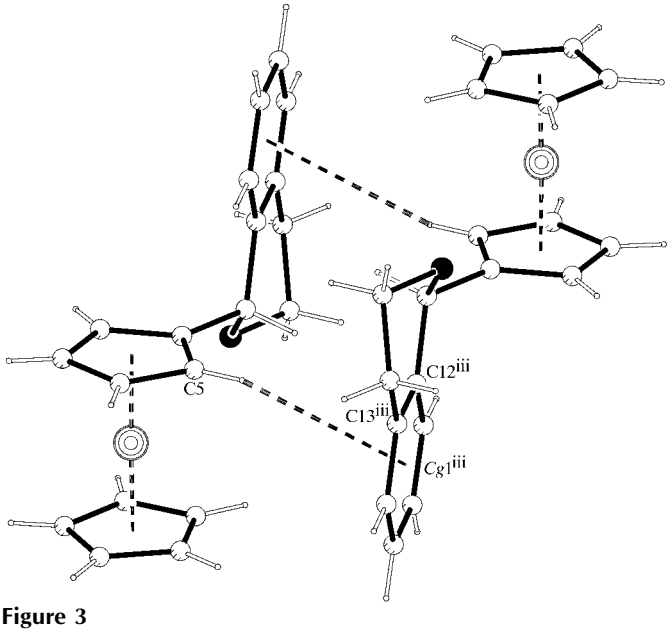

Figure 3
Part of the crystal structure of (I), showing the cyclic motif generated by the C5—H5···$Cg1^{iii}$ interaction (*Cg*1 is the centroid of ring C12/C13/C16–C19), which links the (010) sheets into a three-dimensional framework. C—H···π interactions are indicated by dashed lines, and the unit-cell box has been omitted for clarity. [Symmetry code: (iii) $1-x, -y, 2-z$.]

Experimental

$NaBH_4$ (253 mg, 6.7 mmol) was added gradually to a solution of methyl 2-(ferrocenoyl)benzeneacetate (326 mg, 0.9 mmol) in a mixture of EtOH and Et_2O (1:1 *v*/*v*; 5 ml). The mixture was refluxed for 2 h and worked up in the usual manner. Separation by preparative thin-layer chromatography on silica gel (Merck, Kieselgel 60 HF_{254}) yielded 2-(α-hydroxyferrocenyl)benzeneethanol (237 mg; yield 78%) and orange crystals of 1-ferrocenylisochromane (57 mg; yield 20%; m.p. 365–366 K). Single crystals of the title compound were obtained by slow evaporation from a cyclohexane solution at room temperature. IR (CH_2Cl_2, cm^{-1}): υ 3081 (*w*) and 3020 (*w*) (C—H, ferrocene), 2942 (*m*) (C—H, aliphatic), 1278 (*m*) (C—O—C); ^{1}H NMR (DMSO, p.p.m.): δ 7.18 (*d*, 1H, H16), 7.12 (*d*, 1H, H17), 7.14 (*d*, 1H, H18), 7.16 (*d*, 1H, H19), 4.23 (*s*, 5H, unsubstituted ferrocene ring), 4.13–4.20 (*m*, 4H, substituted ferrocene ring), 3.97 (*m*, 1H, H15*A*), 3.77 (*m*, 1H, H15*B*), 2.78 (*m*, 2H, H14), 5.58 (*s*, 1H, H11); ^{13}C NMR (DMSO, p.p.m.): δ 137.29 (C12), 132.91 (C13), 128.5 (C17), 126.25 (C18), 125.98 (C16), 125.36 (C19), 90.21 (C1), 73.63 (C11), 68.62 (unsubstituted ferrocene ring), 68.56–66.31 (substituted ferrocene ring), 61.55 (C15), 27.99 (C14).

Crystal data

$[Fe(C_5H_5)(C_{14}H_{13}O)]$	D_x = 1.442 Mg m^{-3}
M_r = 318.18	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3411 reflections
a = 11.5053 (2) Å	θ = 2.6–27.5°
b = 18.5095 (3) Å	μ = 1.02 mm^{-1}
c = 7.1941 (1) Å	T = 293 (2) K
β = 106.933 (1)°	Prism, orange
V = 1465.62 (4) Å^3	0.80 × 0.40 × 0.15 mm
Z = 4	

Data collection

Nonius KappaCCD area-detector diffractometer	3334 independent reflections
φ and ω scans	2662 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)	R_{int} = 0.064
T_{min} = 0.630, T_{max} = 0.857	θ_{max} = 27.4°
16 885 measured reflections	$h = -14 \rightarrow 14$
	$k = -23 \rightarrow 23$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.3545P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.030	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.076	$\Delta\rho_{max}$ = 0.25 e Å^{-3}
S = 1.03	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
3334 reflections	
190 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C11	1.4236 (19)	C13—C19	1.392 (3)
O1—C15	1.432 (2)	C13—C14	1.504 (3)
C1—C11	1.503 (2)	C14—C15	1.501 (3)
C11—C12	1.523 (2)	C16—C17	1.384 (3)
C12—C16	1.388 (2)	C17—C18	1.380 (3)
C12—C13	1.397 (2)	C18—C19	1.379 (3)
C11—O1—C15	110.39 (13)	C1—C11—C12	112.14 (13)
C2—C1—C11	127.61 (14)	C13—C12—C11	119.77 (14)
C5—C1—C11	124.78 (14)	C12—C13—C14	120.38 (16)
O1—C11—C1	109.37 (13)	C15—C14—C13	111.24 (15)
O1—C11—C12	111.64 (13)	O1—C15—C14	110.04 (15)

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

*Cg*1 and *Cg*2 are the centroids of rings C12/C13/C16–C19 and C6–C10, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14*A*···*Cg*1^{i}	0.97	2.85	3.627 (2)	138
C18—H18···*Cg*2^{ii}	0.93	2.88	3.660 (2)	142
C18—H18···C7^{ii}	0.93	2.86	3.760 (3)	163
C18—H18···C6^{ii}	0.93	3.03	3.874 (3)	151
C5—H5···*Cg*1^{iii}	0.93	3.14	3.984 (2)	152
C5—H5···C12^{iii}	0.93	2.98	3.840 (2)	154
C5—H5···C13^{iii}	0.93	3.02	3.949 (2)	177

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

All H atoms were included in calculated positions as riding atoms, with *SHELXL*97 (Sheldrick, 1997) defaults *viz.* C—H = 0.93 Å for aromatic H atoms, 0.98 Å for methine H atoms, and 0.97 Å for methylene H atoms. For all H atoms, the isotropic displacement parameters were set at 1.2 times the equivalent anisotropic displacement parameters of the attached non-H atoms.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1251). Services for accessing these data are described at the back of the journal.

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