

Intermolecular O—H...O and C—H... π (C₅H₅), and intramolecular C—H...O interactions in 2-(ferrocenyl)thiophene-3-carboxylic acid

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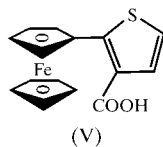
Received 25 September 2000

Accepted 13 October 2000

The title compound, [Fe(C₅H₅)(C₁₀H₇O₂S)], an important precursor *en route* to organometallic donor- π -acceptor systems, forms dimers in the solid state through cyclic intermolecular carboxylic acid O—H...O hydrogen bonds, graph set $R_2^2(8)$ [O...O 2.661 (2) Å and O—H...O 175°]. Intermolecular C_{Cp}—H... π C_{Cp} interactions between the unsubstituted cyclopentadienyl (Cp) rings and C_{thiazole}—H... π C_{Cp} interactions link neighbouring molecules into a three-dimensional network [C...C_g 3.753 (7) Å and C—H...C_g 156°, and C...C_g 3.687 (3) Å and C—H...C_g 129°; C_g is the ring centroid]. Intramolecular C—H...O interactions are present, graph set $S(7)$ [C...O 2.925 (3) Å and C—H...O 120°, and the closest C—H...S_{thienyl} contact has a C...S distance of 3.058 (2) Å].

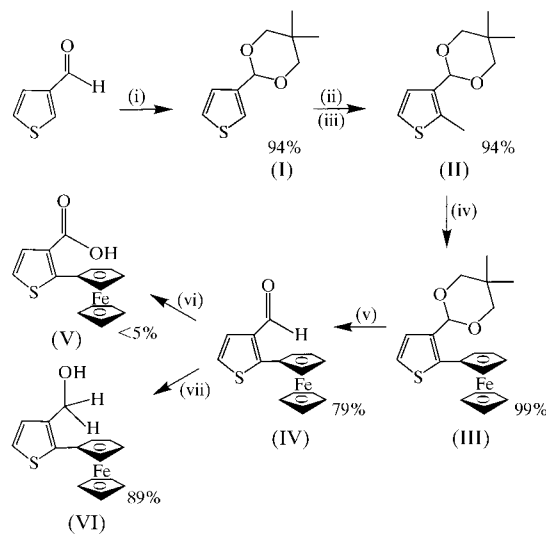
Comment

The design of new redox-active compounds for application in materials science has engaged chemists in recent years. Ferrocene derivatives which are efficient redox systems have been studied extensively as charge-transfer complexes, in molecular recognition science, in peptide chemistry and as non-linear optical materials (Moore *et al.*, 1993; Chesney *et al.*, 1998; Glidewell *et al.*, 1997; Kraatz *et al.*, 1999; Hudson *et al.*,



2001). An understanding of the interactions present in the crystal structure of a new material can provide valuable information on the hydrogen-bonding modes, thus facilitating an understanding of solid-state effects and the subsequent design and improvement of currently available systems. The structure of 2-(ferrocenyl)thiophene-3-carboxylic acid, (V), an

important precursor *en route* to organometallic donor- π -acceptor systems, is reported herein.



Reagents and conditions: (i) neopentyl glycol, catalytic *p*-toluenesulfonic acid, toluene, reflux, 1.5 h; (ii) BuLi, Et₂O, 195–293 K; (iii) I₂, Et₂O, 195–293 K; (iv) ferrocenyllithium, ZnCl₂, tetrahydrofuran–hexane (50/50), Pd(PPh₃)₄, 18 h; (v) oxalic acid, water–tetrahydrofuran (50/50), reflux, 30 min; (vi) 5% KMnO₄, ethanol–water (50/50), 12 d, 293 K; (vii) LiAlH₄, diethyl ether, room temperature, 12 h.

The synthesis of compound (V) is detailed in the *Experimental* section and the molecular structure is depicted, with the atomic numbering scheme, in Fig. 1; selected geometric dimensions are given in Table 1. Bond lengths are in accord with the anticipated values (Orpen *et al.*, 1994). The unsubstituted cyclopentadienyl (Cp) ring is disordered over two sites, with occupancies of 0.691 (18) and 0.309 (18) for the major and minor orientations, respectively. Rotational disorder is often observed in the unsubstituted C₅H₅ ring of ferrocene derivatives, *e.g.* 1-ferrocenyl-1-phenylethanol (Ferguson *et al.*, 1993). The Fe1—C bond lengths for the substituted Cp ring of (V) are in the range 2.028 (2)–2.050 (2) Å, which is similar to that observed for the major orientation of the unsubstituted Cp ring [2.039 (4)–2.051 (7) Å]. The Fe1...C_g1 and Fe1...C_g2 distances are 1.6435 (10) and 1.656 (3) Å, respectively, and the

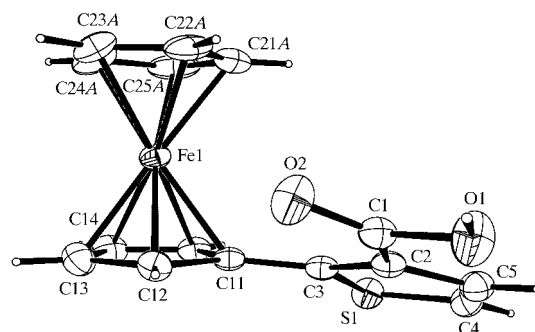


Figure 1
An ORTEX (McArdle, 1995) view of (V) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The minor Cp-ring disorder form has been omitted for clarity.

$Cg1 \cdots Fe1 \cdots Cg2$ angle is $178.42(11)^\circ$, where $Cg1$ and $Cg2$ are the centroids of the substituted and unsubstituted Cp rings in the major orientation, *A*. The Cp rings deviate from eclipsed geometry, as indicated by the $C1nA/B \cdots Cg1 \cdots Cg2 \cdots C2nA/B$ torsion angles, which are in the ranges $20.6(5)$ to $21.3(5)^\circ$ for *A* ($n = 1-5$) and $-5.1(10)$ to $-16.0(7)^\circ$ for the minor orientation, *B*.

There is significant bending of the thienyl group with respect to the substituted Cp ring, with C3 bent away by $0.098(3) \text{ \AA}$ from the C11–C15 plane and on the opposite side to Fe1; the $C3-C11 \cdots Cg1$ angle is $175.21(15)^\circ$. The thienyl system is oriented at an angle of $20.94(12)^\circ$ to the C_5H_4 ring and $5.95(15)^\circ$ to the O1/O2/C1/C2 carboxylic acid plane. The angles involving the COOH group are normal (Gallagher *et al.*, 2000). However, the angles centred at C2 are noteworthy. The C1–C2–C3 and C1–C2–C5 angles are $126.48(18)$ and $120.82(18)^\circ$, respectively, while the C2–C3–C11 angle is $135.23(17)^\circ$, compared with $115.32(14)^\circ$ for S1–C3–C11. Analysis of the C3–C11–C12 and C3–C11–C15 angles, which are $129.38(17)$ and $123.97(18)^\circ$, respectively, also suggests that the former C–C–C angles expand considerably due to the combined effects of hydrogen bonding and repulsion about the C3–C11 bond. The angle expansion on the carboxylic acid side of the substituted Cp ring arises where a C–H \cdots O intramolecular interaction is present, graph set $S(7)$ [C12 \cdots O2 $2.925(3) \text{ \AA}$ and C12–H12 \cdots O2 120°], resulting in a twist by $20.94(12)^\circ$ of the thienyl ring from coplanarity with the C_5H_4 group about the C3–C11 bond.

Compound (V) assembles as hydrogen-bonded dimers through cyclic intermolecular carboxylic acid O1–H1 \cdots O2ⁱ hydrogen bonding, graph set $R_2^2(8)$, in the solid state (Fig. 2) [O1 \cdots O2ⁱ $2.661(2) \text{ \AA}$ and O1–H1 \cdots O2ⁱ 175° ; symmetry code: (i) $1 - x, 2 - y, 1 - z$]. Intermolecular $C_{Cp}-H \cdots \pi_{Cp}$

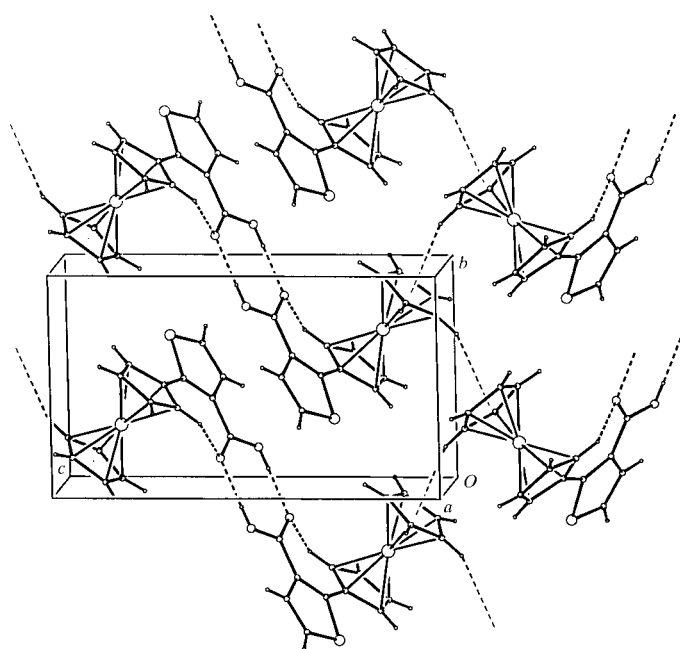


Figure 2
A view of the primary interactions in the crystal structure of (V).

interactions between the unsubstituted Cp rings link neighbouring molecules into a zigzag chain and, in combination with the dimers, form a two-dimensional network [C25A \cdots Cg2ⁱⁱ $3.753(7) \text{ \AA}$ and C25A–H25A \cdots Cg2ⁱⁱ 156° ; symmetry code: (ii) $\frac{1}{2} - x, y - \frac{1}{2}, -z$]. Stacking of the thiophene carboxylic moieties about inversion centres occurs, with an interplanar spacing of 3.46 \AA . A $C4_{\text{thiazole}}-H4 \cdots Cg1^{\text{iii}}$ interaction extends the interactions to form a three-dimensional network [symmetry code: (iii) $\frac{1}{2} + x, \frac{1}{2} - y, z$]. The closest C–H \cdots S contact is C15 \cdots S1 $3.058(2) \text{ \AA}$, with C15–H15 \cdots S1 97° (Table 2).

A search of the Cambridge Structural Database (Allen & Kennard, 1993) for molecules containing the ferrocenyl group directly bonded to a thienyl ring, suggests that such compounds are rare. Current research on chiral ferrocene derivatives implies that (V) may be of interest as a precursor to heterobimetallic systems, as it contains both thienyl and COOH donor groups.

Experimental

Compound (V) was prepared as follows: 3-thiophene carboxaldehyde was protected as its neopentyl acetal, (I), in excellent yield (94%) and *o*-directed metallation with BuLi (Slocum & Gierer, 1976) gave the 2-iodo isomer, (II), exclusively (94%), after quenching with molecular iodine. Pd-catalysed cross coupling with ferrocenyl zinc chloride (Guillaneux & Kagan, 1995; Hudson *et al.*, 2000) afforded the ferrocenyl adduct, (III), in quantitative yield as an orange oil. Deprotection with oxalic acid in a 1:1 mixture of tetrahydrofuran and water at reflux gave the aldehyde, (IV), in good yield (79%) as a red gum. Oxidation of substituents in direct electronic communication with ferrocene is known (Rosenblum, 1965); however, oxidation of (IV) under varying conditions to form (V) resulted either in complete decomposition of the starting material or in no reaction. Compound (V) could only be obtained in very low yield (<5%) by the action of ethanolic potassium permanganate on (IV) for 2 weeks. It is worth noting that the reduction of (IV) was extremely facile and proceeded in high yield (89%) with $LiAlH_4$ in diethyl ether to afford (VI) as an orange crystalline solid. The detailed synthesis of (V) from (IV) is as follows: compound (IV) (0.1 g, 0.34 mmol) was added to a 5% solution of $KMnO_4$ in ethanol/water (50/50; 5 ml) and stirred for 12 d at room temperature. The mixture was extracted with diethyl ether ($2 \times 50 \text{ ml}$) and the organic portions were combined and washed with water ($2 \times 50 \text{ ml}$) before being dried over magnesium sulfate and evaporated to dryness. The black residue was purified by column chromatography on silica gel with CH_2Cl_2 as the eluant, to afford (V) as a red solid (0.005 g, <5%). Careful evaporation of a CH_2Cl_2 solution afforded red crystals of (V). Spectroscopic analysis, 1H NMR (270 MHz; δ p.p.m., $CDCl_3$): 7.39 (*d*, 1H, $J = 5.50 \text{ Hz}$, thiophene), 7.09 (*d*, 1H, $J = 5.31 \text{ Hz}$, thiophene), 4.82 (*m*, 2H, α - C_5H_4), 4.37 (*m*, 2H, β - C_5H_4), 4.16 (*s*, 5H, C_5H_5).

Crystal data

[Fe(C_5H_5)($C_{10}H_7O_2S$)]
 $M_r = 312.16$
 Monoclinic, $P2_1/a$
 $a = 12.7108(8) \text{ \AA}$
 $b = 7.4801(6) \text{ \AA}$
 $c = 14.2397(9) \text{ \AA}$
 $\beta = 110.542(5)^\circ$
 $V = 1267.80(15) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.635 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 75 reflections
 $\theta = 6.2-20.2^\circ$
 $\mu = 1.346 \text{ mm}^{-1}$
 $T = 294(1) \text{ K}$
 Plate, red
 $0.48 \times 0.28 \times 0.05 \text{ mm}$

Table 1

Selected geometric parameters (Å, °).

Fe1—C11	2.0488 (19)	O1—C1	1.316 (2)
Fe1—C12	2.050 (2)	O2—C1	1.222 (3)
Fe1—C13	2.045 (2)	C1—C2	1.472 (3)
Fe1—C14	2.032 (2)	C2—C3	1.388 (3)
Fe1—C15	2.028 (2)	C2—C5	1.430 (3)
S1—C3	1.7296 (19)	C3—C11	1.460 (3)
S1—C4	1.712 (2)	C4—C5	1.344 (3)
C3—S1—C4	93.29 (11)	C3—C2—C5	112.63 (18)
O1—C1—O2	122.11 (19)	S1—C3—C2	109.31 (15)
O1—C1—C2	113.14 (18)	S1—C3—C11	115.32 (14)
O2—C1—C2	124.74 (18)	C2—C3—C11	135.23 (17)
C1—C2—C3	126.48 (18)	S1—C4—C5	111.17 (17)
C1—C2—C5	120.82 (18)	C2—C5—C4	113.6 (2)
O1—C1—C2—C5	−5.7 (3)	C2—C3—C11—C12	−19.8 (4)
C1—C2—C3—C11	−8.0 (4)	S1—C3—C11—C15	−18.6 (2)
S1—C3—C11—C12	155.42 (18)	C2—C3—C11—C15	166.2 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

Cg1 and Cg2 are the centroids of the substituted and unsubstituted Cp rings in the major orientation, A.

<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>
O1—H1...O2 ⁱ	0.82	1.84	2.661 (2)	175
C12—H12...O2	0.93	2.34	2.925 (3)	120
C15—H15...S1	0.93	2.80	3.058 (2)	97
C25A—H25A...Cg2 ⁱⁱ	0.93	2.88	3.753 (7)	156
C4—H4...Cg1 ⁱⁱⁱ	0.93	3.03	3.687 (3)	129

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

Data collection

Bruker P4 diffractometer	$R_{\text{int}} = 0.020$
ω scans	$\theta_{\text{max}} = 28^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -16 \rightarrow 1$
$T_{\text{min}} = 0.64$, $T_{\text{max}} = 0.99$	$k = -9 \rightarrow 1$
3919 measured reflections	$l = -17 \rightarrow 18$
3032 independent reflections	3 standard reflections
2431 reflections with $I > 2\sigma(I)$	every 197 reflections
	intensity variation: $\pm 0.5\%$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.5075P]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.082$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.30 \text{ e } \text{Å}^{-3}$
3032 reflections	$\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{Å}^{-3}$
203 parameters	
H-atom parameters constrained	

All H atoms were allowed for as riding atoms with O—H = 0.82 Å and C—H = 0.93 Å using *SHELXL97* (Sheldrick, 1997) defaults. Disorder in the unsubstituted ring was treated by generating coor-

dinates for the minor component and subsequent use of the *AFIX59* command in *SHELXL97* with appropriate *DELU/ISOR* controls, to give site occupancies of 0.691 (18) and 0.309 (18) in the final refinement cycles. Examination of the structure with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *ORTEX* (McArdle, 1995) and *PLATON*; software used to prepare material for publication: *SHELXL97* and *PREP8* (Ferguson, 1998).

This research was supported by the EU under the TMR network CT-98-0166. JFG thanks Dublin City University for the purchase of a Bruker P4 diffractometer in 1999. Elemental analyses were performed by Ms A. Connolly (UCD).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1424). Services for accessing these data are described at the back of the journal.

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