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

John F. Gallagher, a* Richard D. A. Hudson b and A. R. Manning b

a School of Chemical Sciences, Dublin City University, Dublin 9, Ireland, and b Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

Correspondence e-mail: john.gallagher@dcu.ie

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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 R₂(8) [O⋯O 2.661 (2) Å and O–H⋯O 175°]. Intermolecular C₅H₅–H⋯πC₅P interactions between the unsubstituted cyclopentadienyl (C₅P) rings and C₅H₅–H⋯S interactions link neighbouring molecules into a three-dimensional network [C⋯Cg 3.753 (7) Å and C–H⋯Cg 156°, and C⋯Cg 3.687 (3) Å and C–H⋯Cg 129°; Cg 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 thiienyl 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-toluenesulphonic 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 (C₅P) 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 Fe–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 Fe⋯Cg1 and Fe⋯Cg2 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.
Interactions between the substituted Cp rings link neighbouring molecules into a zigzag chain and, in combination with the dimers, form a two-dimensional network [C25A-...Cg2^ii 3.753 (7) Å and C25A-...H25A-...Cg2^ii 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 Å. A C4^thiazole-...H4•••Cg1^ii interaction extends the interactions to form a three-dimensional network [symmetry code: (iii) \( \frac{3}{2} - x, \frac{1}{2} - y, z \)]. The closest C1-...H^•••S contact is C15•••S1 3.058 (2) Å, with C15—H15•••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 \( \sigma \)-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 (Rosenthal, 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 LiAlH4 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 KMnO4 in ethanol/water (50/50; 5 ml) and stirred for 12 d at room temperature. The mixture was extracted with ethyl ether (2 × 50 ml) and the organic portions were combined and washed with water (2 × 50 ml) before being dried over magnesium sulfate and evaporated to dryness. The black residue was purified by column chromatography on silica gel with CH2Cl2 as the eluant, to afford (V) as a red solid (0.005 g, <5%). Careful evaporation of a CH2Cl2 solution afforded red crystals of (V). Spectroscopic analysis, \(^1\)H NMR (270 MHz; \( \delta \) p.p.m., CDCl3): 7.39 (d, 1H, \( J = 5.50 \) Hz, thiophene); 7.09 (d, 1H, \( J = 5.31 \) Hz, thiophene), 4.82 (m, 2H, \( \alpha \)-C5H4), 4.37 (m, 2H, \( \beta \)-C5H4), 4.16 (s, 5H, C5H5).

**Crystal data**

\[
\begin{align*}
\text{[Fe(C5H4)(C10H7O2S)]} \\
M_r = 312.16 \\
\text{Monoclinic, } P2_1/a \\
a = 12.7108 (8) \text{ Å} \\
b = 7.4801 (6) \text{ Å} \\
c = 14.2397 (9) \text{ Å} \\
\beta = 110.542 (5)° \\
V = 1267.80 (15) \text{ Å}^3 \\
Z = 4
\end{align*}
\]

\( D_r = 1.635 \text{ Mg m}^{-3} \)

\( \alpha \)-KCl radiation

Cell parameters from 75 reflections

\( \theta = 6.2-20.2° \)

\( \mu = 1.346 \text{ mm}^{-1} \)

\( T = 294 \text{ (1) K} \)

Plate, red

\( 0.48 \times 0.28 \times 0.05 \text{ mm} \)

Figure 2

A view of the primary interactions in the crystal structure of (V).
metal-organic compounds

Table 1
Selected geometric parameters (Å, °).

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<tr>
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<tbody>
<tr>
<td>Fe1—C11</td>
<td>2.0488 (19)</td>
<td>O1—C1</td>
<td>1.316 (2)</td>
</tr>
<tr>
<td>Fe1—C12</td>
<td>2.050 (2)</td>
<td>O2—C1</td>
<td>1.222 (3)</td>
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<tr>
<td>Fe1—C13</td>
<td>2.045 (2)</td>
<td>C1—C2</td>
<td>1.472 (3)</td>
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<tr>
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<td>2.032 (2)</td>
<td>C2—C3</td>
<td>1.388 (3)</td>
</tr>
<tr>
<td>Fe1—C15</td>
<td>2.028 (2)</td>
<td>C2—C5</td>
<td>1.430 (3)</td>
</tr>
<tr>
<td>S1—C3</td>
<td>1.7296 (19)</td>
<td>C3—C11</td>
<td>1.460 (3)</td>
</tr>
<tr>
<td>S1—C4</td>
<td>1.712 (2)</td>
<td>C4—C5</td>
<td>1.344 (3)</td>
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C3—S1—C4 93.29 (11)  C2—C3—C11 112.63 (18)
O1—C1—C2 122.11 (19)  S1—C3—C2 109.31 (15)
O1—C1—C2 113.14 (14)  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)
O1—C1—C2—C3 −8.0 (4)  S1—C3—C11—C15 −18.6 (2)
S1—C1—C2—C3 155.42 (18)  S2—C3—C11—C15 166.2 (2)

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

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<tr>
<td>D—H—A</td>
<td>D—H</td>
<td>H—A</td>
</tr>
<tr>
<td>O1—H1—O2'</td>
<td>0.82</td>
<td>1.84</td>
</tr>
<tr>
<td>C12—H12—O2</td>
<td>0.93</td>
<td>2.34</td>
</tr>
<tr>
<td>C15—H15—S1</td>
<td>0.93</td>
<td>2.80</td>
</tr>
<tr>
<td>C25A—H25A—Cg2</td>
<td>0.93</td>
<td>2.88</td>
</tr>
<tr>
<td>C4—H4—Cg1</td>
<td>0.93</td>
<td>3.03</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) 1 — x, 2 — y, 1 — z; (ii) 1/2 — x, y — 1/2, — z; (iii) 1/2 + x, 1/2 — y, z.

Data collection

Bruker P4 diffractometer
ω scans
Absorption correction: ψ scan
(North et al., 1968)
Tmin = 0.64, Tmax = 0.99
3919 measured reflections
3032 independent reflections
2431 reflections with I > 2σ(I)

Refinement

Refinement on F2
R[F2 > 2σ(F2)] = 0.033
wR(F2) = 0.082
S = 1.05
3032 reflections
203 parameters
H-atoms 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.

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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.

References