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Ethyl and isopropyl 4-ferrocenylbenzoate

Frankie P. Anderson,[a] John F. Gallagher,[a]* Peter T. M. Kenny,[a]* Clodagh Ryan[b] and David Savage[b]

[a]School of Chemical Sciences, National Institute for Cellular Biotechnology, Dublin City University, Dublin 9, Ireland, and [b]School of Chemical Sciences, Dublin City University, Dublin 9, Ireland
Correspondence e-mail: john.gallagher@dcu.ie

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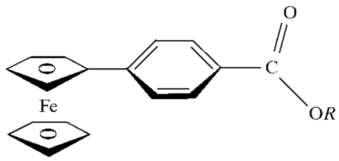
The title compounds, $[Fe(C_5H_5)(C_{14}H_{13}O_2)]$ and $[Fe(C_5H_5)(C_{15}H_{15}O_2)]$, respectively, contain the ferrocenyl $\eta^5(C_5H_4)$ and phenylene $–C_6H_4–$ rings in a nearly coplanar arrangement, with interplanar angles of 6.88 (12) and 10.5 (2)°, respectively. Molecules of the ethyl ester form dimers through $\eta^5(C_5H_5)C—H\cdots O{=}C$ hydrogen bonds, with graph set $R_2^2(20)$, and, together with $Csp^3—H\cdots\pi(C_5H_5)$ interactions, generate a one-dimensional column (irregular ladder). Molecules of the isopropyl ester aggregate through $\eta^5(C_5H_5)C—H\cdots\pi(C_6H_4)$ interactions.

Comment

The design of new redox-active ligands for application in diverse research areas, such as medicinal chemistry and materials science, has engrossed scientists in recent years. Ferrocene (Fc) derivatives, which are efficient redox systems, have been studied extensively in charge-transfer chemistry, hydrogen bonding and molecular-recognition science, peptide chemistry, non-linear optical materials, and liquid crystal research (Chesney *et al.*, 1998; Glidewell *et al.*, 1997; Zakaria *et al.*, 2002; Kraatz *et al.*, 1999; Gallagher *et al.*, 1999*a*,*b*; Hudson, Asselsbergh *et al.*, 2001; Hudson, Manning *et al.*, 2001; Even *et al.*, 2001; Seo *et al.*, 2001). Our interest in ferrocenylbenzoyl derivatives stems from their use as precursors to ferrocenylbenzoyl amino acid ester and dipeptide derivatives. We have recently reported the crystal structure of methyl 4-ferrocenylbenzoate, (I) (Savage *et al.*, 2002).

An understanding of the interactions present in a given crystal structure can provide valuable information on the hydrogen-bonding and aggregation modes not just in the solid state but also in the liquid-crystalline state. The structures of ethyl 4-ferrocenylbenzoate, (II), and the isopropyl analogue, (III), are reported herein for comparison with both the methyl analogue, (I), and our ongoing research on longer chain alkyl derivatives.

The Fe1—C bond lengths for the $\eta^5(C_5H_4)$ ring of (II) are in the range 2.0341 (16)–2.0452 (14) Å, similar to the $\eta^5(C_5H_5)$ ring, with a range of 2.0315 (18)–2.0407 (17) Å. For (III), these values are in the ranges 2.024 (3)–2.044 (3) and 2.023 (4)–2.033 (4) Å, respectively. In (II), the $Fe1\cdots Cg1$ and $Fe1\cdots Cg2$ distances are 1.6425 (8) and 1.6463 (9) Å, respectively, and the $Cg1\cdots Fe1\cdots Cg2$ angle is 179.49 (5)°, where $Cg1$ and $Cg2$ are the centroids of the $\eta^5(C_5H_4)$ and $\eta^5(C_5H_5)$ rings, respectively. In (III), these values are 1.6413 (15) and 1.643 (2) Å, and 178.88 (9)°, respectively. In (II), the cyclopentadienyl C—C bond-length ranges are small, being 1.413 (3)–1.435 (2) and 1.398 (3)–1.420 (3) Å for the $\eta^5(C_5H_4)$ and $\eta^5(C_5H_5)$ rings, respectively. In (III), these ranges are 1.407 (5)–1.428 (4) and 1.389 (6)–1.410 (6) Å, respectively. These results are as expected and highlight the similarity in the ferrocenyl bond lengths and angles in the esters (I) (Savage *et al.*, 2002), and (II) and (III), described herein.



(II) R = ethyl
(III) R = isopropyl

The cyclopentadienyl rings deviate slightly from an eclipsed geometry in (II), as evidenced by the $C1n\cdots Cg1\cdots Cg2\cdots C2n$ (n = 1–5) torsion angles ranging from −2.87 (14) to −3.61 (14)°. In (III), the angles are in the range 6.1 (3)–7.0 (3)°, similar to the eclipsed geometry in (I), where the range is 0.8 (4)–2.3 (4)°. In contrast, this range of angles is 13.7 (2)–15.4 (3)° in *para*-ferrocenylbenzoyl-L-alanine methyl ester (Savage *et al.*, 2002).

The essentially linear molecular conformations adopted by (II) and (III) are comparable, with interplanar angles of 6.88 (12)° between the $\eta^5(C_5H_4)$ and $–C_6H_4–$ rings in (II), 10.5 (2)° in (III) and 9.35 (13)° in (I). The major differences are in the terminal O1—C1—C34—C33 torsion angles, the value of which is −0.8 (2)° in (II), −18.2 (5)° in (III) and 171.2 (3)° in (I). However, the disposition of the terminal alkoxy group, which gives a C1—O1—C2—C3 torsion angle of

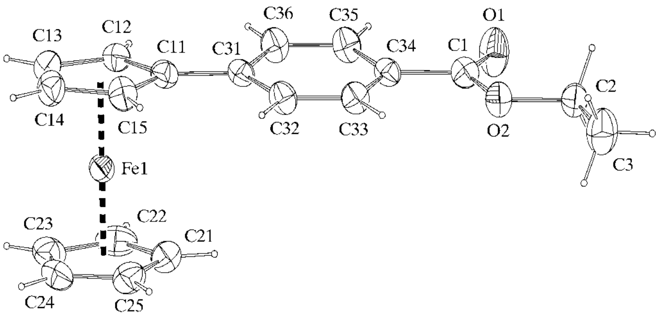


Figure 1
A view of the molecule of (II) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

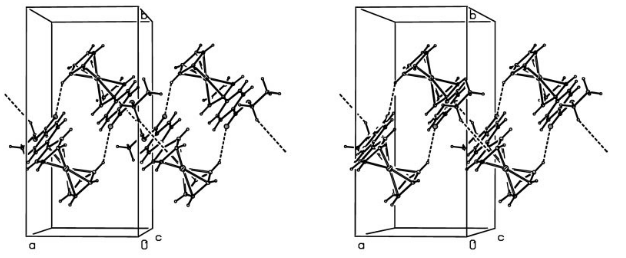


Figure 2
A stereoview of the interactions in the crystal structure of (II).

179.76 (16)° in (II) and 112.0 (5)° in (III), means that the methyl groups of the isopropyl moiety in (III) are oriented almost orthogonal to the ester CO_2 plane (Figs. 1 and 3).

Analysis of the hydrogen bonding in (II) shows only two interactions of note, involving the substituted ring and the ester O═C group as $\eta^5(C_5H_4)C—H\cdots O═C$ interactions (Table 2 and Fig. 2). Molecules of the ethyl ester form dimers through $\eta^5(C_5H_5)C—H\cdots O═C$ hydrogen bonds, graph set $R_2^2(20)$ and, together with $Csp^3—H\cdots\pi(C_5H_5)$ interactions, these generate a one-dimensional column (irregular ladder). The molecules of the isopropyl ester, (III), aggregate through $\eta^5(C_5H_5)C—H\cdots\pi(C_6H_4)$ interactions (Table 4 and Fig. 4).

Analysis of the April 2002 Version of the Cambridge Structural Database using *ConQuest* Version 1.4 (Allen, 2002) for the mono-substituted *para*-Fc–C_6H_4–*X* group (*X* is any atom) was undertaken for structures which fulfil the three-dimensional coordinates and $R < 0.10$ criteria. A total of 13 relevant structures were found. The interplanar angle between the C_5H_4 and C_6 rings varies between 2.2 and 29.1° for 17 examples, with a median of 12.8° (11 examples are within the range 7.7–19.3°). Our results above compare favourably with these values.

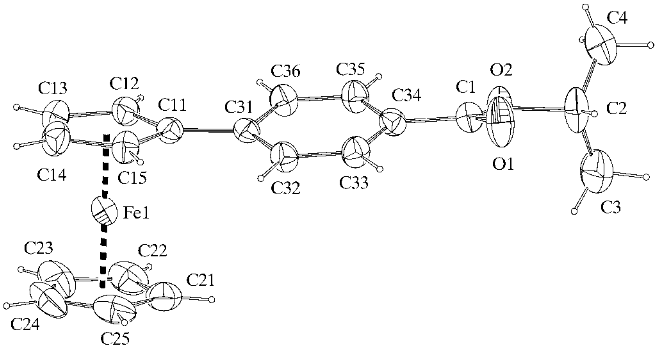


Figure 3
A view of the molecule of (III) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

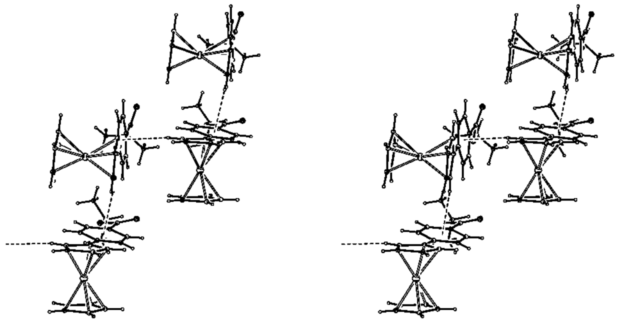


Figure 4
A stereoview of the interactions in the crystal structure of (III). For the sake of clarity, the unit-cell box has been omitted.

Experimental

Compounds (II) and (III) were prepared according to standard literature procedures. Analytical data for (II): m.p. 358–359 K (uncorrected); IR (KBr, ν, cm^{-1}): 1678 (C═O); UV–vis, λ_{max} (CH_3CN): 360 (880), 445 (290) nm; ^{1}H NMR (400 MHz, $CDCl_3$, δ, p.p.m.): 7.86 (2H, *d*, *J* = 8.4 Hz, Ar-H), 7.66 (2H, *d*, *J* = 8.4 Hz, Ar-H), 4.89 [2H, *t*, *J* = 1.8 Hz, *o*-$\eta^5(C_5H_4)$], 4.44 [2H, *t*, *J* = 1.8 Hz, *m*-$\eta^5(C_5H_4)$], 4.32 (2H, *q*, *J* = 7 Hz, –OCH_2CH_3), 4.03 [5H, *s*, $\eta^5(C_5H_5)$], 1.33 (3H, *t*, –OCH_2CH_3); ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 166.1, 145.5, 129.6, 127.2, 126.0, 83.0, 70.2, 69.9, 67.2, 60.9, 14.6. Analytical data for (III): m.p. 351–352 K (uncorrected); IR (KBr, ν, cm^{-1}): 1710 (C═O); UV–vis, λ_{max} (CH_3CN): 360 (1120), 458 (302) nm; ^{1}H NMR (400 MHz, $CDCl_3$, δ, p.p.m.): 7.87 (2H, *d*, *J* = 8.4 Hz, Ar-H), 7.44 (2H, *d*, *J* = 8.4 Hz, Ar-H), 5.18 [1H, *m*, $OCH(CH_3)_2$], 4.64 [2H, *s*, *o*-$\eta^5(C_5H_4)$], 4.32 [2H, *s*, *m*-$\eta^5(C_5H_4)$], 3.96 [5H, *s*, $\eta^5(C_5H_5)$], 1.30 [6H, *t*, $OCH(CH_3)_2$]; ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 166.6, 145.2, 130.0, 128.5, 126.0, 83.9, 70.2, 70.1, 68.5, 67.3, 22.4.

Compound (II)

Crystal data

$[Fe(C_5H_5)(C_{14}H_{13}O_2)]$
$M_r = 334.18$
Monoclinic, $P2_1/c$
$a = 7.9563$ (5) Å
$b = 16.3464$ (11) Å
$c = 12.0088$ (10) Å
$\beta = 94.128$ (5)°
$V = 1557.78$ (19) Å^3
$Z = 4$

$D_x = 1.425$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 80 reflections
$\theta = 5.5$–20.7°
$\mu = 0.97$ mm^{-1}
$T = 294$ (1) K
Block, orange
0.50 × 0.45 × 0.45 mm

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.629$, $T_{max} = 0.646$
4875 measured reflections
3780 independent reflections
3276 reflections with $I > 2\sigma(I)$

$R_{int} = 0.012$
$\theta_{max} = 28°$
$h = -10 \rightarrow 1$
$k = -21 \rightarrow 1$
$l = -15 \rightarrow 15$
4 standard reflections every 296 reflections
intensity variation: ±1%

Table 1
Selected geometric parameters (Å, °) for (II).

O1—C1	1.200 (2)	C1—C34	1.489 (2)
O2—C1	1.3282 (19)	C2—C3	1.486 (3)
O2—C2	1.4503 (19)	C11—C31	1.470 (2)
C1—O2—C2	115.63 (13)	O2—C2—C3	107.37 (15)
O1—C1—O2	123.17 (16)	C1—C34—C33	122.85 (14)
O1—C1—C34	124.07 (15)	C1—C34—C35	118.07 (14)
O2—C1—C34	112.76 (13)		
C2—O2—C1—C34	−178.95 (13)	C12—C11—C31—C36	7.9 (2)
C1—O2—C2—C3	179.76 (16)	O1—C1—C34—C33	178.40 (17)

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.079$
$S = 1.05$
3780 reflections
200 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 0.319P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

Table 2
Hydrogen-bonding and short-contact geometry (Å, °) for (II).

*Cg*1 is the centroid of the substituted cyclopentadienyl ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C22—H22···O1^{i}	0.93	2.54	3.360 (3)	147
C2—H2*A*···*Cg*1^{ii}	0.97	2.87	3.770 (2)	155

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

Compound (III)

Crystal data

$[Fe(C_5H_5)(C_{15}H_{15}O_2)]$
$M_r = 348.21$
Monoclinic, $P2_1/a$
$a = 9.3406$ (9) Å
$b = 10.1663$ (6) Å
$c = 17.9072$ (10) Å
$\beta = 90.136$ (6)°
$V = 1700.5$ (2) Å^3
$Z = 4$
$D_x = 1.360$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 72 reflections
$\theta = 6.1$–15.3°
$\mu = 0.89$ mm^{-1}
$T = 294$ (1) K
Block, red
0.39 × 0.26 × 0.15 mm

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.769$, $T_{\max} = 0.875$
4440 measured reflections
3355 independent reflections
2439 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.006$
$\theta_{\max} = 26°$
$h = -11 \rightarrow 1$
$k = -1 \rightarrow 12$
$l = -22 \rightarrow 22$
4 standard reflections every 296 reflections intensity variation: ±1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.109$
$S = 1.04$
3355 reflections
210 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 0.7638P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (III).

O1—C1	1.186 (4)	C1—C34	1.485 (4)
O2—C1	1.321 (4)	C2—C3	1.440 (7)
O2—C2	1.481 (4)	C2—C4	1.448 (6)
C1—O2—C2	117.7 (2)	O2—C2—C4	108.2 (3)
O1—C1—O2	124.1 (3)	C3—C2—C4	114.8 (4)
O1—C1—C34	123.8 (3)	C1—C34—C33	118.2 (3)
O2—C1—C34	112.1 (3)	C1—C34—C35	123.7 (3)
O2—C2—C3	107.9 (4)		
C2—O2—C1—O1	5.9 (5)	C1—O2—C2—C3	112.0 (5)

Table 4
Hydrogen-bonding and short-contact geometry (Å, °) for (III).

*Cg*3 is the centroid of the phenylene ring system.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1	0.98	2.25	2.696 (4)	106
C12—H12···*Cg*3^{i}	0.93	2.75	3.658 (3)	167

Symmetry code: (i) $x - \frac{3}{2}, -\frac{1}{2} - y, z$.

For compounds (II) and (III), space groups $P2_1/c$ and $P2_1/a$, respectively, were uniquely assigned from the systematic absences and confirmed by the analyses. H atoms were treated as riding atoms, with C—H distances in the range 0.93–0.98 Å.

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *PLATON* (Spek, 1998); software used to prepare material for publication: *SHELXL*97 and *PREP*8 (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1238). Services for accessing these data are described at the back of the journal.

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