

Functionalised acyl ferrocenes: crystal and molecular structures of 4-aminobenzoylferrocene, 4-hydroxybenzoylferrocene and 1,1'-bis(4-hydroxybenzoyl) ferrocene

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Received 27 November 1996; revised 14 January 1997; accepted 14 January 1997

Abstract

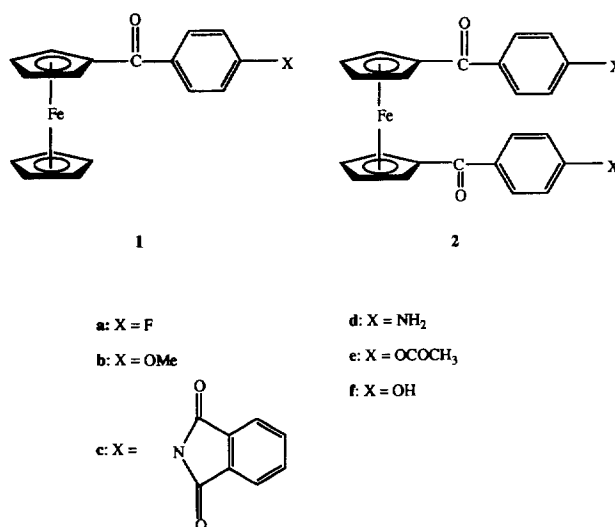
Improved methods of synthesis are reported for $\text{FcCOC}_6\text{H}_4\text{F}$ -4 **1a**, $\text{FcCOC}_6\text{H}_4\text{OMe}$ -4 **1b** and $\text{Fcd}(\text{COC}_6\text{H}_4\text{OMe}-4)_2$ **2b** [$\text{Fc} = (\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)$; $\text{Fcd} = (\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4)$]: demethylation of **1b** and **2b**, using AlCl_3 in 1,1,2-trichloroethane, yields $\text{FcCOC}_6\text{H}_4\text{OH}$ **1f** and $\text{Fcd}(\text{COC}_6\text{H}_4\text{OH})_2$ **2f** respectively. Acylation of ferrocene using 4-phthalimidobenzoyl chloride yields 4-(phthalimidobenzoyl)ferrocene **1c**, hydrazinolysis of which yields $\text{FcCOC}_6\text{H}_4\text{NH}_2$ -4 **1d**. Crystal structures are reported for **1d**, **1f** and **2f**: in **1d** and **1f** the molecules are linked into spiral chains by means of $\text{N-H} \cdots \text{O}=\text{C}$ and $\text{O-H} \cdots \text{O}=\text{C}$ hydrogen bonds respectively; in **2f** the $\text{O-H} \cdots \text{O}=\text{C}$ hydrogen bonds link the centrosymmetric molecules into continuous two-dimensional nets, two independent sets of which are interwoven. © 1997 Elsevier Science S.A.

Keywords: Acyl ferrocenes; 4-Aminobenzoylferrocene; 4-Hydroxybenzoylferrocene; 1,1'-bis(4-Hydroxybenzoyl)ferrocene; Crystal structure; Molecular structure

1. Introduction

Functionalised diacyl ferrocenes of type $\text{Fcd}(\text{COAr})_2$ [$\text{Fcd} = -(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4)-$] in which the aryl group carries a reactive functionality, such as OH, NH_2 or halogen, are potentially useful intermediates for the synthesis of high-performance organometallic polymers. The corresponding mono-acyl species FcCOAr [$\text{Fc} = (\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)-$] are thus ideal models for the study of the reaction chemistry centred upon the aryl functionality, which might be exploitable in subsequent polymer synthesis. In this paper we report improved syntheses for a number of the monoacyl compounds **1**, of which **1a**, **1d** and **1f** are of particular interest in model synthetic reactions, and for the diacyl species **2a** and **2f**, of interest as potential intermediates for polymer synthesis; some studies of the reactivity of **1a** and **2a**; and the

crystal structures of **1d**, **1f** and **2f**, which exhibit interesting hydrogen-bonding interactions in the solid state.



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2. Experimental

NMR spectra were recorded at ambient temperatures, in CDCl₃ solution unless stated otherwise, on a Bruker AM-300 spectrometer operating at 300.135 MHz for ¹H and 75.469 MHz for ¹³C. Diethyl ether and light petroleum (b.p. 40–60 °C) were dried over sodium wire; chromatography was performed on silica gel (60H TLC grade for dry flash chromatography, and Kieselgel 30–70 mesh for standard flash columns).

2.1. Preparation of 4-phthalimidobenzoyl chloride

Phthalic anhydride (44.40 g, 0.3 mol) was added to a solution of *p*-aminobenzoic acid (41.10 g, 0.3 mol) in warm 1,4-dioxan (250 cm³). The suspension was heated to 90 °C (on a water bath), with vigorous agitation for 3 h. The slurry was allowed to cool to room temperature and the white solid collected by filtration, washed with warm (60 °C) 1,4-dioxan (2 × 100 cm³), ether (100 cm³) then dried at the pump. The crude 4-(2-carboxybenzamido)benzoic acid (48.4 g, 64%; m.p. 288–291 °C) was pure by NMR and was used without recrystallisation in the next stage. NMR: δ(H) (DMSO-*d*₆) 3.4 (1H, br s, NH), 7.55–7.54 (3H, m, benzamido H-4,5,6), 7.82 (2H, d, *J* 8.4, AB, *m*-H), 7.89–7.99 (3H, m, *o*-H and benzamido H-3), 10.68 (1H, s, COOH); δ(C) (DMSO-*d*₆) 118.9 (Ar *m*-C), 125.4 (benzamido 2-C), 128.0 (benzamido 4-C), 129.8 (benzamido 3- and 6-C), 130.0 (Ar *ipso*-C), 130.5 (Ar *o*-C), 132.1 (benzamido 5-C), 138.8 (benzamido 1-C), 143.8 (Ar *p*-C), 167.2, 167.5 and 168.0 (3 × C=O). A suspension of 4-(2-carboxybenzamido)benzoic acid (25.00 g, 88 mmol) in thionyl chloride (150 cm³) was heated under reflux for 6 h, allowed to cool and then left at room temperature overnight. The excess thionyl chloride was removed under reduced pressure and the residual pale green–yellow solid dried in vacuum over potassium hydroxide pellets. Recrystallisation from *N,N*-dimethylformamide gave 4-phthalimidobenzoyl chloride as a white crystalline solid (12.8 g, 51%), m.p. 262–264 °C. Anal. Found: C, 63.4; H, 3.0; N, 5.1. C₁₅H₈ClNO₃ Calc.: C, 63.1; H, 2.8; N, 4.9%. δ(H) (DMSO-*d*₆) 7.72 (2H, d, AA'BB', *J* 8.2, Ar *m*-H), 8.02–8.07 (2H, m, phthalimido β-H), 8.07–8.13 (2H, m, phthalimido α-H), 8.20 (2H, d, *J* 8.2, AA'BB', Ar *o*-H); δ(C) (DMSO-*d*₆) 123.8 (phthalimido 2-C), 127.2 (Ar *m*-C), 130.0 (Ar *o*-C), 130.2 (Ar *ipso*-C), 131.7 (phthalimido 1-C), 135.1 (phthalimido 3-C), 136.0 (Ar *p*-C), 166.8 and 166.9 (2 × C=O).

2.2. Preparation of compounds **1a**, **1b**, **2a** and **2b**

Monoacyl ferrocenes **1a** and **1b** were prepared in yields of 54% and 62% respectively by the usual Friedel–Crafts procedure, employing equimolar quanti-

ties of ferrocene and ArCOCl/AlCl₃ in dichloromethane and reaction times of 16 h at ambient temperature. M.p. **1a** 115–117 °C (lit. [1] 117–118 °C), **1b** 78–81 °C (lit. [2] 82–83 °C). NMR: **1a** δ(H) 4.18 (5H, s, Cp), 4.59 and 4.88 (each 2H, s, α- and β-CH of C₅H₄), 7.15 (2H, overlapping dd, ³J_{FH} = J_{HH} = 7.4, Ar *m*-H), 7.95 (2H, overlapping dd, ⁴J_{FH} = J_{HH} = 7.4, Ar *o*-H); δ(C) 70.1 (Cp), 71.4 and 72.5 (α- and β-CH of C₅H₄), 78.0 (1-C), 115.1 (Ar *m*-C, ³J_{CF} 21.8), 130.4 (Ar *o*-C, ⁴J_{CF} 8.8), 135.9 (Ar *ipso*-C), 163.0 and 166.4 (Ar *p*-C, ²J_{CF} 252.5), 197.4 (C=O). **1b** δ(H) 3.80 (3H, s, OCH₃), 4.16 (5H, s, Cp), 4.51 and 4.87 (α- and β-CH of C₅H₄), 6.91 (2H, d, *J* 9.6, AA'BB', Ar *m*-H), 7.94 (2H, d, *J* 9.6, AA'BB', Ar *o*-H); δ(C) 55.1 (OCH₃), 69.0 (Cp), 71.3 and 71.9 (α- and β-CH of C₅H₄), 78.4 (1-C), 113.2 (Ar *m*-C), 130.2 (Ar *o*-C), 130.8 (Ar *ipso*-C), 162.2 (Ar *p*-C), 197.2 (C=O).

Diacyl ferrocenes **2a** and **2b** were similarly prepared, in yields of 59% and 72%, by use of three equivalents of ArCOCl/AlCl₃ and reaction times of 40 h at room temperature. M.p. **2a** 130–133 °C (lit. [3] 129–131 °C), **2b** 139–141 °C (lit. [4] 141–142 °C). NMR: **2a** δ(H) 4.60 and 4.86 (each 2H, s, α- and β-CH of C₅H₄), 7.13 (4H, overlapping dd, ³J_{FH} = J_{HH} = 7.5, Ar *m*-H), 7.82 (4H, overlapping dd, ⁴J_{FH} = J_{HH} = 7.5, Ar *o*-H); δ(C) 72.5 and 73.6 (α- and β-CH of C₅H₄), 79.2 (1- and 1'-C), 115.2 (Ar *m*-C, ³J_{CF} 22.0), 130.5 (Ar *o*-C, ⁴J_{CF} 8.9), 136.0 (Ar *ipso*-C), 163.1 and 166.5 (Ar *p*-C, ²J_{CF} 255.0), 197.1 (C=O). **2b** δ(H) 3.88 (2 × OCH₃), 4.56 and 4.90 (each 4H, s, α- and β-CH of C₅H₄), 6.90 (4H, d, *J* 8.2, AA'BB', Ar *m*-H), 7.83 (4H, d, *J* 8.2, AA'BB', Ar *o*-H); δ(C) 55.3 (OCH₃), 73.0 and 74.1 (α- and β-CH of C₅H₄), 80.0 (1- and 1'-C), 113.4 (Ar *m*-C), 130.5 (Ar *o*-C), 131.6 (Ar *ipso*-C), 162.6 (Ar *p*-C), 196.2 (C=O).

2.3. Preparation of compound **1c**

Aluminium chloride (0.47 g, 3.5 mmol) was added to a hot (60 °C) solution of 4-phthalimidobenzoyl chloride (1.0 g, 3.5 mmol) in 1,2-dichloroethane (25 cm³) and the mixture stirred at 75 °C until all the solid had dissolved (ca. 45 min). A solution of ferrocene (0.65 g, 3.5 mmol) in dichloromethane (4 cm³) was added dropwise and the resulting dark purple mixture stirred at 75 °C for 3 h then room temperature for 12 h. The reaction mixture was poured onto ice (40 g), stirred until the ice had melted, then diluted with ethyl acetate (100 cm³) before the layers were separated. The aqueous layer was extracted with ethyl acetate (50 cm³) and the combined extracts were dried over MgSO₄. Removal of the solvent under reduced pressure gave crude **1c**, a red solid which was purified by dry flash column chromatography with 50% ether–petrol as eluent. Yield 0.62 g, 40%; m.p. 196–197 °C. Anal. Found: C, 69.1; H, 3.9; N, 3.1. C₂₅H₁₇FeNO₃ Calc.: C, 69.0; H, 3.9; N, 3.2%. δ(H)

4.24 (5H, s, Cp), 4.62 and 4.95 (each 2H, α - and β -CH of C₅H₄), 7.61 (2H, d, *J* 7.5, AA'BB', Ar *m*-H), 7.80–7.88 (2H, m, phthalimido α -H), 7.96–8.02 (2H, m, phthalimido β -H), 8.06 (2H, d, *J* 7.5, AA'BB', Ar *o*-H); δ (C) 70.2 (Cp), 71.4 and 72.6 (α - and β -CH of C₅H₄), 77.8 (1-C), 123.8 (phthalimido 2-C), 125.8 (Ar, *m*-C), 128.8 (Ar *o*-C), 131.5 (Ar *ipso*-C), 134.4 (phthalimido 1-C), 134.5 (phthalimido 3-C), 138.7 (Ar, *p*-C), 166.8 (2 \times phthalimido C=O), 197.9 (C=O).

Attempts to prepare 1,1'-bis(4-phthalimidobenzoyl)ferrocene **2c** from aluminium chloride (2.80 g, 21 mmol) and 4-phthalimidobenzoyl chloride (6.00 g, 21 mmol) in 1,2-dichloroethane (150 cm³) with ferrocene (0.93 g, 5 mmol) in dichloromethane (10 cm³) led solely to the formation of the mono derivative **1c**, even when the reaction mixture was heated under reflux for prolonged periods.

2.4. Preparation of compound **1d**

A suspension of 4-phthalimidobenzoylferrocene (0.40 g, 0.9 mmol) and hydrazine monohydrate (98%; 0.05 g, 1.0 mmol) in ethanol (20 cm³) was heated under reflux, with stirring, for 3 h. The solvent was evaporated (reduced pressure), the residue suspended in water (30 cm³) and the pH adjusted to 2.0 using aqueous hydrochloric acid (1 mol dm⁻³). The suspension was filtered, the pH of the filtrate adjusted to 8.0 with aqueous sodium carbonate (1 mol dm⁻³) and the orange precipitate extracted into ethyl acetate (2 \times 70 cm³). The extracts were dried (MgSO₄) and concentrated under reduced pressure to give an orange solid which was purified by chromatography (diethyl ether) then recrystallised from a mixture of ethyl acetate and petroleum. Yield 0.14 g, 50%; m.p. 181–183 °C (dec., softened > 170 °C). Anal. Found: C, 67.1; H, 4.9; N, 4.5. C₁₇H₁₅FeNO Calc.: C, 66.9; H, 4.95; N, 4.5%. δ (H) 4.05 (2H, br s, NH₂), 4.19 (5H, s, Cp), 4.51 and 4.89 (each 2H, s, α - and β -CH of C₅H₄), 6.68 (2H, d, *J* 8.4, AA'BB', Ar *m*-CH), 7.86 (2H, d, *J* 8.4, AA'BB', Ar *o*-CH); δ (C) 70.0 (Cp), 71.4 and 71.6 (α - and β -CH of C₅H₄), 77.3 (1-C), 113.6 (Ar *m*-C), 129.6 (Ar *ipso*-C), 130.7 (Ar *o*-C), 149.4 (Ar *p*-C), 197.0 (C=O).

2.5. Preparation of compound **1e**

Using the general procedure described earlier for mono-arylation, aluminium chloride (13.34 g, 0.1 mol), 4-acetoxybenzoyl chloride (20.00 g, 0.1 mol) in dichloromethane (100 cm³) and ferrocene (18.60 g, 0.1 mol) in dichloromethane (125 cm³) were reacted together. TLC indicated that there were two major products which were almost coincident on the plate and which could not be separated by chromatography. ¹H NMR [δ (H) 2.31 (s, OCOCH₃), 2.38 (s, COCH₃), 4.19 (s, 2 \times Cp), 4.50 and 4.75 (each s, α - and β -CH of

acetyl ferrocene), 4.59 and 4.90 (each s, α - and β -CH of benzoyl derivative), 7.19 (d, *J* 8.0, AA'BB', Ar *m*-H), 7.94 (d, *J* 8.0, AA'BB', Ar *o*-H)] showed that this was a mixture (ca. 3:1) of acetylferrocene and 4-acetoxybenzoyl ferrocene. Total yield 11.96 g; this mixture was used directly for hydrolysis of **1e** to form **1f**.

2.6. Preparation of compound **1f**

(a) By hydrolysis of **1e**. To a solution of the above mixture (11.96 g) in methanol (20 cm³) was added a solution of potassium hydroxide (0.79 g, 14 mmol) in methanol (20 cm³). The mixture was heated under reflux for 15 min after which time no 4-acetoxybenzoyl ferrocene was apparent by TLC. The reaction mixture was poured into water (100 cm³) and then extracted with ether until these extracts were colourless. The aqueous phase was then acidified to pH 1.0 with conc. hydrochloric acid and extracted with ethyl acetate (150 cm³). Removal of the solvent under reduced pressure gave a red solid which was purified by dry flash column chromatography (20% ether–petrol to 60% ether–petrol, gradient) to give first acetylferrocene and then **1f**. Yield of **1f** 0.64 g, 2.1% from ferrocene; m.p. 186–188 °C (lit. [5] 190–191 °C). Anal. Found: C, 66.9, H, 4.9. C₁₇H₁₄FeO₂ Calc.: C, 66.7, H, 4.6%. NMR δ (H) 4.21 (5H, s, Cp), 4.60 and 4.95 (each 2H, s, α - and β -CH of C₅H₄), 6.98 (2H, d, *J* 7.5, AA'BB', 2 \times Ar *m*-H), 7.92 (2H, d, *J* 7.5, AA'BB', 2 \times Ar *o*-H), 7.90–8.10 (1H, br s, OH); δ (C) 70.9 (Cp), 72.3 and 73.1 (α - and β -CH of C₅H₄), 78.8 (1-C), 115.8 (Ar *m*-C), 131.4 (Ar *o*-C), 132.0 (Ar *ipso*-C), 160.8 (Ar *p*-C), 199.8 (C=O). The structure was confirmed by single-crystal X-ray diffraction (see below).

(b) By demethylation of **1b**. Aluminium chloride (1.40 g, 10.5 mmol) was added to a solution of 4-(methoxybenzoyl)ferrocene (1.60 g, 5 mmol) in 1,1,2-trichloroethane (10 cm³) and the suspension was heated under reflux for 15 min. The blue–black reaction mixture was allowed to cool to room temperature, diluted with dichloromethane (20 cm³), poured onto ice (20 g) then stirred for 1 h. The layers were separated and the organic layer stirred with aqueous sodium hydroxide (10% w/w; 30 cm³). The aqueous layer was acidified to pH 1.0 using conc. hydrochloric acid and the red–brown precipitate extracted into dichloromethane (2 \times 50 cm³). The combined extracts were dried (MgSO₄) then filtered through a short (ca. 1 cm) bed of silica (60H TLC grade). Evaporation of the solvent under reduced pressure gave a red solid (0.5 g, 32%), which was purified and characterised as in (a) above.

2.7. Preparation of compound **2f**

Aluminium chloride (2.67 g, 20 mmol) was added to a solution of 1,1'-bis(4-methoxybenzoyl)ferrocene

(2.27 g, 5 mmol) in 1,1,2-trichloroethane (20 cm³) and the violet blue suspension stirred at 80 °C under nitrogen for 2 h: when the reaction was attempted at reflux decomposition was observed, while at 40 °C only unchanged starting material was isolated after several hours. The reaction mixture was cooled to room temperature then poured onto ice (40 g). A black solid mass which remained in the flask was dissolved in aqueous sodium hydroxide (2 mol dm⁻³; 30 cm³) and the resultant red solution was added to the ice-containing portion. The (now basic) mixture was stirred for 10 min before the layers were separated and the aqueous solution washed with dichloromethane (2 × 30 cm³). The aqueous solution was made acidic (pH 1.0) by the addition of conc. hydrochloric acid and the resulting brick-red precipitate was extracted into ethyl acetate (100 cm³). This solution was washed with water (2 ×

50 cm³), dried (MgSO₄) and then concentrated under reduced pressure to give a red-brown solid (0.59 g). Crystallisation of this from the minimum of ethanol gave the pure bis-phenol (0.37 g, 17%) as red blocks which decompose without melting above 270 °C. Anal. Found: C, 67.7; H, 4.4. C₂₄H₁₈FeO₄ Calc.: C, 67.6; H, 4.3%. δ (H) (DMSO-*d*₆) 4.58 and 4.78 (each 4H, s, 2 × Cp α - and β -CH of C₅H₄), 6.80 (4H, d, *J* 5.8, AA'BB', 4 × Ar *m*-H), 7.73 (4H, d, *J* 5.8, AA'BB', 4 × Ar *o*-H), 9.95–10.45 (2H, br s, 2 × OH); δ (C) (DMSO-*d*₆) 72.7 and 73.8 (Cp α - and β -CH of C₅H₄), 80.1 (1,1'-C), 115.1 (Ar *m*-C's), 129.8 (Ar *ipso*-C's), 130.7 (Ar *o*-C's), 161.3 (Ar *p*-C's), 194.7 (2 × C=O).

2.8. Reactions using 1a and 2a

(a) **1a** with sodium methoxide. Sodium methoxide (0.22 g, 4.0 mmol) was added to a solution of (4-fluoro-

Table 1
Summary of crystal data, data collection and refinement details

	1d	1f	2f
<i>(a) Crystal data</i>			
empirical formula	C ₁₇ H ₁₅ FeNO	C ₁₇ H ₁₄ FeO ₂	C ₂₄ H ₁₈ FeO ₄
molar mass	305.16	306.14	426.25
colour, habit	orange, block	red, block	red, block
crystal size, mm ³	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.20 × 0.20 × 0.10
crystal system	monoclinic	orthorhombic	orthorhombic
<i>a</i> (Å)	10.448(7)	10.460(6)	15.713(8)
<i>b</i> (Å)	9.596(8)	12.972(4)	8.414(8)
<i>c</i> (Å)	13.913(8)	10.080(3)	14.235(7)
α (°)	90	90	90
β (°)	108.09(5)	90	90
γ (°)	90	90	90
<i>V</i> (Å ³)	1326(1)	1367.7(9)	1882(1)
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Pbcn</i>
<i>Z</i>	4	4	4
<i>F</i> (000)	632	632	880
<i>d</i> _{calc} (g cm ⁻³)	1.528	1.487	1.504
μ (mm ⁻¹)	1.129	1.098	0.830
<i>(b) Data acquisition^a</i>			
temperature (K)	293(1)	293(1)	293(1)
unit-cell reflections (θ range (°))	9 (7.5–11.9)	25 (23.8–25.0)	20 (7.7–12.8)
max. 2θ (°) for reflections	50.0	50.0	50.0
<i>hkl</i> range of reflns	0, 12; –10, 11; –16, 15	0, 12; 0, 15; 0, 11	0, 18; –10, 8; –16, 0
variation in three standard reflections	decay, 4.7%	< 0.2%	< 0.2%
reflections measured	3071	1417	2719
unique reflections	2648	1416	1921
<i>R</i> _{int}	0.076	0.019	0.169
reflections with $I > n\sigma(I)$, <i>n</i>	1716, 3	1190, 3	1456, 3.3
Abs. corr.; <i>T</i> _{max} , <i>T</i> _{min}	1.000, 0.878	1.000, 0.939	—
<i>(c) Structure solution and refinement^b</i>			
solution method	direct	direct	direct
no. of variables in LS	181	182	138
<i>R</i> (<i>F</i>), <i>R</i> _w (<i>F</i>)	0.062, 0.065	0.034, 0.029	0.109, 0.138
density range in final Δ map (e Å ⁻³)	–0.47, 0.41	–0.25, 0.27	–0.99, 2.41
final shift/error ratio	0.032	0.004	0.222

^a Data collection on a Rigaku AFC7S diffractometer with graphite-monochromated Mo K α radiation (λ , 0.7107 Å).

^b Calculations done using the TeXsan suite [7]. Refinement was on *F* in all cases, with all non-H atoms allowed anisotropic vibration.

Table 2

Atomic coordinates for $\text{FcCOC}_6\text{H}_4\text{NH}_2$ **1d**, $\text{FcCOC}_6\text{H}_4\text{OH}$ **1f** and $\text{Fe}(\text{C}_5\text{H}_4\text{COC}_6\text{H}_4\text{OH})_2$ **2f**

Atom	x	y	z	U_{eq}
(a) $\text{FcCOC}_6\text{H}_4\text{NH}_2$ compound 1d				
Fe(1)	0.8091(1)	-0.3224(1)	0.05666(9)	0.0459(4)
O(1)	0.5105(5)	-0.1520(5)	0.0624(4)	0.056(2)
N(1)	0.7344(6)	0.3375(8)	0.3752(5)	0.058(2)
C(1)	0.6216(8)	-0.0910(9)	0.0846(7)	0.050(3)
C(2)	0.6570(7)	0.0177(8)	0.1627(6)	0.042(2)
C(3)	0.7462(7)	0.1264(9)	0.1596(6)	0.047(3)
C(4)	0.7707(7)	0.2307(9)	0.2317(7)	0.049(3)
C(5)	0.7092(7)	0.2336(9)	0.3044(6)	0.045(3)
C(6)	0.6178(7)	0.1253(9)	0.3066(6)	0.052(3)
C(7)	0.5946(7)	0.0212(9)	0.2362(6)	0.049(3)
C(8)	0.7133(8)	-0.1329(8)	0.0302(6)	0.043(3)
C(9)	0.8613(8)	-0.1168(8)	0.0586(7)	0.054(3)
C(10)	0.9066(8)	-0.1903(9)	-0.0131(7)	0.059(3)
C(11)	0.7947(9)	-0.2514(9)	-0.0857(6)	0.057(3)
C(12)	0.6775(8)	-0.2169(8)	-0.0602(6)	0.054(3)
C(13)	0.7485(8)	-0.4146(9)	0.1671(7)	0.053(3)
C(14)	0.8885(8)	-0.3981(8)	0.2003(6)	0.051(3)
C(15)	0.9426(7)	-0.4716(9)	0.1317(6)	0.054(3)
C(16)	0.8339(9)	-0.5357(8)	0.0563(6)	0.055(3)
C(17)	0.7142(7)	-0.4978(9)	0.0798(7)	0.059(3)
(b) $\text{FcCOC}_6\text{H}_4\text{OH}$ compound 1f				
Fe(1)	-0.62821(5)	-0.11787(4)	0.27799(5)	0.0547(1)
O(1)	-0.4781(2)	-0.0899(2)	-0.0757(2)	0.0701(8)
O(2)	-0.6805(2)	-0.5304(2)	-0.2319(2)	0.0801(8)
C(1)	-0.5678(3)	-0.1369(3)	-0.0267(3)	0.0522(9)
C(2)	-0.6036(3)	-0.2389(2)	-0.0798(3)	0.0506(9)
C(3)	-0.6670(3)	-0.3145(3)	-0.0073(3)	0.067(1)
C(4)	-0.6906(4)	-0.4109(3)	-0.0589(3)	0.073(1)
C(5)	-0.6556(3)	-0.4348(3)	-0.1871(3)	0.0591(9)
C(6)	-0.5947(3)	-0.3593(3)	-0.2620(3)	0.0597(10)
C(7)	-0.5690(3)	-0.2645(3)	-0.2092(3)	0.0576(9)
C(8)	-0.6374(3)	-0.0875(2)	0.0814(3)	0.0534(7)
C(9)	-0.7637(3)	-0.1070(2)	0.1344(3)	0.0570(9)
C(10)	-0.7896(3)	-0.0351(2)	0.2347(4)	0.068(1)
C(11)	-0.6826(3)	0.0310(2)	0.2445(4)	0.074(1)
C(12)	-0.5915(3)	-0.0004(2)	0.1522(4)	0.070(1)
C(13)	-0.6311(6)	-0.2594(3)	0.3617(5)	0.111(2)
C(14)	-0.6577(4)	-0.1834(4)	0.4573(4)	0.095(2)
C(15)	-0.5550(5)	-0.1186(4)	0.4632(4)	0.100(2)
C(16)	-0.4639(4)	-0.1516(4)	0.3749(5)	0.122(2)
C(17)	-0.5101(6)	-0.2395(4)	0.3109(5)	0.131(2)
(c) $\text{Fe}(\text{C}_5\text{H}_4\text{COC}_6\text{H}_4\text{OH})_2$ compound 2f				
Fe(1)	0.5000	-0.5000	0.5000	0.0393(7)
O(1)	0.2865(6)	-0.340(1)	0.5049(6)	0.060(3)
O(2)	0.3301(7)	-0.010(1)	0.8971(7)	0.058(3)
C(1)	0.3519(10)	-0.285(2)	0.5361(9)	0.049(5)
C(2)	0.3505(8)	-0.207(1)	0.6322(8)	0.040(4)
C(3)	0.2953(8)	-0.275(1)	0.6981(10)	0.050(4)
C(4)	0.2897(9)	-0.212(2)	0.7874(9)	0.050(4)
C(5)	0.3349(8)	-0.078(1)	0.8109(10)	0.043(4)
C(6)	0.3882(8)	-0.007(1)	0.745(1)	0.048(4)
C(7)	0.3958(9)	-0.072(1)	0.6569(10)	0.050(4)
C(8)	0.4346(9)	-0.293(1)	0.4864(9)	0.047(4)
C(9)	0.5154(8)	-0.262(1)	0.519(1)	0.054(5)
C(10)	0.575(1)	-0.315(2)	0.452(1)	0.071(6)
C(11)	0.529(1)	-0.383(2)	0.378(1)	0.068(6)
C(12)	0.442(1)	-0.373(2)	0.3976(9)	0.059(5)

Table 3

Selected geometric parameters for $\text{FcCOC}_6\text{H}_4\text{NH}_2$ **1d**, $\text{FcCOC}_6\text{H}_4\text{OH}$ **1f** and $\text{Fe}(\text{C}_5\text{H}_4\text{COC}_6\text{H}_4\text{OH})_2$ **2f** (distances in Å, angles in °)

	1d	1f	2f
O(1)–C(1)	1.252(8)	1.223(5)	1.21(1)
C(1)–C(2)	1.47(1)	1.476(6)	1.52(2)
C(1)–C(8)	1.449(10)	1.459(6)	1.48(2)
X ^a –C(5)	1.368(9)	1.345(5)	1.36(2)
O(1)–C(1)–C(2)	121.2(8)	119.7(5)	118(1)
O(1)–C(1)–C(8)	117.1(8)	117.7(5)	123(1)
C(2)–C(1)–C(8)	121.8(7)	122.6(4)	117(1)
X ^a –C(5)–C(4)	121.3(8)	118.1(5)	122(1)
X ^a –C(5)–C(6)	119.9(8)	123.8(5)	117(1)
C(4)–C(5)–C(6)	118.8(8)	118.1(5)	120(1)
O(1)–C(1)–C(2)–C(3)	-151.6(7)	-154.7(6)	34(1)
O(1)–C(1)–C(2)–C(7)	23(1)	22.6(8)	-141(1)
O(1)–C(1)–C(8)–C(9)	-158.3(8)	-160.5(6)	-167(1)
O(1)–C(1)–C(8)–C(12)	13(1)	14.9(8)	-2(1)
C(2)–C(1)–C(8)–C(9)	21(1)	18.1(9)	11(1)
C(2)–C(1)–C(8)–C(12)	-166.9(7)	-166.5(5)	176(1)
C(3)–C(2)–C(1)–C(8)	28(1)	26.8(8)	-143(1)
C(7)–C(2)–C(1)–C(8)	-156.7(7)	-155.9(5)	39(1)

^a X = N(1) in **1d**; O(2) in **1f** and **2f**.

benzoyl)ferrocene (1.00 g, 3.25 mmol) in chlorobenzene (10 cm³) and the mixture heated under reflux for 24 h. After this period only unreacted starting material was present by TLC.

(b) **1a** with bis-phenol A (4,4'-isopropylidene-diphenol) and bis-phenol S (4,4'-sulfonyldiphenol). An intimate mixture of (4-fluorobenzoyl)ferrocene (3.0814 g, 10.00 mmol), mixed sodium and potassium carbonates (Na:K 50:1; 1.0875 g, 10.00 mmol) and the bisphenol (5.00 mmol) was heated, with stirring under a nitrogen atmosphere, rapidly to 150 °C and kept at this temperature for 3 h. The dark brown melt was allowed to cool before being shaken vigorously with dichloromethane and water (40 cm³ of each). The layers were separated and the organic layer dried (MgSO₄). Analysis of the solution by TLC showed that it contained only unreacted starting materials in both cases. When the procedure was repeated using higher temperatures (such as are used in the preparation of PEEK) decomposition was observed and no products were identified or starting materials recovered.

(c) **2a** with 2-naphthol. An intimate mixture of 1,1'-bis(4-fluorobenzoyl)ferrocene (1.00 g, 2.3 mmol), 2-naphthol (0.66 g, 4.6 mmol) and mixed sodium/potassium carbonates (0.50 g, 4.6 mmol) was heated to 150 °C for 3 h then worked up in the same way as above. Examination by TLC of the dichloromethane solution obtained after work-up showed that only unreacted starting materials were present. Once again when a higher temperature was used the result was decomposition and the formation of an intractable black solid.

2.9. X-ray crystallography

Crystals of compound **1d**, **1f** and **2f** suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in ethyl acetate/light petroleum, dichloromethane/light petroleum, and ethanol respectively.

Details of crystal data, data collection, and structure solution and refinement are summarised in Table 1. For compounds **1d**, **1f** and **2f** the space groups were uniquely determined as $P2_1/c$, $P2_12_12_1$ and $Pbcn$ respectively by the systematic absences: for **1d**, $0k0$ absent if k is odd and $h0l$ absent if l is odd; for **1f**, $h00$ absent if h is odd, $0k0$ absent if k is odd, and $00l$ absent if l is odd; and for **2f**, $0kl$ absent if k is odd, $h0l$ absent if l is odd and $hk0$ absent if $(h+k)$ is odd. The intensity data for **1d** showed a decrease in intensity of 4.7% during the course of the data collection: a linear correction factor was applied to take account of this. For compound **2f** the crystal quality proved to be consistently very poor, despite the excellent external appearance of the crystals. Six different crystals were investigated but, despite this, the quality of the diffraction data is somewhat indifferent. While the metrical precision of the structure analysis for **2f** is not high, there is no doubt that the principal features of the structure, especially the details of the hydrogen-bonding scheme, are correct in all particulars.

2.10. Structure solution and refinement

The structures were solved by direct methods using SIR92 [6], and refined by full-matrix least-squares on F [7]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference maps; except for the hydroxyl hydrogen in **2f**, the positions of H atoms were not refined, but they were all included in the refinements as riding atoms with the CNH_2 fragment in compound **1d** held planar.

Final refined coordinates are given in Table 2, and selected bond lengths and angles in Table 3. Additional material deposited at the Cambridge Crystallographic Data Centre includes displacement parameters and hydrogen atom coordinates: copies of the structure factor listings are available from the authors.

3. Results and discussion

3.1. Syntheses and reactivity

Although the Friedel–Crafts reaction is long-established as the method of choice for the preparation of mono- and di-acylferrocenes, the published procedures often give scope for considerable improvement in terms of both experimental convenience and yield. Function-

alised di-acylferrocenes **2** are attractive intermediates for polymer synthesis, while their mono-acyl analogues **1** are useful models for studies of reactivity at the aryl substituent, and we have therefore sought improved syntheses for a range of potentially useful derivatives **1** and **2**.

The use of equimolar quantities of ferrocene and of $ArCOCl/AlCl_3$ mixtures in dichloromethane as solvent provides satisfactory yields of both **1a** and **1b**, in overnight reactions at room temperature. Compound **1a** has previously been reported as formed in yields in the range 60–75% [1]. However, there must be some doubt about this reported yield as the same paper also described a similar yield of the 4-nitro analogue, using 4-nitrobenzoyl chloride/ $AlCl_3$, although it is well-established [3,8] that acylium ions carrying strongly electron-withdrawing groups, such as $(4-O_2NC_6H_4CO)^+$ [3], effect electron-transfer rather than acylation, giving high yields of the ferricinium cation rather than an acylferrocene. Compound **1b** has previously been prepared in 26% yield using CS_2 as solvent [2] and in 13% yield using CH_2Cl_2 [4]: the present procedure not only improves the yield considerably, but avoids the use of the noxious CS_2 as solvent. Demethylation of compound **1b** proved to be the preferred route to **1f**, but a wide range of reagents established as demethylating agents for aryl methyl ethers failed to demethylate **1b**; thus with chlorotrimethylsilane and sodium iodide [9] **1b** was recovered unchanged, while both HBr /acetic acid [10] and iodotrimethylsilane [11] caused complete decomposition. Eventually it was found that brief treatment with $AlCl_3$ in refluxing 1,1,2-trichloroethane was the most effective route to **1f**. The previous route [5] to **1f** required irradiation of $Fc-COOPh$, which itself requires a lengthy preparative route from ferrocene, via acylation with 2-chlorobenzoyl chloride followed by hydrolysis and esterification.

At the same time as the demethylation of compound **1b** was under investigation, we also explored the possibility of hydrolysing compound **1e** as a more convenient way to produce **1f**. However, room-temperature Friedel–Crafts acylation of ferrocene using 4-acetoxycarbonyl chloride [12] gave not only **1e**, but acetylferrocene also, in approximately three times the yield of **1e**; these two products proved to be inseparable by chromatography. Accordingly, the entire crude mixture was subjected to hydrolysis, using potassium hydroxide in methanol; subsequent chromatographic separation of the acetylferrocene from the much more polar **1f** did indeed yield pure **1f**, whose constitution was confirmed by single-crystal X-ray diffraction (see Section 3.2). Nonetheless, demethylation of **1b** is both more efficient and more convenient.

Use of 4-phthalimidobenzoyl chloride/ $AlCl_3$ as the acylating agent yielded compound **1c**, again under very mild conditions, and hydrazinolysis of **1c** straightfor-

wardly gave, in 20% overall yield from ferrocene, compound **1d** whose structure was confirmed by single-crystal X-ray diffraction (see below Section 3.2).

While we have been unable to improve upon the 76% yield previously reported for compound **2a** [3], we have certainly improved upon the previously reported yield of 0.5% for compound **2b** [4], by the use of three equivalents of $\text{ArCOCl}/\text{AlCl}_3$ in CH_2Cl_2 solution and a reaction time of 40 h at room temperature. The demethylation of **2b** to **2f** required careful control of the reaction conditions. Use of four equivalents of AlCl_3 in 1,1,2-trichloroethane gave rapid and complete decomposition at the reflux temperature (110°C), with no demethylation at all at 40°C , or during prolonged reflux in CH_2Cl_2 (44°C); however, reaction with AlCl_3 for 2 h in 1,1,2-trichloroethane at 80°C , under a dinitrogen atmosphere, gave an isolable yield of pure **2f**, whose structure was confirmed by single-crystal X-ray diffraction (see below Section 3.2). Attempted preparation of **2c** gave only the mono-substituted product **1c**, even after prolonged reaction times at elevated temperatures: evidently, the 4-phthalimidobenzoyl substituent associated with one cyclopentadienyl ring very powerfully deactivates the unsubstituted cyclopentadienyl ring in **1c** towards further electrophilic attack. Similarly, attempts to prepare compound **2e** yielded only 1,1'-diacetylferrocene, so ruling out **2e** as a possible alternative precursor

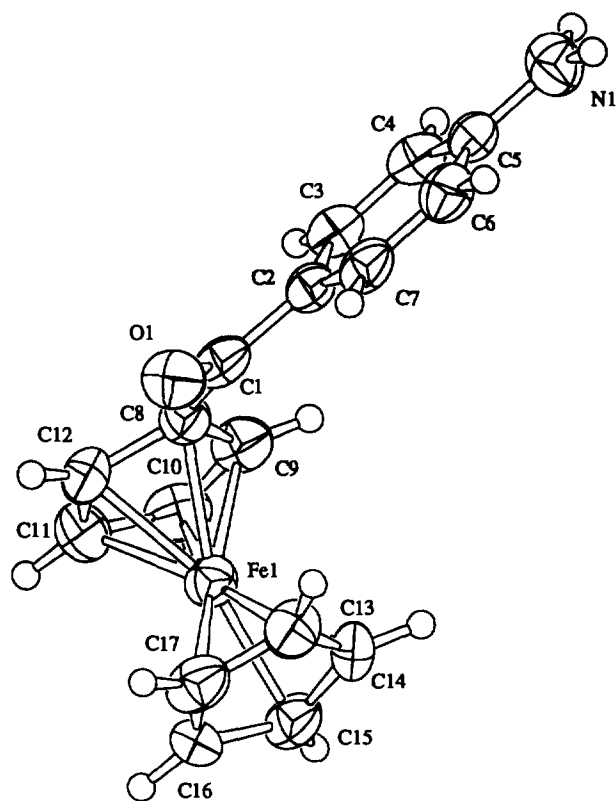


Fig. 1. Perspective view of one molecule of compound **1d**, showing the atom-labelling scheme.

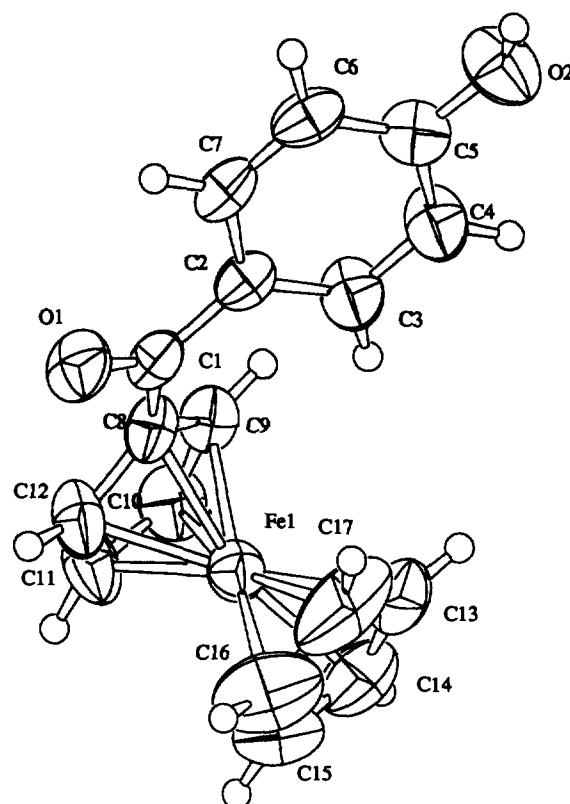


Fig. 2. Perspective view of one molecule of compound **1f**, showing the atom-labelling scheme.

to **2f**: as in the reaction to form **1e**, formation and reaction of the acylium salt $[\text{CH}_3\text{COOC}_6\text{H}_4\text{CO}]^+[\text{AlCl}_4]^-$ by cleavage of a carbon–chlorine bond competes ineffectively with formation and reaction of the presumed alternative $[\text{CH}_3\text{CO}]^+[\text{Cl}_3\text{AlOC}_6\text{H}_4\text{COCl}]^-$.

The reactions, under basic conditions, between bisphenols and bis-(4-fluorophenyl) derivatives such as $(\text{FC}_6\text{H}_4)_2\text{CO}$ are of importance in the synthesis of PEEK-type polymers [13]. We have therefore briefly explored the behaviour of compounds **1a** and **2a** in reactions of this type. Reflux of **1a** with sodium methoxide in chlorobenzene during 24 h effected no reaction, while for reactions of **1a** with either $(\text{HOC}_6\text{H}_4)_2\text{CMe}_2$ or $(\text{HOC}_6\text{H}_4)_2\text{SO}_2$ or of **2a** with 2-naphthol, in a mixed alkali carbonate medium [13], no temperature conditions were found which gave other than recovery of unchanged starting materials on the one hand, or complete decomposition on the other.

3.2. Crystal and molecular structures of compounds **1d**, **1f** and **2f**

Compound **1d** crystallises in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Fig. 1). The crystal structure reveals two points of

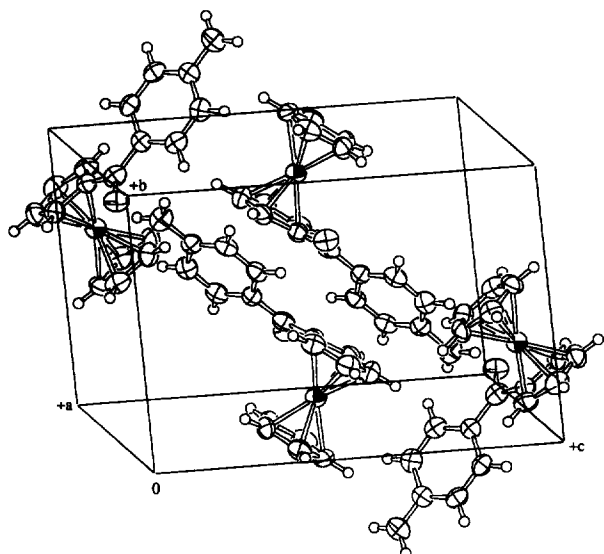


Fig. 3. Perspective view of part of the unit-cell contents for **1f**.

interest. First, the four molecules in the unit cell are arranged in two pairs lying across the centres of inversion at $(0.5,0,0)$ and $(0.5,0.5,0.5)$ such that the two C=O groups of such a pair lie anti-parallel but coplanar, with intermolecular non-bonded C...O distances of only 3.127(9) Å, just less than the sum, 3.22 Å, of the van der Waal's radii for carbon and oxygen [14]: the expected polarities of the atoms indicate that these pairs of carbonyl groups are subject to attractive interactions. Scrutiny of the crystal structures of other simple monoacylferrocenes using the Cambridge Structural Database [15,16] revealed no other example in this series of close intermolecular contacts between carbonyl groups: thus in the structures of FcCOR having R = CH₃ [17], CMe₃ [18], Ph [19], CH₂Ph [20] and Fc [21] the shortest intermolecular C...O distances involving the carbonyl groups are 3.89 Å, 4.93 Å, 4.89 Å, 4.42 Å and 4.95 Å respectively.

This pairwise arrangement of the molecules of **1d** appears to be independent of the second feature of the crystal structure, the connection of the molecules into chains by means of N–H...O hydrogen bonds. The nitrogen atom N1 in the molecule at (x,y,z) acts as

hydrogen-bond donor, via a single N–H bond, to the oxygen atom in the molecule at $(1-x,0.5+y,0.5-z)$; the nitrogen atom in this second molecule in turn acts as donor to the oxygen atom in the molecule at $(x,1+y,z)$, so that repetition of this interaction leads to the formation of chains lying around the 2₁ screw axes parallel to the *b* direction: two such spiral chains, one of each hand, run through each unit cell, generated by the screw axes at $(0.5,y,0.25)$ and $(0.5,y,0.75)$ and related to one another by the centre of inversion at $(0.5,0.5,0.5)$ (Fig. 2). The N...O distance is 2.966(8) Å, and the corresponding H...O distance and N–H...O angle are 2.15 Å and 143° respectively: the second N–H bond plays no part in the hydrogen-bonding scheme. The hydrogen bonding can be described by a single chain-forming motif, whose graph set [22–24] is C(8).

Compound **1f**, although very similar in constitution to **1d**, crystallises in an entirely different space group *P*₂₁₂₁. Although the molecules of both **1d** and **1f** adopt conformations in the solid state of C₁ symmetry, and are therefore chiral, the centrosymmetric space group *P*₂₁/*c* of **1d** accommodates equal numbers of both enantiomers, while in *P*₂₁₂₁ all the molecules in a given crystal have the same chirality. The conformation depicted for **1f** in Fig. 2 is that appropriate to the crystal chosen for X-ray data collection, as demonstrated by the refinement of the Flack parameter [25]. The molecules of **1f** are linked into chains by rather strong O–H...O hydrogen bonds. Atom O2 in the molecule at (x,y,z) acts as hydrogen-bond donor towards atom O1 in the molecule at $(-1-x,-0.5+y,-0.5-z)$, while atom O2 in this latter molecule acts as hydrogen-bond donor towards O1 in the molecule at $(x,-1+y,z)$. These hydrogen bonds thus generate chains around the screw axes parallel to the *b* direction. The O...O distance is 2.672(5) Å, and the corresponding H...O distance and O–H...O angle are 1.72 Å and 155° respectively: the hydrogen bonding in **1f** can thus be described by the same C(8) motif as that in **1d**, and Fig. 3 showing the close contact between the hydrogen-bond donors and acceptor groups of neighbouring molecules serves to illustrate the chain-formation in both **1d** and **1f**.

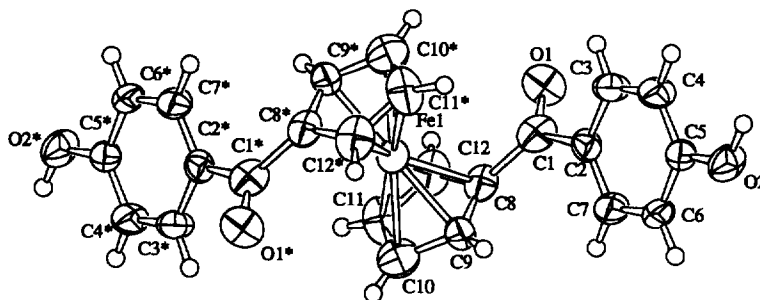


Fig. 4. Perspective view of one molecule of compound **2f**, showing the atom-labelling scheme; atoms labelled with * are generated by the symmetry operation $(1-x, -1-y, 1-z)$.

Compound **2f** crystallises in the centrosymmetric space group *Pbcn* with a Z' value [26] of 0.5, so that the molecules lie on centres of inversion; hence the relative disposition of the substituents on the cyclopentadienyl rings is *trans*. The primary hydrogen-bonding motif in **2f** is similar to that in **1f**; thus the hydroxyl oxygen atom O2 in the half-molecule at (x, y, z) [whose iron atom is at $(0.5, -0.5, 0.5)$, Table 2] acts as hydrogen-bond donor towards atom O1 in the half-molecule at $(0.5 - x, -0.5 - y, 0.5 + z)$, while atom O2 in this second unit acts as donor towards atom O1 in the unit at $(x, y, 1 + z)$. The molecules are thus linked into C(8) spiral chains, generated by the 2_1 screw axis parallel to the c direction; the $O \cdots O$ distance in the hydrogen bonds is $2.70(1)$ Å. The hydrogen-bonding scheme is however seriously complicated by the centrosymmetry of the molecules of **2f**. The symmetry-related carbonyl oxygen atom O1* (Fig. 4) lies at the equivalent position $(1 - x, -1 - y, 1 - z)$: this accepts a hydrogen bond from atom O2 in the unit at $(0.5 + x, -0.5 + y, 0.5 - z)$, while atom O1 in this latter unit accepts a hydrogen bond from O2 in the unit at $(1 - x, -1 - y, 2 - z)$. This last-named unit and that at $(x, y, 1 + z)$, which features in the original spiral chain, are in fact symmetry-related halves of the same molecule, whose iron atom is located at $(0.5, -0.5, 1.5)$. The molecules based on the iron atoms at $(0.5, -0.5, 0.5)$ and $(0.5, -0.5, 1.5)$ thus participate in two anti-parallel chain motifs parallel to the c direction, around the screw axes at $(0.25, -0.25, z)$ and $(0.75, -0.75, z)$ and inter-related by a centre of inversion. These chain motifs are propagated throughout the structure by the centres of inversion within the molecules, and actually generate continuous square nets which lie parallel to the $(1-10)$ plane and are based upon an $R_4^4(40)$ motif [22–24]: these nets describe openings ca. 10 Å in diameter. Fig. 5 shows a schematic view of one of the centrosymmetric $R_4^4(40)$ rings making up the nets.

The formation of these $R_4^4(40)$ nets utilises only two of the four molecules within the unit cell, and there is a similar but entirely independent set of nets, parallel to (110) , which is completely interwoven with the first set and generated from it by the action of the two-fold rotation axes parallel to the b direction. At the centre of the $R_4^4(40)$ ring containing the ferrocenediphenol molecules whose iron atoms lie at $(0.5, -0.5, 0.5)$ and $(0.5, -0.5, 1.5)$ lies the ferrocenediphenol molecule whose iron atom lies at $(0.0, -0.5, 1.0)$: from this molecule, whose oxygen atom O2 lies at $(1 - x, y, 1/5 - z)$, can be generated the entire description of the second set of nets, precisely as the first set was generated but utilising the other two independent screw axes parallel to the c direction. Hence there are two sets of completely interwoven square nets, inclined at around 56° to one another, but with no bonding interactions between them, not even hydrogen bonds. At the centre

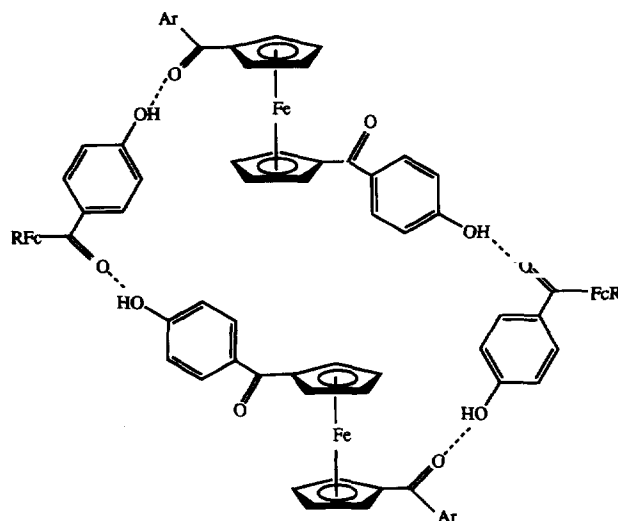


Fig. 5. Schematic view of one of the centrosymmetric $R_4^4(40)$ rings making up the two-dimensional nets in **2f**. In this, Ar represents the fragment C_6H_4OH , and RfC and FcR both represent the fragment $C_5H_4FeC_5H_4COC_6H_4OH$.

of each square, in either net, lies a ferrocenediphenol molecule belonging to the other net.

Within the molecules of **1d**, **1f** and **2f**, the bond lengths are all typical of their types [27,28]. The conformations of **1d** and **1f** are extremely similar (Table 3, Figs. 1 and 2): in each compound, the phenyl ring and the substituted cyclopentadiene ring of the ferrocenyl fragment are slightly twisted away from the C(2)–C(1)–C(8) plane with dihedral angles (Table 3) indicating disrotatory twists of the two groups bonded to C(1). A similar twist, of 17° , was observed [21] in the symmetrical diferrocenyl ketone Fc_2CO , where the molecules lie on a two-fold rotation axis coincident with the C=O bond: in Fc_2CO the displacement from coplanarity, favoured on electronic grounds, was ascribed to intramolecular steric interference between the two hydrogen atoms on the carbon atoms adjacent to those bearing the ring substituent [21]. Despite the very similar molecular structures and conformations of **1d** and **1f**, and their very similar crystal structures as manifested in their hydrogen-bonding schemes, these two compounds crystallise in entirely different space groups, as noted earlier: in particular, **1d** adopts a centrosymmetric space group, while **1f** in a chiral space group is an example of conglomerate crystallisation [29]. The occurrence of very similar crystal structures in different space groups is a well-recognised phenomenon [26]. Chain structures similar to that observed in compound **1f**, albeit built of $O-H \cdots O$ hydrogen bonds involving only hydroxyl groups, are observed in a number of simple ferrocenyl alcohols including $FcCH(OH)CH_3$ [30], $FcCH(OH)Ph$ [31] and $FcCH(OH)CMe_3$ [32].

The crystal structure of compound **2f**, containing two-dimensional networks built from $R_4^4(40)$ rings, dif-

fers markedly from those of simple ferrocenediols, which either form hydrogen-bonded cyclic dimers [32–34] or do not aggregate at all [35]. On the other hand, functionalised bis-phenols containing hydrogen-bond acceptor groups can form similar two-dimensional networks: in $\text{OC}(\text{C}_6\text{H}_4\text{OH})_2$ single networks are built from a combination of $\text{R}_4^4(20)$ and $\text{R}_4^4(40)$ rings [36], while in $\text{O}_2\text{S}(\text{C}_6\text{H}_4\text{OH})_2$ there is pairwise interweaving of networks built from $\text{R}_4^4(32)$ rings [37].

Acknowledgements

A.C.B. is grateful to the Foundation for Hungarian Higher Education and Research for the award of a Zoltán Magyary Fellowship; support for his visit to St. Andrews from TEMPUS Grant No. JEP-9252-95 is also gratefully acknowledged. C.G., B.J.L.R. and D.M.S. thank EPSRC for financial support under the ROPA scheme.

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