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Hydrogen bonding in ferrocene derivatives: crystal structure of racemic ferrocenyl(phenyl)methanol

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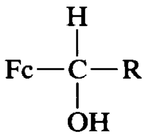
Abstract

A single-crystal X-ray diffraction study has been carried out on racemic ferrocenyl(phenyl)methanol. There are two independent chiral molecules A and B in the asymmetric unit, and the molecules are linked by OH ··· O hydrogen bonds into zigzag chains characterized by the motif –*S*(A)–*R*(B)–*R*(A)–*S*(B)–; within these chains the two independent hydrogen-bonded O ··· O distances are 3.059(2) and 3.150(2) Å.

Key words: Ferrocene; Hydrogen bonding; Crystal structure

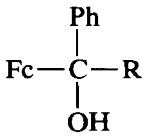
1. Introduction

Monoalcohols ROH exhibit an extremely wide range of intermolecular aggregation patterns in the solid state. Hydrogen bonding of the type of O–H ··· O can lead to finite aggregates that are dimeric [1–3], trimeric [4] or tetrameric [5,6], or to extended chains, often in the form of spirals generated by crystallographic screw axes [7]. An alternative mode of dimer formation employs O–H ··· π(arene) hydrogen bonding [8,9]. In yet other examples [3,10] there is no intermolecular aggregation. Amongst α-ferrocenyl alcohols, examples have been observed of dimers, containing four-membered $(OH)_2$ rings [2,3], and of systems with no intermolecular aggregation [3]. In this paper, we report the crystal and molecular structure of racemic ferrocenyl(phenyl)methanol FcCH(OH)Ph (**1a**) (Fc = $(C_5H_5)Fe(C_5H_4)$), in which the hydrogen bonding results in a zigzag pattern generated by a crystallographic glide plane. We also report details of the preparation and spectroscopic characterisation of some related ferrocenyl alcohols (**1** and **2**); the crystal and molecular structures of **2a** and **2b** have already been reported [3], and structural studies are in progress on other members of these series:



$$\mathrm{Fc-\overset{H}{\underset{OH}{C}}-R}$$

(**1**)



$$\mathrm{Fc-\overset{Ph}{\underset{OH}{C}}-R}$$

(**2**)

(R = Ph (**a**), CH_3 (**b**), CMe_3 (**c**), CH_2Ph (**d**))

2. Experimental details

NMR spectra were recorded at ambient temperature in $CDCl_3$ solution on a Bruker AM-300 spectrometer operating at 300.135 MHz for ^1H and 75.469 MHz for ^{13}C. Acylferrocenes were prepared by the usual Friedel–Crafts methods.

2.1. Preparation of ferrocenyl(phenyl)methanol (1a)

A solution of benzoylferrocene (2.9 g, 0.01 mol) in dry tetrahydrofuran (THF) (20 cm^3) was added with stirring to a cooled solution of $LiAlH_4$ (0.014 g, 0.015 mol) in dry THF (50 cm^3). The mixture was refluxed for 2 h, ethyl acetate was added to destroy the excess of reductant, and then water (0.5 cm^3), ethanol (2.5

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cm^3) and diethyl ether (5 cm^3) were added. The resulting suspension was filtered through Hyflo-supercel, and the filtrate was dried (Na_2SO_4). After removal of the solvent, the resulting deep-yellow oil was dissolved in hot hexane; slow cooling of this solution gave **1a** (83% yield) as deep-yellow plates, m.p. 80–81°C. Anal. Found: C, 70.3; H, 5.8. $C_{17}H_{16}FeO$ calc.: C, 69.9; H, 5.5%. δ(H) 2.52 (s, 1H, OH); 4.18 (m, 4H, C_5H_4); 4.20 (s, 5H, C_5H_5); 5.46 (s, 1H, CH); 7.2–7.4 (m, 5H, C_6H_5) ppm. δ(C) 66.0 (d), 67.4 (d), 68.0 (d), 68.1 (d) and 94.2 (s) (C_5H_4); 68.5 (d, C_5H_5); 72.0 (d, COH); 126.2 (d), 127.4 (d), 128.2 (d) and 143.2 (s) (C_6h_5) ppm.

In a similar fashion the following were prepared.

1c, m.p., 60–61°C (from methanol). Anal. Found: C, 67.3; H, 8.2. $C_{15}H_{20}FeO$ calc.: C, 66.2; H, 7.2%. δ(H) 0.88 (s, 9H, CH_3); 2.15 (s, 1H, OH); 4.00 (s, 1H, CH); 4.18 (m, 2H) and 4.26 (m, 2H) (C_5H_4); 4.20 (s, 5H, C_5H_5) ppm. δ(C) 26.4 (q, CH_3); 35.4 (s, $C(CH_3)_3$); 65.9 (d), 67.9 (d), 68.1 (d), 70.3 (d) and 91.9 (s) (C_5H_4); 68.7 (d, C_5H_5); 78.0 (d, COH) ppm.

1d m.p., 70–71°C (from hexane). Anal. Found: C, 70.8; H, 5.8. $C_{18}H_{18}FeO$ calc.: C, 70.6; H, 5.9%. δ(H) 2.08 (s, 1H, OH); 2.95 (m, 2H, CH_2); 4.08 (m, 1H), 4.15 (m, 1H), 4.16 (m, 1H) and 4.28 (m, 1H) (C_5H_4); 4.20 (s, 5H, C_5H_5); 4.55 (m, 1H, CH); 7.1–7.3 (m, 5H, C_6H_5) ppm. δ(C) 44.9 (t, CH_2); 65.4 (d), 67.4 (d), 67.8 (d), 68.0 (d) and 93.3 (s) (C_5H_4); 68.4 (d, C_5H_5); 70.9 (d, COH); 126.3 (d), 128.3 (d), 129.4 (d) and 138.5 (s) (C_6H_5) ppm.

2.2. *Preparation of ferrocenyl(diphenyl)methanol (2a)*

Phenyllithium (3.066 cm^3 of a solution in hexane, 1.8 mol dm^{-3}; 5.50 mmol) was added with stirring to a solution of benzoylferrocene (1.59 g, 5.50 mmol) in dry ether (50 cm^3). The mixture was stirred for 15 h at room temperature and then poured on to a mixture of crushed ice (100 g) and dilute sulphuric acid (2 mol dm^{-3}). When the ice had melted, the mixture was extracted with ether (2 × 50 cm^3), the combined ether extracts were washed with water and dried (Na_2SO_4) and the solvent was removed. Recrystallization from CH_2Cl_2 gave dark-red crystals of **2a** (yield 75%), m.p. 138°C. Anal. Found: C, 75.0; H, 5.3. $C_{23}H_{20}FeO$ calc.: C, 75.0; H, 5.5%. δ(H) 3.48 (s, 1H, OH); 4.04 (m, 2H) and 4.26 (m, 2H) (C_5H_4); 4.15 (s, 5H, C_5H_5); 7.2–7.4 (m, 10H, $2 \times C_6H_5$) ppm. δ(C) 68.4 (d), 68.7 (d) and 99.3 (s) (C_5H_4); 68.5 (d, C_5H_5); 77.3 (s, COH); 126.7 (d), 126.9 (d), 127.4 (d) and 146.9 (s) (C_6H_5) ppm.

In a similar fashion the following were prepared.

2b, m.p., 120°C (from dichloromethane). Anal. Found: C, 70.4; H, 5.5. $C_{18}H_{18}FeO$ calc.: C, 70.6; H, 5.9%. δ(H) 1.84 (s, 3H, CH_3); 2.71 (s, 1H, OH); 4.08 (m, 1H), 4.12 (m, 1H), 4.21 (m, 1H) and 4.30 (m, 1H) (C_5H_4); 4.22 (s, 5H, C_5H_5); 7.1–7.4 (m, 5H, C_6H_5) ppm. δ(C) 31.7 (q, CH_3); 66.1 (d), 67.4 (d), 67.8 (d), 68.3 (d) and 100.4 (s) (C_5H_4); 68.4 (d, C_5H_5); 72.5 (s, COH); 125.0 (d), 126.4 (d), 127.7 (d) and 147.6 (s) (C_6H_5) ppm.

2c, m.p., 80–82°C (from hexane). Anal. Found: C, 72.9; H, 7.3. $C_{21}H_{24}FeO$ calc.: C, 72.4; H, 6.9%. δ(H) 0.90 (s, 9H, CH_3); 2.63 (s, 1H, OH); 3.85 (s, 5H, C_5H_5); 4.16 (m, 1H), 4.20 (m, 1H), 4.32 (m, 1H), and 4.51 (m, 1H) (C_5H_4); 7.2–7.7 (m, 5H, C_6H_5). δ(C) 26.6 (q, CH_3); 39.1 (s, $C(CH_3)_3$); 67.0 (d), 68.6 (d), 68.9 (d), 69.8 (d) and 95.8 (s) (C_5H_4); 68.4 (d, C_5H_5); 79.6 (s, COH); 126.2 (d), 126.7 (d), 127.3 (d) and 146.0 (s) (C_6H_5).

2d, m.p., 99–100°C (from hexane). Anal. Found: C, 76.1; H, 6.0. $C_{24}H_{22}FeO$ calc.: C, 75.4; H, 5.8%. δ(H) 2.72 (s, 1H, OH); 3.36 and 3.40 (AB, $J = 13.3$ Hz, 2H, CH_2); 4.08 (m, 1H), 4.18 (m, 1H), 4.26 (m, 1H) and 4.38 (m, 1H) (C_5H_4); 4.20 (s, 5H, C_5H_5); 6.8–7.3 (m, 10H, $2 \times C_6H_5$) ppm. δ(C) 49.7 (t, CH_2); 67.1 (2 × d), 68.0 (d), 68.4 (d) and 100.3 (s) (C_5H_4); 68.7 (d, C_5H_5); 74.7 (s, COH); 125.8 (d), 126.3 (d), 126.4 (d), 127.4 (d), 127.5 (d), 130.9 (d), 136.6 (s) and 145.5 (s) ($2 \times C_6H_5$) ppm.

2.3. *Preparation of 1,1,2-triphenylethanol (3b)*

Phenyllithium (33.3 cm^3 of a solution in hexane, 1.8 mol dm^{-3}; 60 mmol) was added with stirring to a solution of ethyl phenylacetate (4.9 g, 30 mmol) in dry ether (100 cm^3). The mixture was stirred for 15 h at room temperature and then hydrolysed with dilute sulphuric acid. The mixture was extracted with ether (2 × 50 cm^3), the ether layer was washed with water and dried (Na_2SO_4), and the solvent then removed. Recrystallization from hexane gave white crystals, m.p., 90–91°C (88–89°C [11]). Anal. Found: C, 87.8; H, 6.5. $C_{20}H_{18}O$ calc.: C, 87.6; H, 6.6%. δ(H) 2.48 (s, 1H, OH); 3.71 (s, 2H, CH_2); 6.9–7.6 (m, 15H, Ph) ppm. δ(C) 47.3 (t, CH_2), 77.3 (s, COH); 125.6 (d), 126.2 (d), 126.3 (d), 127.4 (d), 127.5 (d), 130.3 (d), 135.2 (s) and 146.0 (s) ($2 \times C_6H_5$) ppm.

2.4. *Preparation of 1,2,3-triphenylpropan-2-ol (3c)*

A solution of 1,3-diphenylacetone (10.5 g, 53 mmol) in dry ether (20 cm^3) was added slowly to a solution of phenylmagnesium bromide (100 mmol) in dry ether 950 cm^3). The mixture was refluxed for 15 min, cooled and poured on to a mixture of crushed ice (100 g) and dilute sulphuric acid. The mixture was extracted with ether (3 × 50 cm^3) and the ether fraction was dried and evaporated. Recrystallization from methanol gave white crystals, m.p. 82°C. Anal. Found: C, 87.7; H, 7.1. $C_{21}H_{20}O$ calc.: C, 87.5; H, 7.0%. δ(H) 1.89 (s, 1H, OH); 3.10 (d, $J = 15$ Hz) and 3.28 (d, $J = 15$ Hz) (AX, 4H, $2 \times CH_2$); 6.9–7.3 (m, 15H, Ph) ppm. δ(C) 48.6 (t,

CH_2); 76.8 (s, COH); 125.7 (d), 126.5 (d), 127.8 (d) and 136.3 (s) (2 × $C_6H_5CH_2$); 126.4 (d), 127.7 (d), 130.7 (d) and 145.2 (s) C_6H_5CO) ppm.

Triphenylmethanol (**3a**) had δ(C) 82.0 (s, COH); 127.2 (d), 127.8 (d), 127.9 (d) and 146.8 (s) (C_6H_5) ppm.

Tribenzylmethanol (**3d**) had δ(C) 45.8 (t, CH_2); 73.9 (s, COH); 126.4 (d), 128.1 (d), 130.8 (d) and 137.3 (s) (C_6H_5) ppm.

2.5. X-ray crystallography

Crystals of compound **1a** suitable for X-ray examination were grown from hexane solution.

2.6. Crystal data

$C_{17}H_{16}FeO$; $M_r = 292.16$; monoclinic; $a = 9.8985(7)$ Å, $b = 13.2131$ Å and $c = 20.4282(7)$ Å; $\beta = 90.295(4)°$; $V = 2671.8(3)$ Å^3; space group, $P2_1/a$ (No. 14); $Z = 8$; $D_c = 1.45$ g cm^{-3}; μ(Mo Kα) 11.1 cm^{-1}; $\lambda = 0.71073$ Å, $F_{000} = 1216$.

2.7. Data collection

A block-shaped crystal 0.45 mm × 0.45 mm × 0.75 mm was used. Unit-cell dimensions were refined using 25 reflections in the range $30° \leqslant 2\theta \leqslant 36°$. The space group was uniquely determined by the systematic absences $0k0$ if k is odd, and $h0l$ if h is odd. The intensity data were collected at 21°C on an Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. 8151 reflections were measured in the 2θ range $4° < 2\theta < 60°$ with h from -13 to 13, k from 0 to $+18$ and l from 0 to $+28$, of which 7756 were unique and 5914 were labelled observed with $I > 3\sigma(I)$. An absorption correction was applied, using the Ψ scan method; the maximum and minimum values of the transmission coefficient were 0.774 and 0.751, respectively.

2.8. Structure solution and refinement

The structure was solved by direct methods using SHELXS86 [12], which revealed all the non-hydrogen atoms of the two independent molecules and refined using the NRCVAX [13] suite of programs. Hydrogen atoms bonded to carbon were visible in difference maps at an intermediate stage of the refinement and were included in the refinement as riding atoms in geometrically idealized positions with d(C–H) fixed at 0.95 Å. The hydroxyl hydrogen atoms were located in difference maps in the later stages of refinement and were included at these positions in the structure factor calculations. The final R and R_w values were 0.030 and 0.048 for 5914 data and 344 variables. The figures were prepared using ORTEP-II [14].

The final refined coordinates are given in Table 1, bond lengths in Table 2 and bond angles in Table 3.

TABLE 1. Positional and thermal parameters and their

Atom	x	y	z	B_{iso} [a]
Fe(1)	0.305413(23)	0.413814(18)	0.083006(12)	2.627(9)
O(1A)	0.63049(14)	0.32774(10)	0.21790(7)	3.69(5)
C(1A)	0.54199(18)	0.40336(13)	0.19032(8)	2.91(6)
C(11A)	0.12638(22)	0.43989(20)	0.12972(13)	4.79(10)
C(12A)	0.10519(21)	0.43030(19)	0.06133(14)	4.75(11)
C(13A)	0.18089(22)	0.50683(17)	0.03021(11)	4.13(8)
C(14A)	0.25026(23)	0.56241(16)	0.07826(11)	4.08(9)
C(15A)	0.21646(24)	0.52126(19)	0.14028(11)	4.43(9)
C(21A)	0.38212(20)	0.28634(14)	0.12306(10)	3.45(7)
C(22A)	0.35060(22)	0.27001(15)	0.05612(11)	4.05(8)
C(23A)	0.42577(21)	0.33845(17)	0.01874(9)	3.87(8)
C(24A)	0.50717(18)	0.39796(14)	0.06215(9)	3.14(7)
C(25A)	0.47971(16)	0.36552(12)	0.12733(8)	2.74(6)
C(31A)	0.62121(18)	0.49963(13)	0.18154(8)	2.93(6)
C(32A)	0.56275(23)	0.59248(16)	0.19523(12)	4.24(9)
C(33A)	0.63396(28)	0.68171(17)	0.18509(14)	5.29(11)
C(34A)	0.76402(27)	0.67941(17)	0.16209(13)	4.98(10)
C(35A)	0.82331(23)	0.58756(17)	0.14867(12)	4.42(9)
C(36A)	0.75328(20)	0.49826(15)	0.15846(10)	3.60(8)
Fe(2)	−0.226128(25)	0.540424(19)	0.414603(12)	2.828(9)
O(1B)	−0.07156(15)	0.32504(12)	0.27280(7)	4.44(6)
C(1B)	−0.06067(19)	0.42063(14)	0.30590(9)	3.08(6)
C(11B)	−0.32992(24)	0.65677(18)	0.37189(13)	4.75(10)
C(12B)	−0.34404(30)	0.66034(20)	0.44048(14)	5.83(12)
C(13B)	−0.21357(39)	0.67023(19)	0.46786(14)	6.45(15)
C(14B)	−0.12118(27)	0.67238(18)	0.41750(16)	5.76(13)
C(15B)	−0.19163(27)	0.66483(16)	0.35817(13)	4.78(10)
C(21B)	−0.28622(20)	0.40977(14)	0.37041(10)	3.53(7)
C(22B)	−0.32549(23)	0.40965(16)	0.43737(12)	4.20(8)
C(23B)	−0.20688(24)	0.41942(16)	0.47643(10)	3.97(8)
C(24B)	−0.09458(20)	0.42483(14)	0.43435(9)	3.22(6)
C(25B)	−0.14240(18)	0.41887(12)	0.36814(9)	2.80(6)
C(31B)	0.08648(19)	0.44180(14)	0.31938(9)	3.11(6)
C(32B)	0.13495(22)	0.53985(15)	0.31591(11)	3.96(8)
C(33B)	0.26794(24)	0.56114(19)	0.33242(13)	5.05(11)
C(34B)	0.35386(24)	0.48487(22)	0.35183(14)	5.40(11)
C(35B)	0.30763(24)	0.38721(21)	0.35376(13)	5.10(10)
C(36B)	0.17445(22)	0.36561(16)	0.33791(11)	4.12(8)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid

Additional material deposited at the Cambridge Crystallographic Data Centre includes thermal parameters and hydrogen atom coordinates. Copies of the structure factor listing are available from the authors.

3. Results and discussion

The secondary α-ferrocenyl alcohols **1a–1d** were all readily prepared by lithium aluminium hydride reduction of the corresponding acyl ferrocenes, and the tertiary alcohols **2a–2d** were all prepared by the action of phenyllithium on the acyl ferrocenes. The alcohols **1a–1d** and **2b–2d** all contain a stereogenic carbon atom, and all appear to be formed as racemic mixtures containing equal numbers of molecules of R or S configuration (confirmed crystallographically for **1a** and **2b** [3]). The effects of the stereogenic carbon atom are

TABLE 2. Selected bond lengths

Molecule A		Molecule B	
Fe(1)–C(11A)	2.0462(22)	Fe(2)–C(11B)	2.0423(22)
Fe(1)–C(12A)	2.0402(20)	Fe(2)–C(12B)	2.0392(23)
Fe(1)–C(13A)	2.0444(19)	Fe(2)–C(13B)	2.0345(23)
Fe(1)–C(14A)	2.0401(21)	Fe(2)–C(14B)	2.0303(24)
Fe(1)–C(15A)	2.0422(22)	Fe(2)–C(15B)	2.0377(22)
Fe(1)–C(21A)	2.0191(18)	Fe(2)–C(21B)	2.0356(18)
Fe(1)–C(22A)	2.0284(19)	Fe(2)–C(22B)	2.0431(21)
Fe(1)–C(23A)	2.0373(20)	Fe(2)–C(23B)	2.0458(20)
Fe(1)–C(24A)	2.0549(18)	Fe(2)–C(24B)	2.0459(18)
Fe(1)–C(25A)	2.0463(16)	Fe(2)–C(25B)	2.0434(17)
O(1A)–C(1A)	1.4416(21)	O(1B)–C(1B)	1.4363(22)
C(1A)–C(25A)	1.509(2)	C(1B)–C(25B)	1.511(3)
C(1A)–C(31A)	1.505(2)	C(1B)–C(31B)	1.507(3)
C(11A)–C(12A)	1.417(4)	C(11B)–C(12B)	1.410(4)
C(11A)–C(15A)	1.413(4)	C(11B)–C(15B)	1.403(4)
C(12A)–C(13A)	1.412(3)	C(12B)–C(13B)	1.411(5)
C(13A)–C(14A)	1.403(3)	C(13B)–C(14B)	1.380(5)
C(14A)–C(15A)	1.420(3)	C(14B)–C(15B)	1.399(4)
C(21A)–C(22A)	1.418(3)	C(21B)–C(22B)	1.424(3)
C(21A)–C(25A)	1.426(2)	C(21B)–C(25B)	1.430(3)
C(22A)–C(23A)	1.400(3)	C(22B)–C(23B)	1.422(3)
C(23A)–C(24A)	1.431(3)	C(23B)–C(24B)	1.410(3)
C(24A)–C(25A)	1.426(2)	C(24B)–C(25B)	1.433(3)
C(31A)–C(32A)	1.386(3)	C(31B)–C(32B)	1.383(3)
C(31A)–C(36A)	1.392(3)	C(31B)–C(36B)	1.383(3)
C(32A)–C(33A)	1.390(3)	C(32B)–C(33B)	1.386(3)
C(33A)–C(34A)	1.373(4)	C(33B)–C(34B)	1.376(4)
C(34A)–C(35A)	1.376(4)	C(34B)–C(35B)	1.370(4)
C(35A)–C(36A)	1.384(3)	C(35B)–C(36B)	1.385(3)

apparent in the NMR spectra in two ways: first, for the chiral molecules, all five carbon atoms in the substituted cyclopentadienyl ring are chemically non-equivalent and, apart from chance coincidences, are non-isochronous, as are the four hydrogen atoms of the substituted ring; secondly, in each of **1d** and **2d** the CH_2 group of the benzyl substituent constitutes an AB spin system. Subject to these considerations, the ^1H and ^{13}C NMR spectra for **1a–1d** are all readily and unambiguously assignable (see Experimental section). For **2a–2d**, the NMR assignments are straightforward except for the assignment of the two quaternary carbon resonances arising from the *ipso*-carbon of the substituted cyclopentadiene ring and the C–OH carbon, one of which occurs in the range δ 72–80 ppm and the other in the range δ 95–101 ppm for **2a–2d**. We attempted initially, and before the synthesis of **1a–1d**, to make the assignment of these two quaternary carbon atoms by comparison with the ^{13}C NMR spectra of $Ph_{3-x}(PhCH_2)_xCOH$ ($x = 0$, 1, 2, 3 (**3a–3d**)), where the C–OH resonances can be assigned unambiguously, with δ 82.0 ppm, 77.3 ppm, 76.8 ppm and 73.9 ppm for $x = 0$, 1, 2 and 3 respectively. This suggested that, in compounds **2**, the quaternary resonances in the range δ 72–80 ppm correspond to COH, and those in the range δ 95–101 ppm correspond to the ring quarternary carbon; this deduction was subsequently confirmed by the unambiguous assignments for compounds **1**.

3.1. Crystal and molecular structure of 1a

$(C_5H_5)Fe(C_5H_4)CH(Ph)OH$ (**1a**) crystallizes in the centrosymmetric space group $P2_1/a$, with two independent molecules, denoted A and B, in the asymmetric unit. The space group demands equal numbers of molecules with *R* and *S* configurations at the stereogenic carbon; hence **1a** is racemic. The molecules are connected by OH $\cdots$ O hydrogen bonds into zigzag chains, generated by the action of the glide plane, and aligned along the *a* direction. The asymmetric unit was chose to contain one molecule of *S* configuration (molecule A) and one of *R* configuration (molecule B),

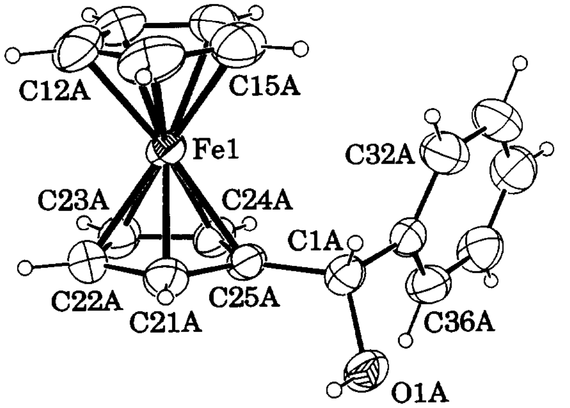

Fig. 1. Molecule A of ferrocenyl(phenyl)methanol, showing the atom numbering scheme. Non-hydrogen atoms are depicted as thermal ellipsoids at the 50% level; hydrogen atoms are depicted as small spheres of arbitrary size.

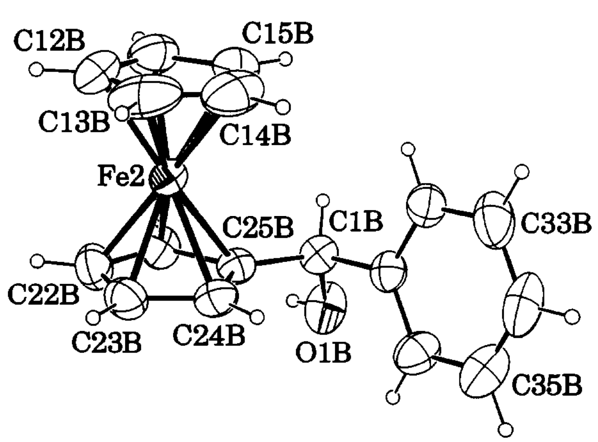

Fig. 2. Molecule B of ferrocenyl(phenyl)methanol. The atoms are depicted as in Fig. 1.

and these are shown in Figs. 1 and 2 respectively; Fig. 3 shows the relationship of A and B in the complete asymmetric unit. If the enantiomeric forms of molecules A and B are denoted A* and B* respectively, the polymeric chain may be described as ···ABA*B* ABA*B*··· with configuration ···SRRSSRRS···; the two independent O···O separations within the chain are 3.059(2) Å and 3.150(2) Å, associated with H···O distances of 2.26 Å and 2.45 Å respectively, and OH···O angles of 164.4° and 157.4° respectively.

A stereoview of the hydrogen bonded chain is provided in Fig. 4, which also shows how the ···OHOH··· chains are wholly isolated from one another by layers of organic groups. The ···OHOH··· chain is generated by the glide plane (at for example $y = 0.25$), and the ···OHOH··· arrays lie approximately parallel to the x–y plane; the molecules of type A all have their ferrocenyl groups on one side of the ···OHOH··· plane and those of type B all have their ferrocenyl groups on the other side, while the phenyl groups all lie in planes nearly parallel to the OHOH array.

It is interesting to contrast the hydrogen bonding patterns observed in the series FcC(H)PhOH (**1a**),

TABLE 3. Selected bond angles (°)

Molecule A		Molecule B	
O(1A)–C(1A)–C(25A)	110.39(14)	O(1B)–C(1B)–C(25B)	110.08(15)
O(1A)–C(1A)–C(31A)	108.44(14)	O(1B)–C(1B)–C(31B)	108.62(15)
C(25A)–C(1A)–C(31A)	112.89(14)	C(25B)–C(1B)–C(31B)	111.73(14)
Fe(1)–C(11A)–C(12A)	69.48(13)	Fe(2)–C(11B)–C(12B)	69.68(13)
Fe(1)–C(11A)–C(15A)	69.63(12)	Fe(2)–C(11B)–C(15B)	69.71(13)
C(12A)–C(11A)–C(15A)	107.99(20)	C(12B)–C(11B)–C(15B)	107.33(23)
Fe(1)–C(12A)–C(11A)	69.93(12)	Fe(2)–C(12B)–C(11B)	69.91(13)
Fe(1)–C(12A)–C(13A)	69.94(12)	Fe(2)–C(12B)–C(13B)	69.56(13)
C(11A)–C(12A)–C(13A)	107.67(21)	C(11B)–C(12B)–C(13B)	107.57(24)
Fe(1)–C(13A)–C(12A)	69.62(12)	Fe(2)–C(13B)–C(12B)	69.92(15)
Fe(1)–C(13A)–C(14A)	69.75(12)	Fe(2)–C(13B)–C(14B)	69.99(14)
C(12A)–C(13A)–C(14A)	108.60(20)	C(12B)–C(13B)–C(14B)	108.37(24)
Fe(1)–C(14A)–C(13A)	70.08(12)	Fe(2)–C(14B)–C(13B)	70.31(16)
Fe(1)–C(14A)–C(15A)	69.72(12)	Fe(2)–C(14B)–C(15B)	70.17(13)
C(13A)–C(14A)–C(15A)	107.89(20)	C(13B)–C(14B)–C(15B)	108.35(24)
Fe(1)–C(15A)–C(11A)	69.94(13)	Fe(2)–C(15B)–C(11B)	70.07(13)
Fe(1)–C(15A)–C(14A)	69.56(12)	Fe(2)–C(15B)–C(14B)	69.60(14)
C(11A)–C(15A)–C(14A)	107.85(21)	C(11B)–C(15B)–C(14B)	108.35(23)
Fe(1)–C(21A)–C(22A)	69.85(11)	Fe(2)–C(21B)–C(22B)	69.85(11)
Fe(1)–C(21A)–C(25A)	70.49(9)	Fe(2)–C(21B)–C(25B)	69.78(10)
C(22A)–C(21A)–C(25A)	108.44(17)	C(22B)–C(21B)–C(25B)	107.94(17)
Fe(1)–C(22A)–C(21A)	69.14(11)	Fe(2)–C(22B)–C(21B)	69.28(11)
Fe(1)–C(22A)–C(23A)	70.20(11)	Fe(2)–C(22B)–C(23B)	69.75(12)
C(21A)–C(22A)–C(23A)	108.23(17)	C(21B)–C(22B)–C(23B)	108.07(18)
Fe(1)–C(23A)–C(22A)	69.52(12)	Fe(2)–C(23B)–C(22B)	69.55(12)
Fe(1)–C(23A)–C(24A)	70.20(11)	Fe(2)–C(23B)–C(24B)	69.84(11)
C(22A)–C(23A)–C(24A)	108.43(17)	C(22B)–C(23B)–C(24B)	108.28(18)
Fe(1)–C(24A)–C(23A)	68.88(11)	Fe(2)–C(24B)–C(23B)	69.83(11)
Fe(1)–C(24A)–C(25A)	69.33(10)	Fe(2)–C(24B)–C(25B)	69.39(10)
C(23A)–C(24A)–C(25A)	107.70(16)	C(23B)–C(24B)–C(25B)	108.36(17)
Fe(1)–C(25A)–C(1A)	127.86(12)	Fe(2)–C(25B)–C(1B)	126.80(12)
Fe(1)–C(25A)–C(21A)	68.44(10)	Fe(2)–C(25B)–C(21B)	69.19(10)
Fe(1)–C(25A)–C(24A)	69.97(9)	Fe(2)–C(25B)–C(24B)	69.58(10)
C(1A)–C(25A)–C(21A)	124.66(15)	C(1B)–C(25B)–C(21B)	124.49(16)
C(1A)–C(25A)–C(24A)	128.13(15)	C(1B)–C(25B)–C(24B)	128.16(16)
C(21A)–C(25A)–C(24A)	107.19(15)	C(21B)–C(25B)–C(24B)	107.35(16)
C(1A)–C(31A)–C(32A)	120.38(17)	C(1B)–C(31B)–C(32B)	119.97(18)
C(1A)–C(31A)–C(36A)	121.33(16)	C(1B)–C(31B)–C(36B)	121.44(17)
C(32A)–C(31A)–C(36A)	118.28(18)	C(32B)–C(31B)–C(36B)	118.54(19)
C(31A)–C(32A)–C(33A)	120.56(21)	C(31B)–C(32B)–C(33B)	120.45(21)
C(32A)–C(33A)–C(34A)	120.62(21)	C(32B)–C(33B)–C(34B)	120.42(21)
C(33A)–C(34A)–C(35A)	119.29(20)	C(33B)–C(34B)–C(35B)	119.49(22)
C(34A)–C(35A)–C(36A)	120.58(21)	C(34B)–C(35B)–C(36B)	120.32(23)
C(31A)–C(36A)–C(35A)	120.66(19)	C(31B)–C(36B)–C(35B)	120.74(21)

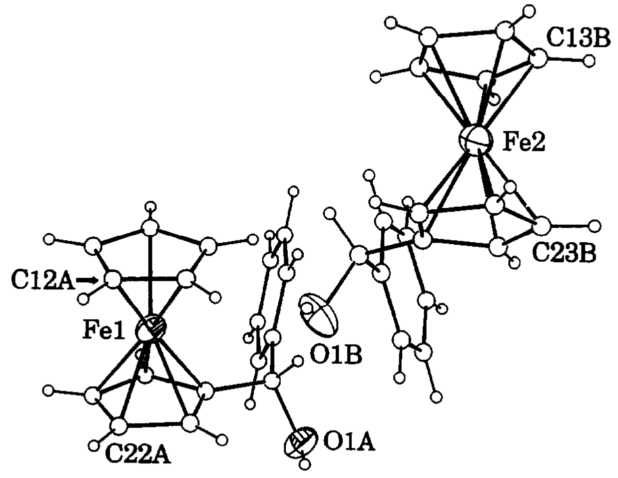

Fig. 3. The asymmetric unit showing molecules A and B.

FcC(CH$_3$)PhOH (**2b**) [3] and FcC(Ph)PhOH (**2a**) [3]; **1a** forms chains, **2b** shows no intermolecular hydrogen bonding at all but instead shows an intramolecular OH ··· π(C$_5$H$_5$) interaction, while **2a** forms dimers based on a rhomboidal (OH)$_2$ fragment. Clearly the hydrogen-bonding patterns observed in this series are not a simple reflection of the steric congestion at the central carbon, and further studies of FcC(R)PhOH are in progress.

Within the molecules A and B the dimensions are largely unexceptional. The overall conformations of molecules A and B are very similar, as demonstrated by the values of the torsion angles: O(1A)–C(1A)–C(25A)–Fe(1), 157.7(2)°; O(1B)–C(1B)–C(25B)–Fe(2), – 153.7(2)° (see also Figs. 1 and 2). In both molecule A and molecule B, the carbon atoms of the unsubstituted C$_5$H$_5$ ring show larger thermal parameters than the substituted ring and these C$_5$ rings are within 5.7(1)° (A) and 10.4(1)° (B) of being eclipsed. The Fe–C bond lengths in molecule A are in the range 2.040(2)–2.046(2) Å (mean, 2.043(2) Å) for the unsubstituted cyclopentadienyl ring C(11A) ··· C(15A), and 2.019(2)–2.055(2) Å (mean, 2.037(2) Å) for the substituted ring C(21A) ··· C(25A). The Fe–C bond lengths in molecule B are in the range 2.030(2)–2.042(2) Å (mean, 2.037(2) Å) for the unsubstituted cyclopentadienyl ring C(11B) ··· C(15B), and 2.036(2)–2.046(2) Å (mean, 2.043(2) Å) for the substituted ring C(21B) ··· C(25B). The C sp^3–O bond lengths are 1.442(2) and 1.436(2) Å. The dihedral angles between the C$_5$ planes in each of the molecules A and B are 3.4(1)° and 0.8(1)° respectively. The C sp^3 carbon atoms C(1A) and C(1B) are displaced 0.032(3) Å and 0.014(3) Å from the plane of their respective C$_5$ rings away from the Fe atom. In the crystal lattice, the contacts between the chains correspond to the normal van der Waals interactions.

The α-ferrocenyl alcohols containing a stereogenic centre whose structures are reported here or in previous publications [3,15] have all been studied as racemic mixtures of enantiomers, and all crystallize in centric space groups. Resolution of these into pure enan-

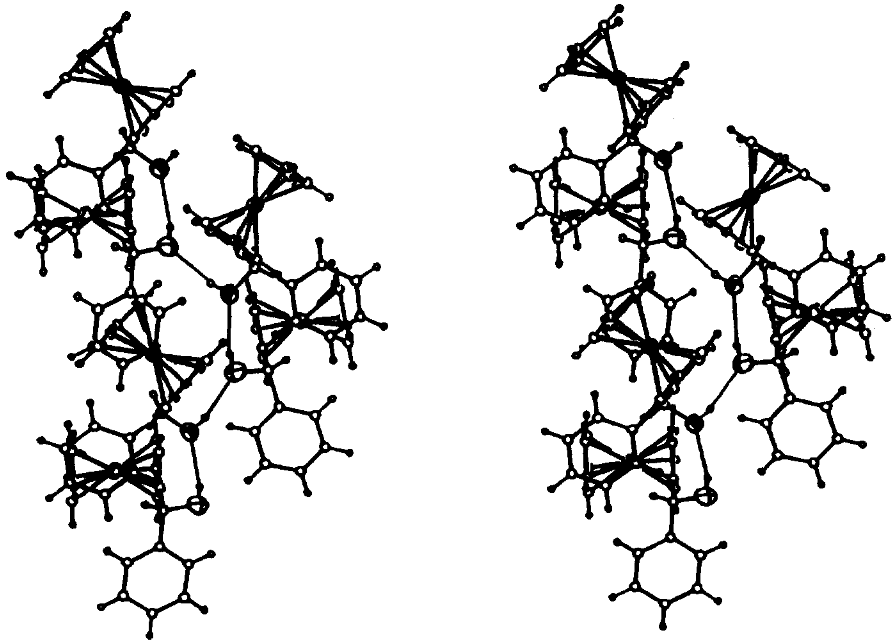

Fig. 4. Stereoview of the hydrogen bonding pattern in ferrocenyl(phenyl)methanol. Iron and oxygen atoms are drawn as thermal ellipsoids; carbon and hydrogen atoms are drawn for clarity as small spheres of arbitrary size.

tiomers offers the possibility of finding materials with non-linear optical properties, found so far very infrequently in structurally characterized organometallics [16]. The ease of assembly of certain ferrocenyl alcohols, such as **1a**, into polymeric aggregates opens up the possibility of self-assembled multistage redox assemblies; ferrocene nuclei have recently been incorporated into covalently bonded assemblies of this type [17].

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