

New ferrocenophanes containing a hydrophobic, aromatic 'pocket'

Richard A. Bartsch ^{a,*}, Piotr Kus ^a, Robert A. Holwerda ^a, Bronislaw P. Czech ^b,
Xiaolan Kou ^c, N. Kent Dalley ^c

^a Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409, USA

^b Bayer Corporation, Diagnostics Division, Tarrytown, NY 10591, USA

^c Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA

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Abstract

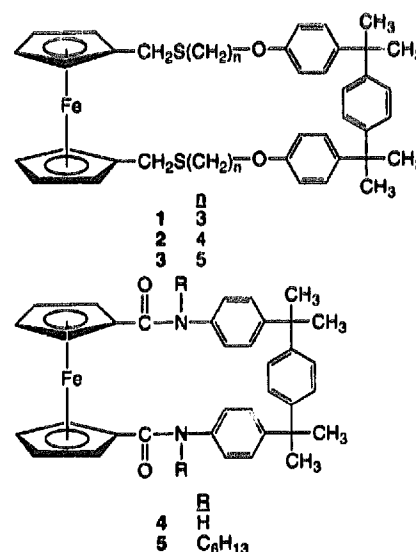
Five novel ferrocenophanes which incorporate a hydrophobic, aromatic 'pocket' derived from α, α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene or α, α' -bis(4-aminophenyl)-1,4-diisopropylbenzene are synthesized. Four of the new ferrocenophanes have been studied by cyclic voltammetry. Solid-state structures of lipophilic ferrocenophane diamide **5**, which has an aromatic 'pocket', and of the reactant 1,1'-di(hydroxymethyl)ferrocene (**13**) have been determined by single-crystal X-ray diffraction analysis and are compared with those for other ferrocenophanes and 1,1'-disubstituted ferrocenes respectively. **13** crystallizes in the space group $P2_1/c$ with $a = 13.395(12)$ Å, $b = 7.714(5)$ Å, $c = 10.497(11)$ Å, $\beta = 105.76(8)^\circ$, $V = 1043.9$ Å³, $Z = 4$, and $R(R_w) = 0.0323$ (0.0354) for 999 reflections ($F > 4.0\sigma(F)$). **5** crystallizes in the space group $P2_1/n$ with $a = 10.948(2)$ Å, $b = 12.387(2)$ Å, $c = 30.425(4)$ Å, $\beta = 90.49(1)^\circ$, $V = 4126.2$ Å³, $Z = 4$, and $R(R_w) = 0.0611$ (0.0723) for 3499 reflections ($F > 4.0\sigma(F)$). For **13**, the structure consists of chains of molecules connected by hydrogen bonds with ferrocene units on the outside of the chains and a hydrogen-bonded network on the interior.

Keywords: Iron; Ferrocenes; Hydrogen bonding; Ferrocenophanes; Electrochemistry; Solid-state structures

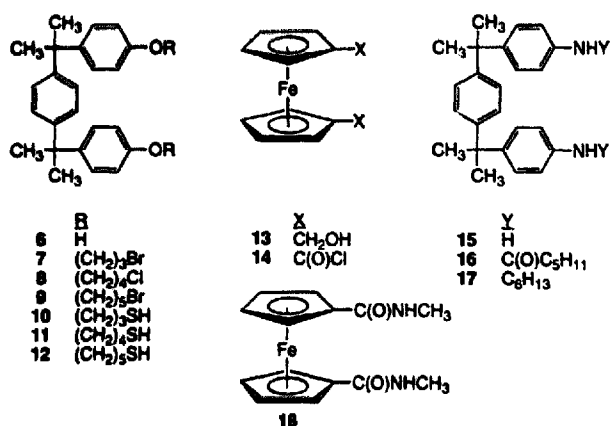
1. Introduction

Most of the ferrocenophanes described recently have crown ether or cryptand-like structures in which a ferrocene redox center is the only aromatic group component of the hydrophilic cavity. Only few reports describe ferrocenophanes which incorporate an aromatic or heteroaromatic subunit in addition to the ferrocene moiety [1–5]. We have recently reported the synthesis and electrochemistry of thiaoxaferrocenophanes [6,7] and thiazaferrocenophanes [8–10]. We have also observed that a triaryl aromatic 'pocket', built into a macrocyclic receptor, participates in complexation of alkylammonium salts [11]. In continuation of our interest in both areas, we have synthesized the new thiaoxaferrocenophanes **1–3** and ferrocenophane diamides **4** and **5** which contain an aromatic 'pocket' in the bridging chain. The hydrophobic character of the triaryl 'pocket' makes these new ferrocenophanes potential

receptors for neutral molecules. Ferrocenophanes **1–3** and **5** have been studied by cyclic voltammetry. Solid-state structures of the reactant 1,1'-di(hydroxymethyl)



* Corresponding author.



ferrocene (**13**) and of lipophilic ferrocenophane diamide **5** have been determined. The results of these studies are now reported.

2. Experimental section

Unless specified otherwise, reagent grade reactants and solvents were used as-received from chemical suppliers. Diol **13** [12] and diacid chloride **14** [13] were prepared by literature procedures. Elemental analyses were performed by Desert Analytics (Tucson, AZ). ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer and chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. Mass spectra were measured with a Hewlett-Packard Model 5982A spectrometer. IR spectra were obtained with a Perkin-Elmer Model 267 spectrophotometer and are reported in wavenumbers (cm⁻¹).

2.1. Preparation of dibromide 7

A mixture of bisphenol **6** (10.00 g, 29.0 mmol), 1,3-dibromopropane (6.96 g, 0.20 mol), K₂CO₃ (20 g), acetone (50 ml) and water (8 ml) was stirred at reflux for 48 h. The mixture was evaporated to dryness in vacuo with a rotary evaporator and then an oil pump. The residue was dissolved in a mixture of dichloromethane and water. The organic layer was separated, washed with water, dried (MgSO₄) and evaporated in vacuo. The residue was chromatographed on silica gel. Elution with hexanes removed the unreacted 1,3-dibromopropane. Subsequent elution with dichloromethane provided 13.48 g (79%) of dibromide **7** containing a small amount of the corresponding mono-dehydrobromination product which could not be removed by repeated chromatography. Therefore, the slightly impure dibromide **7** was utilized for the preparation of dithiol **10**. ¹H NMR (CDCl₃): δ 1.62 (s, 12H), 2.84 (q, 4H), 3.58 (t, 4H), 4.06 (t, 4H), 6.97 (ABq, 8H), 7.09 (s, 4H).

2.2. Preparation of dichloride 8

Bisphenol **6**, NaOH and 1,4-dichlorobutane were reacted in 1-butanol by a published procedure for an analogous modification of a different bisphenol [14] to produce dichloride **8** in 66% yield as white crystals with m.p. 104–105 °C. Anal. Found: C, 73.11; H, 7.48. C₃₂H₄₀Cl₂O₂. Calc.: C, 72.85; H, 7.64%. ¹H NMR (CDCl₃): δ 1.63 (s, 12H), 1.88–2.07 (m, 8H), 3.61 (t, 4H), 3.97 (t, 4H), 6.97 (ABq, 8H), 7.10 (s, 4H). ¹³C NMR (CDCl₃): δ 28.48, 31.13 (CH₂), 32.65 (CH₃), 43.65 (C), 46.58 (CH₂Cl), 68.69 (CH₂O), 115.75, 128.24, 129.82, 145.11, 149.95, 158.81 (Ar).

2.3. Preparation of dibromide 9

By the procedure described above for the preparation of dibromide **7**, but with 1,5-dibromopentane in place of 1,3-dibromopropane, dibromide **9** was realized in 71% yield as white crystals with m.p. 86–88 °C. Anal. Found: C, 63.58; H, 6.77. C₃₄H₄₄Br₂O₂. Calc.: C, 63.36; H, 6.88%. ¹H NMR (CDCl₃): δ 1.63 (s, 12H), 1.69–1.99 (m, 12H), 3.43 (t, 4H), 3.94 (t, 4H), 6.96 (ABq, 8H), 7.09 (s, 4H).

2.4. Preparation of dithiol 10

Dibromide **7** (2.30 g, 3.91 mmol) and thiourea (0.66 g, 8.68 mmol) were refluxed in 95% EtOH (15 ml) and dioxane (3 ml) for 3 h. The white crystals which precipitated after cooling to room temperature were filtered and refluxed with 2.5 N NaOH (6 ml) under argon for 2 h. The mixture was cooled, acidified with 2 N HCl and extracted with Et₂O (2 × 10 ml). The combined extracts were dried (MgSO₄) and the solvent was removed in vacuo. The residue was chromatographed on silica gel with CH₂Cl₂-petroleum ether (1 : 1 → 7 : 3) as eluent to give dithiol **10** (1.39 g, 72%) as waxy crystals with m.p. 88–90 °C. Anal. Found C, 72.87; H, 7.73. C₃₀H₃₈O₂S₂. Calc.: C, 72.83; H, 7.74%. ¹H NMR (CDCl₃): δ 1.38 (t, 2H), 1.63 (s, 12H), 2.06 (pentet, 4H), 2.73 (t, 4H), 4.05 (t, 4H), 6.97 (ABq, 8H), 7.10 (s, 4H). ¹³C NMR (CDCl₃): δ 23.04 (CH₃), 32.65, 35.21, 43.66 (C), 67.37 (CH₂O), 115.80, 128.25, 129.83, 145.19, 149.95, 158.76 (Ar).

2.5. Preparation of dithiol 11

A solution of dichloride **8** (2.11 g, 4.00 mmol), thiourea (0.67 g, 8.80 mmol), 95% ethanol (15 ml), and dioxane (3 ml) was refluxed for 2 days. A solution of 5 N aqueous NaOH (5 ml) was added and the reaction mixture was refluxed under argon for 2 h. After cooling, excess 2 N HCl was added and the mixture was extracted with Et₂O (2 × 10 ml). The combined extracts

were dried (MgSO_4), the solvent was removed in vacuo and the residue was chromatographed on silica gel with CH_2Cl_2 –petroleum ether (1:1 \rightarrow 7:3) as eluent to afford dithiol **11** (0.91 g, 44%) as white crystals with m.p. 91–93 °C. Anal. Found: C, 73.45; H, 8.16. $\text{C}_{32}\text{H}_{42}\text{O}_2\text{S}_2$. Calc.: C, 73.52; H, 8.10%. ^1H NMR (CDCl_3): δ 1.34 (t, 2H), 1.55–1.95 (m, 20H), 2.57 (q, 4H), 3.92 (t, 4H), 6.94 (AB q, 8H), 7.07 (s, 4H); ^{13}C NMR (CDCl_3): δ 24.63, 28.27, 30.90, 31.11 ($\text{CH}_3 + \text{CH}_2$), 42.10 (C), 67.46 (CH_2O), 114.21, 126.70, 128.27, 143.49, 148.43, 157.33 (Ar).

2.6. Preparation of dithiol **12**

Dithiol **12** was obtained from dibromide **9** by the same procedure as that given above for dithiol **10**. Chromatography on silica gel with petroleum ether– CH_2Cl_2 (1:1) as eluent provided **12** (90%) as white crystals with m.p. 77–79 °C. Anal. Found: C, 73.97; H, 8.66. $\text{C}_{34}\text{H}_{46}\text{O}_2\text{S}_2$. Calc.: C, 74.13; H, 8.42%. ^1H NMR (CDCl_3): δ 1.35 (t, 2H), 1.45–1.88 (m, 24H), 2.56 (q, 4H), 3.93 (t, 4H), 6.97 (ABq, 8H), 7.10 (s, 4H). ^{13}C NMR (CDCl_3): δ 24.36, 24.79, 28.65, 30.74, 33.60 ($\text{CH}_3 + \text{CH}_2 + \text{CH}_2\text{S}$), 41.72 (C), 67.48 (CH_2O), 113.83, 126.31, 127.87, 143.02, 148.05, 157.02 (Ar).

2.7. General procedure for the preparation of ferrocenophanes **1–3**

A solution (22 ml) of the dithiol (1.63 mmol) in CH_2Cl_2 and a solution (22 ml) of 1,1'-di(hydroxymethyl)ferrocene (**13**) (0.40 g, 1.63 mmol) in CH_2Cl_2 –THF (21:1) were simultaneously added dropwise to 150 ml of vigorously stirred and refluxing CH_2Cl_2 which contained five drops of trifluoroacetic acid. Following completion of the addition, the mixture was stirred at reflux overnight. The mixture was washed with 5% aqueous NaOH and water and dried (MgSO_4). The solvent was removed in vacuo and the residue was chromatographed on basic alumina with benzene as eluent to produce the ferrocenophane.

2.7.1. Ferrocenophane **1**

Yield: 12%; yellow-orange crystals with m.p. 140–142 °C. Anal. Found: C, 71.45; H, 7.02. $\text{C}_{42}\text{H}_{48}\text{FeO}_2\text{S}$. Calc.: C, 71.57; H, 6.86%. ^1H NMR (CDCl_3): δ 1.68 (s, 12H), 1.98 (pentet, 4H), 2.67 (t, 4H), 3.47 (s, 4H), 3.92–4.20 (m, 12H), 6.95 (ABq, 8H), 7.11 (s, 4H). ^{13}C NMR (CDCl_3): δ 30.67, 30.73, 32.21, 34.13 ($\text{CH}_3 + \text{CH}_2 + \text{CH}_2\text{S}$), 43.51, (C), 67.80 (CH_2O), 70.68, 71.15, 87.44 (Fe), 115.89, 128.16, 129.73, 145.04, 150.17, 158.73 (Ar). MS (m/e): 704.55 (M^+).

2.7.2. Ferrocenophane **2**

Yield: 56%; an amorphous, yellow solid with m.p. 182–184 °C. Anal. Found: C, 73.32; H, 7.45.

$\text{C}_{44}\text{H}_{52}\text{FeO}_2\text{S}_2 \cdot 0.5\text{C}_6\text{H}_6$. Calc.: C, 73.13; H, 7.18%. ^1H NMR (CDCl_3): δ 1.60–2.35 (m, 20H), 2.45 (t, 4H), 3.44 (s, 4H), 3.91 (t, 4H), 4.03 (d, 8H), 6.92 (ABq, 8H), 7.08 (s, 4H), 7.35 (s, C_6H_6). ^{13}C NMR (CDCl_3): δ 26.75, 29.06, 31.45, 31.79 ($\text{CH}_3 + \text{CH}_2 + \text{CH}_2\text{S}$), 42.59, (C), 67.95 (CH_2O), 69.64, 70.27, 86.26 (Fc), 114.85, 127.23, 128.81, 143.99, 149.19, 157.89 (Ar), 129.43 (C_6H_6). MS (m/e): 732.60 (M^+).

2.7.3. Ferrocenophane **3**

Yield: 59%; m.p. 134–135.5 °C. Anal. Found: C, 72.55; H, 7.63. $\text{C}_{46}\text{H}_{56}\text{FeO}_2\text{S}_2$. Calc.: C, 72.61; H, 7.42%. ^1H NMR (CDCl_3): δ 1.45–1.83 (m, 24H), 2.50 (t, 4H), 3.48 (s, 4H), 3.93 (t, 4H), 4.09 (d, 8H), 6.94 (ABq, 4H), 7.09 (s, 4H). ^{13}C NMR (CDCl_3): δ 25.14, 28.58, 28.79, 30.53, 31.65, 32.05 ($\text{CH}_3 + \text{CH}_2 + \text{CH}_2\text{S}$), 41.65, (C), 67.42 (CH_2O), 68.62, 69.27, 85.68 (Fc), 113.83, 126.28, 127.83, 142.97, 148.17, 156.99 (Ar). MS (m/e): 762.00 ($\text{M} + 1$).

2.8. Preparation of ferrocenophane **4**

A solution (75 ml) of diacid chloride **14** (1.55 g, 5.00 mmol) in benzene and a solution (75 ml) of diamine **15** (1.72 g, 5.0 mmol) and triethylamine (1.10 g, 10.7 mmol) in benzene–THF (6:1) were added simultaneously to vigorously stirred benzene (250 ml) at room temperature over a 7 h period. The mixture was stirred overnight and the solvent was removed in vacuo. The residue was chromatographed on silica gel with CHCl_3 –MeOH (9:1) as eluent to give diamide ferrocenophane **4** (0.30 g, 10%) as a yellow, amorphous solid with m.p. 245 °C (dec.). Anal. Found: C, 74.22; H, 5.90. $\text{C}_{46}\text{H}_{34}\text{FeN}_2\text{O}_2$. Calc.: C, 74.23; H, 5.88%. IR (nujol): 3280–3190 (N–H), 1640 ($\text{C}=\text{O}$) cm^{-1} . ^1H NMR (d_5 -pyridine + D_2O): δ 1.67 (s, 12H), 4.42 (s, 4H), 5.06 (s, 4H), 7.25 (d, 8H), 7.77 (ABq, 8H). ^{13}C NMR (d_5 -pyridine): δ 31.04 (CH_3), 42.51 (C), 71.66, 72.29, 80.51 (Fc), 120.75, 127.07, 128.12, 138.41, 146.29, 149.00 (Fc), 170.02 ($\text{C}=\text{O}$).

2.9. Preparation of diamide **16**

A solution of hexanoyl chloride (1.57 g, 11.7 mmol) in THF (7 ml) was added dropwise at 0 °C to a solution of diamine **15** (2.00 g, 5.80 mmol) and triethylamine (1.47 g, 14.6 mmol) in THF (7 ml). The mixture was stirred overnight at room temperature and the solvent was evaporated in vacuo. The residue was washed with water and recrystallized from ethanol to afford diamide **16** (2.50 g, 80%) as white crystals with m.p. 193–194 °C. Anal. Found: C, 79.92; H, 8.98. $\text{C}_{36}\text{H}_{48}\text{N}_2\text{O}_2$. Calc.: C, 79.96; H, 8.95%. IR (nujol): 3300 (N–H), 1660 ($\text{C}=\text{O}$) cm^{-1} . ^1H NMR ($\text{DMSO}-d_6$): δ 0.88 (t, 6H), 1.20–1.70 (m, 24H), 2.27 (t, 4H), 7.10 (s, 4H).

7.31 (ABq, 8H), 9.78 (s, 2H). ^{13}C NMR (DMSO- d_6): δ 15.37 (CH_3), 23.43, 26.40, 31.93, 32.44 ($\text{CH}_3 + \text{CH}_2$), 37.90 (C), 43.16 ($\text{CH}_2\text{C}=\text{O}$), 120.61, 127.79, 128.43, 138.73, 146.62, 149.30 (Ar), 173.04 ($\text{C}=\text{O}$).

2.10. Preparation of diamine 17

Diamide 16 (2.40 g, 4.44 mmol) was added to a suspension of LiAlH_4 (0.84 g, 22.2 mmol) in THF (250 ml) and the mixture was refluxed overnight. The reaction was quenched by addition of 5% aqueous NaOH. The mixture was filtered and the solvent was removed in vacuo. The residue was chromatographed on silica gel with CH_2Cl_2 as eluent to produce diamine 17 (2.00 g, 88%) as a pale-yellow solid with m.p. 78–78 °C. Anal. Found: C, 84.49; H, 10.25. $\text{C}_{36}\text{H}_{52}\text{N}_2$: Calc.: C, 84.32; H, 10.22%. IR (film): 3400 (N–H) cm^{-1} . ^1H NMR (CDCl_3): δ 0.89 (t, 6H), 1.25–1.70 (m, 28H), 3.07 (t, 4H), 3.48 (br s, 2H), 6.78 (ABq, 8H), 7.10 (s, 4H). ^{13}C NMR (CDCl_3): δ 15.77 (CH_3), 24.38, 28.46, 31.43, 32.67, 33.43 ($\text{CH}_3 + \text{CH}_2$), 43.41 (C), 45.97

(CH_2N), 114.20, 128.17, 129.59, 141.56, 148.25, 150.16 (Ar).

2.11. Preparation of ferrocenophane 5

A solution (50 ml) of diacid chloride 14 (1.09 g, 3.50 mmol) in benzene and a solution (50 ml) of diamine 17 (1.79 g, 3.50 mmol) and triethylamine (0.80 g, 7.90 mmol) in benzene were added simultaneously at 5.1 ml h^{-1} to 200 ml of vigorously stirred benzene at room temperature. After the addition was completed, the mixture was stirred for 20 h. The solvent was removed in vacuo and the residue was chromatographed on alumina with petroleum ether–EtOAc (3:2) to give a slightly impure product which was redissolved in a small amount of EtOAc, triturated with petroleum ether and left overnight at 4 °C. Orange crystals were collected and dried under vacuum to afford ferrocenophane 5 (1.05 g, 40%) with m.p. 199–200 °C. Anal. Found: C, 76.96; H, 7.39. $\text{C}_{48}\text{H}_{54}\text{FeN}_2\text{O}_2$: Calc.: C, 77.20; H, 7.99%. IR (film): 1620 ($\text{C}=\text{O}$) cm^{-1} . ^1H NMR (CDCl_3): δ 0.85

Table 1
Crystal data and structure solution data

	13	5
Formula	$\text{C}_{12}\text{H}_{14}\text{FeO}_2$	$\text{C}_{48}\text{H}_{54}\text{FeN}_2\text{O}_2$
Formula weight	246.1	750.80
Crystal size (mm^3)	$0.10 \times 0.21 \times 0.30$	$0.24 \times 0.38 \times 0.44$
Color	orange-brown	orange
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	13.395(12)	10.948(2)
b (Å)	7.714(5)	12.387(2)
c (Å)	10.497(11)	30.425(4)
β (deg)	105.7(8)	90.49(1)
Volume (Å 3)	1043.9	4126.2
Z	4	4
D_c (g cm^{-3})	1.566	1.208
$F(000)$	512	1608
μ (mm^{-1})	1.42	0.405
Scan mode	$2\theta-\theta$	$2\theta-\theta$
Scan speed (deg min^{-1})	3.00 to 14.65 in θ	3.00 to 14.65 in θ
Scan range	$K\alpha$ separation $\pm 0.60^\circ$ in ω	$K\alpha$ -separation $\pm 0.60^\circ$ in ω
T (K)	293	293
2θ limits (deg)	4.0 to 45.0	4.0 to 45.0
Index range	$-14 \leq h \leq 13, -8 \leq k \leq 0, 0 \leq l \leq 11$	$-11 \leq h \leq 0, 0 \leq k \leq 14, -36 \leq l \leq 36$
Total data	1591	6276
Unique data	1369 ($R_{\text{int}} = 1.25\%$)	5543 ($R_{\text{int}} = 4.25\%$)
Observed data	999 ($F > 4.0\sigma(F)$)	3499 ($F > 4.0\sigma(F)$)
Data/parameter ratio	7.3:1	7.5:1
Largest and mean shift/ σ	0.001, 0.000	0.097, 0.007
R	0.0323	0.0611
R_w	0.0354	0.0723
Weights	$w^{-1} = \sigma^2(F) + 0.003F^2$	$w^{-1} = \sigma^2(F) + 0.0007F^2$
Extinction correction	$X = 4(2) \times 10^{-4}$, where $F^* = F[1 + 0.002XF^2/\sin(2\theta)]^{-1/4}$	$X = 4(2) \times 10^{-4}$, where $F^* = F[1 + 0.002XF^2/\sin(2\theta)]^{-1/4}$
Goodness-of-fit	1.30	1.64
Largest difference peak (e Å^{-3})	0.28	0.72
Largest difference hole (e Å^{-3})	-0.23	-0.46

(t, 6H), 1.20–1.65 (m, 16H), 1.84 (s, 12H), 3.48 (s, 4H), 3.70 (t, 4H), 3.74 (s, 4H), 7.20 (s, 4H), 7.29 (ABq, 8H). ^{13}C NMR (CDCl_3): δ 15.74 (CH_3), 24.30, 28.30, 29.42, 30.23, 33.36 (CH_2), 43.33 (C), 52.54 (CH_2N), 73.76, 74.74, 77.87 (Fc), 127.63, 128.98, 131.63, 141.98, 149.39, 152.81 (Ar), 171.00 (C=O). MS (m/e): 750.65 (M^+).

2.12. Cyclic voltammetry

Cyclic voltammetric measurements were carried out and quantitatively interpreted as previously described [8]. Ferrocenophane oxidation products precipitated at the platinum working electrode which made it necessary to clean the electrode with aqua regia after every voltammetric measurement.

2.13. X-ray diffraction studies

A suitable crystal of diol **13** [12] was grown from EtOAc–petroleum ether and mounted on a Siemens R3m/V automated diffractometer which utilized graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Lattice parameters and the orientation matrix of the crystal were obtained using a least squares procedure involving 22 carefully centered reflections ($6.84 \leq 2\theta \leq 26.50^\circ$). The crystallographic data and structure solution and refinement parameters are listed in Table 1. The trial structure was obtained by a combination of Patterson and Fourier methods. Positions for the hydrogen atoms bonded to carbon atoms were calculated, while the alcohol hydrogen atoms were located in difference maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were allowed to ride on the atoms to which they were bonded in the refinement process. The hydrogen atoms were assigned isotropic thermal parameters which were not refined.

A suitable crystal of lipophilic ferrocenophane diamide **5** was grown from EtOAc–petroleum ether. The crystallographic data and experimental conditions for **5** are given in Table 1. These data were obtained in a procedure similar to that described above for diol **13**. For **5**, 31 reflections ($9.40 \leq 2\theta \leq 24.68^\circ$) were used to obtain the lattice parameters and the orientation matrix. The structure was solved by a combination of Patterson and direct methods. The magnitude of the thermal parameters of the carbon atoms included in the hexyl side chains increases as the distance of the atom from the amide nitrogen increases (see Table 2). It was possible to refine atoms Ca1 to Ca3 and Cb1 to Cb6 anisotropically. However, the large isotropic thermal parameters for Ca4, Ca5 and Ca6 and the unrealistic calculated bond distances involving these atoms suggested that these three atoms were disordered. It was not possible to resolve the disorder. In the final refinement process, Ca4, Ca5 and Ca6 were refined isotropically and their

Table 2
Ferrocenophane electrochemical data^a

Compound	$E_{1/2}$ (V vs. NHE)	ΔE_p (V)	Solvent
1	0.44	0.08	CH_3CN
1	0.45	0.12	CH_2Cl_2
2	0.46	0.14	CH_2Cl_2
3	0.44	0.10	CH_2Cl_2
5	0.72	0.07	CH_3CN

^a At 25.0°C with 0.1 M (*n*-Bu)₄NClO₄ as supporting electrolyte. Pt working and auxiliary electrodes; SCE reference electrode in aqueous 0.1 M NaNO₃; sweep rate 50 mV s⁻¹. The uncertainty in $E_{1/2}$ is estimated as ± 0.01 V. $E_{1/2}$ was calculated as $(E_{pa} + E_{pc})/2$ and referenced to NHE with hydroxyethylferrocene internal calibrant, $\Delta E_p = \Delta E_{pa} - E_{pc}$. The solubility of **4** in both CH_3CN and CH_2Cl_2 was too low to permit the measurement of an $E_{1/2}$ value.

bond distances were refined to give reasonable values. The remainder of the non-hydrogen atoms were refined anisotropically. Positions for all hydrogen atoms were calculated, except for those bonded to the disordered atoms and those hydrogen atoms which were not included in the refinement process. In the final refinement, the hydrogen atoms of **5** were treated in a manner similar to those bonded to the carbon atoms of **13**.

All programs used in the solution, refinement and display of **13** and **5** are contained in the SHELXTL-PLUSTM program [15] package. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [16].

3. Results and discussion

3.1. Synthesis

Reactions of commercially available bisphenol **6** with K_2CO_3 and 6.9-fold excesses of 1,3-dibromopropane and 1,5-dibromopentane in acetone produced dibromides **7** and **9** in 79% and 71% yields respectively. Dichloride **8** was obtained in 66% yield by reacting bisphenol **6** with NaOH and a large excess of 1,4-dichlorobutane using an adaptation of a reported procedure for a similar modification of a different bisphenol [14]. Treatment of dibromides **7** and **9** and dichloride **8** with thiourea gave dithiols **10–12** in 72%, 44%, and 90% yields respectively. Utilizing the methodology of Czech and Ratajczak [17], cyclization of the dithiols with 1,1'-di(hydroxymethyl)ferrocene (**13**) was conducted in the presence of trifluoroacetic acid and produced ferrocenophanes **1–3** in 12%, 56% and 59% yields respectively. Ferrocenophane **2** retained benzene, the column chromatographic eluent, even after heating at 60–80 °C under vacuum. Results of both ^1H NMR and combustion analysis were consistent with the presence of a complex involving two molecules of **2** and one of benzene. Re-examination of the crystals by ^1H

NMR after 1 year showed benzene to still be present, but in a lesser amount. No association of benzene with the smaller or larger-cavity ferrocenophane analogues, 1 and 3 respectively, was evident.

The diamide ferrocenophane 4 was prepared in low yield (10%) by high dilution cyclization of diacid chloride 14 with diamine 15. Since compound 4 was found to be only sparingly soluble in common organic solvents, lipophilic hexyl groups were incorporated into the phane structure to enhance its solubility. Thus, diamine 15 was allowed to react with hexanoyl chloride to give an 80% yield of diamide 16, which was reduced with LiAlH_4 to form diamine 17 in 88% yield. High dilution cyclization of acyclic diamine 17 with diacid chloride 14 produced ferrocenophane 5 in 40% yield. Attempts to reduce 5 to the corresponding ferrocenophane diamine by treatment with LiAlH_4 in THF resulted in cleavage of the cyclic structure.

Structural compactness in ferrocenophanes 4 and 5 is suggested by comparison of the ^1H NMR spectra of acyclic diamide 16 and macrocycle 5 in CDCl_3 . The chemical shift of the singlet for the four hydrogens on the central benzene unit moves downfield from 7.08 δ to 7.20 δ on going from 16 to 5. Similarly, the singlet for the 12 hydrogens on the isopropylidene groups shift downfield from 1.63 δ to 1.84 δ . These downfield shifts result from deshielding by the ferrocene moiety in macrocycle 5 caused by its proximity to the central benzene ring and isopropylidene groups. No differences in chemical shifts for the hydrogens on the central benzene units or of the isopropylidene groups are ob-

served in going from the acyclic compounds 6–12 and the larger ring ferrocenophanes 1–3.

Structures of the new compounds were verified by combustion analyses and by NMR spectra. Molecular ions were observed in the MS spectra of ferrocenophanes 1–3 and 5. Confirming IR spectra were obtained for ferrocenophanes 4 and 5 and acyclic intermediates 16 and 17.

3.2. Electrochemical studies on ferrocenophane 1–3 and 5

The half-wave Fe(III-II) potentials of ferrocenophanes 1, 2 and 3 in CH_2Cl_2 (Table 2) are essentially identical at 0.45 ± 0.01 V vs. NHE, independent of n within the $\text{S}(\text{CH}_2)_n$ structural unit and similar to the $E_{1/2}$ of unsubstituted ferrocene (0.42 V vs. NHE). Cyclic ferrocenophane diamide 5 is remarkably resistant to both reduction and oxidation, as evidenced by its degradation in the presence of LiAlH_4 and the observation of an exceptionally positive $E_{1/2}(\text{Fe(III,II)})$ value. This half-wave potential is substantially more positive than those of related cyclic and acyclic ferrocene diamides, but smaller than that of 1,1'-ferrocenediacarboxylic acid (0.805 V vs. NHE) [8]. On this basis, we conclude that the $E_{1/2}$ value observed for 5 falls within the range expected for the inductive influences of ferrocene carbonyl substituents, but could also reflect, in part, rigidity of the cyclopentadienyl rings imposed by the aromatic spacer and amide linkages [18].

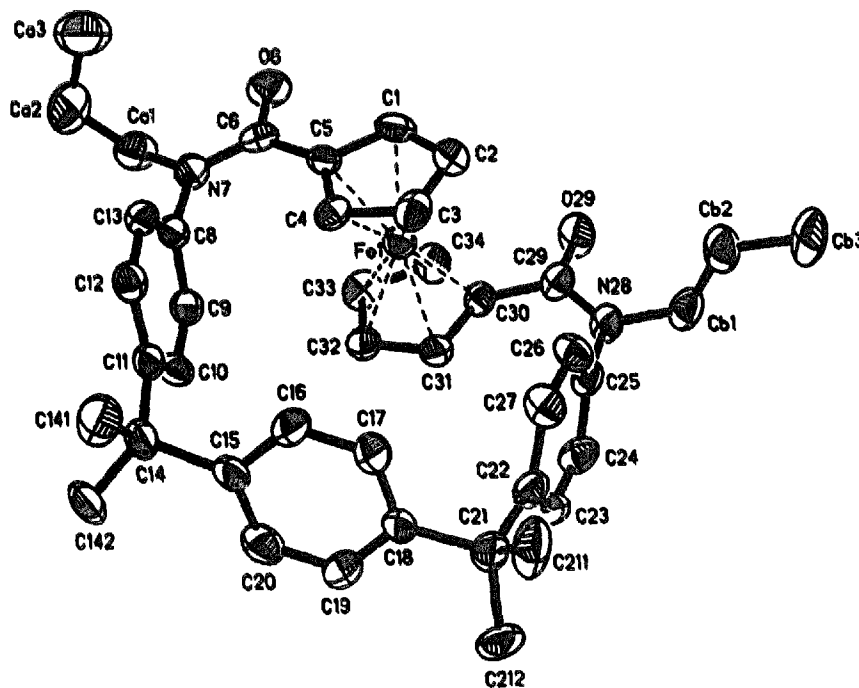


Fig. 1. A view of the molecular structure of lipophilic ferrocenophane diamide 5 showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

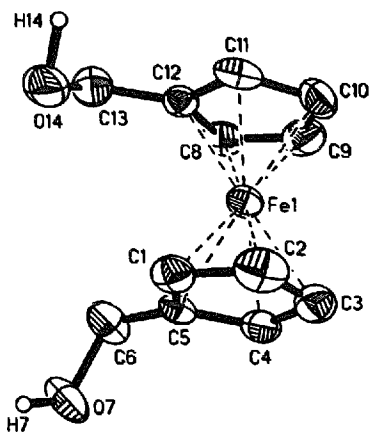


Fig. 2. A view of the molecular structure of 1,1'-di(hydroxymethyl)ferrocene (**13**) showing the atom numbering scheme. Thermal ellipsoids are drawn at the 35% probability level.

3.3. X-ray diffraction studies of ferrocenophane diamide **5** and reactant **13**

Although 1,1'-di(hydroxymethyl)ferrocene (**13**) was first reported more than two decades ago [19], its solid-state structure has not been reported. Therefore the solid-state structures of both reactant **13** and lipophilic ferrocenophane diamide **5** are described. Computer drawings of **5** and **13** are shown in Figs. 1 and 2 respectively, and give the conformations of the two compounds and the atom labels. For **5**, the hexyl groups bonded to the amide nitrogens point away from the cavity, and their conformations are of little importance to the overall structure of the molecule. Therefore, only the first three carbon atoms of each chain are included in the figure. Positional and thermal parameters for the atoms of **5** and **13** are listed in Tables 3 and 4 respectively. Bond lengths and angles for the non-hydrogen atoms of **13** are listed in Tables 5 and 6 respectively. Owing to the size of **5**, and the large number of bonds and angles which have been well characterized, only the bond lengths (Table 7) and the bond angles (Table 8) in the ferrocene and amide portions of the molecules are included in the tables. Comparison of bond lengths and angles for the ferrocene units in **5** and **13** (Tables 5–8) and with other ferrocene-containing compounds reveals that these bonding parameters are typical of the class.

When discussing or comparing the structures of disubstituted ferrocenes, the structural features that are of particular interest, as illustrated in Fig. 3, are: α , the relative angle of tilt of the two cyclopentadienyl rings; β , the orientation of the carboxyl plane or amide plane (if relevant) relative to the cyclopentadienyl ring; γ , the relative disposition of the two cyclopentadienyl rings [20].

In the structure of **13**, α is 1.7° , β is not relevant, since the molecule does not contain carbonyl groups, and γ has a value of 43.9° . The value of α is normal,

but the γ value is uncommon. When there are no strong intermolecular forces in the crystal structures of 1,1'-disubstituted ferrocenes, these molecules frequently adopt a 1,3'-conformation ($108 < \gamma < 180^\circ$). Thus, for 1,1'-ferrocene diketones and diamides, the γ values range from 129 – 142° (see Table 9) [20]. However, when intermolecular forces, such as hydrogen bonds, are present, the γ values may lie outside this range. For example,

Table 3

Atomic positional parameters ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for atoms of **5**

Atom	x	y	z	U_{eq}^a
Fe	3103(1)	174(1)	2116(1)	47(1)
C1	1405(6)	585(6)	2333(2)	69(3)
H1A	696	129	2335	80 ^b
C2	1745(6)	1257(6)	1988(2)	72(3)
H2A	1322	1340	1712	80
C3	2825(6)	1803(5)	2117(2)	59(3)
H3A	3253	2330	1945	80
C4	3165(5)	1445(4)	2537(2)	48(2)
H4A	3870	1677	2702	80
C5	2272(5)	670(5)	2680(2)	47(2)
C6	2125(6)	18(5)	3087(2)	52(2)
O6	1195(4)	-526(4)	3125(2)	78(2)
N7	2997(4)	31(4)	3410(2)	52(2)
Ca1	2848(6)	-672(6)	3795(2)	73(3)
H1A1	2176	-1151	3739	100
H2A1	3584	-1084	3833	100
Ca2	2613(8)	-87(7)	4210(3)	101(4)
H1A2	3306	368	4268	100
H2A2	2545	-616	4439	100
Ca3	1511(8)	590(8)	4226(3)	124(5)
H1A3	1557	1104	3991	100
H2A3	811	135	4183	100
Ca4	1325(12)	1226(11)	4656(4)	218(6) ^b
Ca5	257(15)	1989(14)	4560(5)	270(9) ^b
Ca6	-125(18)	2546(17)	4947(7)	331(11) ^b
C8	4103(5)	635(5)	3389(2)	44(2)
C9	5136(5)	180(5)	3210(2)	49(2)
H9A	5122	-567	3125	80
C10	6165(5)	798(5)	3154(2)	55(2)
H10A	6886	476	3033	80
C11	6213(5)	1873(6)	3280(2)	51(2)
C12	5200(6)	2301(5)	3486(2)	50(2)
H12A	5229	3032	3590	80
C13	4166(5)	1682(5)	3543(2)	49(2)
H13A	3478	1974	3696	80
C14	7360(6)	2559(6)	3179(2)	65(3)
C141	7263(7)	3693(6)	3384(2)	94(4)
H14A	6553	4046	3265	80
H14B	7199	3652	3698	80
H14C	7979	4097	3309	80
C142	8478(6)	1986(7)	3376(2)	99(4)
H14D	9202	2404	3327	80
H14E	8388	1860	3686	80
H14F	8543	1307	3226	80
C15	7442(5)	2639(5)	2674(2)	54(2)
C16	6577(6)	3234(6)	2442(2)	66(3)
H16A	5959	3599	2607	80
C17	6590(6)	3318(6)	1993(2)	68(3)
H17A	5977	3755	1852	80
C18	7445(6)	2796(5)	1735(2)	55(3)

Table 3 (continued)

Atom	x	y	z	U_{eq}^a
C19	8301(6)	2222(6)	1960(2)	71(3)
H19A	8908	1830	1799	80
C20	8297(6)	2156(6)	2412(3)	73(3)
H20A	8933	1760	2559	80
C21	7393(6)	2857(6)	1232(2)	67(3)
C211	7185(7)	4028(6)	1081(2)	102(4)
H21A	6430	4273	1204	80
H21B	7839	4485	1180	80
H21C	7131	4055	766	80
C212	8609(6)	2503(7)	1034(2)	110(4)
H21D	8771	1774	1124	80
H21E	8551	2533	719	80
H21F	9260	2964	1133	80
C22	6339(6)	2137(6)	1071(2)	57(3)
C23	6500(6)	1149(6)	878(2)	67(3)
H23A	7317	912	819	80
C24	5527(6)	480(5)	766(2)	62(3)
H24A	5667	-208	630	80
C25	4355(6)	796(5)	847(2)	51(2)
C26	4157(6)	1820(5)	1017(2)	58(3)
H26A	3335	2066	1061	80
C27	5128(6)	2468(5)	1130(2)	62(3)
H27A	4984	3173	1250	80
N28	3329(4)	97(4)	783(2)	56(2)
Cb1	2718(6)	130(6)	352(2)	72(3)
H1B1	3328	240	132	100
H2B1	2316	-548	302	100
Cb2	1779(7)	1023(6)	314(2)	81(3)
H1B2	1127	869	514	100
H2B2	2164	1691	396	100
Cb3	1238(8)	1114(7)	-149(2)	92(4)
H1B3	941	422	-243	100
H2B3	1877	1348	-340	100
Cb4	234(9)	1945(8)	-196(3)	122(5)
H1B4	-47	1911	-495	120
H2B4	-410	1723	-4	120
Cb5	469(12)	3139(9)	-88(4)	160(7)
H1B5	852	3175	197	160
H2B5	-304	3503	-80	160
Cb6	1177(12)	3737(12)	-372(4)	187(8)
H1B6	1650	3087	-351	160
H2B6	1698	4349	-322	160
H3B6	813	3787	-659	160
C29	2848(6)	-507(5)	1110(2)	61(3)
O29	1897(4)	-1017(4)	1050(2)	84(2)
C30	3478(5)	-613(5)	1543(2)	49(2)
C31	4571(5)	-126(5)	1729(2)	55(2)
H31A	5076	404	1589	80
C32	4763(6)	-576(5)	2152(2)	57(2)
H32A	5427	-400	2347	80
C33	3837(6)	-1320(5)	2236(2)	63(3)
H33A	3752	-1729	2502	80
C34	3054(6)	-1353(5)	1872(2)	65(3)
H34A	2345	-1804	1844	80

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b U value for each hydrogen atom and for each non-hydrogen atom with superscript ^b is an isotropic U .

for 1,1'-ferrocene-dicarboxylic acid, which crystallizes as hydrogen-bonded dimeric units, the γ value is 1.6° [20,23]. In the structure of 1,1'-di(hydroxymethyl)ferro-

Table 4

Atomic positional parameters ($\times 10^{-4}$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for atoms of 13

Atom	x	y	z	U_{eq}^a
Fe1	8077(1)	4955(1)	2616(1)	30(1)
C1	7173(4)	4148(6)	3778(4)	40(2)
H1	6551	4706	3852	80 ^b
C2	8197(4)	4487(6)	4564(4)	48(2)
H2	8385	5302	5280	80
C3	8890(4)	3408(6)	4136(4)	43(2)
H3	9631	3380	4482	80
C4	8298(4)	2387(6)	3087(4)	39(2)
H4	8561	1522	2607	80
C5	7230(3)	2846(5)	2854(4)	33(2)
C6	6330(3)	2090(6)	1826(5)	52(2)
H6A	6571	1622	1115	80
H6B	5842	2996	1472	80
O7	5820(2)	745(4)	2350(3)	57(1)
H7	5336	1119	2864	80
C8	7849(4)	5534(5)	655(4)	41(2)
H8	7567	4775	-79	80
C9	8909(4)	5711(7)	1330(5)	53(2)
H9	9475	5099	1138	80
C10	8991(4)	6942(6)	2331(5)	52(2)
H10	9622	7313	2953	80
C11	7977(4)	7556(6)	2276(4)	42(2)
H11	7804	8411	2845	80
C12	7266(3)	6673(5)	1233(4)	32(2)
C13	6126(3)	6939(6)	729(5)	57(2)
H13A	5822	5891	300	80
H13B	5995	7845	78	80
O14	5630(3)	7354(5)	1714(4)	79(2)
H14	5809	8729	1882	80

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b U value for each hydrogen atom is an isotropic U .

Table 5

Bond lengths (\AA) for non-hydrogen atoms of 13

Fe1-C1	2.036(6)	Fe1-C8	2.047(5)
Fe1-C2	2.039(5)	Fe1-C9	2.054(6)
Fe1-C3	2.052(5)	Fe1-C10	2.034(6)
Fe1-C4	2.043(5)	Fe1-C11	2.036(5)
Fe1-C5	2.038(5)	Fe1-C12	2.047(4)
C1-C2	1.419(6)	C8-C9	1.410(6)
C2-C3	1.408(7)	C9-C10	1.398(7)
C3-C4	1.409(6)	C10-C11	1.425(7)
C4-C5	1.428(6)	C11-C12	1.415(6)
C5-C1	1.413(6)	C12-C8	1.417(7)
C5-C6	1.500(6)	C12-C13	1.489(6)
C6-O7	1.432(6)	C13-O14	1.409(7)

Table 6

Bond angles (deg) for non-hydrogen atoms of 13

C2-C1-C5	107.8(4)	C9-C8-C12	108.7(4)
C1-C2-C3	108.8(4)	C8-C9-C10	107.9(5)
C2-C3-C4	107.4(4)	C9-C10-C11	108.4(4)
C3-C4-C5	108.7(4)	C10-C11-C12	107.8(4)
C1-C5-C4	107.2(4)	C8-C12-C11	107.2(4)
C1-C5-C6	126.0(4)	C8-C12-C13	124.4(4)
C4-C5-C6	126.8(4)	C11-C12-C13	128.2(4)
C5-C6-O7	112.7(4)	C12-C13-O14	114.4(4)

Table 7
Selected bond lengths (Å) for **5**

Fe–C1	2.042(6)	Fe–C34	2.032(6)
Fe–C2	2.037(7)	Fe–C33	2.050(6)
Fe–C3	2.040(6)	Fe–C32	2.044(6)
Fe–C4	2.031(6)	Fe–C31	2.035(6)
Fe–C5	2.044(6)	Fe–C30	2.041(6)
C1–C2	1.392(10)	C33–C34	1.397(10)
C2–C3	1.414(10)	C32–C33	1.396(9)
C3–C4	1.402(9)	C31–C32	1.416(9)
C4–C5	1.439(8)	C30–C31	1.450(8)
C5–C1	1.419(9)	C30–C34	1.436(9)
C5–C6	1.488(9)	C30–C29	1.488(9)
C6–O6	1.227(8)	C29–O29	1.231(8)
C6–N7	1.365(8)	C29–N28	1.355(8)
N7–C8	1.426(7)	N28–C25	1.431(8)
N7–Ca1	1.469(9)	N28–Cb1	1.467(8)

Table 8
Selected bond angles (deg) for **5**

C2–C1–C5	109.5(6)	C30–C34–C33	109.5(6)
C1–C2–C3	107.8(6)	C34–C33–C32	108.3(6)
C2–C3–C4	108.4(6)	C33–C32–C31	109.0(6)
C3–C4–C5	108.1(5)	C32–C31–C30	107.8(5)
C1–C5–C4	106.1(5)	C34–C30–C31	105.4(5)
C1–C5–C6	120.1(5)	C34–C30–C29	121.5(5)
C4–C5–C6	133.8(5)	C31–C30–C29	133.0(6)
C5–C6–O6	118.2(5)	O29–C29–C30	118.1(6)
C5–C6–N7	120.8(5)	C30–C29–N28	121.3(6)
O6–C6–N7	121.0(6)	O29–C29–N28	120.5(6)
C6–N7–Ca1	119.0(5)	Cb1–N28–C29	119.7(5)
C6–N7–C8	124.3(5)	C25–N28–C29	122.9(5)
Ca1–N7–C8	116.6(5)	C25–N28–C61	117.1(5)

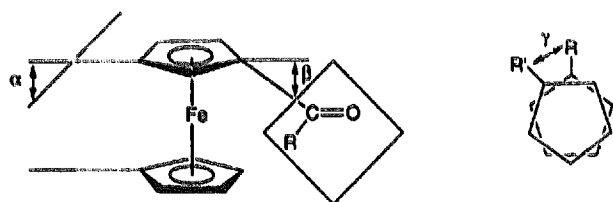


Fig. 3. Schematic diagram depicting the angles α , β and γ as listed in Table 9, α being a measure of the noncoplanarity of the two cyclopentadienyl rings, β the angle of the carbonyl group relative to the cyclopentadienyl ring, and γ the relative orientation of the two cyclopentadienyl rings in a ferrocene derivative.

Table 9
Structural features for 1,1'-disubstituted ferrocenes

Substituents		α (deg)	β (deg)		γ (deg)	Ref.
1	1'		Cp(1)	Cp(2)		
–C(O)CH ₃	–C(O)CH ₃	1.0	11.5	8.9	139.3	[21]
–C(O)CH ₃	–C(O)C ₆ H ₅	1.5	10.8	6.3	129.1	[22]
–C(O)NHCH ₃	–C(O)NHCH ₃	1.4	15.6	6.0	142.0	[20]
–CO ₂ H	–CO ₂ H	1.3	0.8	4.7	1.6	[23]
–CH ₂ OH	–CH ₂ OH	1.7	–	–	43.9	this work

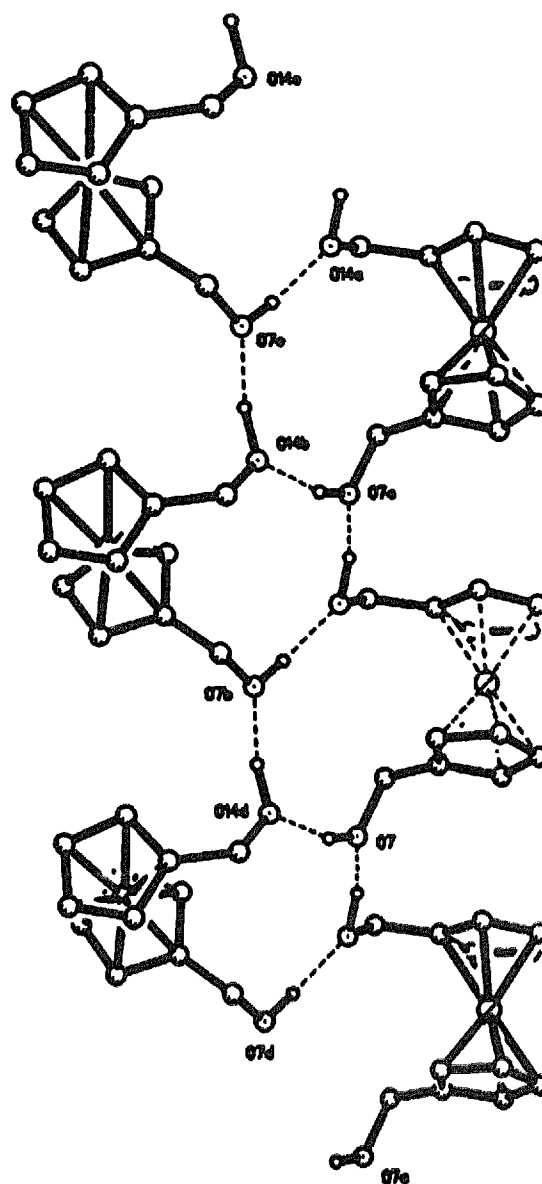


Fig. 4. A view of the hydrogen-bonding network for 1,1-dihydroxy-methylferrocenophane (**13**).

cene (**13**) (Fig. 2), the ferrocene unit has a 1,2'-conformation with a γ value of 43.9°. This is a result of an interesting intermolecular hydrogen-bonding arrangement for **13** which is shown in Fig. 4.

Table 10
Hydrogen bond data for 13

D	H	A	D...A (Å)	H...A (Å)	D-H...A (deg)
O7	H7	O14	2.705	1.76	158
O14	H14	O7	2.694	1.63	164

In the solid-state structure of **13**, the alcohol portion of the hydroxymethyl group attached to each ring of the ferrocene units participates in an intermolecular hydrogen-bonding network. Each alcohol function is involved in two intermolecular hydrogen bonds, acting as both a hydrogen atom donor and acceptor. The hydrogen bond data are given in Table 10. The first hydrogen bond listed in Table 10 joins molecules related by the symmetry operation $-x, 0.5 + y, 0.5 - z$, while the second joins molecules related by a cell translation in the b direction. Thus, the structure consists of chains of molecules connected by hydrogen bonds with ferrocene groups on the outside of the chains and the hydrogen-bonding network on the interior (Fig. 4).

A molecule of **5** contains several planar fragments which include three benzene groups, two amide groups and two cyclopentadiene rings. Also, the backbone of the molecule, which consists of C8, C11, C14, C15, C18 and C21, is nearly planar. Least-squares planes have been calculated for the eight fragments. Table 11 lists the average deviation of an atom used in the calculation of the plane from the plane and also the dihedral angles between the respective planes. It can be seen from the data in Table 11 that the β values (Fig. 3) for the two cyclopentadiene-amide groups in **5** are similar at 5.4 and 5.7°. It is also interesting to note that the dihedral angles between the plane of the backbone and the plane of the cyclopentadiene rings and amide fragments are all less than 26°, while similar angles between the plane of the backbone and the planes of the benzene rings are all within the range $90 \pm 26^\circ$.

For the lipophilic ferrocenophane diamide **5**, the α value is 1.0° and the β values are nearly equal at 5.4 and 5.7°, as mentioned earlier. In contrast, for **18**, which is an acyclic analogue of **5**, the β values of 6.0 and 15.6° [20] differ by almost 10° . The γ value for **5** is 149.9° . This value is similar to that reported for structurally related acyclic analogue **18** and other 1,1'-disubstituted ferrocenes in which there are no strong intermolecular forces (Table 9) [20], but it is considerably different from the cyclic ferrocene cryptand [Fc.2.2] for which $\gamma = 79.1^\circ$ [20]. The β values for [Fc.2.2] differ considerably from each other and from those of **5**, being 15.7 and 50.2° .

Fig. 1 shows that lipophilic ferrocenophane diamide **5** has a small, but open, cavity. Three sides of the cavity are formed by the three benzene rings, while the ferrocene unit provides the fourth side. It appears that the

Table 11
(a) Least-squares planes of planar groups of **5** and (b) dihedral angles between those planes

Plane	Atoms of plane	Average deviation of an atom from the plane (Å)
A	C1, C2, C3, C4, C5	0.005
B	C5, C6, O6, N7	0.001
C	C8, C9, C10, C11, C12, C13	0.020
D	C15, C16, C17, C18, C19, C20	0.007
E	C22, C23, C24, C25, C26, C27	0.017
F	N28, C29, O29, C30	0.007
G	C30, C31, C32, C33, C34	0.001
H	C8, C11, C14, C15, C18, C21, C22, C25	0.055

Planes	A	B	C	D	E	F	G
A							
B	5.4						
C	92.2	89.5					
D	72.3	67.6	89.6				
E	86.8	85.6	18.8	105.1			
F	5.1	6.9	96.2	69.2	91.6		
G	1.0	6.3	92.3	73.3	86.6	5.7	
H	22.7	25.2	114.7	71.2	109.0	18.5	22.7

cavity in **5** is not likely to accommodate a guest ion or molecule because of its small size.

The solid-state structure of the lipophilic ferrocenophane **5** indicates that neither **4** nor **5** will be able to function as sequestering agents. Owing to the structural differences between ferrocenophanes **1–3** compared with **4** and **5**, whether or not the former can sequester neutral molecules remains an open question.

4. Supplementary information available

Additional experimental details and structural data for the X-ray diffraction studies of **5** and **13** can be obtained for N.K.D.

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