

2-(3-Chlorophenyl)-1-ferrocenylmethyl-1H-1,3-benzimidazole: an electroactive agent for anion sensor and malarial parasite studies

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Key indicators

Single-crystal X-ray study

$T = 297\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.041

wR factor = 0.105

Data-to-parameter ratio = 18.5

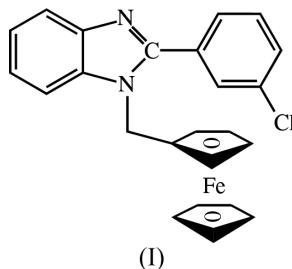
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_{19}\text{H}_{14}\text{ClN}_2)]$, a model electroactive agent for anion sensor and malarial parasite studies, has $\text{Fe}-\text{C}$ bond lengths in the range 2.020 (3)–2.0543 (18) Å. The $\text{Fe}\cdots\text{Cg}$ distances (Cg indicates a ring centroid) are essentially similar, with values of 1.6467 (10) and 1.6487 (11) Å for the substituted and unsubstituted cyclopentadienyl rings, respectively, with a linear $\text{Cg}\cdots\text{Fe}\cdots\text{Cg}$ angle of $179.12(7)^\circ$. The $\text{Fe}-\text{C}_{\text{Cp}}-\text{Csp}^3$ angle is $128.43(13)^\circ$ and the $\text{Fe1}-\text{C}_{\text{Cp}}-\text{Csp}^3-\text{N}_{\text{Bz}}$ torsion angle $110.27(17)^\circ$ (Cp is cyclopentadienyl and Bz is benzimidazole). Weak $\text{C}-\text{H}\cdots\text{Cl}$ contacts form the only intermolecular interactions of significance.

Comment

The synthesis of anion receptors is currently an area of intense research activity due primarily to the ubiquitous roles which anions play in both chemical and biological processes, for example, as substrates or co-factors for enzymes and as nucleophiles, redox agents and phase transfer catalysts. In the past decade, combinations of an organometallic moiety with an amide $\text{N}-\text{H}$ group have been demonstrated to be essential components in many anion-recognition receptors (Beer, 1998; Kingston *et al.*, 1999). 1,3-Disubstituted imidazolium cations have been utilized as such recently (Sato *et al.*, 1999; Thomas *et al.*, 2000) and their synthetic intermediates (imidazolin-2-ylidenes) are also of interest as carbenes and the subject of several synthetic and structural investigations (Benito *et al.*, 1995; Bildstein *et al.*, 1998, 1999).

Recently, benzimidazole systems have attracted our considerable attention in synthetic and applied biological research (Howarth *et al.*, 2000; Thomas *et al.*, 2000; Howarth & Hanlon, 2001). Compound (I), depicted in Fig. 1, is obtained from 2-(3-chlorophenyl)benzimidazole and (trimethyl)ammoniumferrocenylmethyl iodide (Pauson *et al.*, 1966; Ferguson *et al.*, 1994a) and is an important electroactive model compound for application in anion sensor studies (Thomas *et al.*, 2000), as well as in malarial parasite research (Howarth & Hanlon, 2001).



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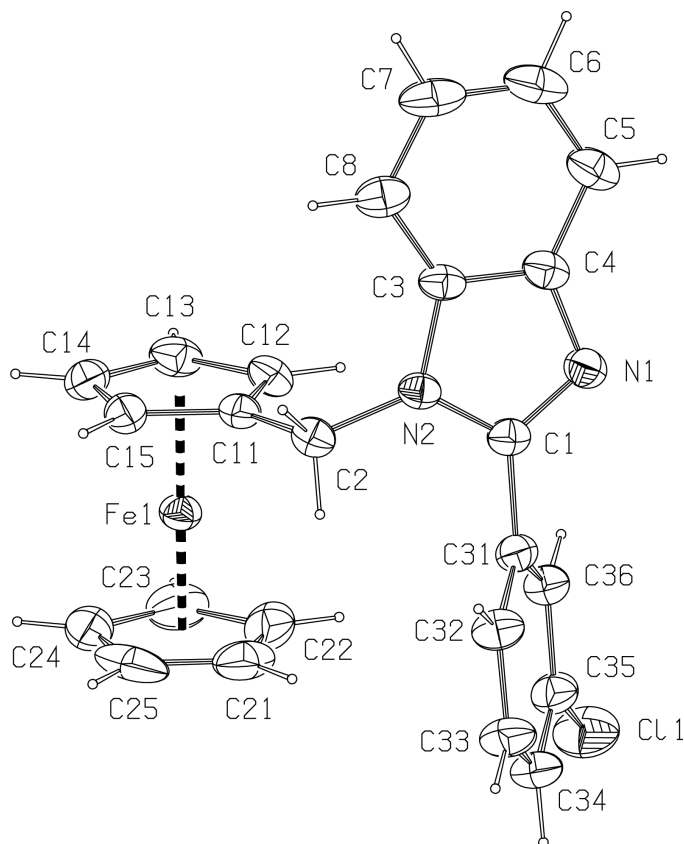


Figure 1
A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

In (I), selected bond lengths and angles are listed in Table 1. The Fe—C bond lengths are in the range 2.020 (3)–2.0543 (18) Å; the Fe1...Cg(1,2) distances (Cg1 and Cg2 are centroids of the cyclopentadienyl rings) are comparable, 1.6467 (10) and 1.6487 (11) Å for the substituted and unsubstituted rings, respectively, with a linear Cg1...Fe1...Cg2 angle of 179.12 (7)°. The cyclopentadienyl rings are essentially eclipsed, with a C21—Fe1—C11—C2 torsion angle of -2.8 (2)° and there is no evidence for disorder in the unsubstituted C₅H₅ ring. The Fe—C_{Cp}—Csp³ angle is 128.43 (13)° and similar to 128.3 (3)° in *N*-ferrocenylmethyl-2-ferrocenylbenzimidazole, (II) (Benito *et al.*, 1995), or 127.86 (12) and 126.80 (12)° in the two independent molecules of racemic ferrocenyl(phenyl)methanol (Ferguson *et al.*, 1994*b*). The benzimidazole is twisted with respect to the ferrocenyl moiety, with Fe1—C_{Cp}—Csp³—N2 = 110.27 (17)° and C_{Cp}—Csp³—N2—C3 = 71.7 (2)° [the N1—C1—C31—C32 angle is 126.9 (2)°], and due to the bulky ferrocenyl and benzimidazole groups avoiding possible sterically hindered H...H contacts. In the crystal structure, the shortest H...Cl1 contacts and involving C25—H25 and C36—H36 [C...Cl 3.802 (5) and 3.670 (2) Å] are listed in Table 2.

A search of the October 2000 version of the Cambridge Structural Database using ConQuest Version 1.1 (Allen & Kennard, 1993) for molecules similar to (I) shows that such

compounds are relatively rare and include *N*-ferrocenylmethyl-2-ferrocenylbenzimidazole (ZIJPIR; Benito *et al.*, 1995) and *N*-ferrocenylmethyl-2-ferrocenylbenzimidazolium tetrafluoroborate (GIFLUC; Li *et al.*, 1998), which differ from (I) primarily through replacement of the chlorophenyl group by a ferrocenyl group.

Experimental

To a mixture of 2-(chlorophenyl)benzimidazole (2.5 g, 10 mmol) and K₂CO₃ (2.07 g, 15 mmol) in CH₃CN (100 ml) was added (trimethyl)ammoniumferrocenylmethyl iodide (4.05 g, 10.5 mmol) (Pauson *et al.*, 1966; Ferguson *et al.*, 1994*a*), and the mixture was refluxed for 12 h. The reaction was cooled to room temperature, water added and the suspension extracted into CHCl₃. The organic layer was washed with water, dried (MgSO₄) and evaporated under vacuum to leave a brown solid. The crude product was purified by column chromatography on silica gel using CH₂Cl₂—CH₃OH (97:3) as eluent. The title compound was obtained as a light-brown powder. Yield 2.8 g (64%), m.p. 435–438 K (uncorrected). Analysis for C₂₄H₁₉ClFeN₂, calculated: C 67.57, H 4.45, N 6.56%; found: C 67.47, H 4.51, N 6.52%. IR (KBr, ν cm⁻¹), 3051, 2971, 2308, 1708, 1639, 1456, 1422, 1364, 1330, 1261, 1153, 1101, 1027, 1008, 895, 741, 706, 695. ¹H NMR [400 MHz, δH (p.p.m.), CDCl₃], 7.82 (*m*, 2H, aryl-H), 7.69 (*m*, 1H, C₆H₄), 7.56–7.48 (*m*, 3H, aryl-H and C₆H₄), 7.34 (*m*, 2H, C₆H₄), 5.22 (*s*, 2H, Fc-CH₂), 4.13–4.07 (*m*, 9H, Fc-H). ¹³C NMR (δC, CDCl₃), 152.27, 143.27, 136.04, 135.08, 132.79, 130.4, 130.35, 130.08, 128.21, 123.49, 123.05, 120.48, 110.86, 83.36, 69.25, 69.14, 68.71, 44.95.

Crystal data

[Fe(C₅H₅)(C₁₉H₁₄ClN₂)]
M_r = 426.71
Monoclinic, P2₁/n
a = 11.6838 (9) Å
b = 9.9220 (6) Å
c = 16.7493 (14) Å
β = 90.542 (6)°
V = 1941.6 (2) Å³
Z = 4

D_x = 1.46 Mg m⁻³
Mo Kα radiation
Cell parameters from 27 reflections
θ = 4.5–16.1°
μ = 0.93 mm⁻¹
T = 297 (1) K
Block, orange
0.37 × 0.24 × 0.21 mm

Data collection

Bruker P4 diffractometer
ω–2θ scans
Absorption correction: ψ scan
(North *et al.*, 1968)
T_{min} = 0.682, T_{max} = 0.746
5483 measured reflections
4669 independent reflections
3646 reflections with I > 2σ(I)

R_{int} = 0.033
θ_{max} = 28.0°
h = -15 → 1
k = -13 → 1
l = -22 → 22
3 standard reflections every 197 reflections
intensity decay: 2%

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.041
wR(F²) = 0.105
S = 1.03
4669 reflections
253 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.0495P)² + 0.6062P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.70 e Å⁻³
Δρ_{min} = -0.55 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Fe1—C11	2.0543 (18)	Fe1—C25	2.020 (3)
Fe1—C12	2.0419 (19)	C11—C35	1.742 (2)
Fe1—C13	2.038 (2)	N1—C1	1.310 (3)
Fe1—C14	2.034 (2)	N1—C4	1.389 (3)
Fe1—C15	2.040 (2)	N2—C1	1.378 (3)
Fe1—C21	2.031 (3)	N2—C2	1.456 (2)
Fe1—C22	2.034 (3)	N2—C3	1.386 (2)
Fe1—C23	2.032 (2)	C1—C31	1.480 (3)
Fe1—C24	2.026 (2)	C2—C11	1.504 (3)
C1—N1—C4	104.77 (17)	N1—C1—C31	123.68 (19)
C1—N2—C2	128.44 (16)	N2—C1—C31	122.80 (18)
C1—N2—C3	105.85 (16)	N2—C2—C11	111.86 (15)
C2—N2—C3	124.26 (17)	C2—C11—Fe1	128.43 (13)
N1—C1—N2	113.52 (17)		
C3—N2—C2—C11	71.7 (2)	C21—Fe1—C11—C2	−2.8 (2)
N2—C2—C11—C12	18.6 (3)	N2—C1—C31—C36	128.8 (2)
N2—C2—C11—Fe1	110.27 (17)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C25—H25 \cdots Cl1 ⁱ	0.93	3.05	3.802 (5)	139
C36—H36 \cdots Cl1 ⁱⁱ	0.93	3.03	3.670 (2)	127

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $2 - x, -y, 1 - z$.

All H atoms bound to C atoms were treated as riding, with *SHELXL97* (Sheldrick, 1997) defaults for C—H distances and with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for the remainder. Examination of the structure with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

ORTEPIII (Burnett & Johnson, 1996) and *PLATON* (Spek, 1998); software used to prepare material for publication: *SHELXL97* and *PREP8* (Ferguson, 1998).

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