O(3)—Cu—O(5)	102.3 (2)	O(2)—C(12)—C(11)	121.5 (4)
O(1ⁱ)—Cu—N(1)	91.9 (2)	O(4)—C(12)—C(11)	116.3 (4)
O(2)—Cu—N(1)	90.4 (2)	C(10)—C(11)—C(12)	115.3 (4)
O(3)—Cu—N(1)	162.9 (2)		

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

Table 3. Hydrogen-bonding geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O(5)—H(51)···O(4ⁱ)	0.93	1.84 (1)	2.748 (5)	167 (1)
O(5)—H(52)···O(3ⁱⁱ)	0.93	2.16 (1)	2.742 (5)	121 (1)
N(3)—H(3)···O(4ⁱⁱⁱ)	0.86	1.98 (1)	2.797 (5)	159 (1)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 2 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, 2 - z$; (iii) $-x, y - \frac{1}{2}, \frac{3}{2} - z$.

The structure was solved by the conventional Patterson method and refined by full-matrix least-squares calculations. The H atoms of the H₂O groups were located from a difference synthesis; all other H atoms were included in calculated positions (C—H and N—H of benzimidazole = 0.93 and 0.86 Å and C—H of malonate ion = 0.97 Å) and refined isotropically using a riding model, with fixed isotropic displacement parameters. All other non-H atoms were refined anisotropically.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990).

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2-Ferrocenylquinoxaline

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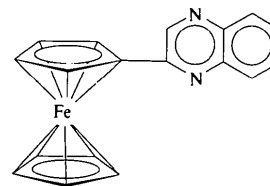
Abstract

In the title compound, [Fe(C₁₃H₉N₂)(C₅H₅)], the heterocyclic ring is almost coplanar with the cyclopentadienyl ring to which it is bonded. The molecules are arranged in a herringbone pattern generated by a 2₁ axis and there are no significant intermolecular interactions.

Comment

Ferrocenyl alcohols show a strong propensity both to self-assemble into oligomeric or polymeric aggregates (Sharma, Cervantes-Lee & Pannell, 1992; Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*, 1994; Li, Ferguson, Glidewell & Zakaria, 1994; Gallagher, Ferguson, Glidewell & Zakaria, 1994) and to form host–guest complexes (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*; Glidewell, Ferguson, Lough & Zakaria, 1994; Ferguson, Glidewell, Lewis & Zakaria, 1995). Following the observation of a very wide range of hydrogen-bonding patterns in adducts of ferrocenyl alcohols with amines, where the ferrocene acts as a hydrogen-bond donor (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*; Glidewell, Ferguson, Lough & Zakaria, 1994; Ferguson, Glidewell, Lewis & Zakaria, 1995), we have now embarked on a study of functionalized ferrocenes, which are potentially strong hydrogen-bond acceptors. We report here the structure of one such ferrocene, 2-ferrocenylquinoxaline, (I), where the structural features of interest, aside from confirmation of the molecular constitution, include the relative orientation of the ferrocene and heterocyclic portions of the molecule, and the nature of the intermolecular interactions.

(I)

The title compound crystallizes in the monoclinic space group $P2_1/a$ with a single molecule (Fig. 1) in the asymmetric unit. The mean value of the torsion angles $C1n$—$Cp1$—$Cp2$—$C2n$ ($n = 1$–5, $Cp1$ and $Cp2$ are the centroids of the cyclopentadienyl rings) is $-0.7 (3)°$, indicating an almost perfectly eclipsed average conformation of the two cyclopentadienyl rings, as generally found in monosubstituted ferrocenes. However, the displacement parameters for atoms $C2n$ ($n = 1$–5) indicate significant rotational motion of this ring about the local fivefold axis relative to the rest of the molecule. The angle $Cp1$—Fe—$Cp2$ is $177.8 (2)°$, while the dihedral angle between the best planes through $C1n$ and $C2n$ ($n = 1$–5) is $1.9 (2)°$.
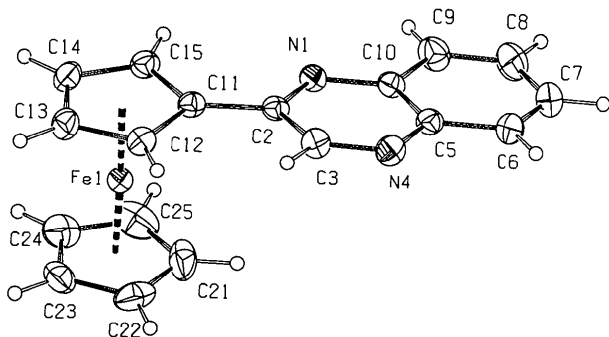

Fig. 1. A view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The quinoxaline fragment shows marked bond fixation of the naphthalene type; the mean value of the $C5$—$C6$ and $C9$—$C10$ distances $[1.410 (4) Å]$ exceeds the mean of the $C6$—$C7$ and $C8$—$C9$ distances $[1.360 (8) Å]$ by $0.050 Å$, and the mean of the $N1$—$C10$ and $N4$—$C5$ distances $[1.366 (3) Å]$ similarly exceeds the mean of the $N1$—$C2$ and $C3$—$N4$ distances $[1.316 (8) Å]$. In hexachloroquinoxaline, probably the simplest quinoxaline for which an accurate structure is available, the corresponding mean C—C distances are 1.413 and 1.372 Å, respectively, and the mean N—C distances are 1.290 and 1.368 Å, respectively (Vermeulen & Huiszoon, 1979).

The internal angles at the N atoms, $C2$—$N1$—$C10$ and $C3$—$N4$—$C5$, have values of $116.6 (2)$ and $116.2 (2)°$, respectively, typical of the values found in simple uncoordinated pyrazines (Ro & Sorum, 1972a,b; De With, Harkema & Feil, 1976) and quinoxalines (Vermeulen & Huiszoon, 1979; Cushman, Patel & McKenzie, 1988). However, of the four N—C—C angles in the pyrazino ring, only one $[N4$—$C3$—$C2$ $123.6 (2)°]$ shows the large enhancement over 120° typical of such angles. The angles $N1$—$C10$—$C5$ and $N4$—$C5$—$C10$ are to some extent constrained by the ring fusion and it is tempting to associate the disparity between the angles $N1$—$C2$—$C3$ $[120.7 (2)°]$ and $N4$—$C3$—$C2$ with the strongly electron-donating ferrocenyl substituent at $C2$.

It has been found that the magnitude of the *ipso* C—C—C angle in monosubstituted benzenes is markedly dependent upon the electron donor or acceptor properties of the substituent (Domenicano, Vaciago & Coulson, 1975), with electron-donor substituents leading to an *ipso* C—C—C angle below 120°. Hence, the geometric effects of the N1 atom and the ferrocenyl substituent at $C2$ essentially cancel each other.

The quinoxaline ring is nearly coplanar with the $C1n$ ring of the ferrocene fragment; the dihedral angle between these rings is $7.1 (4)°$. Similar near planarity has been observed in a bis(quinolyl)ferrocene (Gelin & Thummel, 1992). The $C2$—$C11$ distance, $1.464 (3) Å$, is significantly shorter than the corresponding C—C distances in octaphenylferrocene [range 1.481 (3)–1.500 (4) Å; mean 1.490 Å] (Castellani, Wright, Geib, Rheingold & Trogler, 1986). This may be indicative of some conjugation between the rings (Allen *et al.*, 1987).

The molecules fit closely together in a herringbone pattern generated by the 2_1 screw axis. However, none of the intermolecular contact distances is significantly shorter than the sum of the van der Waals radii (Bondi, 1964) and, in particular, there is no evidence for any C—$H \cdots \pi$(arene) interactions.

Experimental

The title compound was prepared by boiling under reflux for 20 h a methanol solution containing equimolar quantities of chloroacetylferrocene and o-phenylenediamine, followed by chromatography on alumina with toluene as eluant. Suitable crystals were grown by slow evaporation of a solution in dichloromethane/light petroleum (b.p. 313–333 K).

Crystal data

[Fe(C13H9N2)(C5H5)]	Mo $K\alpha$ radiation
$M_r = 314.16$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 25
$P2_1/a$	reflections
$a = 11.101 (2)$ Å	$\theta = 9.50$–$15.30°$
$b = 8.6795 (7)$ Å	$\mu = 1.079$ mm^{-1}
$c = 14.648 (2)$ Å	$T = 294 (1)$ K
$\beta = 100.457 (11)°$	Needle
$V = 1387.9 (3)$ Å^3	$0.40 \times 0.18 \times 0.18$ mm
$Z = 4$	Ruby red
$D_x = 1.504$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4	2141 observed reflections
diffractometer	$[I > 2\sigma(I)]$
$\omega/2\theta$ scans	$R_{int} = 0.019$
Absorption correction:	$\theta_{max} = 26.8°$
four ψ scans at 4°	$h = -14 \rightarrow 13$
steps (North, Phillips &	$k = 0 \rightarrow 11$
Mathews, 1968)	$l = 0 \rightarrow 18$
$T_{min} = 0.796$, $T_{max} =$	3 standard reflections
0.844	frequency: 120 min
3129 measured reflections	intensity decay: no decay,
2984 independent reflections	variation 0.5%

Refinement

Refinement on F^2
$R(F) = 0.0347$
$wR(F^2) = 0.0962$
$S = 1.042$
2984 reflections
190 parameters
H atoms riding (C—H 0.93 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 0.1337P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.294$ e Å^{-3}
$\Delta\rho_{min} = -0.417$ e Å^{-3}
Atomic scattering factors from International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe1	0.29193 (3)	0.04290 (4)	0.34779 (2)	0.03556 (12)
C11	0.2471 (2)	−0.1852 (3)	0.3490 (2)	0.0349 (5)
C12	0.1534 (2)	−0.0930 (3)	0.3778 (2)	0.0403 (5)
C13	0.2082 (3)	−0.0085 (3)	0.4571 (2)	0.0487 (6)
C14	0.3342 (3)	−0.0474 (3)	0.4779 (2)	0.0479 (6)
C15	0.3591 (2)	−0.1557 (3)	0.4114 (2)	0.0415 (5)
C21	0.3158 (5)	0.1048 (4)	0.2191 (2)	0.0909 (15)
C22	0.2220 (3)	0.1945 (4)	0.2458 (2)	0.0683 (9)
C23	0.2746 (3)	0.2741 (3)	0.3255 (2)	0.0562 (7)
C24	0.3969 (3)	0.2345 (4)	0.3472 (2)	0.0674 (9)
C25	0.4224 (4)	0.1310 (4)	0.2832 (3)	0.0805 (11)
N1	0.3306 (2)	−0.3525 (2)	0.24546 (13)	0.0363 (4)
C2	0.2323 (2)	−0.2885 (2)	0.2687 (2)	0.0333 (5)
C3	0.1131 (2)	−0.3197 (3)	0.2168 (2)	0.0419 (6)
N4	0.0930 (2)	−0.4072 (3)	0.14289 (15)	0.0458 (5)
C5	0.1939 (2)	−0.4716 (3)	0.1170 (2)	0.0386 (5)
C6	0.1799 (3)	−0.5650 (3)	0.0371 (2)	0.0529 (7)
C7	0.2793 (3)	−0.6298 (4)	0.0113 (2)	0.0626 (8)
C8	0.3963 (3)	−0.6059 (4)	0.0624 (2)	0.0635 (8)
C9	0.4132 (3)	−0.5158 (3)	0.1403 (2)	0.0543 (7)
C10	0.3117 (2)	−0.4454 (3)	0.1689 (2)	0.0368 (5)
Cp1†	0.2604 (2)	−0.0980 (3)	0.4146 (2)	
Cp2†	0.3263 (4)	0.1878 (4)	0.2842 (2)	

† Cp1 and Cp2 are the centroids of rings C1n and C2n ($n = 1$–5), respectively.

Table 2. *Selected geometric parameters* (Å, °)

Fe1—Cp1	1.643 (2)	C24—C25	1.365 (5)
Fe1—Cp2	1.651 (3)	N1—C2	1.323 (3)
C11—C2	1.464 (3)	N1—C10	1.366 (3)
C11—C12	1.436 (3)	C2—C3	1.427 (3)
C11—C15	1.426 (3)	C3—N4	1.308 (3)
C12—C13	1.414 (4)	N4—C5	1.365 (3)
C13—C14	1.417 (4)	C5—C6	1.409 (4)
C14—C15	1.417 (3)	C5—C10	1.407 (3)
C21—C22	1.412 (5)	C6—C7	1.352 (4)
C21—C25	1.390 (6)	C7—C8	1.393 (4)
C22—C23	1.390 (4)	C8—C9	1.368 (4)
C23—C24	1.380 (4)	C9—C10	1.410 (4)
Cp1—Fe1—Cp2	177.8 (2)		

Examination of the structure with PLATON (Spek, 1994a) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: CAD-4/PC Software (Enraf–Nonius, 1992). Cell refinement: SET4 (de Boer & Duisenberg, 1984) and CELDIM (Enraf–Nonius, 1992). Data reduction: DATRD2 in NRCVAX (Gabe, Le Page, Charland, Lee & White, 1989).

Program(s) used to solve structure: Patterson vector using NRCVAX. Program(s) used to refine structure: NRCVAX and SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976) as implemented in PLATON (Spek, 1994a) and PLUTON (Spek, 1994b). Software used to prepare material for publication: NRCVAX and SHELXL93.

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