Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A highly functionalized ferrocenyl-pyrazolo[2,3-*a*]pyridine[1]

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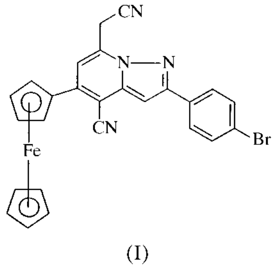
Received 17 January 2000
Accepted 11 February 2000

Data validation number: IUC0000047

The crystal structure of [2-(4-bromophenyl)-4-cyano-5-ferrocenylpyrazolo[2,3-*a*]pyridin-7-yl]acetonitrile, $C_{26}H_{17}N_4FeBr$ or $[Fe(C_5H_5)(C_{21}H_{12}BrN_4)]$, shows that the pyrazolopyridine ring system (PP), the bromophenyl ring (BP) and the cyclopentadiene ring (Cp) are nearly planar. The PP ring system is twisted out of the plane of the BP and Cp rings by about 20°.

Comment

In view of the recent growing interest in the field of asymmetric synthesis, ferrocene and its derivatives occupy an important place in synthetic and materials chemistry due to their unique non-linear optical, liquid and crystalline and ferromagnetic properties (Hayashi, 1995). The 1,2- and 1,3-disubstituted ferrocene derivatives, having planar chirality, are suitable chiral reference systems for asymmetric induced synthesis (Marquarding *et al.*, 1970). The unique properties of these compounds encouraged the synthesis of ferrocene derivatives with highly functionalized ring systems directly linked to one of the cyclopentadiene moieties. These compounds do not exhibit optical activity due to lack of restricted rotation. The title compound was synthesized following a procedure reported earlier (Nath *et al.*, 1998). The structure of the title compound, (I), was assigned by IR, NMR and mass spectra, but the conformation of the ferrocene moiety with respect to the heterocyclic ring was of particular interest and prompted us to undertake the present X-ray diffraction study.



(I)

The title molecule contains one pyrazolo[2,3-*a*]pyridine fused-ring system (PP), one bromo-phenyl ring (BP) and one ferrocenyl moiety. The two individual rings [inclined to each other by an angle 1.9 (2)°] in the PP system and the BP ring are planar [the deviations of the atoms from the least-squares planes are within the range −0.012 (3)–0.006 (3) Å]. The —CN group at C12 lies slightly out of the PP ring system [torsion angle C6—C7—C12—C13 −7.2 (6)°]. The cyclopentadiene rings of the ferrocene moiety are essentually elipsed [the mean value of the five torsion angles $CnA—CgA—CgB—CnB$ (where n = 1–5, and CgA and CgB are the Cp ring centroids) is 4.9 (6)°]. The Cp rings are parallel [dihedral angle 2.4 (3)°] and each lies equidistant [1.65 (1) Å] from the Fe atom. Both the BP and Cp rings adopt a twist conformation with respect to the PP ring system [torsion angle N1—C2—C1′—C6′ −17.8 (6)° and C6—C5—C1*A*—C5*A* 20.6 (6)°]. There are no short contacts or intermolecular stacking interactions in the lattice.

Experimental

The synthesis of (I) was carried out by the reaction of 3-cyano-6-ferrocenyl-4-methylthio-2*H*-pyran-2-one with 5-(4-bromophenyl)-3-cyanomethyl-1*H*-pyrazole in a 1:1 molar ratio in dry DMF in the presence of KOH (Nath *et al.*, 1998). Diffraction quality crystals were grown by slow evaporation from a mixture of dichloromethane and hexane at room temperature.

Crystal data

$[Fe(C_5H_5)(C_{21}H_{12}BrN_4)]$
$M_r = 521.20$
Triclinic, $P\overline{1}$
$a = 7.96080 (10)$ Å
$b = 10.68440 (10)$ Å
$c = 12.8215 (3)$ Å
$\alpha = 93.5770 (10)°$
$\beta = 97.7370 (10)°$
$\gamma = 99.0460 (10)°$
$V = 1063.28 (3)$ Å^3
$Z = 2$
$D_x = 1.628$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 509 reflections
$\theta = 2.99–25.55°$
$\mu = 2.610$ mm^{-1}
$T = 150 (2)$ K
Plate, red
0.25 × 0.15 × 0.06 mm

Data collection

Bruker SMARTCCD diffractometer
ω scans
Absorption correction: ψ scan (*XPREP*; Sheldrick, 1994)
$T_{min} = 0.606$, $T_{max} = 0.855$
7790 measured reflections
4823 independent reflections
3953 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0403$
$\theta_{max} = 27.49°$
$h = -10 \rightarrow 9$
$k = -13 \rightarrow 10$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.140$
$S = 1.028$
4783 reflections
289 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 4.8638P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

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[1] CDRI Communication No. 5997.

Table 1
Selected geometric parameters (Å).

Fe—C5*B*	2.031 (5)	Fe—C2*A*	2.050 (4)
Fe—C4*B*	2.045 (4)	Fe—C1*B*	2.044 (5)
Fe—C2*B*	2.049 (5)	Fe—C4*A*	2.055 (4)
Fe—C1*A*	2.054 (4)	Fe—C3*B*	2.054 (5)
Fe—C5*A*	2.048 (4)	Fe—C3*A*	2.062 (5)

All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, to which each was bonded for the final cycles of refinement. Nine reflections [most disagreeable, $\Delta(F^2)/\sigma > 5.0$] were suppressed during the last cycles of refinement.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *NRCVAX* (Gabe *et al.*, 1989); software used to prepare material for publication: *SHELXL*93.

SS and PS thank CSIR, India, for a Senior Research Fellowship. CKB and JAKH thank the EPSRC for their support.

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