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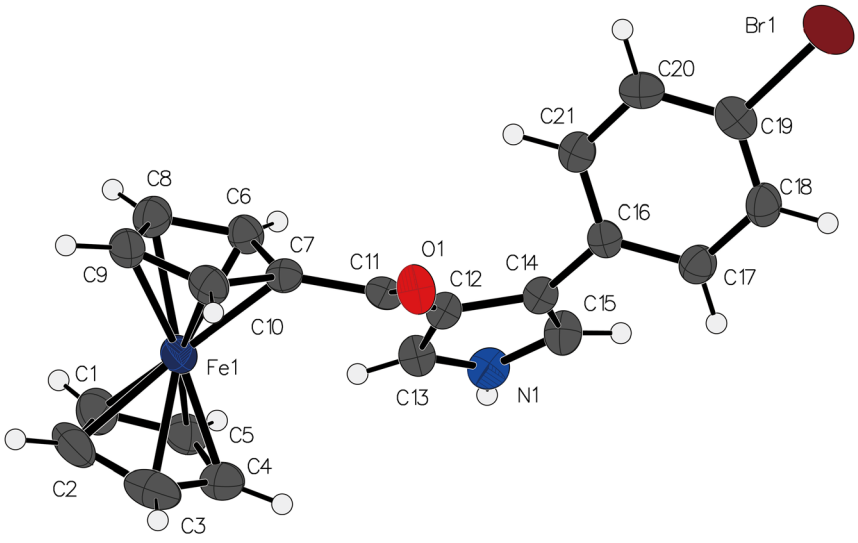
Crystal structure of ((4-(4-bromophenyl)-1*H*-pyrrol-3-yl)methyl)ferrocene, $C_{21}H_{16}BrFeNO$



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Abstract

$C_{21}H_{16}BrFeNO$, monoclinic, $P2_{1/c}$ (no. 14), a = 14.6736(9) Å, b = 9.5595(6) Å, c = 12.7860(7) Å, β = 105.579(2)°, V = 1727.63(18) Å^3, Z = 4, $R_{gt}(F)$ = 0.0452 w$R_{ref}(F^2)$ = 0.0919, T = 170 K.

CCDC no.: 2419220

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.19 × 0.13 × 0.08 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	3.19 mm^{-1}
Diffractometer, scan mode:	Bruker APEX II, φ and ω scans
θ_{max}, completeness:	26.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18980, 3524, 0.074
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2341
$N(param)_{refined}$:	226
Programs:	Bruker,[1] SHELX,[2,3] Olex2[4]

1 Source of materials

To a solution of 1-ferrocenyl-3-(4-bromophenyl)-2-propen-1-one (3.93 g, 10 mmol) and tosylmethyl isocyanide (2.15 g, 11 mmol) in N,N-dimethylformamide (25 mL) was added potassium tert-butoxide (2.24 g, 20 mmol). The mixture was stirred at room temperature for 12 h, until the TLC indicated the reaction was completed. The mixture was diluted with brine, and then extracted with ethyl acetate (3 × 30 mL). The organic phase was washed with brine (30 mL), dried with anhydrous sodium sulphate, and then concentrated under pressure. The title compound was separated by silica-gel column chromatography with ethyl acetate-petroleum ether (25 %) gradient solvent system. The target product was obtained as a white solid. For crystal growth, the product was dissolved in a minimal amount of hot ethanol and slowly cooled to room temperature (Table 1).

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2 Experimental details

The crystal structure was determined using the SHELXT program,[2] and refinement was performed with the SHELXL program[3] in Olex2 software.[4] Non-hydrogen atoms underwent anisotropic refinement, while hydrogen atoms were positioned based on idealized geometry and refined using a riding model.

3 Comment

Ferrocene derivatives are of interest in organic electronics, catalysis, and material science.[5] The iron(II)-centered sandwich structure of ferrocene, where two cyclopentadienyl anions surround a central metal atom, confers a high degree of stability.[6–10] Specifically, the functionalization of ferrocene, such as introducing aromatic rings or heteroatoms, allows for enhanced electronic and chemical characteristics, making it useful in the design of molecular switches, sensors, and catalysts. In this context, the compound ((4-(4-bromophenyl)-1*H*-pyrrol-3-yl)methyl) ferrocene presents an intriguing example of ferrocene modification, featuring a bromophenyl and a pyrrole group attached to the ferrocene backbone.

The central iron atom (Fe1) is coordinated symmetrically by two cyclopentadienyl rings (C1–C5 and C2–C6), forming a classical sandwich-like structure typical of ferrocene derivatives. The bond lengths between the iron center and the carbon atoms of the cyclopentadienyl rings (Fe–C) are consistent with the typical ferrocene scaffold, averaging around 2.0 Å. These Fe–C bond distances indicate the maintenance of the characteristic electronic structure of the ferrocene core.[11–16]

The structure features a (4-(4-bromophenyl)-1H-pyrrol-3-yl)methyl group, which is attached to the ferrocene core via a methylene linker (C11). The pyrrole ring (C11, C12, C13, N1) exhibits planarity, as expected for an aromatic heterocyclic system. The nitrogen atom (N1) is slightly displaced from the plane, likely due to electron-donating effects from the methyl group attached to C13. The pyrrole group, together with the adjacent bromophenyl unit, serves as an electron-rich region that modulates the reactivity of the ferrocene core, potentially allowing for further functionalization or interactions with electrophilic reagents.

The bromophenyl group (C14–C16, C18–C21) is attached to the pyrrole ring at position 4. The bond lengths and angles in this aromatic region follow typical values for a substituted phenyl ring, with C–C bond lengths around 1.39 Å and bond angles close to 120°, consistent with the sp^2 hybridization of the carbon atoms.

The C11–O1 bond between the pyrrole ring and the oxygen atom (O1) adds a distinctive feature to the structure. The bond length for C11–O1 is approximately 1.236 Å, which is typical for a C–O single bond. The oxygen atom (O1) is positioned in such a way that it could participate in potential hydrogen bonding or dipole-dipole interactions, especially in polar solvents.

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