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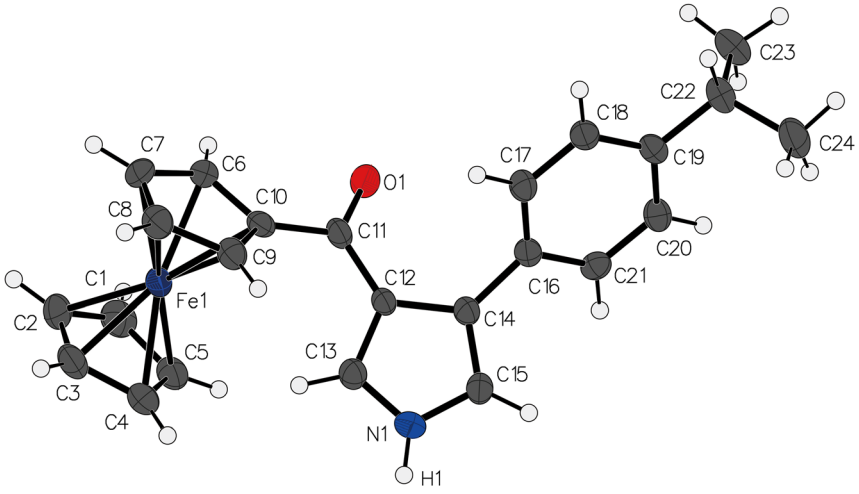
Crystal structure of (4-(4-isopropylphenyl)-1H-pyrrol-3-yl)(ferrocenyl)methanone, $C_{24}H_{23}FeNO$



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Abstract

$C_{24}H_{23}FeNO$, monoclinic, $P2_1/c$ (no. 14), a = 15.4240(10) Å, b = 10.2113(7) Å, c = 12.2776(7) Å, β = 105.808(2)°, V = 1860.6(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0564 w$R_{ref}(F^2)$ = 0.1804, T = 170 K.

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Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.09 × 0.05 × 0.04 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.82 mm^{-1}
Diffractometer, scan mode:	Bruker D8 VENTURE, φ and ω scans
θ_{max}, completeness:	26.4°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13720, 3742, 0.093
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2,268
$N(param)_{refined}$:	246
Programs:	Bruker,[1] SHELX,[2,3] Olex2[4]

The molecular structure is shown in the figure. Table 1 contains the crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif- file attached to this article.

1 Source of materials

To a solution of 1–ferrocenyl-3-(4-isopropylphenyl)-2-propen-1-one (3.58 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 yellow solid. For crystal growth, the product was dissolved in a minimal amount of hot ethanol and slowly cooled to room temperature.

2 Experimental details

The crystal structure was determined using Direct Methods with the SHELXT program.[2] The initial solution was refined

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using full-matrix least squares on F^2 with the SHELXL program,[3] implemented within the Olex2 software.[4] The hydrogen atoms were placed at their idealized positions based on standard geometrical constraints.

3 Comment

Ferrocene, consisting of a central iron atom sandwiched between two cyclopentadienyl rings, exhibits remarkable stability and symmetry, making it a model compound for understanding metal-organic interactions and the behavior of metallocenes.[5] Over the years, various functionalized ferrocene derivatives have been synthesized to explore their potential in a wide range of applications, including catalysis, materials science, and organic electronics.[6–10] Crystallographic studies of these compounds are particularly valuable as they provide detailed insights into the molecular arrangement, intermolecular interactions, and packing behavior within the solid state, which are critical for tailoring their properties for specific applications.

The structure of the title compound is characterized by a ferrocenyl moiety conjugated with a pyrrole core via a ketone bridge. The ferrocene unit exhibits an almost ideal sandwich structure, with the iron center symmetrically coordinated between the two cyclopentadienyl rings.[11–17] The Fe–C bond lengths range from 2.04 to 2.07 Å, consistent with previously reported ferrocenyl derivatives. The ketone (C=O) bond length is approximately 1.24 Å, indicative of a typical carbonyl functional group, while the pyrrole ring remains nearly planar, suggesting strong conjugation within the system.

The pyrrole core is functionalized at the 3-position with the ferrocenyl ketone group and at the 4-position with a *para*-substituted isopropylphenyl unit. The torsion angle between the pyrrole and phenyl rings is 44.3°. The isopropyl group is positioned in a staggered conformation, with the adjacent phenyl hydrogen atoms. The C–N bond in the pyrrole ring remains within the expected range 1.34–1.37 Å.

Intermolecular interactions in the crystal lattice are primarily governed by weak N–H···O interaction (N1–H1···O1), which contribute to the overall packing stability. The bond length of H1···O1 is 2.08 Å, and the angle of N1–H1···O1 is 138.0°. The torsion angle between the pyrrole and phenyl rings is 44.3°, and the torsion angle between the pyrrole and cyclopentadienyl rings is 52.4°. This contrasts with the corresponding dihedral angle in a similar structure, (4-(2-chlorophenyl)-1*H*-pyrrol-3-yl)(ferrocenyl) methanone,[12] due to differences in the substituents and the intermolecular hydrogen bonding, which exert a significant influence on the molecular stereochemistry.

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