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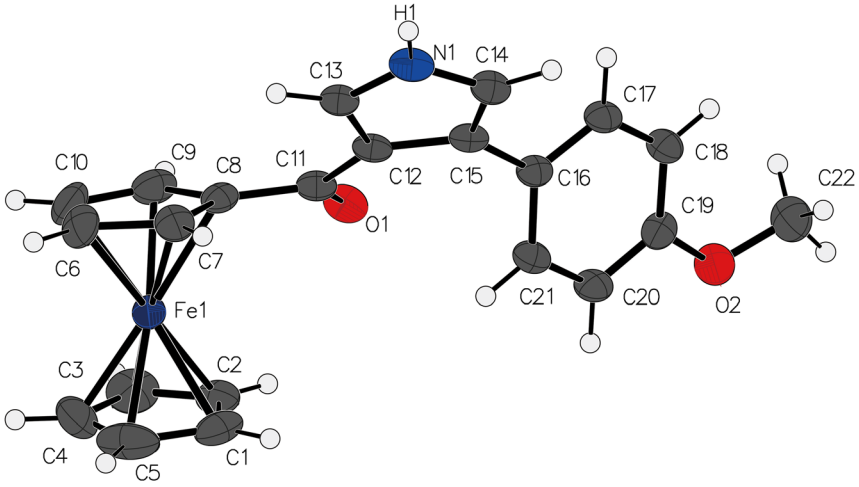
Crystal structure of (4-(4-methoxyphenyl)-1H-pyrrole-3-carbonyl)ferrocene, $C_{22}H_{19}FeNO_2$



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Abstract

$C_{22}H_{19}FeNO_2$, tetragonal, $P4_2/n$ (no. 86), a = 21.7903(7) Å, c = 7.3022(4) Å, V = 3467.2(3) Å^3, Z = 8, $R_{gt}(F)$ = 0.0385, w$R_{ref}(F^2)$ = 0.1009, T = 170 K.

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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-methoxyphenyl)-2-propen-1-one (3.46 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).

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.12 × 0.08 × 0.07 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	0.89 mm^{-1}
Diffractometer, scan mode:	Bruker D8, φ and ω scans
θ_{max}, completeness:	26.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	38473, 3557, 0.081
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2,584
$N(param)_{refined}$:	240
Programs:	Bruker,[1] SHELX,[2,3] Olex2[4]

2 Experimental details

The crystal structure was determined with the SHELXT program.[2] Subsequent refinement was performed using the

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SHELXL program,[3] within the Olex2 software environment.[4] The hydrogen atoms were positioned based on idealized geometry and refined using a riding model.

3 Comment

Ferrocene and its derivatives have garnered significant attention in the different fields properties.[5] The incorporation of functional groups into the ferrocene structure can lead to enhanced stability, tunable electronic characteristics, and reactivity, making them valuable candidates for a range of applications, including molecular switches, sensors, and catalysts.[6–11] Here, we present the study of the crystal structures of such derivatives, like the title structure.

The single crystal of the title compound consists of a ferrocene backbone, where the iron atom (Fe1) is coordinated to two cyclopentadienyl anions. It is consistent with previously reported related structures. The key bond lengths within the molecule include the length of Fe–C bonds all 2.04 Å approximately, consistent with typical values for iron-carbon bonds.[12–14] The C15–C16 bond is 1.47 Å, indicating a single bond between the pyrrole and the phenyl group, while the C13–N1 bond length is 1.34 Å, typical for a C–N bond in pyrrole derivatives. The carbonyl group attached to the pyrrole ring adopts an almost planar geometry with a C=O bond length of 1.23 Å, typical for such functional groups.

The angles around the central iron atom (Fe1) are consistent with a distorted trigonal bipyramidal geometry, where the bond angles of C1–Fe1–C7 and C1–Fe1–C8 are approximately 112.5° and 115.9°, respectively. The dihedral angle between the ferrocene and the pyrrole group is approximately 46.7°, showing a significant twist in the molecule. Additionally, the dihedral angle between the pyrrole ring and the benzene ring is 43.5°.

Intermolecularly, a significant hydrogen bond is formed between H1 and O1, with the N1–H1–O1 bond angle measuring 169° and the H1–O1 bond length being 2.05 Å. In comparison with the structurally related (4-(2-chlorophenyl) -1*H*-pyrrol-3-yl)(ferrocenyl)methanone,[13] the bond angle is smaller, and the bond length is longer, suggesting a slightly weaker hydrogen bond.

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