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N-(4-Ferrocenylphenyl)-4-piperidino-1,8-naphthalimide

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The title compound, $[Fe(C_5H_5)(C_{28}H_{23}N_2O_2)]$, contains a 1,8-naphthalimide system, substituted in the 4-position with an N-bound piperidine ring. The imide N atom of the naphthalimide group carries a 4-ferrocenylphenyl substituent. The compound crystallizes with the plane of the naphthalimide moiety orthogonal to those of the benzene and cyclopentadiene rings, which facilitates intermolecular π stacking interactions between adjacent pairs of naphthalimide rings.

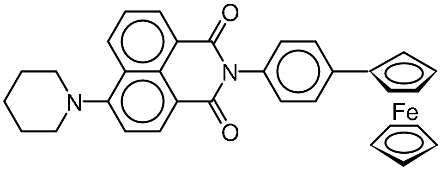
Key indicators

Single-crystal X-ray study
T = 163 K
Mean σ(C–C) = 0.005 Å
R factor = 0.045
wR factor = 0.090
Data-to-parameter ratio = 12.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

We have a long-standing interest in molecules that contain both fluorescent and redox centres, particularly when such centres are joined by potentially conductive links (McAdam *et al.*, 1999, 2000, 2003, 2004, McGale *et al.*, 2003). As part of these investigations, the title compound, (I), in which the ferrocene redox centre is linked to the naphthalimide fluorophore *via* a phenylene bridge, was prepared from the reaction of 4-bromonaphthalic anhydride and ferrocenylaniline followed by replacement of the bromo substituent in boiling piperidine.



(I)

A perspective view of (I) is shown in Fig. 1. The 1,8-naphthalimide moiety carries a 4-ferrocenylbenzene substituent on the N atom of the dicarboximide ring, with a piperidine substituent, in a classic chair conformation, N-bound to atom C4 of the naphthalimide moiety. Bond length variations in the dicarboximide ring are consistent with considerable electron delocalization over the naphthalimide unit but, unsurprisingly (Easton *et al.*, 1992), this does not extend to the N1—C13 bond. In contrast, the C4—N2 bond is relatively short [1.376 (4) Å], commensurate with some degree of delocalization between the naphthalimide and piperidine units, and with a likely effect on the donor ability of the substituent.

The cyclopentadienyl rings of the ferrocene are approximately eclipsed, with a mean C*m*—*Cg*1—*Cg*2—C*n* torsion angle of 4.3 (3)° (*Cg*1 and *Cg*2 are the centroids of the cyclopentadienyl rings, m = 21–25 when n = 31–35). The dihedral angle between the Cp ring planes is 3.7 (3)°. The average Fe—C distance [1.995 (8) Å] is not unusual and atom Fe1 lies 1.607 (2) and 1.611 (2) Å, respectively, from the C21–C25 and C31–C35 ring planes.

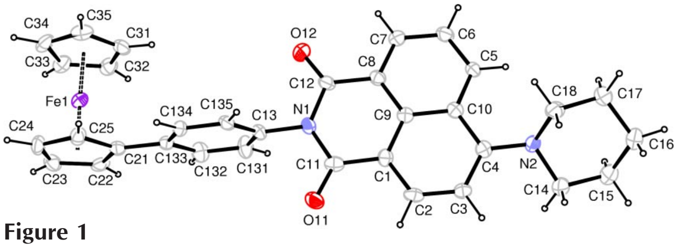


Figure 1
Perspective drawing of (I), showing the atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles with arbitrary radii.

The substituted cyclopentadienyl ring of the ferrocene moiety and its benzene substituent are almost coplanar [interplanar angle 5.1 (2)°]. The naphthalimide unit, in contrast, is almost orthogonal to the aromatic ring, with a dihedral angle of 89.37 (9)° between the naphthalimide and benzene ring planes. This conformation may be preferred in order to accommodate π stacking between pairs of naphthalimide units. We have shown previously that the solid-state structures of naphthalimide systems are often stabilized by extensive π stacking interactions (Batchelor *et al.*, 1997, McAdam *et al.*, 1999, 2000, Cavigiolo *et al.*, 2004). In this system, offset π stacking (Janiak, 2000) interactions are found between pairs of molecules arranged in a head-to-tail fashion (Fig. 2). The orthogonal placement of the phenylferrocene moieties with respect to the naphthalimide rings facilitates these interactions, which show displacement angles in the range 22.2–47.6° and perpendicular distances between the naphthalimide ring planes in the range 3.45–3.54 Å.

Experimental

4-Bromonaphthalic anhydride (0.138 g, 0.5 mmol) was heated in ferrocenylaniline (literature melting point 432–433 K) (0.167 g, 0.6 mmol) for 1 h. Column chromatography (SiO_2/CH_2Cl_2) and recrystallization from boiling EtOH yielded 0.16 g (60%) of orange crystals of 4-bromo-*N*-(*p*-phenylferrocenyl)-1,8-naphthalimide. Analysis calculated for $C_{28}H_{18}BrFeNO_2$: C 62.72, H 3.38, N 2.61%; found: C 62.36, H 3.10, N 2.78%. APCI-MS: *m*/*e* 536 (*M*+). ^1H NMR: δ 4.11 (*s*, 5H, $-C_5H_5$), 4.35, 4.67 [2 × (*t*, 2H, Fc—H)], 7.23, 7.64 [2 × (*m*, *J* = 8 Hz, 2H, phenyl H)], 7.90 (*dd*, *J* = 9 and 7 Hz, naphth. H6), 8.10 (*d*, *J* = 8 Hz, naphth. H3), 8.48 (*d*, *J* = 8 Hz, naphth. H2), 8.65 (*dd*, *J* = 9 and 1 Hz, naphth. H5), 8.72 (*dd*, *J* = 7 and 1 Hz, naphth. H7). IR (KBr): $\nu_{C=O}$ 1711, 1673 cm^{-1}. This product was heated in piperidine (5 ml) at 403 K for 3 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography (SiO_2/CH_2Cl_2) to give an orange band. Recrystallization from CH_2Cl_2 gave orange crystals of (I) (yield 0.149 g, 95%). Analysis calculated for $C_{33}H_{28}FeN_2O_2$: C 73.34, H 5.22, N 5.18%; found: C 73.26, H 5.10, N 5.30%. APCI-MS: *m*/*e* 542 (*M*H+). ^1H NMR: δ 1.7 (*m*, 2H, pip. H), 1.9, 3.27 [2 × (*m*, 4H, pip. H)], 4.11 (*s*, 5H, $-C_5H_5$), 4.34, 4.67 [2 × (*t*, 2H, Fc—H)], 7.22 (*m*, 2H, phenyl H), 7.25 (*d*, *J* = 8 Hz, naphth. H3), 7.62 (*m*, 2H, phenyl H), 7.72 (*dd*, *J* = 8 and 7 Hz, naphth. H6), 8.45 (*dd*, *J* = 8 and 1 Hz, naphth. H5), 8.55 (*d*, *J* = 8 Hz, naphth. H2), 8.63 (*dd*, *J* = 7 and 1 Hz, naphth. H7). IR (KBr): $\nu_{C=O}$ 1702, 1662 cm^{-1}. E-chem (CH_2Cl_2/TBAPF$_6$): $[Fc]^{0/+}$ 0.59 V *versus* Fc*. UV-vis (CH_2Cl_2): λ_{max} nm ($\varepsilon \times 10^{-3}$) 281 (21), 413 (13). Emission (CH_2Cl_2): λ_{flu} 521 nm, φ_{flu} 0.003.

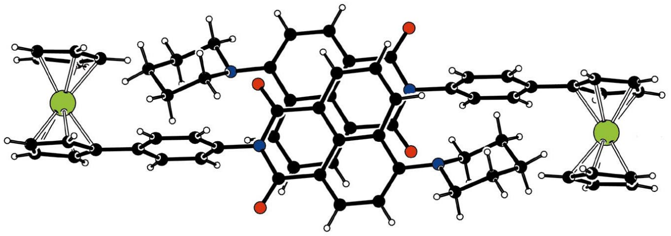


Figure 2
Fig, 2. π stacking in (I); the molecules shown are related by the symmetry operation ($2 - x$, $1 - y$, $-z$).

Crystal data

$[Fe(C_5H_5)(C_{28}H_{23}N_2O_2)]$
$M_r = 540.42$
Triclinic, $P\overline{1}$
$a = 9.238$ (8) Å
$b = 11.112$ (11) Å
$c = 12.164$ (12) Å
$\alpha = 93.904$ (14)°
$\beta = 100.206$ (13)°
$\gamma = 104.154$ (15)°
$V = 1183.4$ (19) Å^3

$Z = 2$
$D_x = 1.517$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3022 reflections
$\theta = 2.7$–24.7°
$\mu = 0.68$ mm^{-1}
$T = 163$ (2) K
Plate, orange
0.30 × 0.14 × 0.02 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker 1999)
$T_{min} = 0.860$, $T_{max} = 1.000$
11 404 measured reflections

4329 independent reflections
2629 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 26.4$°
$h = -11 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.091$
$S = 0.89$
4329 reflections
343 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

All H atoms were included in calculated positions using a riding model with aromatic C—H distances of 0.93 Å, Csp^2—H bond distances of 0.97 Å, and U_{iso}(H) values of 1.2U_{eq}(C).

Data collection: *SMART* (Bruker 1999); cell refinement: *SAINT* (Bruker 1999); data reduction: *SAINT*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) and *TITAN*2000 (Hunter & Simpson, 1999); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek 1995); software used to prepare material for publication: *SHELXL*97.

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