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[η^5-1,2-Bis(4-nitrophenyl)cyclopentadienyl]-(η^5-cyclopentadienyl)iron

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Key indicators

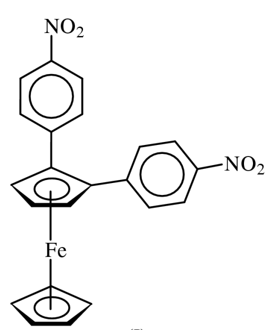
Single-crystal X-ray study
T = 164 K
Mean σ(C–C) = 0.002 Å
R factor = 0.027
wR factor = 0.076
Data-to-parameter ratio = 13.8

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

The title compound, 1,2-bis(4-nitrophenyl)ferrocene, $[Fe(C_5H_5)(C_{17}H_{11}N_2O_4)]$, crystallizes with the planes of the two vicinal 4-nitrophenyl rings subtending angles of 46.04 (6) and 36.30 (7)° at the plane of the substituted cyclopentadiene ring of the ferrocene moiety.

Comment

Our interest in efficient energy transfer between donor–acceptor arrays incorporating redox- or photo-active centres (McAdam *et al.*, 1999, 2000; McGale *et al.*, 2003) prompted us to investigate the use of phenyl substituents on ferrocene redox centres as links to photo-active centres such as naphthalimides. The title compound, (I), with *p*-nitrophenyl substituents in adjacent 1,2-positions on one of the cyclopentadienyl rings, provides a route to further functionalize the ferrocene moiety. Compound (I) was prepared *via* a modified diazonium coupling reaction to the ferrocenium cation (Coe *et al.*, 1994) and the X-ray structure is reported here.



(I)

Both benzene rings are essentially planar, with their nitro substituents inclined at angles of 19.5 (2) and 1.8 (2)° to the C11–C16 and C21–C26 rings, respectively. Each benzene ring is twisted in the same direction with respect to the plane of the substituted C1–C5 cyclopentadienyl ring. Interplanar angles are 46.04 (6) (C1–C5/C11–C26) and 36.30 (7)° (C1–C5/C21–C26). A search of the November 2002 release of the Cambridge Structural Database (Allen, 2002) reveals only one other 1,2-bis(phenyl)ferrocene derivative that has been structurally characterized (Lee *et al.*, 1997), although structures of pentaphenyl- (Aroney *et al.*, 1993) and penta-*p*-tolylferrocenes (Field *et al.*, 1993) have been reported. In these structures, the phenyl substituents are held at varying torsional angles (40–65°) relative to the substituted cyclopentadienyl ligand.

The cyclopentadienyl rings of the ferrocene are approximately eclipsed, with a mean C*m*—*Cg*1—*Cg*2—C*n* torsion angle of 5.3 (4)° ($Cg1$ and $Cg2$ are the centroids of the cyclopentadienyl rings; m = 1–5 when $n = m + 5$). The dihedral angle between the Cp ring planes is 1.28 (14)°. It is noteworthy that the C1—C2 distance and, to a lesser exent, the C1—C5 and C2—C3 distances are longer than those in the unsubstituted C6–C10 ring (Table 1). This, combined with widening of the C2—C1—C11 and C1—C2—C21 angles, suggests some steric interaction between the vicinal nitrophenyl substituents. The average Fe—C distance, 2.042 (6) Å, is not unusual, and the Fe1 atom lies 1.6430 (8) and 1.6529 (9) Å, respectively from the C1–C5 and C6–C10 ring planes.

Extensive π–π-stacking interactions have been shown to stabilize the solid-state structures of ferrocene compounds with vicinal pentafluorophenyl substituents in both cyclopentadienyl rings (Thornberry *et al.*, 2000; Deck *et al.*, 2001) and also to occur between phenyl and pentafluorophenyl rings in related ferrocenes (Blanchard *et al.*, 2000). However, examination of the distances between benzene ring centroids and the angles between the C_6 least-squares planes (Spek, 1995) shows no evidence for significant π–π-stacking interactions in this structure.

Experimental

The title compound was prepared as an additional product of the *in situ* reaction between the ferrocenium cation and and the diazonium salt derived from 4-nitroaniline, using the procedure outlined by Coe *et al.* (1994). Compound (I) was isolated using column chromatography, as the third band with CH_2Cl_2/hexane eluant. Shiny red blocks formed upon slow solvent evaporation. Calculated for $C_{22}H_{16}FeN_2O_4$: C 61.71, H 3.77, N 6.54%; found: C 61.56, H 3.78, N 6.72%; IR [$\nu(NO_2)$ cm^{-1}]: 1517/1508, 1343. UV (CH_2Cl_2) λmax(ε): 313 (20000), 399 (3200), 490 (3100). ^{1}H NMR ($CDCl_3$): δ 4.15 (*s*, 5H, C_5H_5), 4.61 (*t*, 1H, C_5H_3), 4.74 (*d*, 2H, C_5H_3), 7.48, 8.11 [2 × (*m*, 4H, phenyl—H)]. $Fc^{0/+}$ (CH_2Cl_2, $TBAPF_6$): 0.81V.

Crystal data

$[Fe(C_5H_5)(C_{17}H_{11}N_2O_4)]$
M_r = 428.22
Monoclinic, $P2_1/c$
a = 7.4359 (10) Å
b = 14.0883 (19) Å
c = 17.042 (2) Å
β = 92.048 (2)°
V = 1784.1 (4) Å^3
Z = 4
D_x = 1.594 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5205 reflections
θ = 5.5–52.7°
μ = 0.88 mm^{-1}
T = 164 (2) K
Block, red
0.45 × 0.23 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.776, T_{max} = 0.916
22614 measured reflections
3620 independent reflections
2945 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 26.4°
$h = -9 \rightarrow 9$
$k = -17 \rightarrow 17$
$l = -10 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.076
S = 1.06
3620 reflections
262 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

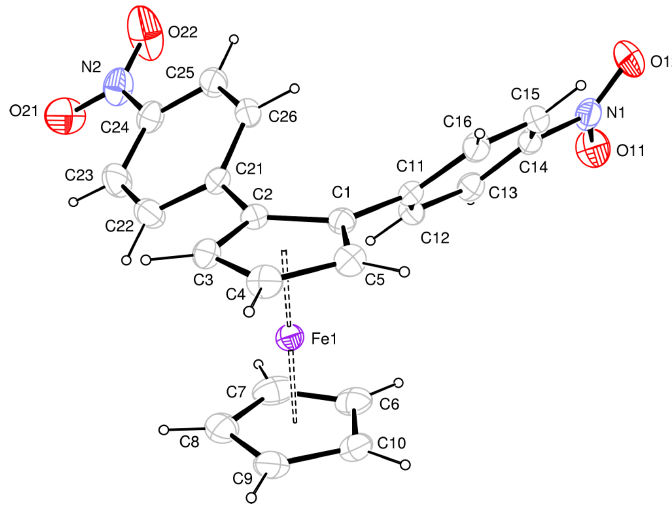


Figure 1
Perspective drawing of the title molecule (Farrugia, 1997), showing the atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles of arbitrary radii.

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.446 (2)	C4—C5	1.413 (2)
C1—C11	1.476 (2)	C6—C7	1.404 (3)
C1—C5	1.425 (2)	C6—C10	1.410 (3)
C2—C3	1.435 (2)	C7—C8	1.414 (3)
C2—C21	1.467 (2)	C8—C9	1.418 (3)
C3—C4	1.407 (2)	C9—C10	1.412 (3)
C2—C1—C11	127.72 (14)	C1—C2—C21	129.25 (15)
C5—C1—C11	124.88 (15)	C3—C2—C21	123.87 (15)

All H atoms were included in calculated positions using a riding model, with Csp^2—H bond distances of 0.95 Å and U_{iso}(H) = 1.2U_{eq}(parent C).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986) and *TITAN*2000 (Hunter & Simpson, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) and *TITAN*2000; molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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