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Intermolecular interactions in *N*-(ferrocenylmethyl)anthracene-9-carboxamide

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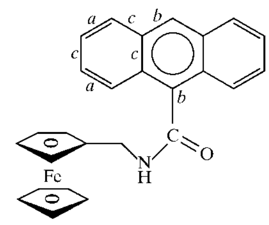
The title compound, [Fe(C_5H_5)($C_{21}H_{16}NO$)], was synthesized from the coupling reaction of anthracene-9-carboxylic acid and ferrocenylmethylamine. The ferrocenyl (Fc) group and the anthracene ring system both lie approximately orthogonal to the amide moiety. An amide–amide interaction (along the *a* axis) is the principal interaction [N···O = 2.910 (2) Å]. A C—H···π(arene) interaction [C···centroid = 3.573 (2) Å] and a C—H···O interaction [C···O = 3.275 (3) Å] complete the hydrogen bonding; two short (Fc)C···C(anthracene) contacts are also present.

Comment

Applications of novel redox-active ligands in diverse research fields, such as medicinal chemistry and materials science, have recently engaged scientists. Ferrocene continues to attract much interest as an electroactive group, with potential applications ranging from sensors to new optical materials to liquid crystals (Chesney *et al.*, 1998; Zakaria *et al.*, 2002; Gallagher *et al.*, 1999; Kraatz *et al.*, 1999; Hudson, Asselsbergh *et al.*, 2001; Hudson, Manning *et al.*, 2001; Seo *et al.*, 2001). Our interest in ferrocene stems from its potential use in both novel sensors and biological systems. We have previously reported the crystal structures of three *para*-(ferrocenyl)benzoyl esters (Savage *et al.*, 2002; Anderson *et al.*, 2003), and the structure of *N*-(ferrocenylmethyl)anthracene-9-carboxamide, (I), is reported here. Selected geometric parameters are presented in Table 1, with hydrogen-bond and contact data in Table 2; the molecular and crystal structures are depicted in Figs. 1–3.

In (I), the ferrocenyl (Fc) group [Fc = (C_5H_5)Fe(C_5H_4)] is normal, with Fe1···*Cg*1/*Cg*2 distances of 1.6498 (10) and 1.6539 (11) Å, and a *Cg*1···Fe1···*Cg*2 angle of 178.51 (6)° (*Cg*1 and *Cg*2 are the ring centroids for the substituted and unsubstituted rings, respectively). The Fe1—C bond lengths for the substituted η^5(C_5H_4) cyclopentadienyl ring are in the range 2.045 (2)–2.047 (2) Å and those in the unsubstituted η^5(C_5H_5) ring are similar [2.034 (2)–2.060 (2) Å]; the C—C bond-length ranges are tight, *viz.* 1.414 (3)–1.428 (3) and 1.417 (3)–1.421 (4) Å for the η^5(C_5H_4) and η^5(C_5H_5) rings, respectively. The C atoms of the η^5(C_5) rings are essentially eclipsed, with the five C1*n*···*Cg*1···*Cg*2···C2*n* angles (*n* = 1–5) ranging from 0.2 (2)° (for the C14/C24 pair) to 0.57 (19)° (for the C13/C23 pair). The C2—C11—Fe1 angle is 126.92 (15)°, which is similar to the mean value (127.2°) reported in the Cambridge Structural Database (CSD version of July 2003, update 5.24; Allen, 2002) for Fe—C—CH_2 angles (from 616 'hits' with coordinates and no disorder for Fe/CH_2).



(I)

The overall molecular geometry in (I) is described by the N1—C2—C11—C12 and N1—C1—C31—C32 angles [79.6 (3) and 115.4 (2)°], which indicate that the three major components in (I), *i.e.* the ferrocene, amide and anthracene groups, are all approximately orthogonal to one another (Fig. 1). The interplanar angle between the η^5(C_5H_4) ring and the anthracene group is 88.45 (8)° (Fig. 1). The rings in the anthracene group are coplanar with the two external rings, at angles of 1.01 (9) and 1.95 (9)° to the central ring (C31–C36). In the C_{14} system, the bond lengths can be arranged in specific groupings, with four in the range 1.353 (3)–1.365 (3) Å (*a* in the scheme), four in the range 1.390 (3)–1.412 (3) Å (*b*) and eight in the range 1.414 (3)–1.441 (3) Å [mean 1.428 (3) Å] (*c*). These bond lengths correspond to the anthracene system as depicted in our scheme and are similar to those found in related anthracene-9-carboxamide structures in the CSD [*e.g.* refcodes CABGAO (Adams *et al.*, 2001) and MEYYOE (Kohmoto *et al.*, 2001)].

The primary intermolecular interaction is the amide–amide interaction along the *a* axis [N···O^i = 2.910 (2) Å; symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z$; Table 2] [graph set *C*(4); Bernstein *et al.*, 1995]. In tandem with the N—H···O═C hydrogen bond, a C—H···π(arene) interaction [C2—H2*A*···*Cg*3^i, with C2···*Cg*3^i = 3.573 (2) Å; *Cg*3 is the centroid of the C31–C36 ring] generates an $R_2^2(8)$ ring, with the two donors on one molecule and the two acceptors on the other (Figs. 2 and 3). The C15—H15 moiety also forms a C—H···π(arene) contact with the anthracene group [H15···*Cg*5 = 3.04 Å (*Cg*5 is the centroid of the anthracene group), some 0.4 Å longer than the C2···π(arene centroid) distance]. However, this contact is directed towards atom C40 atom (H15···C40^i = 2.80 Å and C15—H15···C40^i = 164°). The C25—H25 group is involved in a similar contact with atom C37 (H25···C37 = 2.87 Å and C25—H25···C37^i = 149°). A second type of $R_2^2(8)$ ring can be

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considered to form from two C—H···π(arene) interactions involving atoms C2 and C15. A similar arrangement has been observed previously in the crystal structure of 2,4,6-tris(1′-phenylthio-1-ferrocenyl)boroxin (CSD refcode BOQQAZ; Hua *et al.*, 2001), in which a ferrocene group forms two contacts with a neighbouring C_6 aromatic ring, with (cp)H···C_6 distances of 2.78 and 2.87 Å, and C—H···C angles of 164 and 160° (the two C_6 atoms are *para*-related; cp is the cyclopentadienyl ring). In the structure of OBEWOH (Knoesen *et al.*, 2001), the (cp)H···C distances are 2.73 and 2.81 Å, and the C—H···C angles are 161 and 147°; in PALZOR, bis(2-ferrocenylmethyleneamino)-(benzenethiolato-*S*)mercury(II), the relevant data are 2.84 and 2.71 Å, and 152 and 163° (Kawamoto & Kushi, 1992). Similar C—H···C contacts have been reported in ethynyl steroids (Lutz *et al.*, 1998). A C—H···O hydrogen bond involving atoms C44 and O1^{ii} completes the intermolecular interactions [symmetry code: (ii) $\frac{1}{2} - x, y - \frac{1}{2}, -z$].

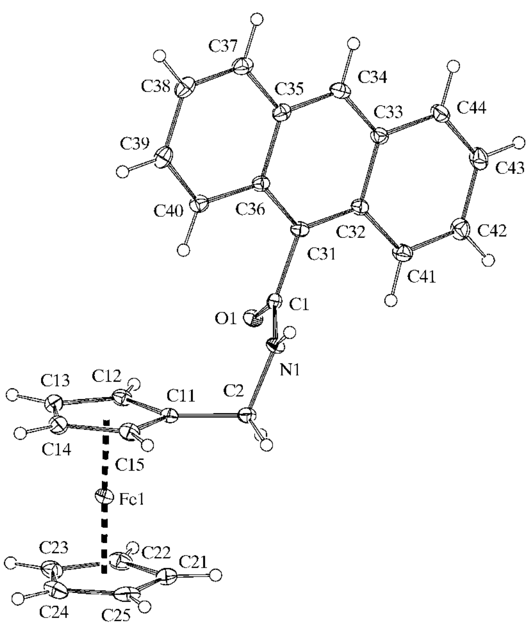

Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

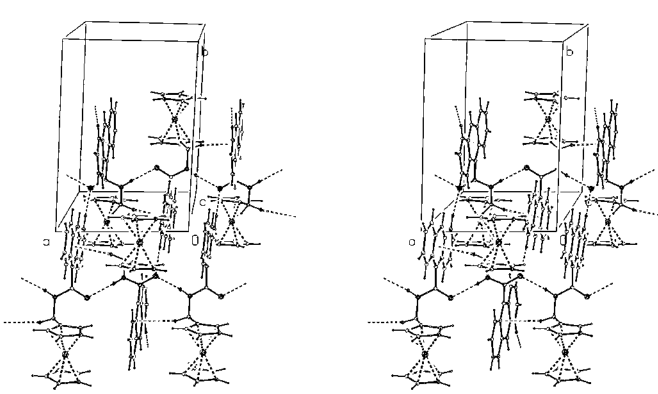

Figure 2
A stereoview of the interactions in the crystal structure of (I) (with a labelled unit cell).

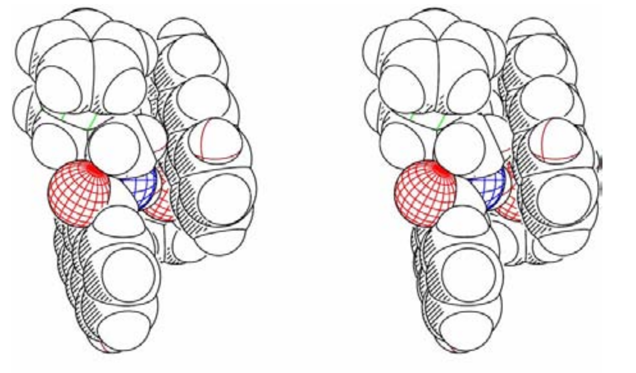

Figure 3
A stereoview of the interactions between the ferrocene moiety and the anthracene ring in (I), with atoms drawn as their van der Waals spheres.

Examination of the structure with *PLATON* (Spek, 2002) showed that there were four niches, each with a volume of 17 Å^3, but these are too small to contain even a water molecule (40 Å^3).

The majority of ferrocene derivatives in the CSD that contain an amide group have the ferrocene group bonded directly to the amide functionality (usually derived from ferrocenecarboxylic acid or acyl chloride reacted with an amine derivative). The combination of Fc and CH_2NHCO moieties is unusual, and currently seven examples are available in the CSD. These include FAMFER (Hall & Brown, 1971), PULDUV (Gale *et al.*, 1998), OHEPUM (Denuault *et al.*, 2002), XULRIF (Laurent *et al.*, 2002), XUZSIU and XUZSUG (Coles *et al.*, 2003). By comparison, there are ten 'hits' for the Fc/NH/CO moiety and 79 'hits' for the Fc/CO/NH moiety. This result can be attributed to the difficulty of obtaining aminoferrocene as a starting material and also the frequency with which ferrocenecarboxylic acid or the acyl chloride are used in condensation reactions with amine derivatives.

Experimental

For the synthesis of (I), ferrocenylmethylamine (0.50 g, 2.3 mmol) was added to a solution of anthracene-9-carboxylic acid (0.56 g, 2.5 mmol), 1-hydroxybenzotriazole (0.38 g, 2.7 mmol) and 1,3-dicyclohexylcarbodiimide (0.55 g, 2.5 mmol) in CH_2Cl_2 (40 ml) at 273 K and the mixture stirred for 30 min. The reaction mixture was warmed to room temperature and stirred for a further 48 h. The precipitated *N*,*N*′-dicyclohexylcarbourea was removed by filtration and the residue was washed with CH_2Cl_2, with the solvent volume reduced *in vacuo*. The mixture was purified on a silica-gel column using a mobile phase of hexane–ethyl acetate (2:1). Recrystallization from methanol furnished (I) as orange needles [0.447 g, 48% yield; m.p. 477–479 K (uncorrected)]. The UV–Vis transition is at 435 nm at a concentration of 1.01 mg ml^{-1} in $CHCl_3$. IR (KBr, cm^{-1}): $\nu_{C=O}$ 1617; ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.19–4.20, 4.26, 4.36–4.37, 4.43–4.44, 7.54–7.58, 7.94–7.96, 8.12–8.15, 8.66, 9.12; ^{13}C NMR (100 MHz, DMSO-d_6): δ 38.75, 67.83, 68.44, 68.82, 86.33, 125.56, 125.93, 126.68, 127.46, 127.63, 128.76, 131.04, 133.61, 168.23.

Crystal data

[Fe(C_5H_5)($C_{21}H_{16}$NO)]	D_x = 1.417 Mg m^{-3}
M_r = 419.29	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 7412 reflections
a = 9.5904 (3) Å	θ = 2.6–27.5°
b = 13.4903 (5) Å	μ = 0.78 mm^{-1}
c = 15.8568 (5) Å	T = 294 (1) K
β = 106.603 (2)°	Block, orange
V = 1965.98 (11) Å^3	0.24 × 0.20 × 0.20 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	4481 independent reflections
φ scans, and ω scans with κ offsets	3287 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)	R_{int} = 0.057
T_{min} = 0.854, T_{max} = 0.907	θ_{max} = 27.5°
13 006 measured reflections	$h = -12 \rightarrow 11$
	$k = -17 \rightarrow 17$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 1.1032P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.040	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.097	$\Delta\rho_{max}$ = 0.46 e Å^{-3}
S = 1.03	$\Delta\rho_{min}$ = −0.43 e Å^{-3}
4481 reflections	Extinction correction: *SHELXL*97
267 parameters	Extinction coefficient: 0.0024 (6)
H atoms: see below	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.245 (2)	C1—C31	1.499 (3)
N1—C1	1.336 (3)	C2—C11	1.504 (3)
N1—C2	1.465 (3)	N1—H1	0.82 (3)
C1—N1—C2	121.03 (18)	N1—C1—C31	117.81 (18)
O1—C1—N1	122.5 (2)	N1—C2—C11	111.85 (18)
O1—C1—C31	119.69 (18)	C2—C11—Fe1	126.92 (15)
C2—N1—C1—O1	−4.1 (3)	N1—C2—C11—Fe1	169.99 (14)
C2—N1—C1—C31	175.43 (18)	O1—C1—C31—C36	108.9 (2)
C1—N1—C2—C11	−79.1 (2)	N1—C1—C31—C36	−70.6 (3)
N1—C2—C11—C15	−99.1 (2)	O1—C1—C31—C32	−65.1 (3)
N1—C2—C11—C12	79.6 (3)	N1—C1—C31—C32	115.4 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

*Cg*3 is the centroid of the C31–C36 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.82 (3)	2.10 (3)	2.910 (2)	169 (2)
C2—H2*A*···*Cg*3^{i}	0.99	2.62	3.573 (2)	161
C15—H15···C40^{i}	0.95	2.80	3.726 (3)	164
C25—H25···C37^{i}	0.95	2.87	3.715 (3)	149
C44—H44···O1^{ii}	0.95	2.41	3.276 (3)	151

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, -z$.

Compound (I) crystallized in the monoclinic system; space group $P2_1/a$ was assigned from the systematic absences and confirmed by the analysis. H atoms attached to C atoms were treated as riding, using *SHELXL*97 (Sheldrick, 1997) defaults, and the H atom attached to the N atom was refined with isotropic displacement parameters [N—H = 0.82 (3) Å].

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PREP*8 (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1288). Services for accessing these data are described at the back of the journal.

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