

## A new polymorph of 1-ferrocenyl-3-(3-nitroanilino)propan-1-one

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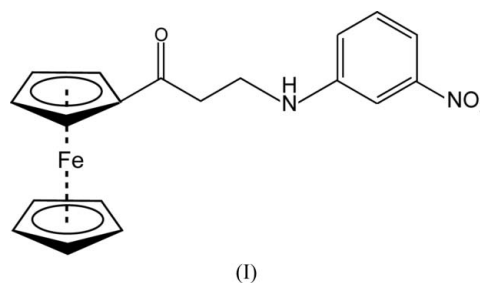
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Recrystallization of the title compound, [Fe(C<sub>5</sub>H<sub>5</sub>)(C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub>)], from a mixture of *n*-hexane and dichloromethane gave the new polymorph, denoted (I), which crystallizes in the same space group (*P* $\bar{1}$ ) as the previously reported structure, denoted (II). The Fe—C distances in (I) range from 2.015 (3) to 2.048 (2) Å and the average value of the C—C bond lengths in the two cyclopentadienyl (Cp) rings is 1.403 (13) Å. As indicated by the smallest C—Cg1—Cg2—C torsion angle of 1.4° (Cg1 and Cg2 are the centroids of the two Cp rings), the orientation of the Cp rings in (I) is more eclipsed than in the case of (II), for which the value was 15.3°. Despite the pronounced conformational similarity between (I) and (II), the formation of self-complementary N—H···O hydrogen-bonded dimers represents the only structural motif common to the two polymorphs. In the extended structure, molecules of (I) utilize C—H···O hydrogen bonds and, unlike (II), an extensive set of intermolecular C—H··· $\pi$  interactions. Fingerprint plots based on Hirshfeld surfaces are used to compare the packing of the two polymorphs.

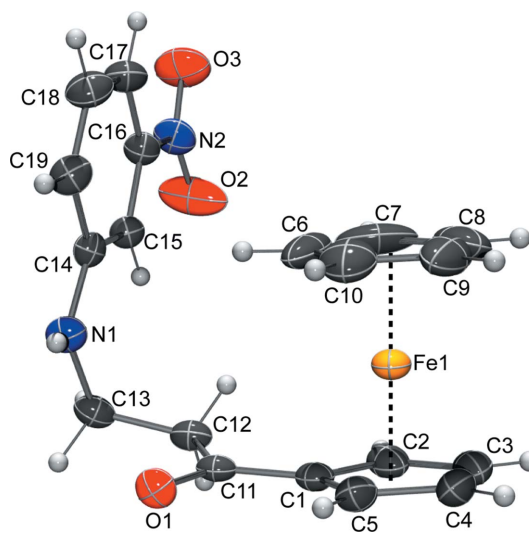
### Comment

Ferrocene, an unnatural compound, has attracted intense attention from chemists since its discovery in 1951 (Kealy & Pauson, 1951; Miller *et al.*, 1952) and particularly after its first functionalization by Friedel–Crafts acylation (Woodward *et al.*, 1952). This interest is a consequence of several unique properties of ferrocene and its derivatives, including nontoxicity, easy handling, outstanding stability in both aqueous and non-aqueous media *etc.* The most attractive feature of these compounds is their ease of functionalization; following classical organic protocols one can synthesize a 'double' of any known compound in which the aromatic unit is substituted by ferrocene.

Ferrocene exists in three polymorphic forms, one at room temperature, which is monoclinic (Seiler & Dunitz, 1979*a*; Takusagawa & Koetzle, 1979), and two at low temperature, *viz.* triclinic and orthorhombic (Seiler & Dunitz, 1979*b*, 1982). At the molecular level, the ferrocene molecules within these forms differ only in the relative orientation of the two cyclopentadienyl (Cp) rings (Braga *et al.*, 1998). The low rotation barrier of the Cp rings accounts for the considerable flexibility of the ferrocene (Fc) unit, which can be further related to the evident structural polymorphism of Fc-containing compounds. Aliphatic substituents, when present on Fc units, add to the overall structural flexibility which plays an important role in the polymorphism of these compounds. A Cambridge Structural Database (CSD, Version 5.31, August 2010; Allen, 2002) survey of Fc-containing crystal structures, for which the special text string 'polymorphism' has been registered, retrieved 78 different compounds. Among these structures there are 16 examples in which the polymorphs crystallize in the same space group.



We report here a new polymorph of 1-ferrocenyl-3-(3-nitroanilino)propan-1-one obtained by recrystallization from a mixture of *n*-hexane and dichloromethane. The novel polymorph, denoted (I) (Fig. 1), as well as the previously described polymorph, denoted (II) (Damljanović *et al.*, 2011), crystallizes in the space group *P* $\bar{1}$ , with one molecule in the asym-



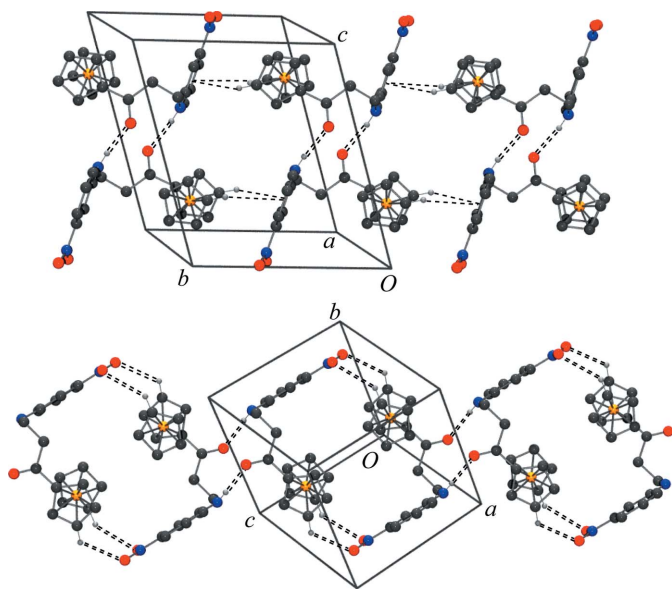
**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level.

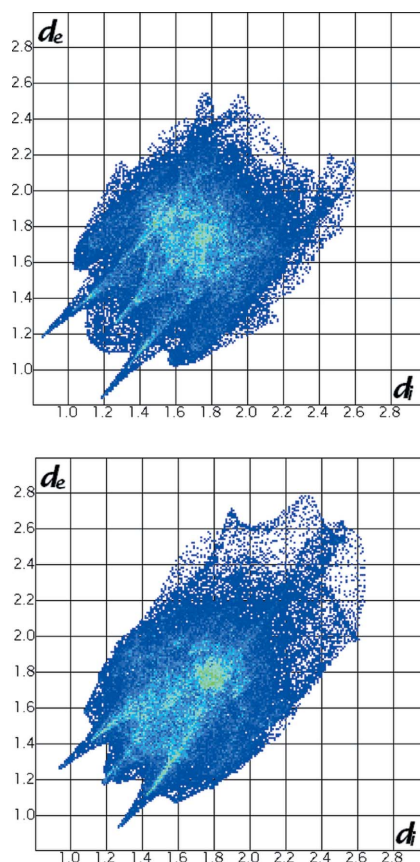
metric unit. The unit cells of (I) and (II) display similar volumes but differ significantly in axis lengths and angles. The previously reported examples of monosubstituted 3-aryl-amino-1-ferrocenylpropan-1-ones (Damljanović *et al.*, 2011) indicate the existence of two molecular conformations, mostly dependent on the position of the substituent on the arylamino group. Molecules (I) and (II) belong to the same conformational type and exhibit only slight structural dissimilarity, but they display a significant packing polymorphism. For (I), the bond distances (Table 1) within the Fc unit are as expected for monosubstituted derivatives. The C–C bonds in the substituted cyclopentadienyl ring, Cp1, are slightly longer than those in the unsubstituted ring, Cp2. One should, however, take into account that the apparently shorter C–C bonds in the unsubstituted ring may be a result of the strong libration in this ring, as demonstrated by the elongated ellipsoids. Disorder of the Cp rings in ferrocene is a well known phenomenon which was initially described by Seiler & Dunitz (1979a). The longest Cp bonds are C1–C2 [1.437 (3) Å] and C1–C5 [1.429 (3) Å] vicinal to the substituent at C1 (Fig. 1). As previously observed in similar monosubstituted Fc-based compounds (Ratković *et al.*, 2010), the metal atom could be considered as positioned slightly closer to the substituted Cp1 ring (Fe1–Cg1 = 1.64 Å and Fe1–Cg2 = 1.65 Å; Cg1 and Cg2 are the centroids of the Cp1 and Cp2 rings, respectively). The Cp1 and Cp2 rings are almost parallel, with a dihedral angle of 1.3 (2)°, similar to the value of 2.3 (4)° in (II). The most pronounced difference in the Fc units of (I) and (II) concerns the mutual orientation of Cp rings. The C1–Cg1–Cg2–C6 torsion angles of 1.4° in (I) and 15.3° in (II) indicate a more significant deviation from an eclipsed conformation in the case of (II). Bond lengths and angles within the substituents are similar in (I) and (II). Torsion angles (Table 2) indicate small

but noticeable differences in the conformation of the C1–C14 chains which are enabled by free rotation around the corresponding single bonds. These differences accompany a slight variation in the Cp2/Ph dihedral angle, *viz.* 85.7 (1) and 82.7 (2)° for (I) and (II), respectively. A good gauge of the conformational differences between (I) and (II) is the relative displacement of arylamino atom N1 from the Fe1/Cg2/C6 plane, which bisects Cp2 and contains the Fe1 atom [0.55 Å in (I) and 2.05 Å in (II), see Fig. S1 in the *Supplementary materials*].

In the packing of the two polymorphs, the strongest intermolecular N1–H1*n*···O1<sup>i</sup> interactions [symmetry code: (i)  $-x + 1, -y + 2, -z + 1$ ], formed between their aliphatic moieties, link the centrosymmetrically related molecules into dimers characterized by the same cyclic  $R_2^2(12)$  motif (Etter, 1990). The N1–H1*n*···O1<sup>i</sup> hydrogen bond in (I) is somewhat shorter [N1···O1<sup>i</sup> = 3.018 (2) Å in (I) and 3.133 (6) Å in (II)] and displays better directionality than the analogous interaction in (II). The N1–H1*n*···O1 interactions in (II) are additionally supported by a C6–H6···O1<sup>i</sup> interaction, while in (I) the relative disposition of the neighbouring molecules obviates this interaction (see Fig. S2 in the *Supplementary materials*). The dimer mediated by N1–H1*n*···O1<sup>i</sup> is the only motif common to the two structures. This interaction involves the strongest donor and acceptor, and represents the best initial aggregation mode for this compound. Beyond that, polymorphs (I) and (II) display pronounced differences. In



**Figure 2**  
The N1–H1···O1 hydrogen-bonded dimers of (I) (top) and (II) (bottom), interconnected by corresponding C–H··· $\pi$  and C–H···O interactions, respectively. H atoms not involved in intermolecular interactions have been excluded for the sake of clarity.



**Figure 3**  
Fingerprint plots of (I) (top) and (II) (bottom).

(II), the strongest remaining acceptors, the nitro O atoms, interact with a pair of C—H donors, one from each Cp ring of the Fc unit. In this manner, the bent configuration of the molecule is utilized to form a macrocyclic motif centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  (Fig. 2, bottom). This motif is not seen for (I); indeed, in (I), the same pair of C—H donors is involved in a pair of C—H $\cdots\pi$  interactions towards the neighbouring benzene ring, forming an infinite chain parallel to *b*. Fig. 2 shows the dimers common to (I) and (II) interconnected by C—H $\cdots\pi$  [(I); Fig. 2, top] and C—H $\cdots$ O [(II); Fig. 2, bottom] interactions, respectively. In (I), the nitro O atoms have a completely different role from that observed in (II). Atom O2 in (I) is involved in an acceptor-bifurcated hydrogen bond (both H $\cdots$ O < 2.6 Å), with the C15—H15 benzene ring and the aliphatic C13—H13a group as donors. The interaction with acceptor atom O3 is weaker and involves the cyclopentadienyl C7—H7 group as donor. This is the only interaction between the Fc moiety and NO<sub>2</sub> in (I), in contrast to (II), where there are three. While Fc in (I) play an important role in C—H $\cdots\pi$  interactions, both as a C—H donor and as a  $\pi$  acceptor, in (II) only one intermolecular C—H $\cdots\pi$  interaction is observed (Table 3, see Fig. S3 in the *Supplementary materials*).

The differences in the overall patterns of interactions in the crystal structures of polymorphs (I) and (II) are best illustrated through Hirshfeld surfaces (see Fig. S4 in the *Supplementary materials*) and the corresponding fingerprint plots (Fig. 3) (Wolff *et al.*, 2007; Spackman & McKinnon, 2002). This two-dimensional mapping summarizes the intermolecular interactions present in the crystal structures and reflects the influences of the different crystal environments on the two polymorphs. The values  $d_e$  and  $d_i$  are defined as the distances from a point on the Hirshfeld surface to the nearest atoms external and internal to the surface, respectively. For each ( $d_e, d_i$ ) pair, the fingerprint plot gives its frequency of occurrence in the structure, using colour to represent frequency. As discussed by Spackman & Jayatilaka (2009), various types of interactions in a molecular structure give rise to characteristic patterns in the fingerprint plot. The fingerprint plots for (I) and (II) show distinctly different shapes; however, the dominant feature with each of them is a pair of sharp spikes corresponding to the shortest O $\cdots$ H contacts. Taking into account the  $d_e$  and  $d_i$  values, it is clear that polymorph (I) exhibits shorter hydrogen-bonding interactions. Moreover, a systematic shift of the whole pattern to shorter contacts in (I) suggests a more dense packing in the case of this polymorph. This accords with the densities  $D_{\text{calc}}$  of 1.475 and 1.462 Mg m<sup>-3</sup> for (I) and (II), respectively. If the density of the different polymorphs is considered as a measure of their relative stabilities (Braga *et al.*, 1998), one can conclude that polymorph (I) is the more stable of the two. An important feature in the fingerprint plot of (I), which is lacking in (II), is the wing-like accumulation at the top left and bottom right of the graph, corresponding to the C—H $\cdots\pi$  interactions. The region between the spikes corresponds to the H $\cdots$ H contacts, which are obviously more numerous for (I). The shortest intermolecular H $\cdots$ H distance (2.42 Å) is found between atom H1*n* (attached to N1) and cyclopentadienyl atom H5

(located in the vicinity of the O-atom acceptor interacting with H1*n*). The percentage contributions of the H $\cdots$ O contacts to the fingerprint plot is 24.8% for (I) and slightly higher in the case of (II) (27.1%). On the other hand, the contribution of H $\cdots$ C contacts is higher for polymorph (I) [19.1% in comparison to 13.1% for (II)], in agreement with the greater number of observed C—H $\cdots\pi$  interactions (see Fig. S3 in the *Supplementary materials*).

In summary, the two polymorphs of 1-ferrocenyl-3-(3-nitroanilino)propan-1-one represent the infrequent case in which polymorphs of Fc compounds crystallize with the same space group. Indeed, the molecules in polymorphs (I) and (II) exhibit almost the same conformation, and form similar centrosymmetric dimers; nevertheless, they display completely different three-dimensional packing which is based entirely on weak noncovalent interactions.

## Experimental

Polymorph (I) was synthesized according to the previously reported procedure of Damjanović *et al.* (2011). The solid product obtained following column chromatography was dissolved in a small amount of dichloromethane (2–3 ml) and *n*-hexane was added carefully to this solution until the first appearance of turbidity. One or two drops of dichloromethane were then added to obtain a clear solution, which was allowed to evaporate slowly at room temperature, producing crystals of (I).

### Crystal data

[Fe(C <sub>5</sub> H <sub>5</sub> )(C <sub>14</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> )]	$\gamma = 75.891 (5)^\circ$
$M_r = 378.20$	$V = 851.55 (8) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.6075 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.1342 (7) \text{ \AA}$	$\mu = 0.91 \text{ mm}^{-1}$
$c = 11.9062 (6) \text{ \AA}$	$T = 293 \text{ K}$
$\alpha = 73.805 (5)^\circ$	$0.22 \times 0.18 \times 0.15 \text{ mm}$
$\beta = 81.350 (4)^\circ$	

### Data collection

Oxford Diffraction Xcalibur	6735 measured reflections
Sapphire3 Gemini diffractometer	3884 independent reflections
Absorption correction: multi-scan	3147 reflections with $I > 2\sigma(I)$
( <i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	$R_{\text{int}} = 0.021$
$T_{\text{min}} = 0.933$ , $T_{\text{max}} = 1.000$	

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	227 parameters
$wR(F^2) = 0.091$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
3884 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

O1—C11	1.219 (2)	N2—C16	1.470 (3)
O2—N2	1.205 (3)	C1—C11	1.463 (3)
O3—N2	1.209 (2)	C11—C12	1.509 (3)
N1—C13	1.449 (3)	C12—C13	1.512 (3)
N1—C14	1.372 (3)		
O1—C11—C1	121.19 (19)	C14—N1—C13	122.85 (17)
O1—C11—C12	120.3 (2)	C1—C11—C12	118.54 (18)
N1—C13—C12	114.00 (18)	C11—C12—C13	112.79 (17)

**Table 2**

Selected torsion angles (°) for (I) and (II).

	(I)	(II)
C1—C11—C12—C13	−167.40 (16)	−164.4 (4)
C5—C1—C11—C12	169.19 (18)	178.8 (5)
C11—C12—C13—N1	65.2 (2)	67.4 (7)
C12—C13—N1—C14	74.4 (3)	68.7 (8)
C13—N1—C14—C15	11.7 (3)	13.0 (9)
O1—C11—C12—C13	12.5 (3)	17.6 (7)

**Table 3**

Geometric parameters (Å, °) for intermolecular interactions.

Only contacts with H...C < 3.0 Å were considered as potential intermolecular C—H...π interactions. H...C<sub>g</sub> represents the distance between the H atom and the centroid of the aromatic ring. See *Refinement* text below for further details of the data for (II).

D—H...A	D—H	H...A	D...A	D—H...A	H...C <sub>g</sub>
<b>(I)</b>					
N1—H1 <sup>n</sup> ...O1 <sup>i</sup>	0.86	2.18	3.018 (2)	165	
C19—H19...O1 <sup>i</sup>	0.93	2.64	3.361 (2)	135	
C13—H13 <sup>a</sup> ...O2 <sup>ii</sup>	0.97	2.55	3.411 (3)	147	
C15—H15...O2 <sup>ii</sup>	0.93	2.51	3.422 (3)	168	
C7—H7...O3 <sup>iii</sup>	0.93	2.62	3.383 (4)	140	
C17—H17...C3 <sup>iv</sup>	0.93	2.90	3.824 (3)	173	2.87
C17—H17...C4 <sup>iv</sup>	0.93	2.73	3.541 (3)	146	2.87
C12—H12A...C7 <sup>v</sup>	0.93	2.90	3.724 (4)	143	3.06
C12—H12A...C8 <sup>v</sup>	0.93	2.91	3.903 (3)	137	3.06
C4—H4...C14 <sup>vi</sup>	0.93	2.94	3.857 (4)	160	3.31
C4—H4...C15 <sup>vi</sup>	0.93	2.74	3.536 (4)	144	3.31
C9—H9...C17 <sup>vi</sup>	0.93	2.87	3.780 (5)	144	3.19
<b>(II)</b>					
N1—H1 <sup>n</sup> ...O1 <sup>i</sup>	0.86	2.34	3.133 (6)	154	
C6—H6...O1 <sup>i</sup>	0.93	2.70	3.601 (6)	163	
C19—H19...O1 <sup>i</sup>	0.93	2.64	3.388 (7)	138	
C9—H9...O2 <sup>ii</sup>	0.93	2.66	3.444 (10)	143	
C4—H4...O3 <sup>ii</sup>	0.93	2.65	3.273 (10)	125	
C18—H18...C7 <sup>iii</sup>	0.93	2.78	3.577 (15)	145	3.23

Symmetry codes for (I): (i)  $-x + 1, -y + 2, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 2$ ; (iii)  $-x + 2, -y + 1, -z + 2$ ; (iv)  $x + 1, y - 1, z$ ; (v)  $x - 1, y, z$ ; (vi)  $x, y + 1, z$ . Symmetry codes for (II): (i)  $-x + 2, -y + 1, -z$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $-x + 2, -y + 1, -z + 1$ .

H atoms bonded to C atoms were placed at calculated positions, with C—H distances fixed at 0.93 Å for aromatic Csp<sup>2</sup> atoms and at 0.97 Å for methylene Csp<sup>3</sup> atoms. The corresponding isotropic displacement parameters of the H atoms were set equal to 1.2U<sub>eq</sub> and 1.5U<sub>eq</sub> of the parent Csp<sup>2</sup> and Csp<sup>3</sup> atoms, respectively. The H atom attached to N1 was located by difference Fourier synthesis, then the N—H bond length was idealized to 0.86 Å and the H atom constrained to ride on its parent atom with its isotropic displacement parameter freely refined.

In order to compare the Hirshfeld fingerprint plots for the two polymorphs on the same grounds, the corresponding N—H bond in (II) was elongated to the identical value of 0.86 Å. The refinement of (II) was then continued until convergence in the same manner as for (I). The parameters for (II) given in Table 3 are slightly altered from the original publication (Damljanović *et al.*, 2011) due to this modification.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PLATON* (Spek, 2009) and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3265). Services for accessing these data are described at the back of the journal.

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