
Impressive 1D (FERROCENYL...C6F5R...)n Stacking Due to Cooperative Interactions in N- (Ferrocenylmethyl)pentafluorobenzenecarboxamide: Four Crystal Structures and Contacts Analyses in N- (Ferrocenylalkyl)benzenecarboxamides

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Keywords: Aggregation; Aromatic Ring Stacking; Columnar; Contact Enrichment Analysis; Crystal Structure; Ferrocene; Fluorine; Hydrogen Bonding



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Article

Impressive 1D (Ferrocenyl...C₆F₅R...) _n Stacking Due to Cooperative Interactions in *N*-(ferrocenylmethyl)pentafluorobenzenecarboxamide: Four Crystal Structures and Contacts Analyses in *N*-(ferrocenylalkyl)benzenecarboxamides

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† This research paper is dedicated to our great friend and colleague, Peter (1958–2022); a passionate and lifelong Glasgow Celtic and Chelsea football supporter.

Highlights:

- Crystal structure analyses of four new ferrocenylcarboxamide derivatives.
- Intricate ring stacking in a penta-fluorinated ferrocene carboxamide derivative.
- Competition between intermolecular interactions with increasing fluorine content.
- Comparisons with a published structure that forms part of the 5 molecule series.
- Comparisons with a known structure **SUFLIR** that exhibits intricate 1D ring stacking.

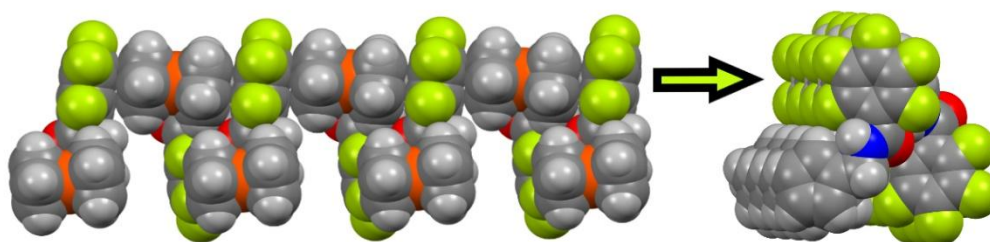
Abstract: The crystal structures, interactions and contacts analyses of four *N*-(ferrocenylalkyl)benzene-carboxamide derivatives are described as the *N*-(ferrocenylmethyl)benzene-carboxamide **4a**, *N*-(ferrocenylmethyl)-2,6-difluorobenzenecarboxamide **4e**, *N*-(ferrocenylmethyl)penta-fluorobenzenecarboxamide **4f** and *N*-(ferrocenylethyl)-4-fluorobenzenecarboxamide **5**. Intermolecular amide...amide hydrogen bonding interactions as 1D intermolecular chains are present in all four crystal structures, with N...O distances ranging from 2.819(2) to 2.924(3) Å. Three of the crystal structures have one molecule per asymmetric unit, except the phenyl **4a** which has *Z'*=2. In the structure of **4a**, Fc(C-H)...(phenyl) and _{phenyl}C-H...π(C₅H₄) ring interactions dominate the interaction landscape, together with (1:1) face-to-face (phenyl)...(phenyl) and (C₅H₅)...(C₅H₅) ring stacked pairs (Fc = ferrocenyl moiety). In **4e**, interlocking ferrocenyls, short C-H...(C-F) and C-H...O hydrogen bonds are the only additional notable intermolecular interactions. In the pentafluorophenyl derivative **4f**, a remarkable selection of interactions is present with interwoven 1D ferrocenyl...(C₆F₅) stacking and C-H...F interactions; molecules aggregate forming impressive 1D columns comprising intertwined (Fc...C₆F₅...) _n ring stacking. In the ethyl bridged system **5**, C-H...F and C-H...π(arene) contacts with (4-fluorobenzene)ring...ring pairs combine and stack about inversion centres. The reported *para*-F substituted structure **REYWOU** (**4d**) is used for comparisons with the **4a**, **4e**, **4f** and **5** crystal structures. In view of the rich interaction chemistry, contacts enrichment analyses of the Hirshfeld surface highlights several interesting features in all five ferrocenylalkylcarboxamide structures.

Keywords: aggregation; aromatic ring stacking; columnar; contact enrichment analysis; crystal structure; ferrocene; fluorine; hydrogen bonding

Graphical Abstract

Diversity of intermolecular interactions influencing aggregation in four (ferrocenylmethyl)benzene-carboxamides with impressive cooperative amide...amide interactions and 1D columnar $(\text{Fc}\cdots\text{C}_6\text{F}_5\text{R}\cdots)_n$ stacking in the *N*-(ferrocenylmethyl)pentafluorobenzenecarboxamide.

From $\text{C-H}\cdots\pi(\text{Fc})$ relays to the $\text{Fc}/\text{C}_6\text{F}_5\text{R}$ alternating stacking rings in a pentafluorobenzene carboxamide.



1. Introduction

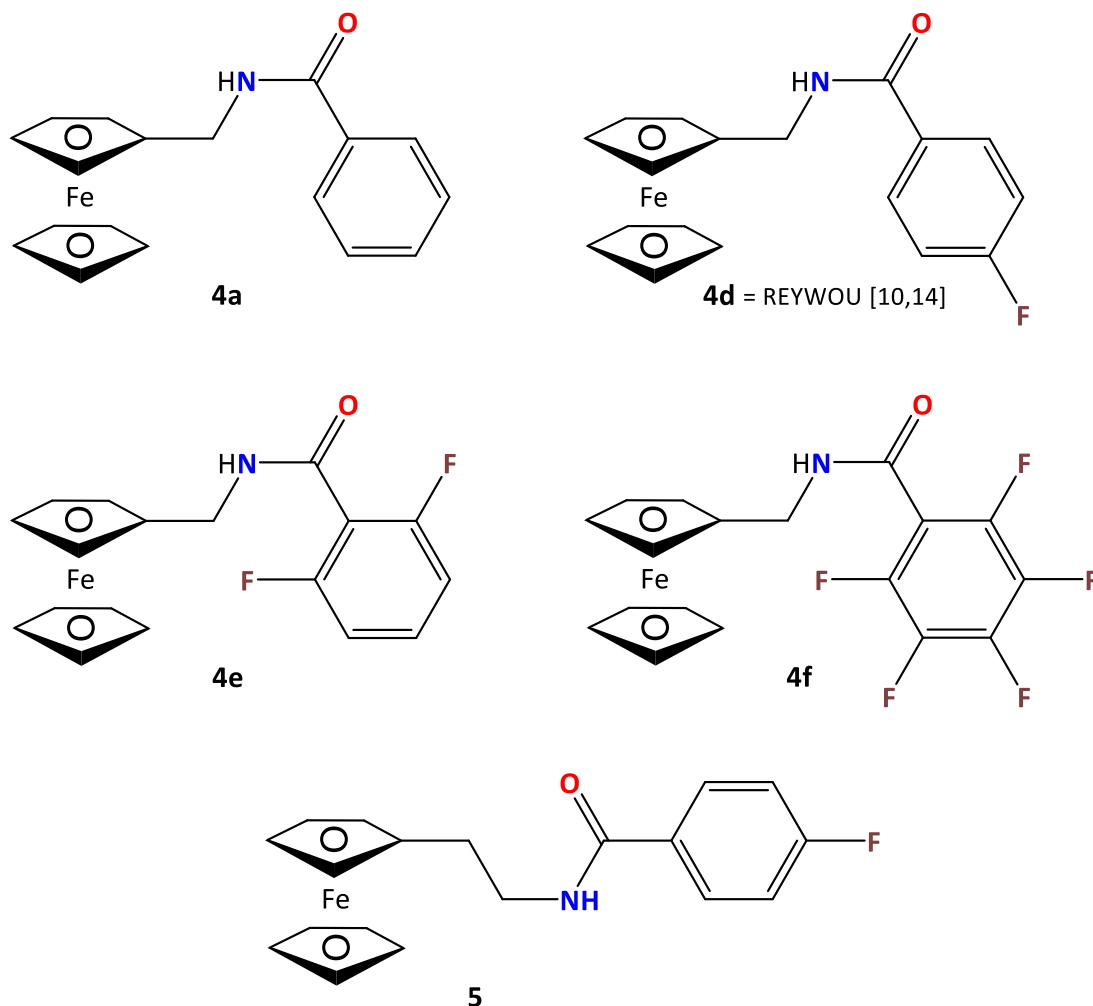
After 70+ years of enormous developments, ferrocene chemistry continues to progress and grow unabated in a multitude of areas in chemistry and science [1–9]. There are many research fields that have overlapped with ferrocenes and aided in its development. Significant branching into expanding multidisciplinary studies has arisen, and overall the growth and study of ferrocene crystal structures diversifies and shows no sign of abating [10]. This is noted by the number of structures incorporating ferrocene or as a derivative which is currently ~19,000 (18797 structures without restrictions and including repeat structures 01/02...) as listed in the Cambridge Structural Database (CSD) in January 2025 [10]. Of on-going interest in structural science, the ferrocene molecule [as $\text{Fe}(\text{cp})_2$] and its derivatives are notable on account of their rich, robust chemistry and remarkable stability [1–3]. It is widely used due to the physicochemical changes and improvements imparted on the molecular systems under study. For example, areas such as bioorganometallic and related chemistry (incorporating the ferrocenyl moiety - Fc) have seen spectacular growth over the past few decades with applications in medicinal and anti-cancer studies [10–18].

Our research interests in ferrocene derivatives has focused on two specific areas as (i) hydrogen bonding and crystal engineering studies [9,19] and (ii) bioorganometallic ferrocene chemistry [13–14,20,21]. In the latter studies, ferrocenyl and ferrocenoyl groups were incorporated with conjugated linker groups such as benzene and naphthalene bonded specifically to amino acids and dipeptides [20,21]. An impetus for this research is their utilisation as new biomaterials and in medicinal chemistry/anti-cancer studies [20,21].

Of note and particular interest to the present manuscript is the recent publication by Cockcroft and co-workers where they reported the structure and properties of $(\text{C}_6\text{F}_6):\text{ferrocene}$ [or $(\text{C}_6\text{F}_6):\text{FeCp}_2$] in a temperature range from 100 K up to ~309 K [5]. In this $\text{C}_6\text{F}_6:\text{FeCp}_2$ solvate adduct (from 100→290 K), the crystal structure comprises closely-packed columns of alternating hexafluorobenzene C_6F_6 and FeCp_2 molecules arranged so that the hexafluorobenzene is sandwiched between the ferrocenes. It is stated that intermolecular quadrupolar forces between the C_6F_6 and FeCp_2 components are the main driving forces in the observed columnar and structural aggregation [5].

In the present manuscript, four new ferrocenecarboxamide crystal structures are reported [13,14] and analysed for comparisons using contacts enrichment analyses (**Scheme 1**). The structural changes that arise on changing the substitution pattern from phenyl to pentafluorobenzene derivatives are analyzed. Comparisons are made with the published 4-fluorobenzene structure **4d** (REYWOU) [14] and related literature [5,10]. Additionally, the ethylene bridged group $(-\text{CH}_2\text{CH}_2-)$ in **5** provides an extra degree of flexibility in molecular structure. Previously, we have published research on conjugated ferrocene derivatives in structural systematic studies and biomaterials [9,19] and have

noted that the number of compounds incorporating the 'FcCH₂NHC=O(arene)' moiety is still relatively low, with only 8 structures available in the CSD, ([Fc = (η⁵-C₅H₅)Fe(η⁵-C₅H₄)] [10]. These structures include **UYENUJ** [15] and **MIRYIZ** [18]. A total of thirty 'FcCH₂NHCO-C' structures are noted in a more general study [10]. In order to further develop and expand this area of ferrocene structural research, four new ferrocene derivatives are presented with their crystal structures. It is noted in particular the diversity of packing modes and the importance of thorough analysis of the 3D structures for comparisons with related molecules [5,10].



Scheme 1. Schematic diagram of the ferrocene derivatives **4a**, **4d** [14], **4e**, **4f** and **5**.

2. Experimental

2.1. Materials and Characterisation

The chemicals, materials, spectroscopic, X-ray diffraction methods and analytical equipment are as reported previously [9,13,14]. All chemicals used in the synthetic reactions were used as purchased from Sigma-Aldrich and the synthetic reactions utilised standard organic synthetic procedures as described in earlier work [14] (ESI). The original numbering system for the compounds and structures presented herein is retained. Compounds **4b** and **4c** are the related *ortho*-F and *meta*-F isomers of the *para*-F substituted structure **REYWOU** (**4d**) [14]. Single crystal X-ray diffraction methods and data collection strategies were routine [22] and structure solution and refinement for **4a**, **4e**, **4f**, **5** undertaken using the SHELXS and SHELXL14 programs [23]. Molecular graphics using the Mercury program provided ORTEP diagrams (with displacement ellipsoids drawn at the 30% probability level) and the hydrogen bonding diagrams [24]. Analyses of the geometric data for comparison purposes were performed using SHELXL14 output together with the 'CALC ALL'

routine in PLATON [25]. Salient features of the four structures are provided in **Tables 1** and **2**. Comparisons and analyses of the CSD [10] were undertaken using the latest version available in 2024 [Conquest version 24.2.0 (5.45 + update 3); build 415171].

Table 1. Selected crystallographic data (full details are available; ESI, Table S01).

Structures	Crystal system; Space group	Z'	Volume (Å ³); KPI	R, wR ₂ R-factors, GoF
4a	Monoclinic; <i>P2₁/n</i>	2	2851.36(18); 71.3	0.044, 0.126, 0.98
4d [ref 14]	Orthorhombic; <i>P2₁2₁2₁</i>	1	1435.97(4); 71.8	0.031, 0.065, 1.05
4e	Monoclinic; <i>P2₁/a</i>	1	1524.92(8); 69.3	0.034, 0.085, 1.05
4f	Monoclinic; <i>P2₁/c</i>	1	1577.44(10); 71.2	0.034, 0.086, 1.06
5	Orthorhombic; <i>Pbca</i>	1	3145.27(16); 69.8	0.037, 0.092, 1.03

Footnote: R-factor definitions as $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$.

Table 2. Selected interplanar angles and intermolecular distances (°, Å).

Structures	C ₅ H ₄ /C ₆ (°)	C ₅ H ₄ /amide (°)	Amide...amide interaction (Å)	O=C-N-C _{torsion}
4a	73.16(11)/79.12(11)	64.77(12)/68.16(12)	2.924(3)/2.869(3)	-1.6(4)/4.1(4)
4d [ref 14]	77.80(8)	69.80(10)	2.972(3)	2.1(3)
4e	81.24(7)	68.55(10)	2.819(2)	-7.6(3)
4f	11.34(11)	57.31(9)	2.892(2)	3.0(3)
5	61.66(7)	34.08(12)	2.853(2)	-3.8(3)

2.2. Methods: Hirshfeld Surface Analysis Details

Analyses of the Hirshfeld surface (**ESI; Figure S10** and **Table S3**) [26] and contacts enrichment ratio were performed to analyse different types of intermolecular interactions using procedures previously reported [27].

The fingerprint plots of contacts around the molecules in the four crystal packings of **4a**, **4e**, **4f**, **5** were computed with the CrystalExplorer17 program [26]. The contact statistics and enrichment ratios were obtained using the MoProViewer program [27]. In the case of compound **4a** (with $Z'=2$), the Hirshfeld surface was computed around two independent molecules not in contact with each other in the crystal packing. In the contacts analysis, the charged H_N hydrogen atoms bound to nitrogen were differentiated from the hydrophobic hydrogen H_C atoms linked to a carbon.

In the asymmetric unit of **4a**, molecules A and B have similar conformations and although PLATON [25] suggests space group *C2/c*, the results do not support this space group assignment (as noted in the following section and **ESI**). Geometric differences between molecules A and B can be demonstrated by the Fe1A–C11A–C2A–N1A dihedral angle = $-179.48(18)^\circ$ and for Fe1B–C11B–C2B–N1B = $175.51(19)^\circ$. This represents a significant 4° angle difference (with a detailed explanation in the **ESI**). Additional differences can be noted between molecules A and B (e.g., amide...amide distances) in the following section on the crystal and molecular structure discussion. The root mean square deviation of molecule A with the inverted B molecule is 0.10 Å and maximum atomic deviation is 0.16 Å.

2.3. Four Crystal and Molecular Structures:

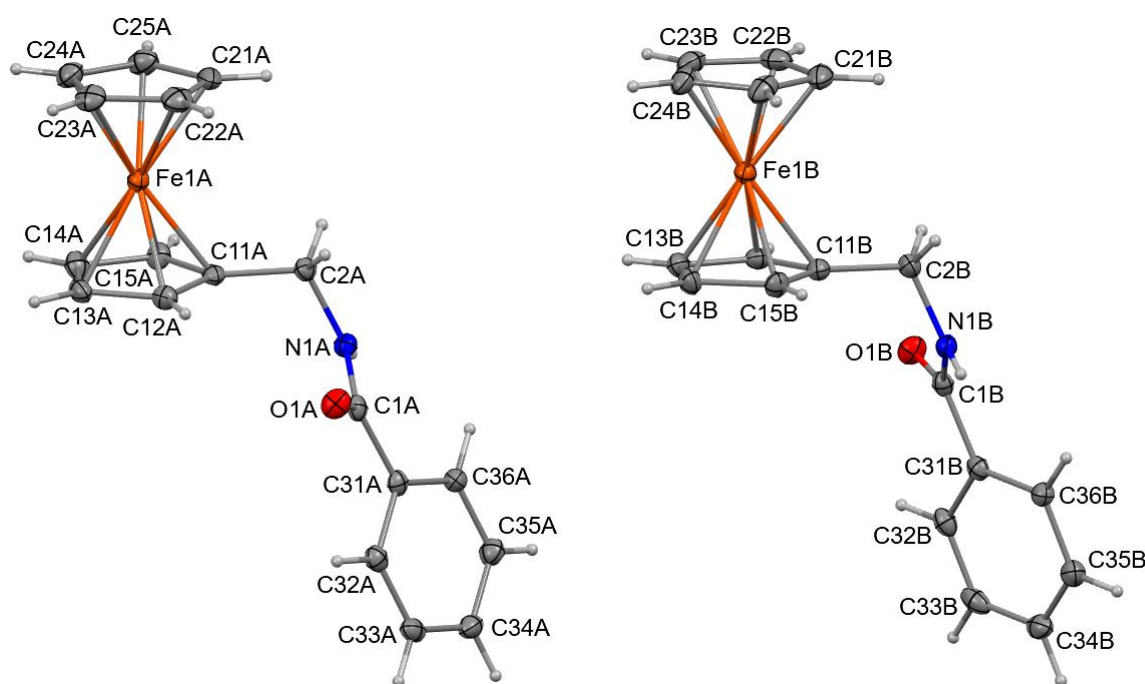
N-(Ferrocenylmethyl)benzenecarboxamide structure (4a) with $Z'=2$

The phenyl derivative **4a** crystallizes with two molecules A and B ($Z'=2$) in the asymmetric unit of space group *P2₁/n* (No. 14) (**Scheme 1; Figure 1**). Molecules A and B adopt similar conformations

and molecular similarities are demonstrated by their root mean square (rms) bond and angle deviations of 0.007 Å and 0.47° (Mercury = 0.10 Å) [25]. In the ferrocenyl moiety the C₅ rings are almost eclipsed as noted by the five HC...CH torsion angles. Pairs of molecules aggregate in a hydrogen bonded cyclic arrangement by face-to-face C₆...C₆ stacked rings and C-H...π(C₅H₄) interactions. The amide conformation is shown by ϕ C-C-N-C=O torsion angles of -80.9(3)° in (A) and 79.0(3)° in (B), as influenced by the C_{2A/B} hinge, whereas the C₅H₄/C₆ interplanar angles are 73.16(11)° and 79.12(11)° (**Table 2**). Molecular differences are exemplified by the cross-molecule Fe1_{A/B}...C34_{A/B} distances of 9.207(3) Å and 9.147(3) Å for A and B, respectively, differing by 0.06 Å. The packing index (KPI) = 71.3 [25].

The asymmetric unit in **4a** comprises A and B molecules in a cyclic arrangement, linked by two phenylC-H...π(C₅H₄) interactions and oriented with their NHCOC₆H₅ groups parallel as a face-to-face C₆...C₆ pair (**Figure 1b**). Geometric data reveal the C-H...C₅(centroid) as C34A-H34A...Cg4ⁱ [2.78 Å, 156°, 3.663(3) Å] and C34B-H34B...Cg1ⁱ [2.84 Å, 158°, 3.744(4) Å]; the C₆...C₅H₄ interplanar angles are 78.19(11)° and 74.12(11)°. For the NHCOC₆H₅...C₆H₅CONH stacked pair, the shortest contacts are C31A...C33B = 3.401(4) Å and C31B...C33A = 3.411(4) Å, with an interplanar angle of 2.93(17)°; the C₆...C₆ centroid distance = 3.8141(18) Å [25]. The A/B molecular C₅H₅ interplanar angle within the asymmetric unit is 5.60(10)°.

4a exhibits a wide range of intermolecular interactions comprising 1D intermolecular amide...amide chains, Fc(C-H)...C₆ ring, C-H...π(C₅H₄) interactions, (1:1) face-to-face (phenyl)ring...ring and (C₅H₅)ring...ring pairs, where [Fc = (η⁵-C₅H₅)Fe(η⁵-C₅H₄)]. These interactions are noted including those in the A, B intricate molecular pair. The 1D amide...amide interactions form (A...A...)_n and (B...B...)_n chains along the *b*-axis direction with hydrogen bonding distances N1A...O1Aⁱ = 2.924(3) Å and N1B...O1Bⁱⁱ = 2.869(3) Å (symmetry operations *i*, *ii*; ESI, **Table S02**). The amide...amide interaction between molecules of A is augmented by a C₅H₄ ring oriented side on and interacting with a symmetry related (C31A,...,C36A)ⁱ phenyl ring as C12A-H12A...π(Cg3)ⁱ; [2.73 Å, 163°, 3.652(3) Å]. The asymmetric Fc-H...C₆ interaction in molecule A differs from that in B, where two FcC-H...C₆ rather than a single C-H...Cg manifest in side-on 2 × (C₅-H)...C₆ contacts. The associated data are C15B-H15B...C31Bⁱⁱ [2.83 Å; 159°; 3.730(4) Å] and C25B-H25B...C34Bⁱⁱ [2.84 Å; 156°; 3.730(5) Å].



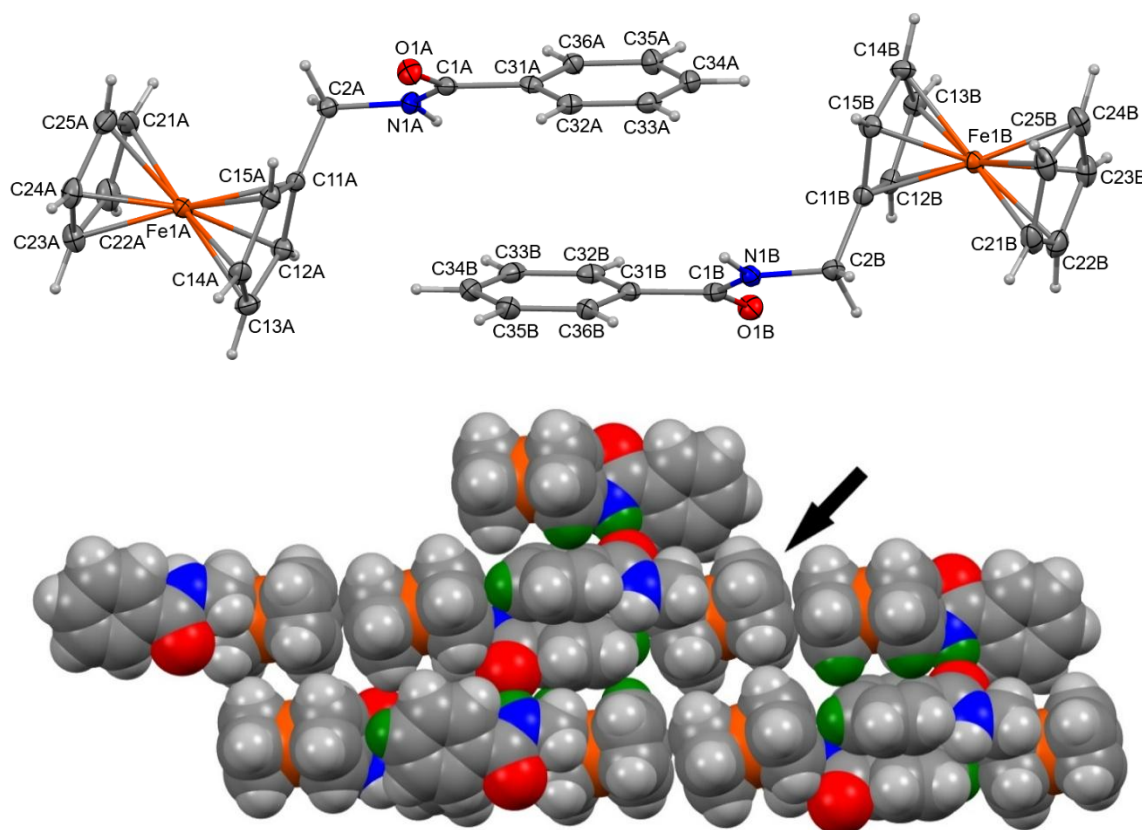


Figure 1. ORTEP diagrams of molecules A and B (top), together with the asymmetric unit (centre) in **4a**. A view of the areneC-H $\cdots\pi$ (cp) and cpC-H $\cdots$ (arene) interactions with the principal interacting H atoms coloured in green (bottom). The arrow highlights both the Fc $\cdots$ Fc stacking and Fc(C-H) $\cdots$ C₆ ring interactions.

Both 1D undulating molecular chains (and interlinked by $\text{phenylC-H}\cdots\pi(\text{C}_5\text{H}_4)$ interactions and (1:1) C₆ $\cdots$ C₆ stacked pairs) generate a 1D column aligned along the *b*-axis and $\frac{1}{2} \times c$ cell length wide. Columns, comprising the (A $\cdots$)_n and (B $\cdots$)_n chains, are linked by face-to-face C₅H₅ $\cdots$ C₅H₅ ring overlaps and paired into slightly ruffled sheets parallel to (2 0 -5). The cpC $\cdots$ C_{cp} contact separations are rather short i.e., C23A $\cdots$ C24B^{xv} = 3.303(5) Å. The C₅H₅ $\cdots$ C₅H₅ interplanar angle is 8.15(19)°, and rings are moderately offset with a C₅H₅ ring centroid with Cg $\cdots$ Cg distance = 3.857(2) Å. This is depicted by face-to-face C₅H₅ $\cdots$ C₅H₅ and C-H $\cdots\pi$ weak H-bonds (**Figure 1c**). Sheets are linked by the remaining face-to-face C₅H₄ $\cdots$ C₅H₄ contacts. In addition, ferrocene moieties interlock (using their C-Hs) and this is particularly notable for molecule A where the cp rings and Fc(C-H) form a dual ‘cog-like’ intermolecular aggregation.

The rmsd of molecular overlap between **4a** (molecule B or inverted A) and the REYWOU (**4d**) structure (*N*-(ferrocenylmethyl)-*para*-fluorobenzene carboxamide) is 0.3 Å [14]. Differences are primarily due to the orientation of the unsubstituted η^5 -C₅H₅ cyclopentadienyl ring. As such REYWOU will therefore be discussed primarily in terms of molecular interactions [14].

***N*-(Ferrocenylmethyl)-4-fluorobenzenecarboxamide [REYWOU; 10], **4d** [14]**

The molecular structure of **4d** has been described [14] (**Figure 2**) and salient features of the crystal structure are only provided herein for comparisons with **4a**, **4e**, **4f** and **5**. It is noted that **4d** has a similar conformation to **4a** with cpC-C-N-C=O torsion angle of 89.6(3)° as influenced by the C2_{A/B} hinge; the C₅H₄/C₆ interplanar angle = 77.80(8)°. Amide $\cdots$ amide interactions dominate with molecules aligning in the *a*-axis direction (N1 $\cdots$ O1^{xvi} = 2.972(2) Å). This H-bond is bifurcated, being augmented by *ortho*-C32-H32 $\cdots$ O1^{xvi} contacts (d_{co} = 3.485(3) Å), generating 1D chains incorporating *R*₁²(7) hydrogen bonded rings (symmetry operations as noted in **Table S02**, ESI). This type of H-bond aggregation is frequently observed in benzamide structures and 1D chains aggregate through a combination of intermolecular contacts [9].

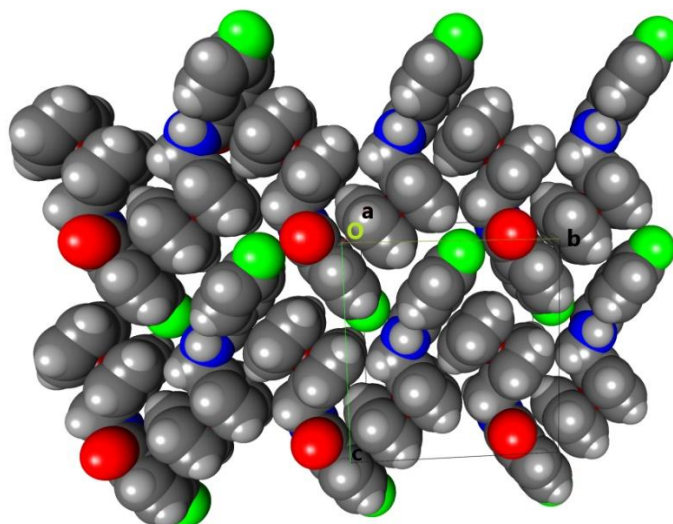


Figure 2. Crystallographic autostereogram of an array of interactions in the (100) plane in **4d** [REYWOU] [14] showing a relay of $[\text{Fe}(\underline{\text{C}}_5\text{-H})\cdots\pi(\text{C}_5\text{H}_4)\text{Fe}(\underline{\text{C}}_5\text{-H})\cdots\pi(\text{C}_5\text{H}_4)\cdots]_n$ contacts. The $\underline{\text{C}}_5$ as indicated highlights the capped (stacked) nature of the (1:1) $\text{C}_5:\text{C}_6$ (face-to-face) ring overlap.

Molecules pack along the *b*-axis [010] direction via an extensive combination of face-to-face $\text{C}_5\text{H}_5\cdots\text{C}_6$ stacked pairs [interplanar angle = $8.45(13)^\circ$], relays of $\text{C}_5\text{-H}\cdots\pi(\text{C}_5\text{H}_4)$ interactions [$\text{C}21\text{-H}21\cdots\text{Cg}1^{xvii}$; 2.75 Å, 176° , 3.680(3) Å] and $\text{HC-H}\cdots\text{C}_5\text{H}_4$ contacts [$\text{H}2\text{B}\cdots\text{C}13^{xvii}$ = 2.79 Å] (**Figure 2**). Weak intermolecular contacts as $\text{F}34\cdots\text{C}1\text{-N}1^{xviii}$ = 3.185(2) Å, with an angle for $\text{C}34\text{-F}34\cdots\text{C}1^{xviii}$ = $134.46(15)^\circ$ augment the interactions. In summary, key interactions involve amide $\cdots$ amide/ $\text{C}32\text{-H}32\cdots\text{O}1^{xvi}$ pairing along [100] and the interaction rich combination of (1:1) stacking and contacts along [010]. The zig-zag relay of $[\text{Fc}(\underline{\text{C}}_5\text{-H})\cdots\pi(\text{C}_5\text{H}_4)\text{Fe}(\underline{\text{C}}_5\text{-H})\cdots]_n$ contacts, with the C_5H_5 capped by a (1:1) stack with the C_6 ring, is notable and can also be denoted simply by $(\text{Fc-H}\cdots\text{Fc-H}\cdots)_n$ (**Figure 2**).

N*-(Ferrocenylmethyl)-2,6-difluorobenzenecarboxamide or **4e*

In the structure of **4e** (**Figure 3**) intermolecular amide $\cdots$ amide hydrogen bonding generate 1D chains along the *a*-axis direction with $\text{N}1\text{-H}1\cdots\text{O}1^{iii}$ data as 2.00(3) Å, $156(2)^\circ$, 2.819(2) Å ($iii = \frac{1}{2}+x, \frac{1}{2}-y, z$; **ESI, Table S02**). The interactions arise in tandem with alkyl $\text{C}2\text{-H}2\text{A}\cdots(\text{C}36\text{-F}36)^{iii}$ interactions [for $\text{C}36$; data are 2.72 Å, 164° , 3.679(2) Å; **ESI, Figure S04**]. The 1D chains are linked by intermolecular $\text{C}35\text{-H}35\cdots\text{O}1^{iv}$ interactions [2.44 Å, 150° , 3.295(3) Å] ($iv = \frac{1}{2}-x, -\frac{1}{2}+y, 1-z$), with the formation of the ($\text{C}31, \dots, \text{C}36$) sandwich about inversion centres, with $\text{Cg}3\cdots\text{Cg}3^{xix}$ = 3.5765(12) Å; $\text{Cg}3\cdots\text{C}6^{xix}$ = 3.3773(9) Å, ($xix = 1-x, -y, 1-z$; **ESI, Table S02**).

The *ortho*-fluorine F32 and F36 atoms do not partake directly in significant intermolecular interactions. However, F36 is positioned at 2.81 Å from H2A (0.15 Å longer than the sum of the van der Waals radii 1.20+1.47 Å) [25]. The $\text{C}2\text{-H}2\text{A}\cdots\text{F}36^{iii}$ angle = 139° and assisting the $\text{C}2\text{-H}2\text{A}\cdots\text{C}36^{iii}$ contact. Of interest is that the unsubstituted C_5H_5 ring does not form any face-to-face stacks with either of the C_5 or C_6 rings. On the other hand, there are two phenyl $\text{C-H}\cdots\pi$ interactions on one side of the C_5H_5 . It can be stated that heterocycles are more likely to be involved in parallel stacking than carbocyclic rings [27,28]. Not surprisingly, the $\text{C}_6\text{H}_3\text{F}_2$ rings form face-to-face pairs about inversion centres and the closest $\text{C}\cdots\text{C}$ contact is $\text{C}34\cdots\text{C}36^{xix}$ = 3.410(3) Å and the centroid $\text{Cg}3\cdots\text{Cg}3^{xix}$ distance is 3.5765(12) Å.

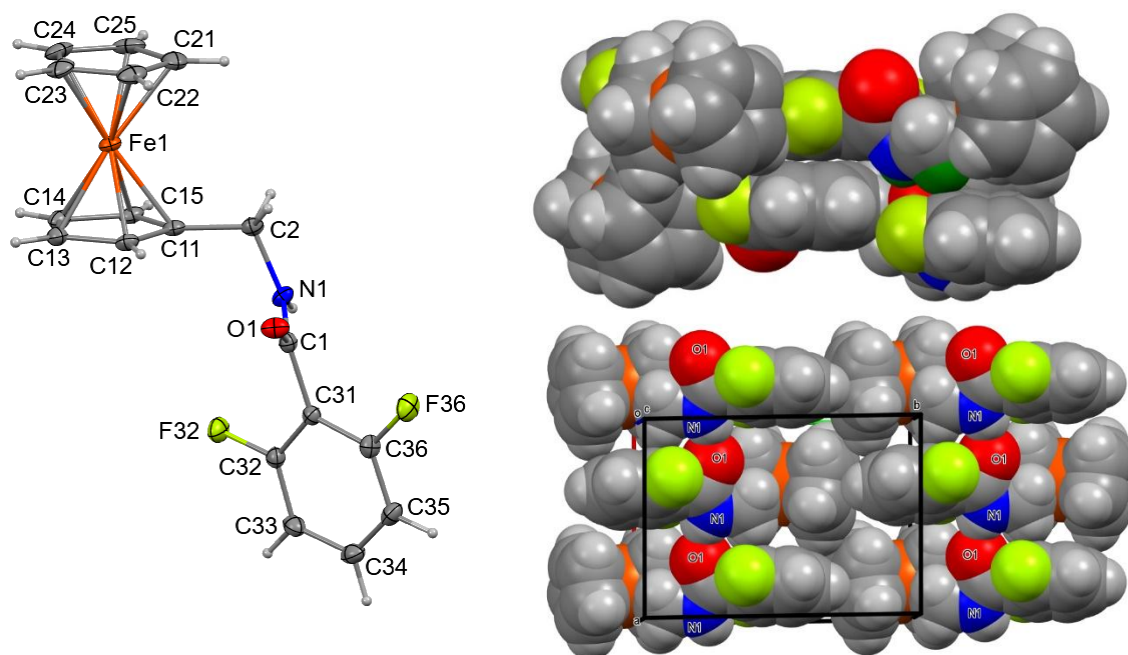
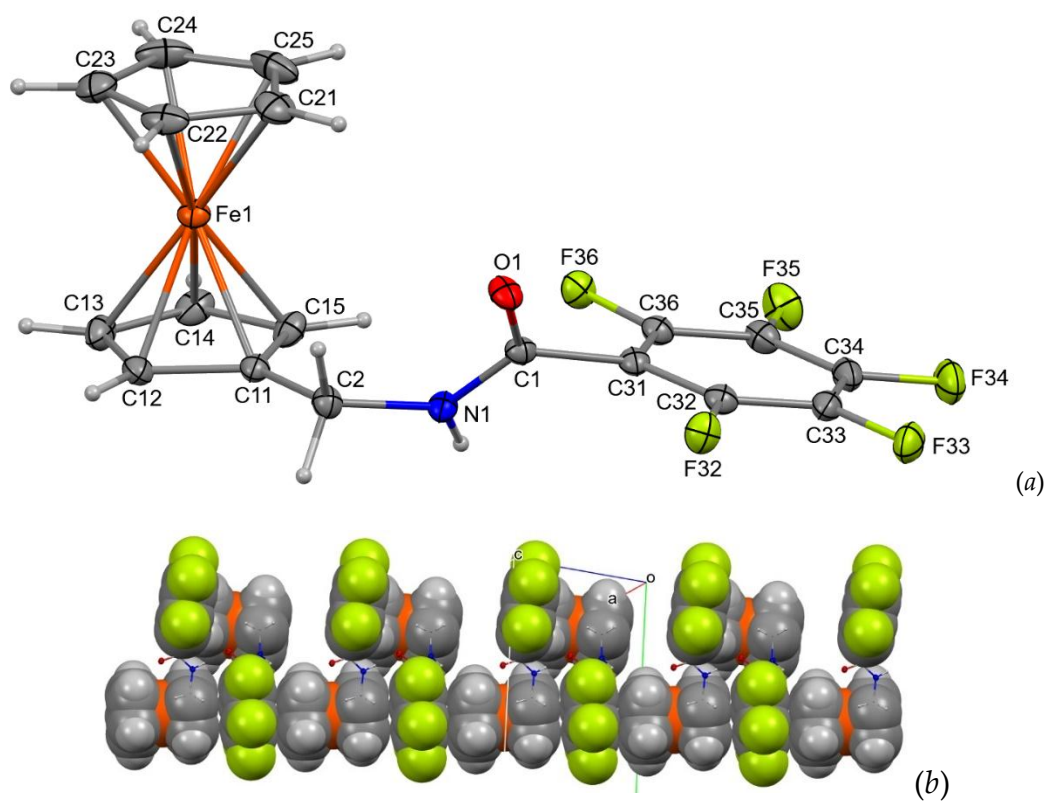


Figure 3. ORTEP diagrams of **4e** with displacement ellipsoids at the 30% probability level. A view of the face-to-face ring...ring stacked pair with tandem amide...amide and C-H...C interactions (interacting H atoms coloured in **dark green**). A general CPK view of the amide...amide (N1...O1) chain and crystal packing.



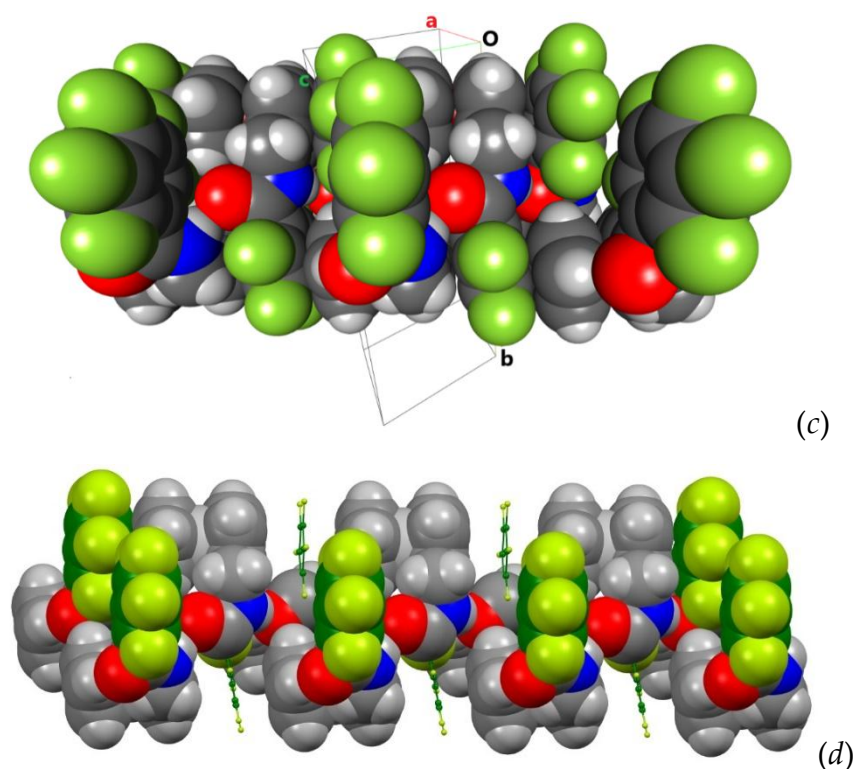


Figure 4. *a)* ORTEP diagram of **4f** with displacement ellipsoids at the 30% probability level. Three CPK packing diagrams of the $(\text{Fc}\cdots\text{C}_6\text{F}_5\cdots)_n$ 1D stacking along the $a+c$ direction (*b*) as a chain with amides (ball and stick) and the space where Fc moieties occupy, (*c*) an autostereogram of the stacking and (*d*) a view of the C_6F_5 groups in green and five C_6F_5 groups depicted as ball and stick.

Impressive, intricate stacking in N-(Ferrocenylmethyl)pentafluorobenzenecarboxamide

The pentafluorobenzene derivative (**4f**) exhibits an array of intermolecular interactions that incorporate $\text{N-H}\cdots\text{O}=\text{C}$ hydrogen bonding as 1D chains in the c -axis direction in tandem with local (1:1) $\text{C}_5\text{H}_4\cdots\text{C}_6\text{F}_5$ ring overlay between the substituted C_5H_4 and C_6F_5 rings. Chains crosslink forming sheets via $\text{C-H}\cdots\text{O}/\text{F}$ contacts and tight $\text{C}_5\text{H}_5\cdots\text{C}_6\text{F}_5$ ring stacking on the opposite side of the C_6F_5 ring. Sheets aggregate by $\text{C-H}\cdots\text{F}$ contacts and sheet formation involves all three carbocyclic rings (as $2 \times \text{C}_5$; C_6). The ferrocenyl (Fc) moiety is effectively sandwiched by C_6F_5 rings forming a 1D stack. Four $\text{C-H}\cdots\text{F}$ interactions per **4f** molecule involve three of the C_6F_5 fluorine atoms as F32, F35 and F36, (symmetry codes vi to ix) with shortest $\text{C-H}\cdots\text{F-C}$ contact being $\text{C13-H13}\cdots\text{F35}^{vi} = 2.55 \text{ \AA}$ for $\text{H}\cdots\text{F}$ (angle = 133°).

Overall, the impressive feature of the **4f** crystal packing is the intricate $(\text{ferrocene}\cdots\text{C}_6\text{F}_5\cdots)_n$ alternating (Fc group) $\cdots$ ring overlap, where the Fc group and C_6F_5 ring alternate as $(1:1)_n$ pairing in 1D columns that lie parallel to the $(-1\ 0\ 1)$ plane (ESI, Figures S05-S08). Each **4f** molecule contributes the ferrocenyl and C_6F_5 to two distinct 1D columns that are reinforced by crosslinking amide $\cdots$ amide interactions (alternate explanation as above), (ESI, Figure S06). At a local level the $\text{C}_6\text{F}_5\text{CONH-}$ moiety can be analysed further. Each amide $\cdots$ amide interaction facilitates formation of a compact, localised (1:1) face-to-face $\text{C}_5\text{H}_4\cdots\text{C}_6\text{F}_5$ ring stacking (per amide $\cdots$ amide link). Therefore, the $\text{C}_5\text{H}_4\cdots\text{C}_6\text{F}_5$ ring overlap as a (1:1) stacked pair arises in tandem with each amide $\cdots$ amide interaction as it propagates in the c -axis direction. The crystal structure aggregation is enhanced as the remaining C_5H_5 ring (in each **4f** molecule) is critical in the formation of sheets with 1D columns of $(\text{Fc}\cdots\text{C}_6\text{F}_5\cdots)_n$ ring stacking. Overall the $(\text{Fc}\cdots\text{C}_6\text{F}_5\cdots)_n$ ring stacking is both elegant and efficient, where the Fc group is sandwiched between two C_6F_5 rings of **4f** molecules from different 1D chains. Diagrams are used to highlight and show how it manifests in the **4f** crystal structure (ESI, Figures S04-S07).

Table 3 highlights details of **4f** and stacking distances $\text{Cg1}\cdots\text{Cg3}^v = 3.5720(12) \text{ \AA}$ between the C_5H_4 (Cg1 centroid) and C_6F_5 rings (Cg3 centroid). The tighter $\text{Cg2}\cdots\text{Cg3}^{xx}$ is $3.5399(13) \text{ \AA}$ ($\text{Cg2} = \text{C}_5\text{H}_5$),

where C_g represents the ring centroids. The perpendicular centroid...ring distances are 3.2530(10) Å and 3.3133(8) Å, with three C...C distances < 3.40 Å [and the shortest is C25...C32^{xx} = 3.319(3) Å]. The C₅ and C₆ ring interplanar angle is 10.05(12)°. For comparison with **4f** and of particular note is the **SUFLIR** crystal structure of a (1:1) co-crystal of ferrocene:C₆F₆ [5,10] and with thirteen datasets collected over a temperature range (from 100 K to 304 K). In **Table 3**, comparisons are made between **SUFLIR** at 100 K (KPI = 72.4 [25]) and the present study of **4f** (at 150 K).

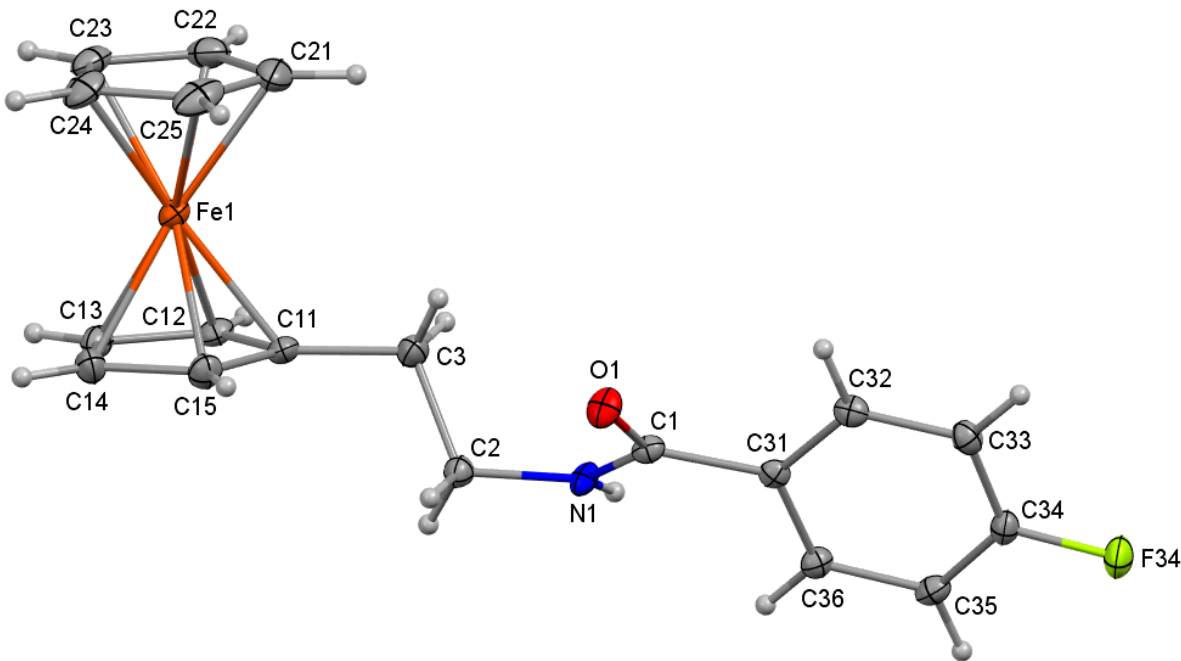
Table 3. Comparative analysis of the Fc...C₆ stacking in **SUFLIR** [5] and **4f** (present work) [25].

Geometric data	SUFLIR (100 K) [5] (Å, °)	4f (Å, °)
Fe...C ₅ (centroid); (Å, °) ^a	1.6467(8), 1.6479(8); 179.53(4)	1.6482(9), 1.6530(10); 178.75(6)
C ₅ ...C ₆ F ₆ [5] or C ₅ ...C ₆ F ₅ ^b	3.5825(10); 3.6052(11)	3.5399(13); 3.5720(12)
Dihedral angle (planes)° ^c	7.67(9); 8.86(9) ^d	2.76(12); 2.88(10)
C-F...C ₅ ring centroid (Å)	3.5949(13); 3.6210(14)	3.5179(16); 3.6620(15)
C-F...C ₅ ring centroid (Å)	3.3342(18); 3.3370(18)	3.257(2); 3.377(2)
C-F...C ₅ (°)	68.05(8); 67.13(8)	67.79(10); 67.22(9)
Shortest stack _{cp} C...C _{arene}	3.310(2), 3.337(2), 3.340(2)	3.319(3), 3.327(3), 3.387(3)
Shortest stack _{cp} H...F-C	3.089, 3.167, 3.176, 3.226	3.21, 3.29, 3.29, 3.35

^a Ferrocene C₅ ring geometric data (distances in Å; angle °). ^b Defined as centroid...centroid (C_g) distances (Å) for the C₅ or C₆ rings. ^c Dihedral angle between the Fc C₅ ring and C₅...C₆F₆ [5] or C₅...C₆F₅ ^{present work} ring planes [25]. ^d As 7.8° and 9.1° using Mercury [5,24].

Structural differences between **SUFLIR** and **4f** (as noted in **Table 3**) are relatively small [25]. Distances between stacked rings (from the centroid...centroid for C₅, C₆F₆) are 0.03–0.04 Å shorter in **4f**, while the interplanar (dihedral) angles are closer to co-planarity and differing by 5–6° from **SUFLIR** [5]. The reason for the differences may be more steric than electronic, and influenced by the carboxamide...carboxamide hydrogen bonding in **4f** and short contacts involving the methylene CH₂ group H2B hydrogen atom. The C-F...C₅ geometric data are more symmetrical in **SUFLIR** [5], but with shorter contact distances in **4f**. However, the _{cp}C-H...F-C distances are shorter in **SUFLIR** (by 0.05–0.10 Å) for their three shortest H...F contacts and this may be influenced to an extent by differences in data collection temperatures (100 *vs* 150 K).

In the stacking behaviour of **SUFLIR** [5] and **4f**, it is important to consider factors that influence their packing. Benzene (-33.3 ± 2.1) [29] and Ferrocene (-30 ± 7) [30] have large negative molecular quadrupole moments (QM), expressed in 10⁻⁴⁰ C m². This contrasts with hexafluorobenzene (C₆F₆) which has a moment of similar magnitude, but with a positive value as determined experimentally as +31.7 (± 1.7) × 10⁻⁴⁰ C m² [29]. Therefore, it can be evaluated that the quadrupole moments for the Fc-C and C-C₆F₅ moieties are relatively similar in magnitude, but opposite in sign. A guideline estimate of quadrupole moments are ca. -20 and +20 × 10⁻⁴⁰ C m⁻² for the Fc-C and C-C₆F₅, respectively [29–31]. Hence the observation for **4f** that favourable ring stacking occurs with conformational change and in tandem with amide...amide directed hydrogen bonding in the crystal state. In **4f**, the methylene -CH₂- spacer group facilitates conformational change and the ability to form interweaved 1D stacked columns using the ferrocenyl moiety (Fc) and the pentafluorobenzene C₆F₅ rings.



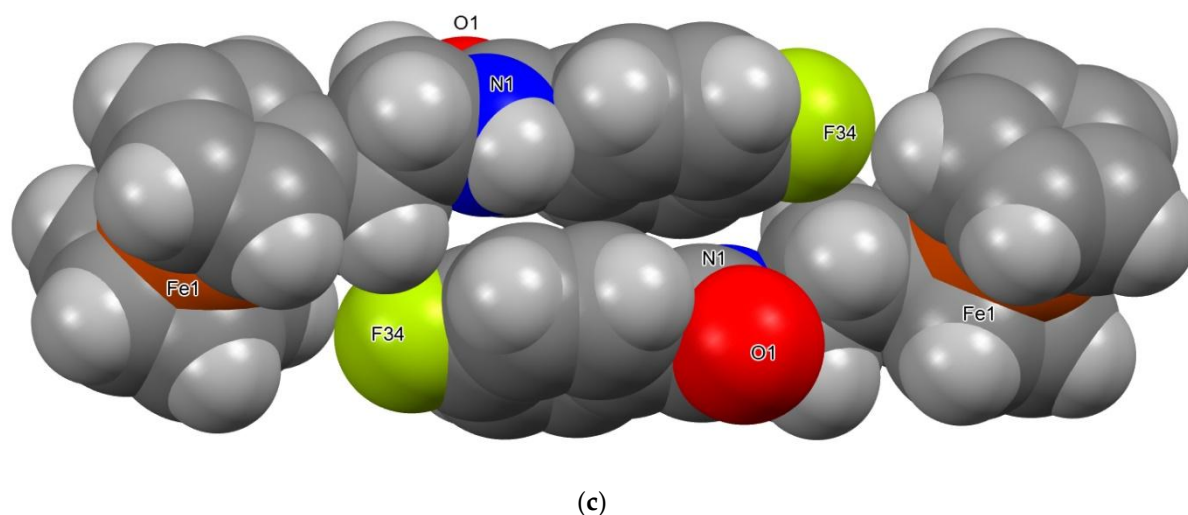


Figure 5. (a) ORTEP diagram of the molecular structure of **5** with displacement ellipsoids at the 30% probability level. **5** differs from **4d** [REYWOU] by an extra $-\text{CH}_2-$ group. (b) An ORTEP diagram of **5** showing the amide...amide 1D chains along the b -axis direction. (c) Two identical views (ORTEP, CPK) of a molecular pair of **5** highlighting the arene ring...ring stacking and C-H...F hydrogen bonding interactions.

***N*-(Ferrocenylethyl)-4-fluorobenzene-carboxamide or 5.**

The molecular conformation of **5** (with an ethylene $-\text{CH}_2\text{CH}_2-$ bridge as compared to the methylene $-\text{CH}_2-$ bridge for the **4x** series) is broadly similar to the pentafluorobenzene derivative **4f**. Having the additional $-\text{CH}_2-$ spacer group provides extra molecular flexibility. In terms of molecular conformation, the C11-C3-C2-N1 torsion angle is $176.19(19)^\circ$ and C3-C2-N1-C1 is $81.0(3)^\circ$. The ferrocenyl C_5 rings are effectively eclipsed and with all five $\text{H-C}\cdots(\text{C})\text{H} < 0.3^\circ$, whereas in **4f** the C_5 rings deviate from being fully eclipsed by $\sim 18^\circ$.

Amide...amide interactions dominate as $\text{N1-H1}\cdots\text{O1}^x$ forming 1D chains along the b -axis direction. These chains are linked about inversion centres by $\text{C21-H21}\cdots\text{F34}^{xii}$ contacts (ESI; Table S02). The F34 atom also engages in a weak contact as $\text{C25-H25}\cdots\text{F34}^{xi} = 3.554(3) \text{ \AA}$ (Table S02); with two $\text{C-H}\cdots\text{F34}$ forming a bifurcated hydrogen bonding system. In addition, compact ring...ring pairing about inversion centres involves the aromatic C_6 groups and with shortest $\text{C31}\cdots\text{C32}^{xii}$ contact distance of $3.451(3) \text{ \AA}$. In addition, weak $\text{C-H}\cdots\pi(\text{arene})$ contacts form as $\text{C36-H36}\cdots\text{C32}^x$ ($\text{H36}\cdots\text{C32}^x = 2.82 \text{ \AA}$; $\text{C36-H36}\cdots\text{C32}^x = 173^\circ$) with $\text{C33-H33}\cdots\text{O1}^{xiii}$ interactions. Of further structural interest is that ferrocene carboxamide structures containing an ethylene ($-\text{CH}_2\text{-CH}_2-$) group or even just a two carbon atom chain as a linker group are relatively rare in the CSD [10].

2.4. Hirshfeld Surface Analysis: Contacts Enrichment Analyses of Five Structures (4a, 4d-f and 5)

MoProViewer software [27] was used to investigate the intermolecular interactions and the contacts enrichment on the Hirshfeld surfaces of the five molecules (**4a**, **4d-f** and **5**) in their crystal packings [26]. The enrichment values (E_{XY}) were obtained as the ratio between the proportions of actual contacts (C_{XY}) and equiprobable (random) contacts (R_{XY}), the latter being obtained via probability products ($R_{XY} = S_X \times S_Y$), where S_X is the surface content in chemical species X. Contacts $X\cdots Y$, which are over-represented with respect to the share of X and Y chemical species on the Hirshfeld surface, have enrichments larger than unity. The chemical nature of the contacts and their enrichment data values in the crystal structures are listed in the ESI (Table S03).

In all five crystal packings, the strong $\text{N-H}\cdots\text{O}=\text{C}$ hydrogen bond between amide groups has extremely high enrichment ratios $E_{\text{O,Hn}}$ greater than 14.8, as it constitutes by far the most attractive electrostatic interaction (ESI, Table S03). The fingerprint plots (ESI, Figure S10) display all two spikes at short distance corresponding to this $\text{N-H}\cdots\text{O}=\text{C}$ hydrogen bond. The hydrophilic content (O and Hn) on the surface is always below 7%. As a consequence of the high hydrophobic content in Hc and C atoms, the most abundant contacts in all cases (except in the fluorine rich **4f**) are $\text{C}\cdots\text{Hc}$

followed by Hc...Hc hydrophobic contacts. All of the fingerprint plots show abundant C...H and H...H contacts (ESI, Figure S10). The next most abundant contacts in the crystal structures of **4a**, **4d**, **4e** and **5** are the C...C and the F...Hc weak hydrogen bonds in **4d**, **4e** and **5**. The H...F contacts show spikes within the fingerprint clouds at the shortest distances of $d_i = 1.2/d_e = 1.4$ Å. In all structures, with the exception of the penta-fluorobenzene derivative **4f**, the enrichments of the hydrophobic contacts C...C, Hc...Hc and C...Hc do not deviate much from the unitary ratios (in the range $0.83 < E < 1.23$).

The penta-fluorinated compound **4f** is peculiar in that the C...C contacts are significantly enriched (with $E_{CC} = 2.2$) due to the (Fc...C₆F₅...) _n 1D ring...ring stacking. The C^δ-H^{δ+} and C^{δ+}-F^{δ-} groups in the two carbocyclic rings form attractive electrostatic interactions. The fluorine content on the surface is 23.9% and with an enrichment value of 1.54. Therefore, the F...Hc weak hydrogen bonds turn out to be the most abundant contact type in the penta-fluorinated **4f** crystal structure. The F...F contact in **4f** is 3.9% whereas all four other structures **4a**, **4d**, **4e**, **5** which contain less fluorine atoms have this value at 0. On the other hand, the C...Hc weak hydrogen bonds are quite under-represented in **4f** ($E = 0.49$), presumably due to competition of the slightly stronger F...Hc interactions. The fingerprint plots for **4f** are depicted in Figure 6 and can be compared with the other four crystal structures (ESI; Figure S10).

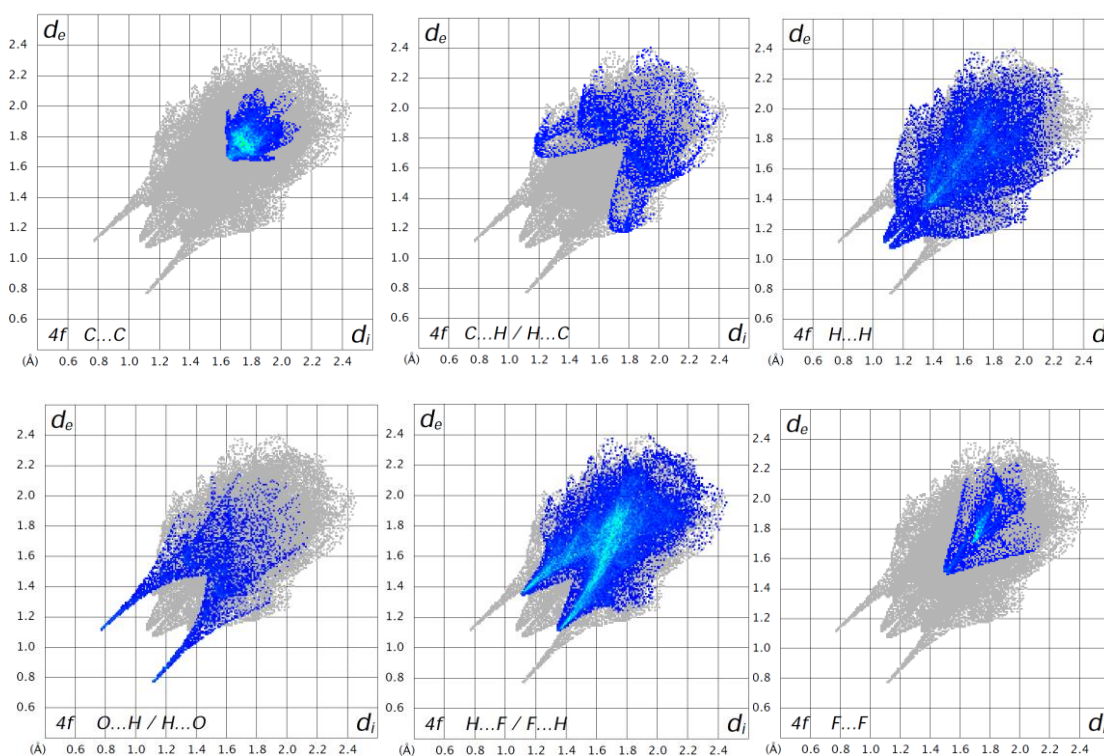


Figure 6. Fingerprint plots of the main contacts on the Hirshfeld surface of **4f** [26].

2.7. Comparisons with Ferrocene Derivatives That Exhibit Distinct Aggregation and Packing

Analysis of the Cambridge Structural Database was performed (with ca. 400 structures retrieved in a search as Fc_C₆F₁) for structures similar to **4f** and C₆F₆•FcCp₂ (SUFLIR) [5]. The search demonstrates that the vast majority of ferrocene derivatives incorporating at least one aromatic fluorine (as C₆F) **do not** stack in extended columns, but rather are 'capped' in a variety of ways by either C-H... π (arene), C-F... π (cp) contacts or (1:1) face to face pairing of aromatic rings [10]. As such, there are several notable examples of a diverse range of packing involving ferrocene groups either on their own or in combination with other rings. Such examples include GEHNAJ (ferrocene•decafluorobiphenyl) [6], LUZJIB (ferrocene• decafluorophenanthrene) [32], SUFLIR01-09 (ferrocene•hexafluorobenzene) [5,10].

The crystal structure of **UNEWES** reveals slight undulating 1D chains incorporating alternating ferrocenyl $\text{Fc}\cdots\text{C}_6\text{FH}_4$ pairs sandwiched and linked between $\text{C-H}\cdots\pi(\text{cp})$ interactions (**ESI, Figure S09**) [33]. At the other extreme, in the crystal structure of **UYIHER** or 3-ferrocenyl-1-(4-fluorophenyl)-5-methyl-1H-pyrazole, zigzag chains of ferrocenyl moieties are linked solely by $\text{C-H}\cdots\pi(\text{cp})$ interactions [34]. In **ADIQAF** or *rac*-1,1'-bis(pentafluorophenyl)-3,3'-di-*t*-butylferrocene the pentafluorobenzene ring forms a 1D column [35], whereas in **LUZJIB**, the decafluorophenanthrene (**X**) forms stacks as $(\text{Fc}\cdots\text{X}\cdots\text{X}\cdots)_n$ [32]. Another structural example is the **FANNUE(01)** (**ESI, Figure S09**) where the ferrocene stacks and interacts with a hexakis(μ -2,3,4,5,6-tetrafluorobenzene-1,2-diyl) Hg_6 (**L**) complex such that the structure consists of $(\text{L}\cdots\text{ferrocene}\cdots\text{L}\cdots)_n$ stacking [36]. In **QAPYAI** [37] the Fc moiety and a pyrrotriazole ring form a stack along the *b*-axis direction and this aggregation arrangement is reminiscent of the **4f** crystal structure.

A related search of the CSD [10] was undertaken specifically for ferrocene centroid... C_6 ring centroid distances that are < 3.60 Å, with C_5/C_6 interplanar angles $< 15^\circ$ (arbitrary values) and with optional fluorine atoms. This CSD search reveals several structures including **MANRIC**, **SAMTEH**, **APUJIH**, **QIGRUW** and **VIBSEF** [10,38]. The vast majority of these structures exhibit a short range stack (depending on the structures and symmetry) and are usually capped at either end by $\text{C-H}\cdots\pi(\text{arene})$ contacts, and thereby preventing 1D stack formation. In the 1D stack of **MANRIC**, the unsubstituted C_5 and C_6 ring [$\text{C}14,\dots,\text{C}19$] centroids are separated by $3.457(2)$ Å with an interplanar angle of $4.22(18)^\circ$, arising in a centrosymmetric stacked dimer that stacks with symmetry related dimers [38]. Dimers link into 1D chains by overlapping rings with interplanar distances of $3.4154(8)$ Å. Much research is on-going and as this is not a review, a more detailed and extensive analysis will be published at a future date. Of additional note is that Horie and co-workers have studied ferrocene ring rotation in interlocked molecules in single crystals [39].

Competition between hydrogen and halogen bonding in intermolecular interactions continues to attract much attention so as to aid in our understanding of intermolecular interactions and aggregation in molecular crystals [40–45]. In this present structural study we show the roles that ferrocenyl moieties and fluorinated benzene rings play in aggregation and stacking [5,10]. Several recent publications have compared series of related structures in terms of the effects of the different types of interactions that can arise with substitution pattern [41–45]. Understanding the competition between intermolecular processes in structures and the profound effects that they can have in aggregation and packing where compounds differ as isomers, or by one atom substitution has been explored in halogenated benzamides [42], carboxamides [43], isophthalamides [44] and Schiff bases [45]. The future of this structural research will expand with even more expansive studies (and resulting structural data) on how substitution patterns influence structure together with the range and types of competition between intermolecular interactions [10].

3. Conclusions and Future Work

In the five ferrocenyl carboxamide crystal structures (including **REYWOU 4d** [14]), the structural effects on the molecular geometry and conformations are assessed in structural packing, including the phenyl **4a**, *para*-fluorobenzene **4d**, 2,6-difluorobenzene **4e** and the penta-fluorobenzene derivatives **4f**. The competition between amide...amide hydrogen bonding and various types of ring...ring stacking, as well as weaker interactions such as $\text{C-H}\cdots\text{O}$ and $\text{C-H}\cdots\pi(\text{arene})$ is analysed and comparisons are made [46,47].

In the series, stacking of C_6 rings of the mono- and di-fluorinated systems and ferrocenyl groups do not dominate in the crystal packing as they are in competition with stronger hydrogen bonding interactions. However, additional fluorine atoms on the aromatic ring promotes 1D ring stacking. The additional fluorine atoms on a benzene ring system push the molecular quadrupole from benzene as negative (–) towards that of the positive (+) hexafluorobenzene molecule [30,31]. This can induce a favourable stacking arrangement with ferrocenes or ferrocenyl moieties (with a negative molecular quadrupole). With the possibility of ferrocenes stacking relatively easily with penta-fluorobenzene based systems and with a favourable stacking conformation, it may be that there is a

strong possibility that trifluoro- or tetra-fluorobenzene derivatives (of whichever F atom substitution pattern) may be enough to influence and participate in stacking patterns such as the tight 1D stacking seen in **4f**.

We recognise that a rich and diverse range of pentafluoro-derived ferrocene systems is available and are examining if they can be further incorporated into various ferrocenyl moieties or alternatively through the formation of co-crystals with ferrocene [5,10,48]. The ability of trifluoro- and tetrafluorinated aromatic rings is currently being examined to study the structural diversity types and the tipping points towards capped or 1D stacked structures. This requires a large number of crystal structures which are closely related so that indepth comparisons can be made [10]. The present series represents a basis for the development of this general class of fluorinated ferrocenyl carboxamides [14]. Indeed there is vast research space for exploring combinations with other halogen atoms and mixed halogenated systems using chlorine, bromine and iodine.

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Supplementary Information: CCDC (Deposition Number **2409147–2409150**) contains the supplementary crystallographic data for this paper. The CIF data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk). The data are available as CIF files from the corresponding author Professor John F. Gallagher (Dublin City University).

Ethical Statement: All ethical guidelines in the experiments have been adhered to.

Declaration of competing interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the research work as reported in this scientific paper.

Credit authorship contribution statement: **John F Gallagher:** Design, Crystal structure analysis, data curation, writing and editing. **Christian Jelsch:** Contacts analysis, Hirshfeld analysis, writing and editing. **Peter TM Kenny[†]:** Concept and design, experimental review. **Alan J Lough:** Data collection and crystal structure analyses.

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