



Crystal packing principles for ferrocenyl groups linked by polyene chains: dimorphism of Fc-C₄-Fc

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Paper

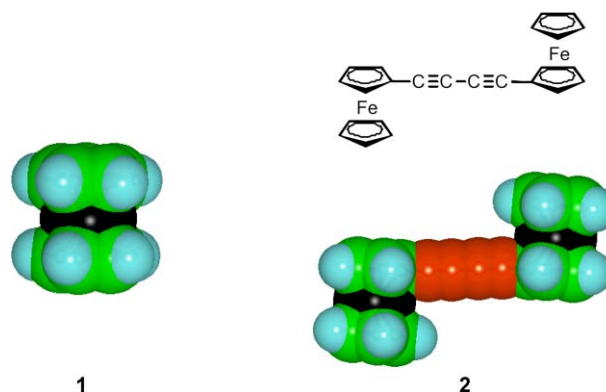
The crystal structure and packing of a new dimorph (**2B**) of 1,4-diferrocenyl-1,3-butadiyne (Fc-C₄-Fc, **2**) is described and analysed, and compared with the different crystal packing of dimorph **2A**. This analysis is made in the context of the polymorphic crystal packing of ferrocene (**1**), and the crystal packing of 1,8-diferrocenyl-octatetrayne, Fc-C₈-Fc. In **2B** the packing is layered, allowing the Fc groups to be organised in approximately square arrays of well-developed edge-to-face (EF) motifs, very similar to the arrangement in the monoclinic and triclinic polymorphs of ferrocene. The C₄ chains are sandwiched between the Fc layers in **2B**. The same molecule in **2A** is packed with some offset-face-to-face (OFF) motifs between Fc groups, and with a motif in which C₄ chains occupy the grooves between cyclopentadienyl rings of Fc. In FcC₈Fc the packing is dominated by the C₈ chains, surrounded by six molecules, two of which present cyclopentadienyl faces to the C₈ chain, and four present the groove in the ferrocenyl group, with no EF or OFF motifs. In this progression of structure types and intermolecular motifs for molecules Fc-C_n-Fc, the members with C₄ occur at the transition between the ferrocenyl dominant intermolecular motifs and the C_n chain dominant features. Dimorph **2A** is like the longer chain structure, while **2B** is like ferrocene.

Introduction

Two chemical functionalities often invoked in the design and development of devices and materials are the ferrocenyl (Fc) group, as a robust redox control unit and appendage, and the extended π -delocalised C_n chain as electronic conductor or connector.¹ In this paper we deal with molecules containing just these two functionalities, and their intermolecular interactions. Ferrocene (**1**) exhibits exemplary electron transfer activity, while the bare carbon chain is the minimal rigid linkage, with the smallest possible contribution to additional intermolecular interaction energy. We report a new crystal polymorph of 1,4-diferrocenyl-1,3-butadiyne (Fc-C₄-Fc, **2**), and analyse the crystal packing in the dimorphs. Further, using the known crystal polymorphism of ferrocene (**1**) and the crystal packing of Fc-C₄-Fc, we use the series Fc, Fc-C₄-Fc, Fc-C₈-Fc, to seek the relevant principles for the intermolecular interactions of Fc and C_n components.

The intramolecular and intermolecular stereochemistry of ferrocene (η^5 -C₅H₅)₂Fe and other metallocenes has been investigated on many occasions. There is intramolecular isomerism of the rotational conformation of the two cyclopentadienyl rings between extremes of staggered and eclipsed, and there is crystal packing isomerism (polymorphism) with different intermolecular interactions.^{2,3} The subtleties of the intramolecular isomerism have complicated crystallographic investigations.^{3,4} Overall, the crystallography of the metallocenes indicates that the energies of intramolecular variation are comparable with the intermolecular energies.

Ferrocene is an equidimensional molecule and, from the perspective of intermolecular interactions and crystal packing, is like a very thick aromatic group, with two aromatic faces and doubled edges, (see **1**), able to engage in the classic offset face-to-face (OFF) and edge-to-face (EF) intermolecular motifs characteristic of aromatic systems.⁵ An equatorial groove occurs between the two cyclopentadienyl rings.



There are two different reports of one crystal structure of **2**, occurring in the Cambridge Structural Database (CSD) as YATDAY⁶ (space group $P2_1/c$) and YATDAY01⁷ ($P2_1/a$). This crystal structure is labelled **2A**. Our discussion of **2A** will utilise the $P2_1/c$ setting (YATDAY). The second form of this compound, **2B**, crystallises in a different $P2_1/c$ cell. In the figures the butadiynyl chain will be coloured orange.

Crystallisation

Compound **2** was obtained as a side product in the reaction of ethynylferrocene and 4-bromo-1,2-dimethoxybenzene in triethylamine using bis(triphenylphosphine)palladium(II) dichloride and copper(I) iodide as catalysts. Crystals of **2B** were obtained by layered diffusion of methanol into a dichloromethane solution of **2**.

Crystal structure

Crystal data for **2B**: C₂₄H₁₈Fe₂, formula weight 418.1, monoclinic, space group $P2_1/c$, $a = 11.049(2)$, $b = 9.568(2)$,

$c = 8.767(2) \text{ \AA}$, $\beta = 102.35(1)^\circ$, $V = 905.4(3) \text{ \AA}^3$, $Z = 2$, $T = 294 \text{ K}$, $\mu = 1.605 \text{ mm}^{-1}$ (MoK α radiation, $\lambda = 0.7107 \text{ \AA}$). Least squares refinement based on 1328 observed reflections with $I > 2\sigma(I)$ converged with $R = 0.025$ and $R_w = 0.038$. CCDC reference number 213338. See <http://www.rsc.org/suppdata/ce/b3/b307082d/> for crystallographic data in CIF or other electronic format.

Crystal packing

The molecule **2** has the same centrosymmetric *trans* conformation of the ferrocenyl groups (which are virtually eclipsed) in both crystals **2A** and **2B**: the molecular dimensions in the two structures are indistinguishable. Along the C_4 chain the C–C distances alternate 1.20, 1.37, 1.20 Å in all three determinations, and are closer to butadiynyl bonding than polyene bonding.

In crystal **2B** the molecules are arranged in bilayers parallel to the *bc*-plane, with the butadiyne C_4 chains linking layers of ferrocenyl groups (see Fig. 1). The linear C_4 chains are inclined to this bilayer plane (angle 42.4° between the chain and the normal to the layer of ferrocenyl groups), which reduces the space between the two halves of the bilayer: note from Fig. 1a that the planes of Fc groups are closer between the bilayers than within the bilayer.

Within the Fc monolayers there is close packing of ferrocenyl groups, as shown in Fig. 2a. All intermolecular contacts within the monolayer are edge-to-face (EF) comprised of C–H \cdots C local contacts. These are double EF interactions, in which the

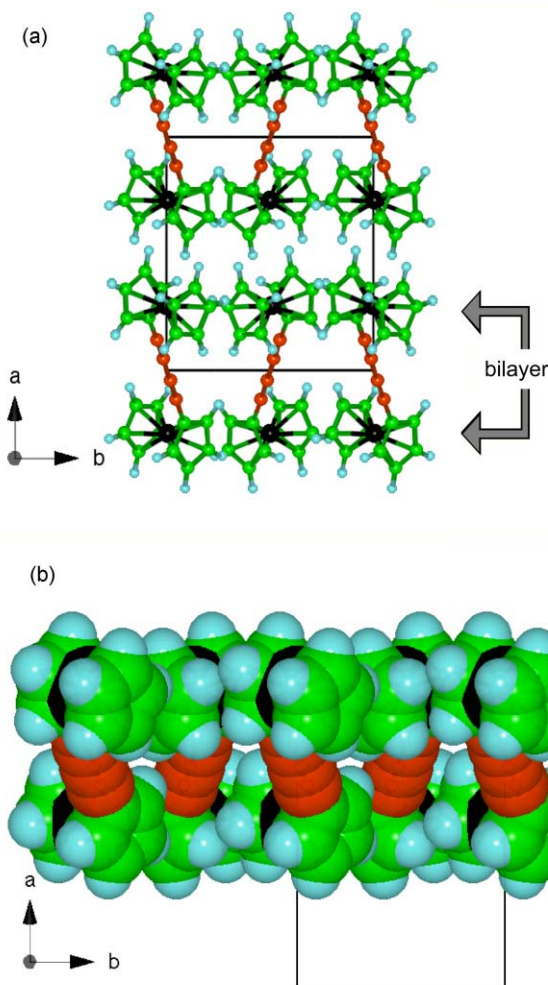


Fig. 1 The bilayered packing of **2** in crystals **2B**, space-group $P2_1/c$. The carbon atoms of the butadiynyl chain are coloured orange. (a) Two bilayers; (b) space-filling within one bilayer, achieved by inclination of the C_4 linkers. Click here to access a 3D image for Fig. 1a.

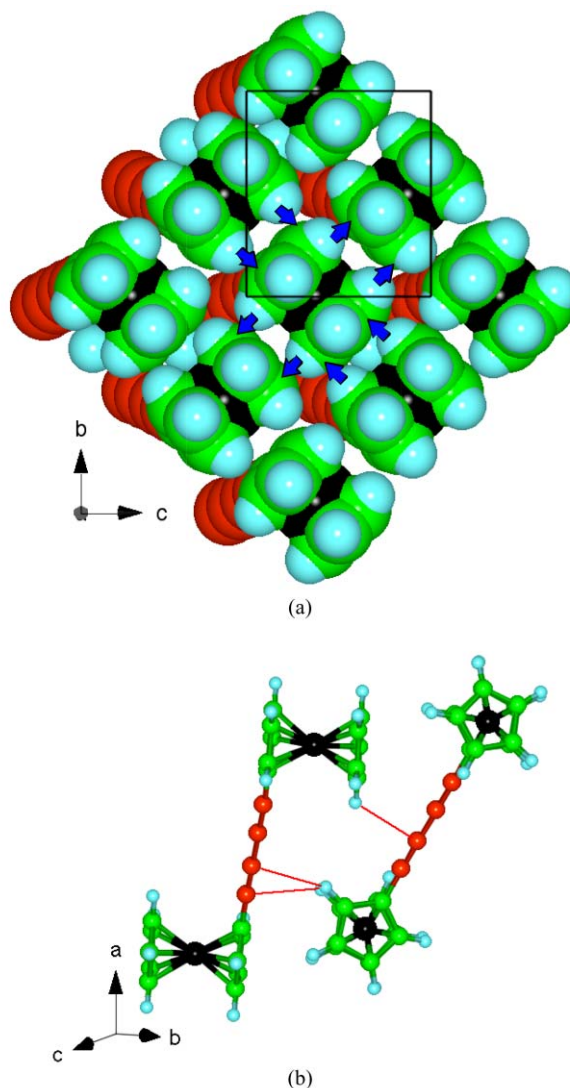


Fig. 2 (a) The approximately square close packing of ferrocenyl groups in the monolayer of **2B**. Every group is engaged in four edge-to-face interactions (blue arrows) with neighbours. (b) The relationship between adjacent molecules in the bilayer, showing the orthogonality of the axes of contiguous ferrocene groups, detail of the EF interactions, and how there is some approach of ferrocenyl H atoms to butadiynyl C atoms. H \cdots C interactions $< 3.3 \text{ \AA}$ are marked with red lines.

edges of the two cyclopentadienyl (Cp) rings in one ferrocenyl group are placed over one Cp ring of the neighbouring ferrocenyl group, as marked on Fig. 2a. The inclination of the molecules to the bilayer affects details of the cyclopentadienyl edges and faces involved, and also places some of the Cp hydrogen atoms near C atoms of the butadiynyl chains, as shown in Fig. 2b.

Figs. 1 and 2 show that the external surfaces of the bilayers are comprised only of Cp hydrogen atoms, and therefore only H \cdots H contacts occur across the interface between bilayers.

The crystal packing in **2A** is quite different from that in **2B**. Fig. 3a shows the arrangement of molecules in **2A**: in contrast to **2B** there are no layers of Fc groups. The molecules occur as chains along the *c*-axis, with an offset-face-to-face (OFF) motif between Cp rings of contiguous molecules in the chain (see Fig. 3b). The chain repeat is one molecule, and therefore the adjacent chain generated by the $c/2$ translation of the *c*-glide symmetry is positioned such that the ferrocenyl groups of one chain are nearest the C_4 atoms of its neighbour (Fig. 3c and 3d). In this way the crystal packing can be regarded as two sets of chains of molecules along the *c*-direction, each chain propagated by OFF between Cp faces, and the chains from the different sets

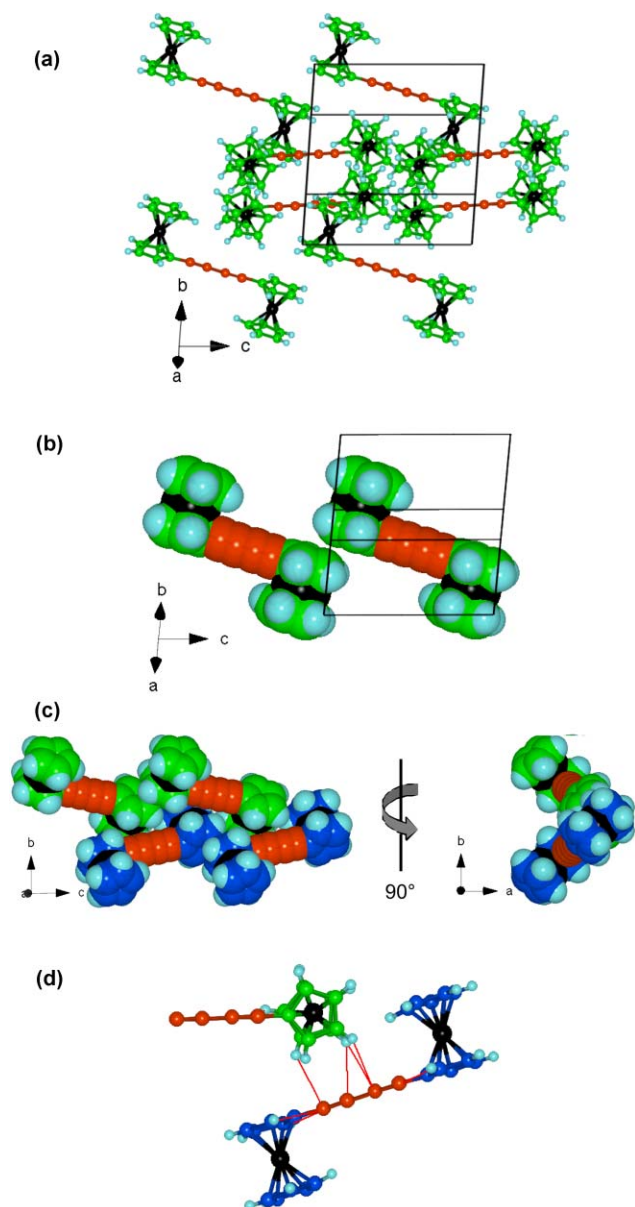


Fig. 3 Aspects of the packing of molecules **2** in crystals **2A** (YATDAY, space group $P2_1/c$). (a) Arrangement of the molecules, translated as chains along the c -axis. (b) The OFF motif connecting molecules in a chain. (c) Two orthogonal views showing the relationship between two chains (Fc carbon atoms green and blue, respectively) related by c -glide symmetry. The ferrocenyl regions of one chain are closest to the butadiyne regions of the other. (d) $\text{CH}\cdots\text{C}$ contacts $< 3.3 \text{ \AA}$ between Fc and C_4 are shown as red lines.

being associated by ferrocenyl \cdots butadiynyl interactions. In Figs. 3c, 3d and Fig. 4, the chains of one set have their ferrocenyl carbon atoms green, while those of the other are blue. The EF motifs that are well-developed in **2B** do not occur in **2A**.

There are further features of the relationship between chains both in the same set and between sets, involving the equatorial groove of the Fc group, and illustrated in Fig. 4a. Firstly, the Cp rings of Fc groups from contiguous chains in the same set mesh together so that the edges of the Cp rings nestle into the grooves of adjacent molecules (light and dark green in Fig. 4a). The second interaction involves the butadiyne chains. While these chains in **2B** are enclosed within the interior of the bilayers, the butadiyne chains in **2A** are surrounded by a pair of ferrocene groups from two different molecules of the opposing set. Fig. 4b shows the way in which two Fc groups surround one C_4 group. The view down the linker group with the top ferrocene group omitted is on the right. The location of the C_4 chain near the groove region of the surrounding Fc groups is clear.

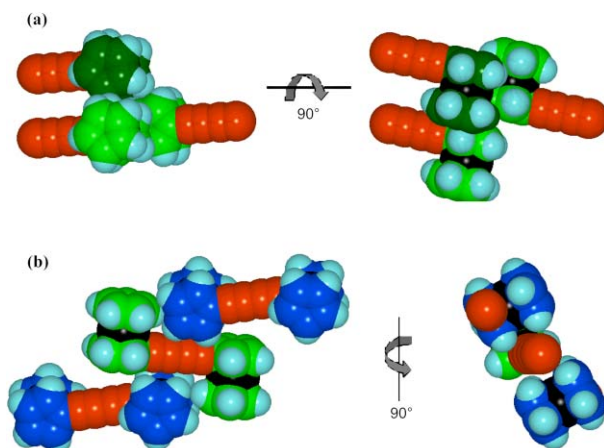


Fig. 4 (a) In **2A**, the intermeshing of Cp sections of contiguous chains in the same set, locating the edge of the Cp rings in the groove of the adjacent Fc. (b) Two orthogonal views of the Fc groups surrounding the central C_4 linker.

Relationship with the crystal packing isomers of ferrocene

The crystal structure of ferrocene stable at room temperature [CSD refcode FEROC12] is monoclinic, $P2_1/a$, and contains layers of ferrocene molecules close-packed in an approximately square array (Fig. 5) very similar to that in **2B**. The only motif within the layers is EF, and between the layers the interactions are essentially $\text{H}\cdots\text{H}$, without the common aryl \cdots aryl motifs.

The low temperature metastable triclinic phase of ferrocene [CSD refcode FEROC16] has a similar layered structure with the same square array of molecules fully engaged in EF motifs.

The very low temperature ($< 100 \text{ K}$) orthorhombic phase of ferrocene [refcode FEROC24], space-group $Pnma$, contains an array of molecules exhibiting a number of the features seen in the structures discussed above. There are layers of Fc molecules engaging in EF motifs, (Fig. 6a), which are oblique rather than orthogonal, as was observed in Fig. 2a for **2B** and Fig. 5a for the higher temperature forms of ferrocene.⁸ Within layers of molecules in the ab -plane (Fig. 6b) the meshed motif, where the edge of a Cp ring is located in the groove of the adjacent Fc molecules, is evident. This is comparable with the motif in **2A** (Fig. 4a).

Crystal packing of 1,8-diferrocenyl-octatetrayne

While no crystal structures of Fc- C_2 -Fc or Fc- C_6 -Fc are known, the crystal structure of 1,8-diferrocenyl-octatetrayne [Fc- C_8 -Fc CSD refcode RARNUT, space group $C2/m$] has been reported.⁹ Like both structural forms of the butadiyne

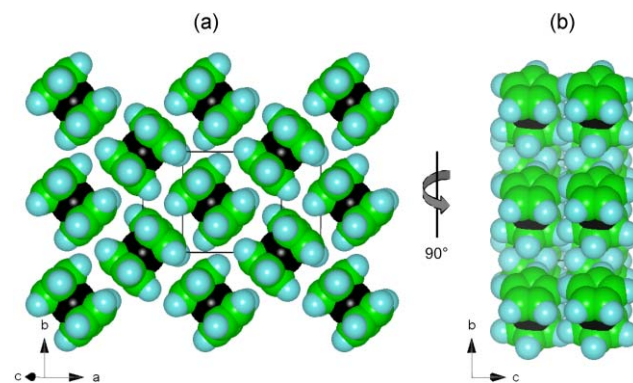


Fig. 5 The close packing of ferrocene molecules in layers in the room temperature monoclinic $P2_1/a$ polymorph (FEROC12). Each molecule participates in four EF motifs (compare with Fig. 2a).

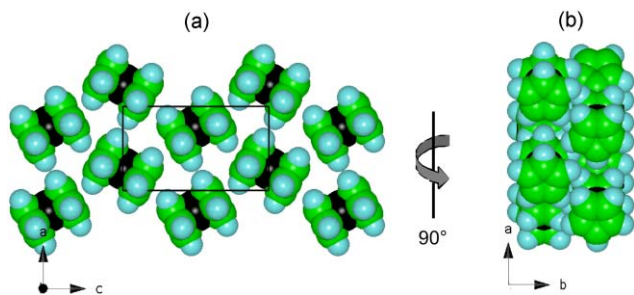


Fig. 6 Aspects of the crystal packing of the low temperature orthorhombic ($Pnma$) polymorph of ferrocene (FEROCE24). (a) The layer of molecules in the ac -plane, in which all molecular fivefold axes are coplanar, and the molecules are linked by EF interactions motifs in pseudo herringbone array. (b) Two adjacent layers which intermesh in the ab -plane so that the edge of the Cp ring is located in the groove of the adjacent Fc.

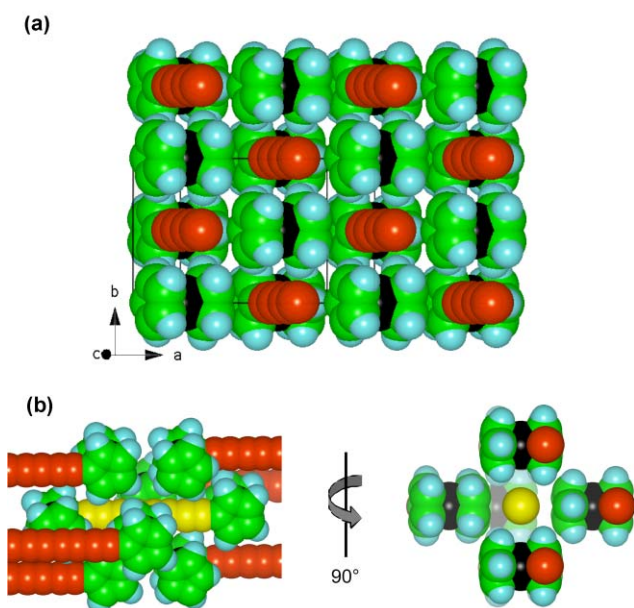


Fig. 7 The packing of 1,8-bis(ferrocenyl)octatetrayne molecules in RARNUT, space group $C2/m$. (a) The parallel alignment of all molecules, each of which has C_{2h} symmetry (some front Fc groups are not included, to reveal the locations of the C_8 chains, coloured orange). Note that there are no EF or OFF motifs between Fc groups. (b) The relative displacements of adjacent molecules along the direction of the parallel rods, showing how the Fc groups of six different molecules are arranged around each C_8 chain (yellow). The orthogonal view (with some Fc groups omitted), shows the $C_{p\text{face-to-}C_8}$ and $Fc_{\text{groove-to-}C_8}$ motifs.

compound, the ferrocene groups are eclipsed, and the molecule is centrosymmetric. The long molecules, which have C_{2h} symmetry, are aligned as parallel rods in the crystal (Fig. 7a). Adjacent molecules are displaced along the rod direction such that the larger ferrocenyl groups fit around the narrower C_8 connectors (Fig. 7b). Each C_8 chain is surrounded by six ferrocene groups from six different molecules, two of which present Cp faces to the C_8 chain, and four present the groove in the ferrocenyl group. There are no EF or OFF motifs between Fc groups in this crystal packing.

Discussion

The packing of Fc molecules in the crystal polymorphs of pure ferrocene is based principally on EF intermolecular motifs. There are no OFF motifs in any of the crystal forms of ferrocene. There is a regular evolution of molecular packing features in molecules where Fc groups are connected by linear

polyene C_n chains. When two Fc groups are connected by a linear C_4 chain in **2**, the molecular conformation is centrosymmetric, and there are two crystal forms. The new crystal form reported here, **2B**, is also packed with EF motifs between Fc groups as the dominant intermolecular feature: the Fc groups are organised in approximately square arrays of EF motifs, very similar to the layered arrangement that occurs in the ambient temperature and metastable low temperature crystalline forms of ferrocene (monoclinic and triclinic, respectively). The C_4 groups in **2B** are arranged obliquely between the layers of Fc groups, in order to minimise their awkwardness. The other crystal dimorph, **2A**, manifests the OFF motif as a significant intermolecular motif, with less significant EF motifs. In order to achieve the OFF motifs in **2A** pairs of Fc groups surround each C_4 chain. However, when the polyene linker is C_8 , all EF and OFF motifs between Fc groups are disrupted and instead six Fc groups are clustered around each polyene chain.

In this progression of structure types and intermolecular motifs for molecules Fc- C_n -Fc, the members with C_4 occur at the transition between the ferrocenyl dominant intermolecular motifs and the C_n chain dominant features. Dimorph **2A** is more like the longer chain structure, while **2B** is more like pure ferrocene. There is limited information on the relative stabilities of **2A** and **2B** and the conditions that control their formation. Solvent is often influential in polymorph formation. We crystallised **2B** from methanol/dichloromethane. In the experiments of Rodriguez *et al.*⁷ **2A** was crystallised from toluene, while during the preparation of **2** it was also crystallised from dichloromethane, but these crystals were not characterised. Yuan *et al.*⁶ crystallised **2A** from hexane.

In conclusion, it is evident that the C_n rod is a geometrically minimal component, even in comparison with the Fc group which is relatively small amongst entities used in molecular design. However the rod controls the rigidity of molecular shape, and on elongation causes the Fc...Fc dominant intermolecular motifs of ferrocene to be modified, in order that the Fc groups can fill space around the C_n rods. To some extent the polymorphism observed is facilitated by the lack of decoration on the Fc groups, which are therefore able to use different parts of their edges. A referee wondered whether Fc- C_8 -Fc might also be polymorphic. We comment that the three known Fc- C_n -Fc crystal packing arrangements involve C_n rods that are aligned parallel or approximately parallel, while alternative crystal packings with orthogonal or approximately orthogonal C_n rods are conceivable with longer C_n such as C_8 .

Acknowledgements

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