

Investigation of the co-crystallisation of N-heterocycles

By

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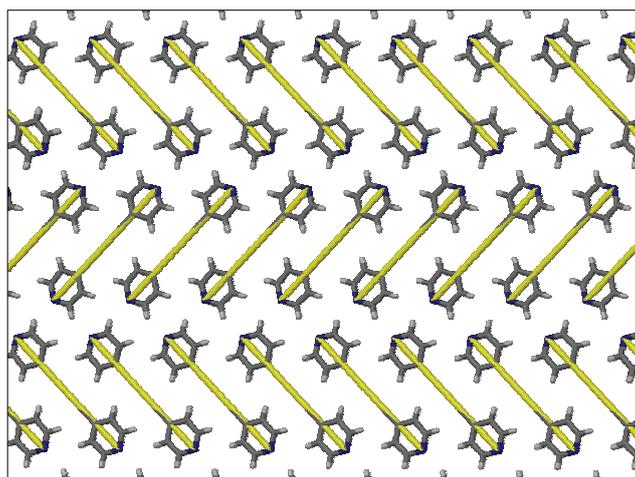


Figure 5.3 A 2-D layer of Ligand **1** showing the herringbone pattern.

The powder diffractogram of Ligand **1** is comparable to that simulated from the single-crystal data (Figure 5.4) and verifies that the single-crystal structure is representative of the bulk material. The discrepancies in intensity can be ascribed to preferred orientation of the crystals. The high angle peaks of the experimental diffractogram are shifted slightly to the left compared to those of the simulated pattern. This is due to the fact that the single-crystal data were collected at 100 K, while the PXRD pattern was measured at 295 K. Therefore, it is reasonable to expect the higher temperature data to be shifted slightly to the left.

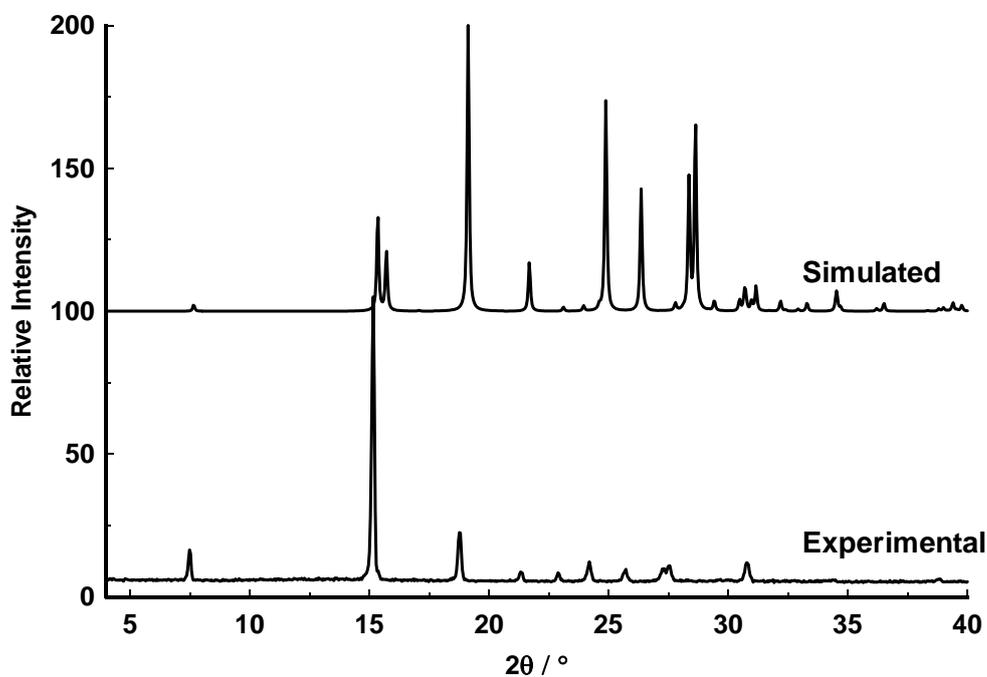
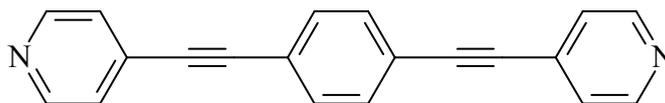


Figure 5.4 The experimental and simulated PXRD of Ligand **1**.

5.2.2 Ligand 2: 1,4-Bis((4-Pyridyl)ethynyl)benzene



Ligand **2** is similar in design to Ligand **1**, with a phenylene ring inserted between two alkyne moieties. Insertion of the phenylene spacer provides additional elongation without compromising rigidity.

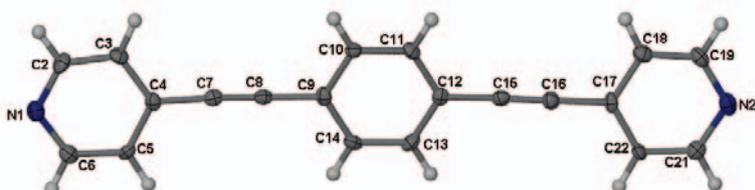


Figure 5.5 Thermal ellipsoid plot of Ligand **2**.

Flat rectangular single-crystals of Ligand **2** were obtained from a dimethyl sulphoxide solution. Although the synthesis of this molecule has been described in the literature,¹¹ the single-crystal structure has not been reported to date. The compound crystallises in the orthorhombic space group $Pna2_1$ with one entire molecule in the ASU (Figure 5.5). Similarly to Ligand **1**, there are no strong H-bond donors available for hydrogen bonding between molecules and, consequently, weaker intermolecular interactions play a significant role in the 3-D arrangement of the molecule.

The fingerprint plot (Figure 5.6) has few distinctive features and is less informative with regard to the intermolecular interactions involved in the crystal structure than is the case with the previous structure. However, the plot does indicate that most interactions are long-range,

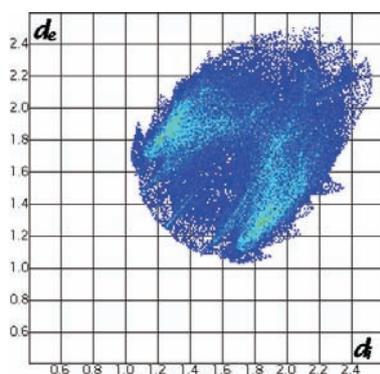


Figure 5.6 Fingerprint plot of Ligand **2**.

apart from H \cdots H interactions, which overshadow the C-H \cdots π wings. The Hirshfeld Surface (Figure 5.7), in this instance, is a more visual tool than the 2-D plot to assist in establishing the interactions between the molecules in the 3-D arrangement. The majority of the intermolecular interactions are of the C-H \cdots π type. The C-H groups interact with the π acceptors of either the aromatic pyridyl rings or the alkyne moieties.

A 2-D herringbone pattern, similar to that in Ligand **1**, results from these interactions (Figure 5.8), although the herringbone angle is more acute than that of Ligand **1**. The C-atom *meta* to the N-atom is involved in the C-H \cdots N interaction, giving rise to a more angular

herringbone pattern. Molecules appear to orient themselves to avoid $\pi \cdots \pi$ stacking and instead promote C–H $\cdots\pi$ interactions between two 2-D layers.

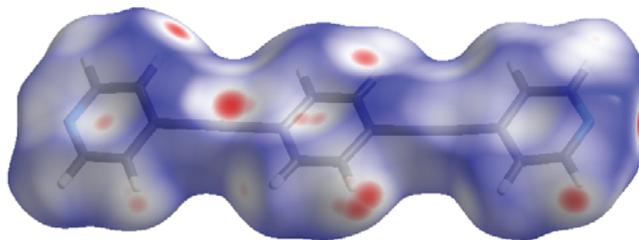


Figure 5.7 Transparent Hirshfeld Surface of Ligand 2. Red areas indicate close intermolecular contacts.

The ligand is intended to be a rigid molecule with limited conformational freedom, thus providing a degree of control over subsequent self-assembly processes in the solid-state. In reality, this molecule experiences some rotational mobility of the pyridyl rings, which may be beneficial in constructing frameworks. It is presumed that the central benzene ring allows for minimal rotation about the alkyne bonds to bring about the added flexibility.

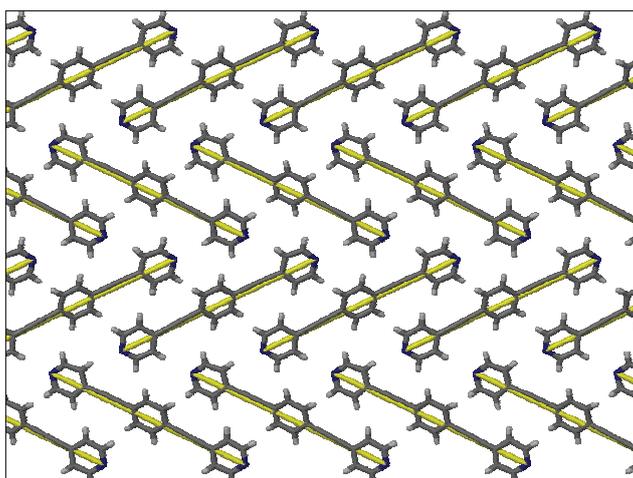


Figure 5.8 A 2-D layer of Ligand 2 viewed along the [001].

The single-crystal data from Ligand 2 were used to simulate a powder diffractogram, which is comparable to the experimental pattern obtained (Figure 5.9). However, as observed for the previous structure, peak positions are slightly offset in the two patterns.

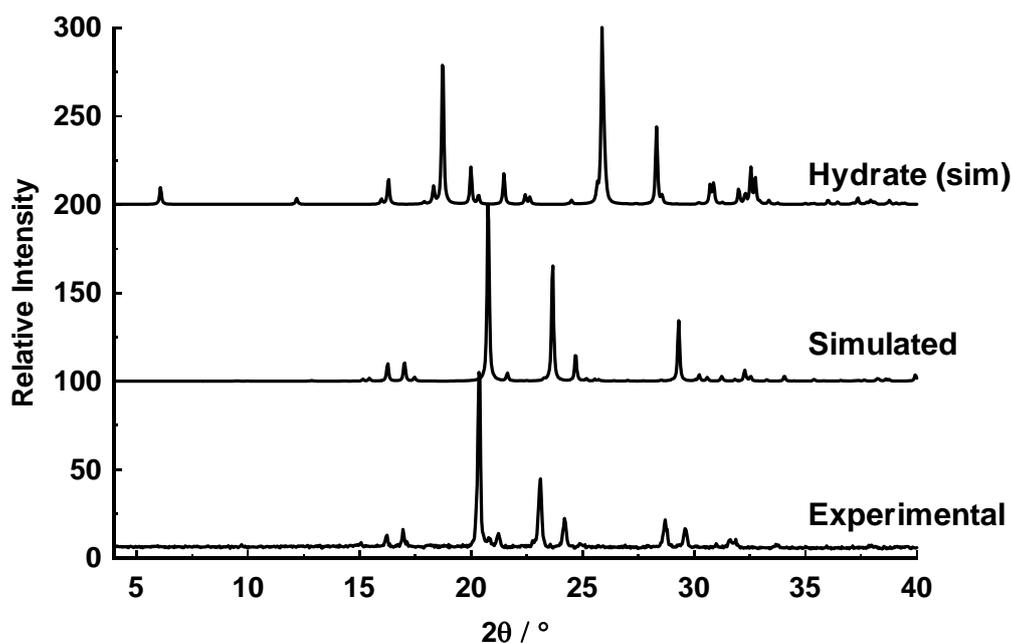


Figure 5.9 PXR D comparison of the experimental pattern with that of the simulated patterns of the pure and hydrated forms of Ligand **2**.

5.2.3 The hydrate of Ligand **2**

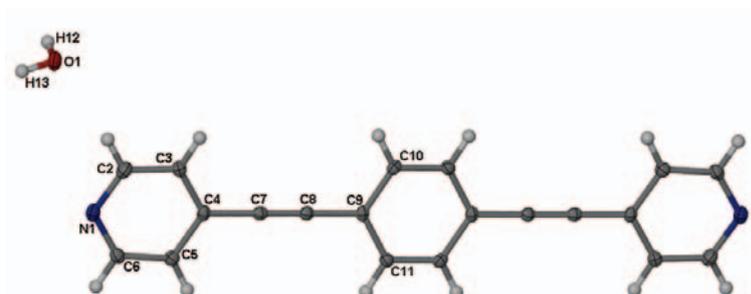


Figure 5.10 Thermal ellipsoid plot of the hydrate of Ligand **2**. Atoms of the ASU are labelled.

Colourless plates of the hydrated form of Ligand **2** were obtained by recrystallisation from a refluxed ethanolic solution. The ASU consists of half a molecule of Ligand **2**, located on the origin and an entire water molecule on a general position in the monoclinic space group $P2_1/c$ (Figure 5.10). The fingerprint plot (Figure 5.11) of the hydrate form, shows two types of short intermolecular interactions involved in the solid-state structure. The outer ‘tails’ indicate the $O-H\cdots N$ hydrogen bonds that exist between the aromatic nitrogen and a water molecule, whilst inner ‘tails’ signify $O-H\cdots O$ interactions between neighbouring water molecules.

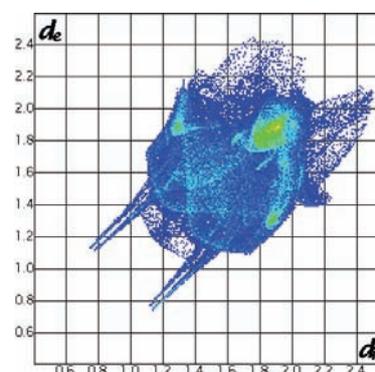


Figure 5.11 Fingerprint plot of the Ligand **2** hydrate

Ligand **2** is more linear in the hydrated than in the

anhydrous form, with aromatic rings being approximately co-planar. The water molecules act as both hydrogen bond donors and acceptors in this structure. Hydrogen bonds between water and the ligand form a staggered chain. The O–H·····O bonds that form between water molecules link the staggered chains to form a 2-D layer resembling a herringbone pattern (Figure 5.12). Offset π ····· π stacking interactions between aromatic rings and alkyne moieties play a minor role in layer construction. These π ····· π interactions are indicated by the green-to-yellow area on the diagonal at approximately 1.9 Å in the fingerprint plot. The 3-D assembly arises from 2-D layers orientated 180° to one another and ligand molecules are positioned for C–H····· π interactions between aromatic rings and alkyne moieties of neighbouring molecules.

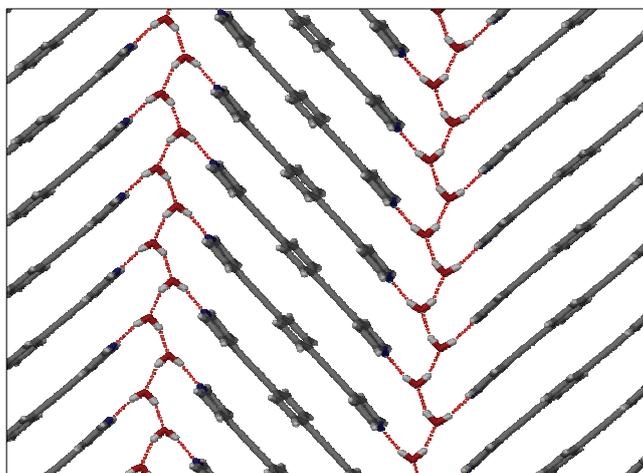


Figure 5.12 A single layer of hydrogen bonded chains of the Ligand 2 hydrate, viewed perpendicular to the *ab*-plane. The herringbone pattern is illustrated.

The inclusion of water in the structure causes ligand molecules to rotate such that π ····· π stacking is present within a hydrogen-bonded layer. However, molecules in the anhydrous form pack into a planar herringbone pattern. The simulated diffractogram of the hydrate form (Figure 5.9) was compared to the experimental diffractogram of the pure form. As expected, the two patterns show distinct differences. Insufficient sample was available for experimental PXRD analysis or thermal studies to be carried out on the hydrated form.

Summary and Discussion

The synthesis of two extended pyridyl based ligands is reported here. Three crystal structures were obtained for the two ligands – pure anhydrous forms of both ligands and a hydrate of Ligand 2. Weak intermolecular interactions dominate the packing of the anhydrous forms owing to the absence of strong hydrogen bond donors. The C–H·····N interactions between