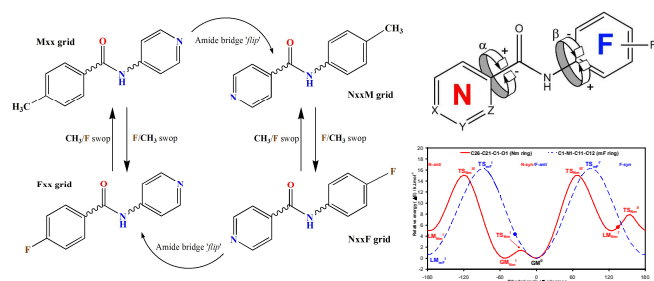




## Introduction

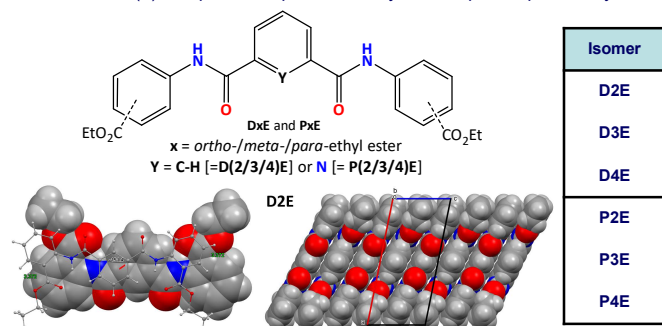
The effects of **X** (CH<sub>3</sub>, F, Cl) and pyridine **N** atom substitution patterns on molecular structure/conformation in benzamides, pyridinecarboxamides and isophthalimides have been reported by us (Figure 1).<sup>1-5</sup> Research integrates crystal structure analyses, computational calculations of conformations, with NMR data and melting point data.<sup>1-5</sup> This poster highlights the crystal structures of six isophthalimides (**DxE**) and pyridine relatives (**PxE**) (**D** = *meta*-C<sub>6</sub>H<sub>4</sub>, **P** = *meta*-pyridine; **xE** = 2-/3-/4-ethyl ester substitution).



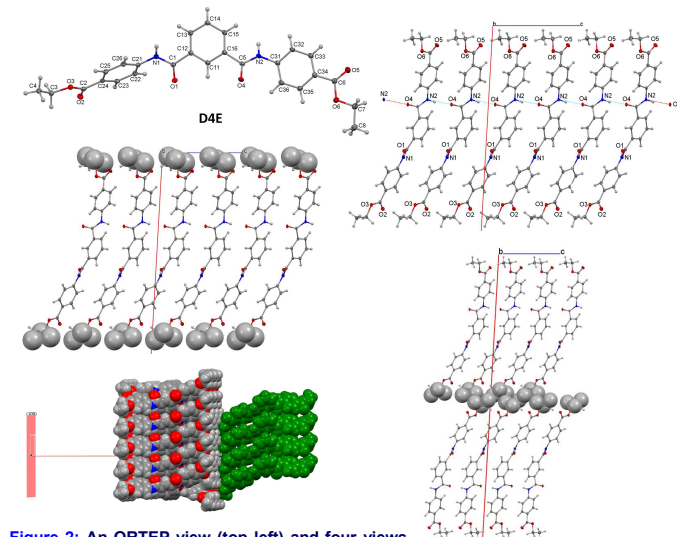
**Scheme 1:** Mxx/NxxM/NxxF/Fxx benzamide and pyridinecarboxamide series; Potential Energy Scans (PES) of the NmmF isomer (*meta*-F and *meta*-N).

## Experimental methods

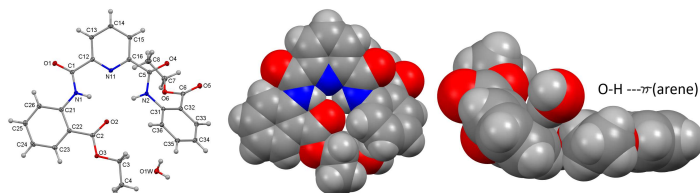
Nucleophilic acyl substitution (condensation) reactions of benzoyl chlorides (or isophthaloyl dichloride) with mono-substituted aminopyridines in the appropriate ratios produces benzamides or isophthalamides. Purification is by standard organic washing techniques, and sometimes chromatography.<sup>1-5</sup> Single crystal X-ray data were collected using a XtaLAB Synergy, Dualflex, ATLAS2 at 100(1) K. Spectroscopic data analysis as reported previously.<sup>1-5</sup>



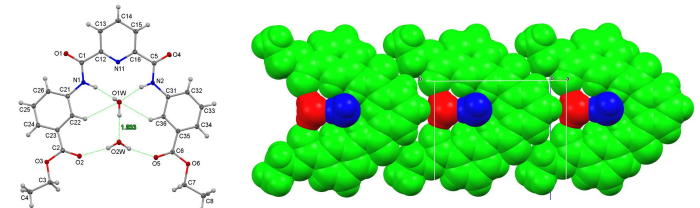
**Figure 1:** A schematic diagram of the DxE/PxE series; view of D2E (overlay with a symmetry related D2E); the D2E crystal structure (as viewed along the *b*-axis).



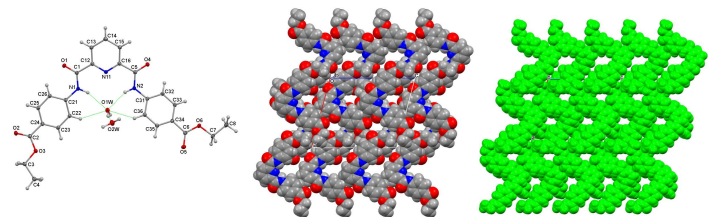
**Figure 2:** An ORTEP view (top left) and four views of the hydrogen bonding and aggregation in D4E.



**Figure 3:** An ORTEP plot and two views of P2E(0.44)H<sub>2</sub>O; with O-H...π(arene) contact.



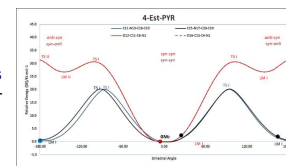
**Figure 4:** An ORTEP plot and view of the 'arrowhead' packing in P3E(2)H<sub>2</sub>O.



**Figure 5:** An ORTEP plot and two packing views of P4E(2)H<sub>2</sub>O (with H<sub>2</sub>O removed)

## Computational analysis

The conformational analysis was performed as previously described and the PES scan for P4E is depicted on the RHS (Figure 7).<sup>1-4</sup>



## Results and Conclusions

Over the past decade we have analysed the structures of several series of organic benzamides, pyridinecarboxamides and carbamates. Comparisons have been made between the (*n* × *m*) isomer grids comprising many crystal structures.<sup>1-5</sup> Recently we expanded the research into isophthalimides and their pyridine relatives, with mono-halo-derivatives as a starting point.<sup>6</sup> Herein, six isophthalamide (**DxE**) and pyridinecarboxamide diesters (**PxE**) are reported as analyzed by single crystal X-ray diffraction (**D** = *meta*-C<sub>6</sub>H<sub>4</sub>, **P** = *meta*-pyridine; **xE** = 2-/3-/4-ethyl ester substitution).

**D2E** (Figure 1) is planar as induced by C-H...O intramolecular interactions. All 34 non-H atoms lie within 0.1 Å of the **D2E** molecular plane. There is extensive intermolecular ring...ring stacking and the closest interplanar C...C is 3.372(2) Å. For **D3E** (*Z*=4) and **D4E** (Figure 2) the hierarchy of intermolecular interactions is an influential factor in driving structure formation. In **P2E** (**GAPTUP**), (Figure 3) the O1W molecule [site occupancy = 0.441(5)] forms four interactions O1W-H...O=C, O1W-H...π(arene) and two aromatic C-H...O1W. The *meta*- and *para*-substituted **P(3/4)E**·2(H<sub>2</sub>O) structures have open conformations with pairs of water molecules hydrogen bonding in molecular *niches* between the side benzamide ester groups (Figures 4 and 5).

The entry point into the diester chemistry has provided six distinct (**DxE/PxE**) compounds and crystal structures. Further reaction yields the acid derivatives **DxA/PxA** which provides a platform for complexation with a range of metals providing new metal complexes.<sup>8</sup>

## References:

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Note: The 298 K crystal structure of P2E has been reported previously as GAPTUP (CSD).