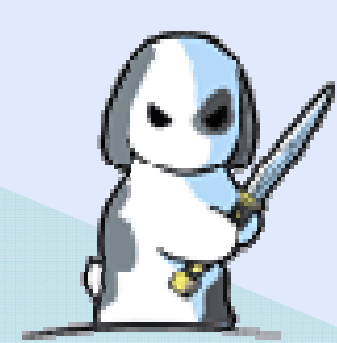


Supramolecular Assembly: *Recorded in 'tape-form'*



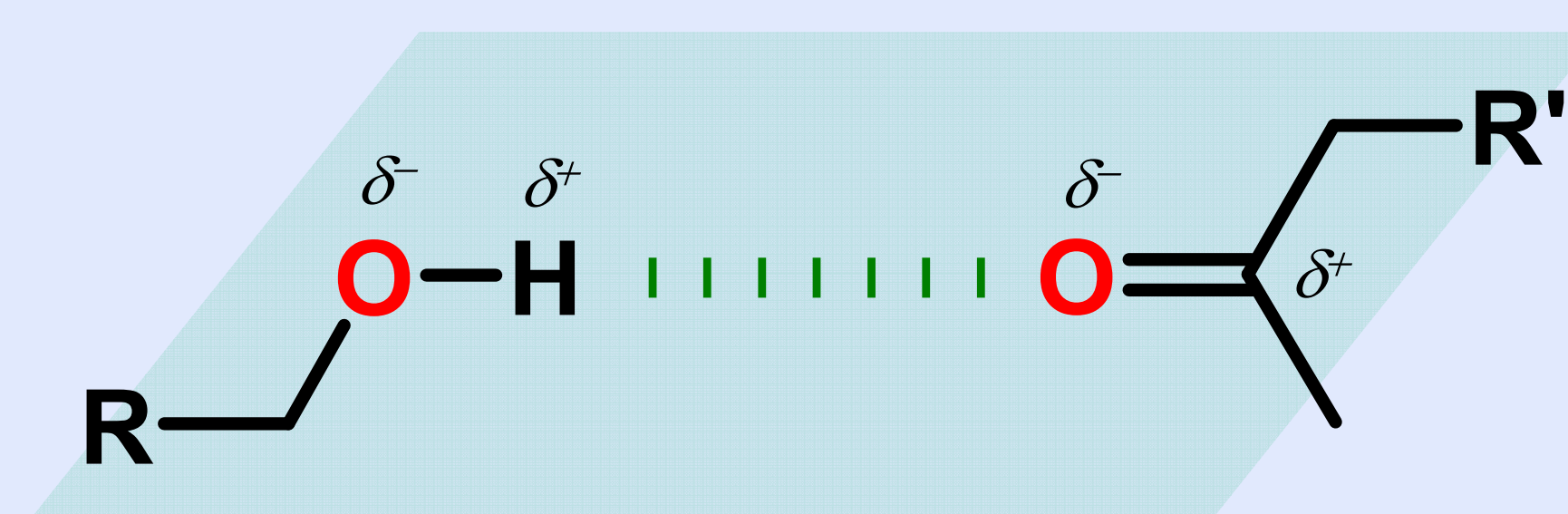
**Prof. Michael B. Hursthouse, Dr. Martin C. Grossel and
*James B. Orton - University of Southampton, UK**



Introduction

The covalent bond is a familiar concept to all chemists as being the fundamental contact between atoms within molecules. Bonding within molecules is well understood theoretically and the manipulation (chemical synthesis), to produce desired arrays of atoms (target molecules), is a well developed science.

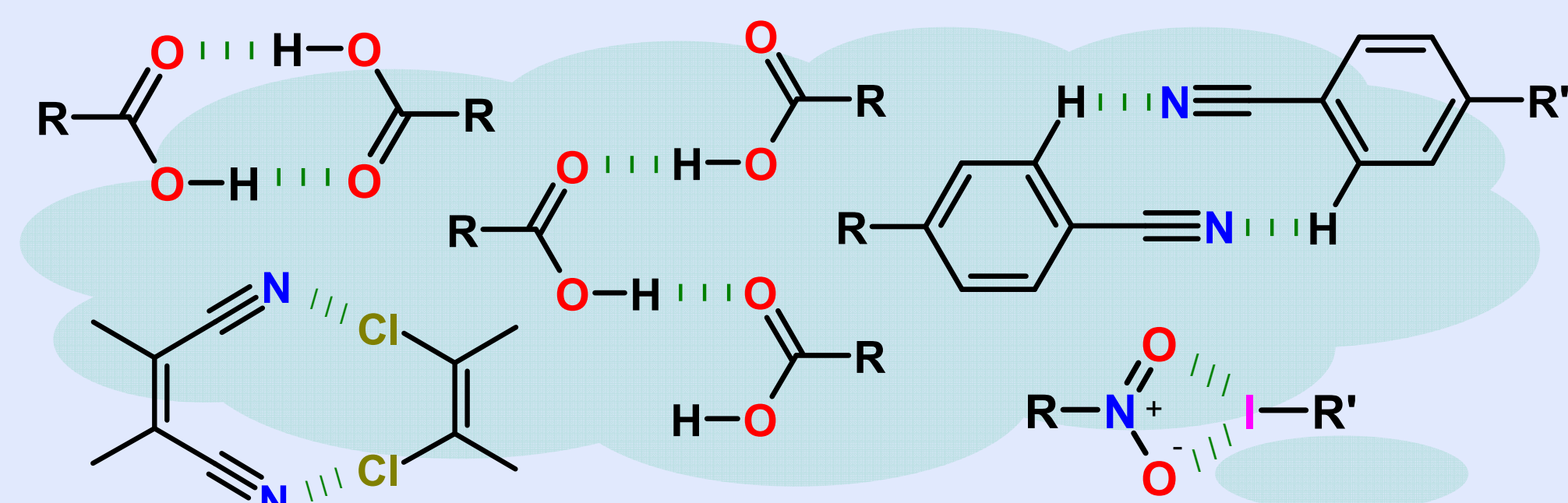
Supramolecular contacts, such as the hydrogen bond, are also well known entities; these constitute the fundamental contacts to the assembly of arrays of molecules (supramolecular assemblies). Though individually explained and predicted by theory, much still remains unknown when these interactions are placed in competition with one-another and ultimately, what the net effect of multiple contacts will confer on intermolecular geometry. It is this void that has spawned the discipline now known as crystal engineering¹: the systematic investigation of supramolecular interactions, how they behave and the effects they cause on molecular packing motifs.



Classic example of a hydrogen bond

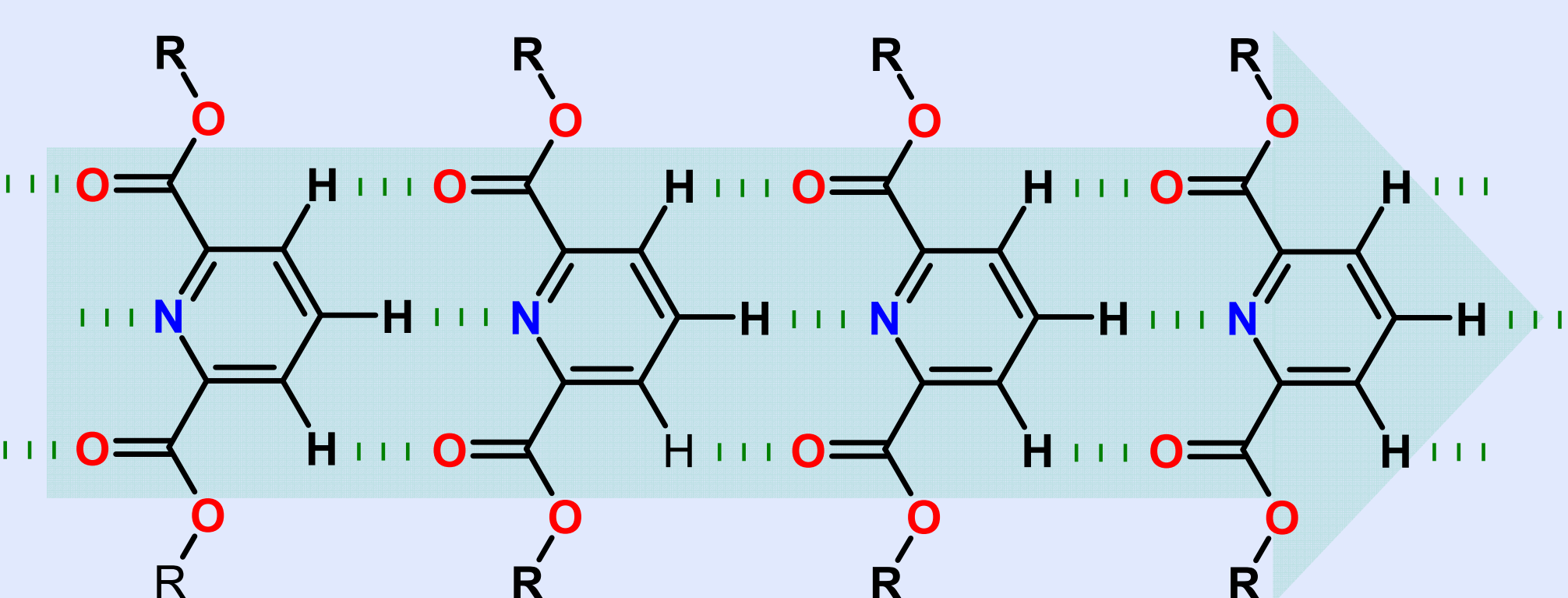
Crystal Engineering

As the knowledge base in this field has increased, it has given rise to the concept of the 'supramolecular synthon' – the spatial arrangements of intermolecular interactions which play the same rôle in supramolecular synthesis as conventional synthons do in organic synthesis. More recently Desiraju^{2,3} and others^{4,5} have described a wide variety of supramolecular synthons which can be used to control the architecture of organic molecules.



Examples of derived supramolecular synthons

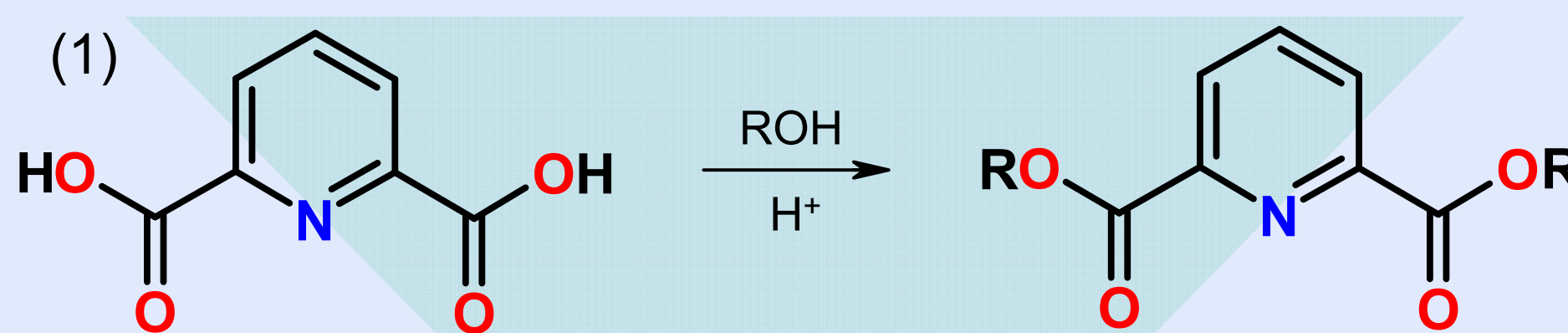
It is on the key principles of crystal engineering that the study of known and robust supramolecular synthons, found to form 'tape-like' assemblies⁵ (below), have been forged. Investigations into the careful addition of various supramolecular contacts, conditions and/or constraints to the periphery of these 'tapes', has led to some interesting discoveries due to their impact on the intermolecular assembly of the primary 'tape-like' architecture and on secondary inter-'tape' structure.



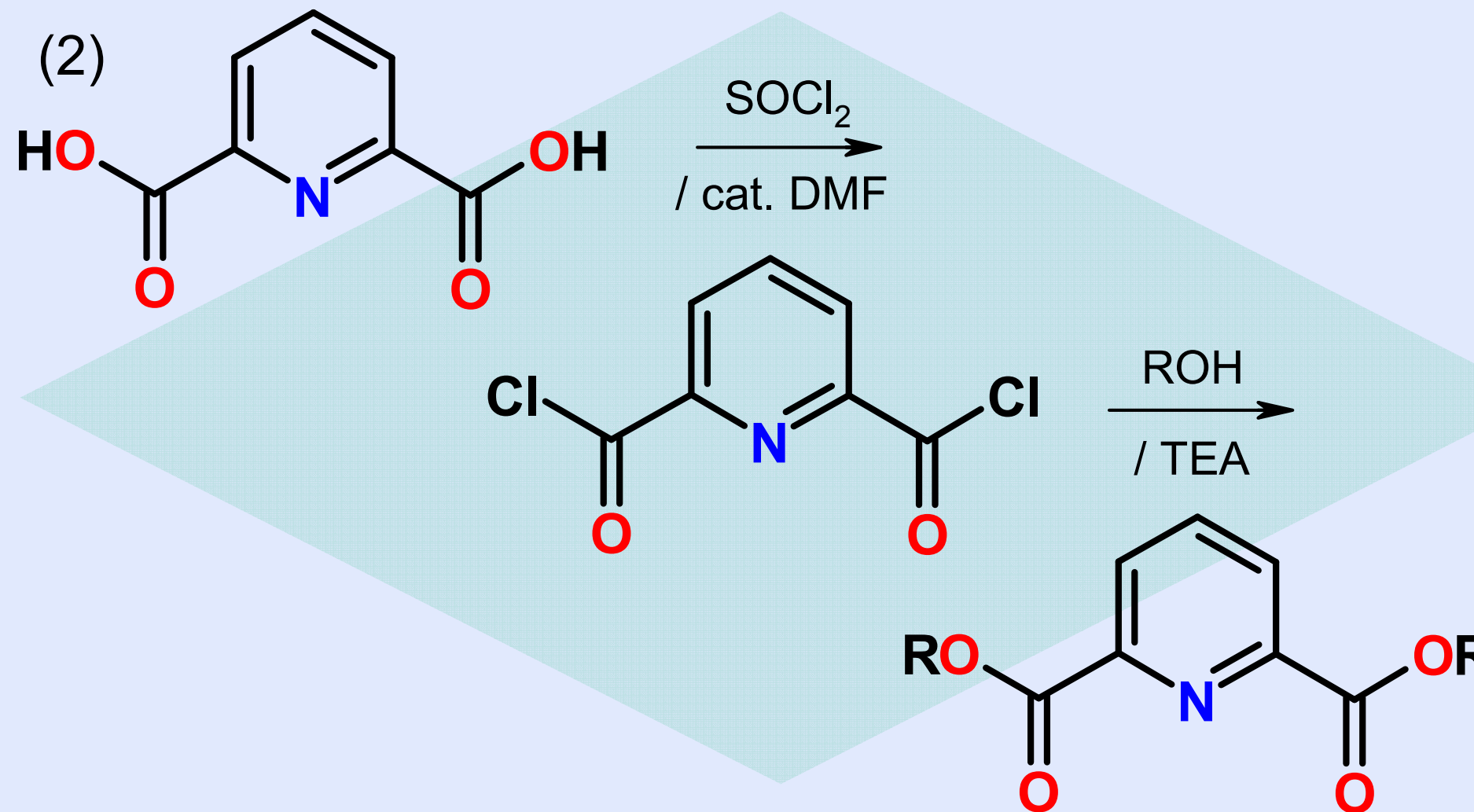
'Tape-like' assembly – 2,6-pyridine core synthon

Synthesis

Achieved *via* one of two routes: (1) direct reaction of the commercially available pyridine-*x,y*-dicarboxylic acid [*x,y* = 2,5; 2,6 or 3,5] under acidic dehydrating conditions with an appropriately substituted alcohol;

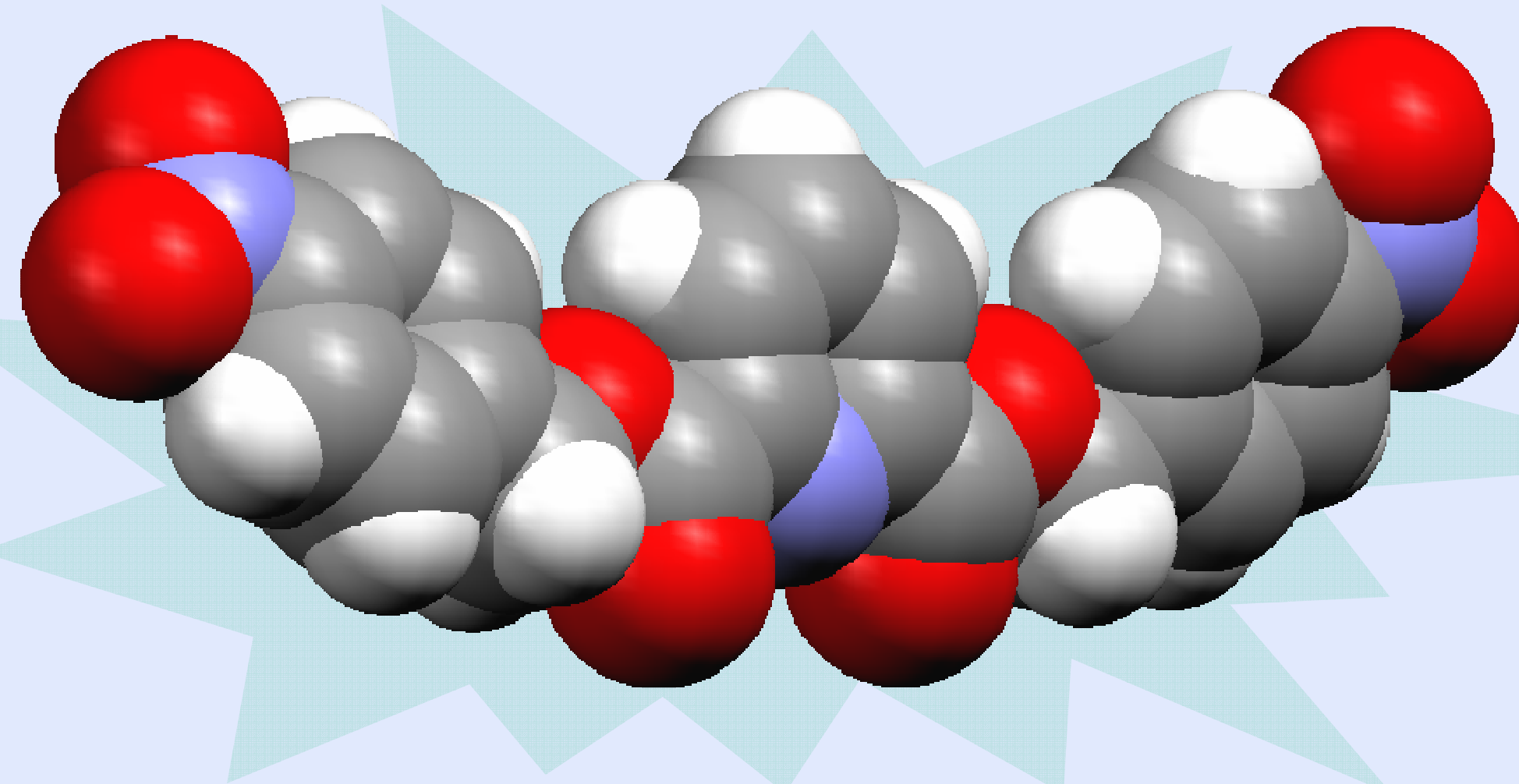


or (2) *via* a two-step procedure by first converting the pyridine-*x,y*-dicarboxylic acid to the corresponding (and more reactive) acid chloride which then may be readily coupled with an appropriately substituted alcohol in the presence of triethylamine (TEA).



Solid-State Behaviour

The geometry of the diesters in the solid-state have been found to adopt an open or *W*-shape (example below), which is in contrast to the pincer or *U*-shaped configuration of the related pyridine-*x,y*-diamides.

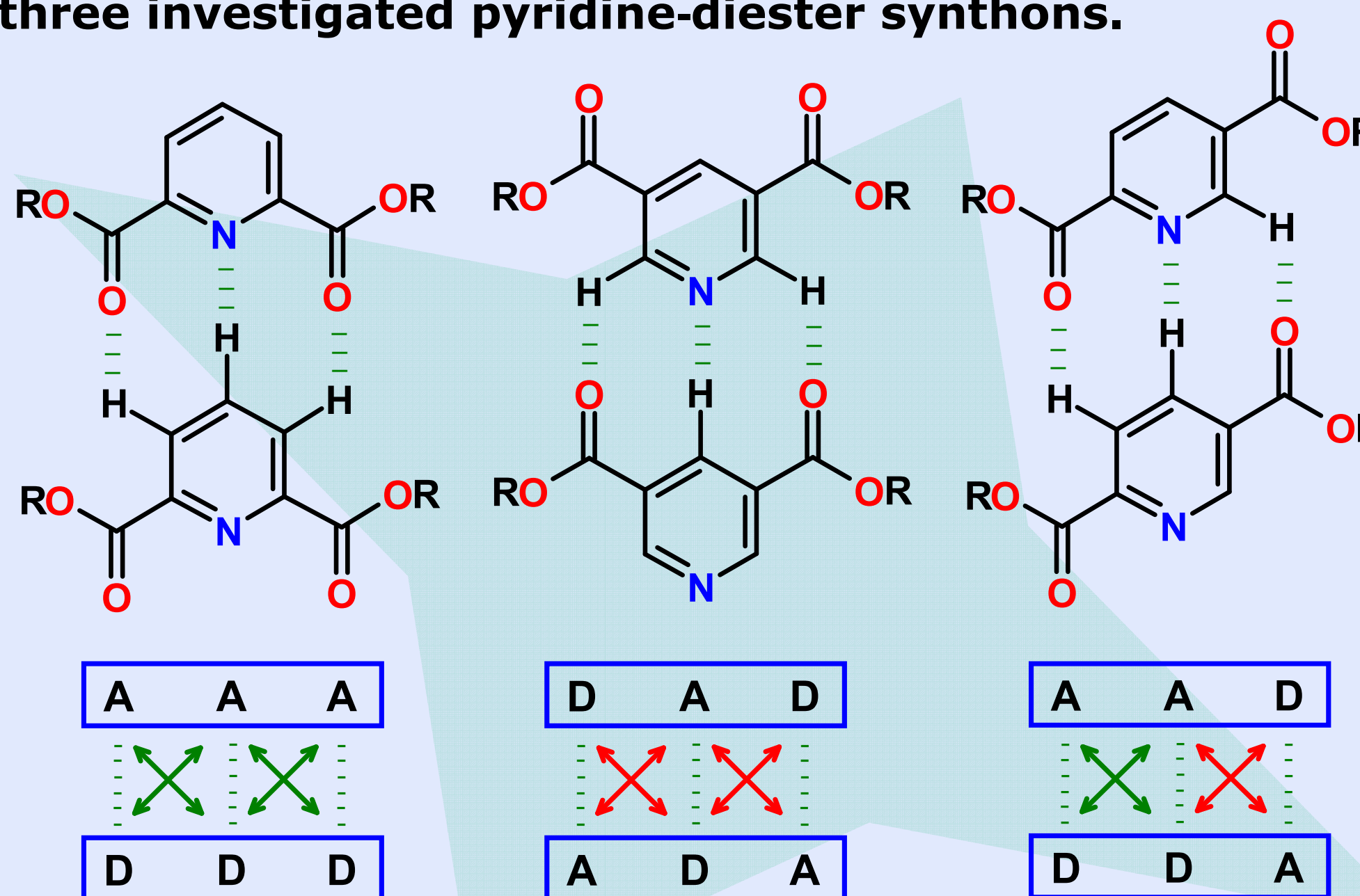


Example diester demonstrating an open conformation

It is this open conformation that permits the formation of infinitely extended tapes in the solid-state through a novel supramolecular contact consisting of 1x N...H-C and 2x C=O...H-C interactions.

Motifs

Three differing bonding motifs are observed from the three investigated pyridine-diester synthons.



KEY: D = 1° H-bond donor; A = 1° H-bond acceptor; X = favourable 2° H-bond; X = unfavourable 2° H-bond

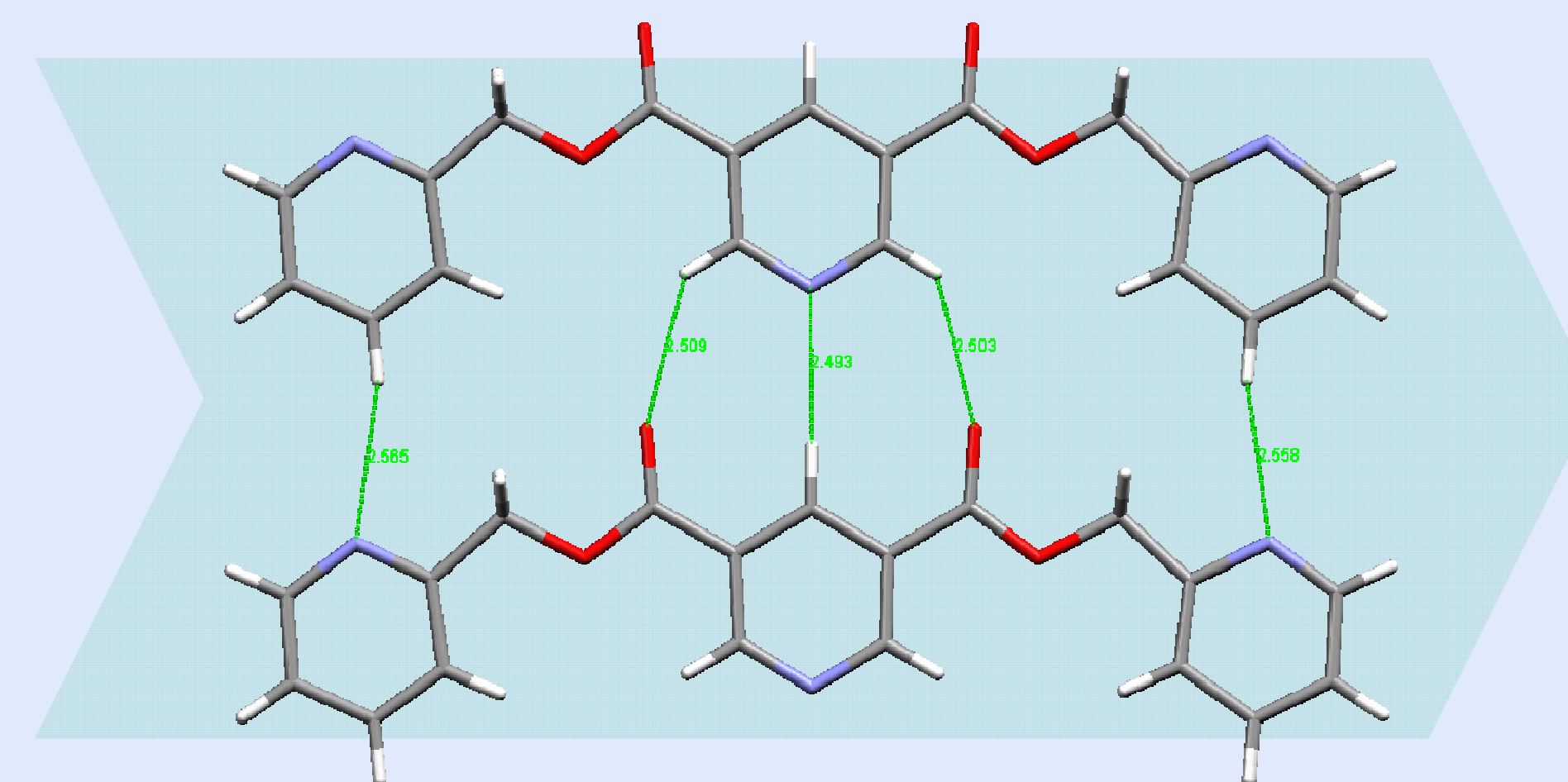
It can be seen that the 2,6 motif is expected to be the strongest interaction, the 3,5 to be less strong due to unfavourable secondary interactions. Unlike the other two motifs the 2,5 imposes only one complementary conformation.

References

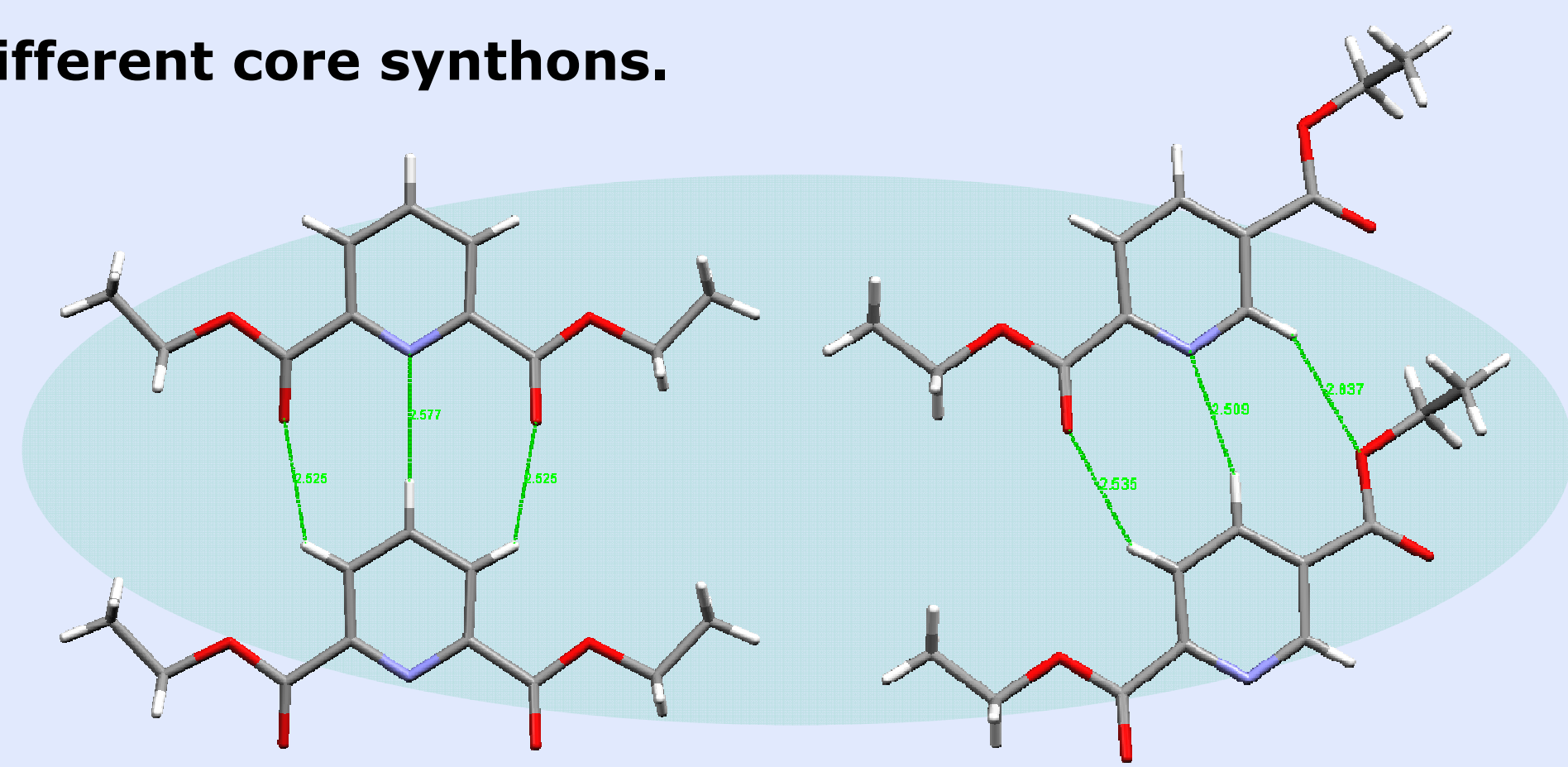
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Primary Assembly

Infinite 'tape-like' assemblies are found to form from these synthons even when a variety of steric, geometric and/or additional supramolecular contacts are added to them.

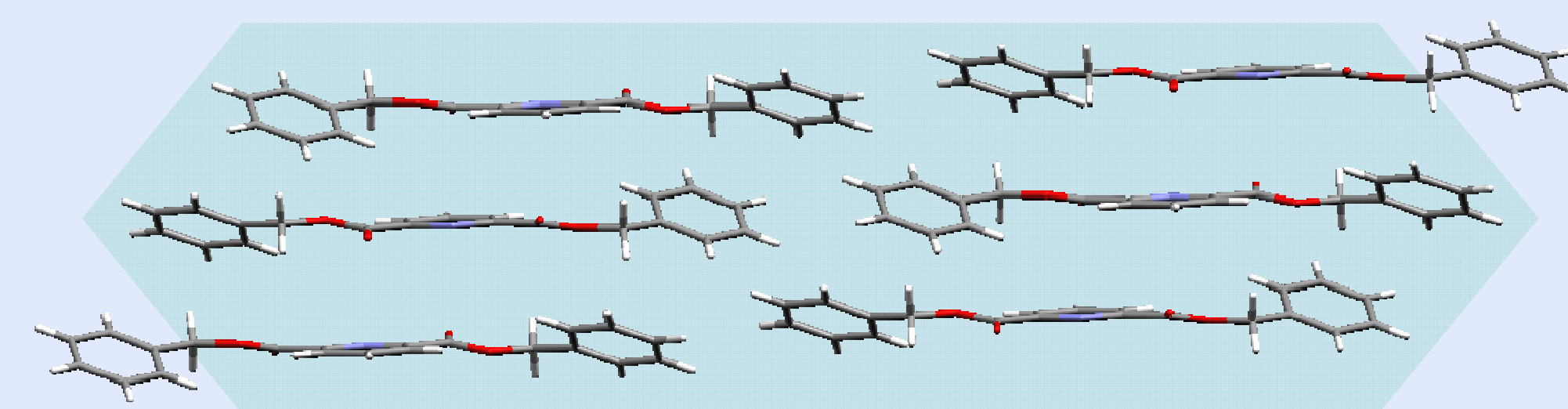


Contrasting behaviour has been seen in some cases between structures containing the same side-arm but different core synthons.

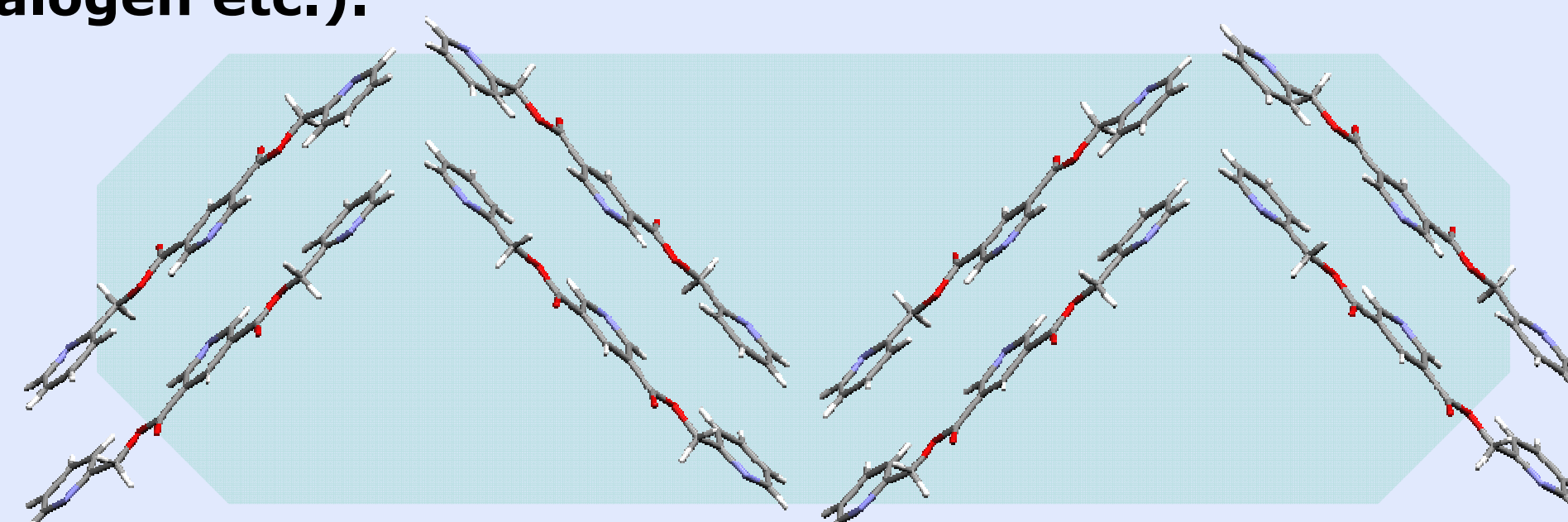


Secondary Assembly

In some cases 'tapes' stack in a face-to-face manner with long molecular axis neighbours arranged in a parallel format;



...in other cases a herringbone array is preferred this difference in architecture is attributed to maximising interplay of the various supramolecular forces present in each system (electrostatic, dispersive, halogen-halogen etc.).



Measuring Tapes

In addition to the solid-state structural studies of these assemblies, further supporting information has been sought through techniques such as VT-Raman, MAS and infinite dilution NMR. Of particular interest, the investigated 2,6 arrays; NMR experiments highlighting the H-bonding present in the system and VT-Raman⁶ yielding evidence for simple H-bonded species in the molten state and in both aprotic and protic solvents.

Summary

In the solid-state, of pyridine-*x,y*-diesters assemble into 'tape-like' assemblies involving a novel triple supramolecular contact consisting of N...H-C and C=O...H-C interactions. These intermolecular contacts are persistent in many of their supramolecular assemblies. Continuing investigation into placing additional interactions contained within the side arms yields interesting effects upon solid-state architecture.⁷ Further evidence for this triple contact has come from various spectroscopic techniques.