Appendix C: Theoretical Frameworks related to the MFI and MEL topologies.

Prompted by the apparent similarities between TNU-9 and the MFI topology indicated from HRTEM images, initial attempts to solve the structure of TNU-9 adopted a model building approach. In these studies, structural units if the MFI topology were rearranged to investigate whether the observed unit cell could be obtained while maintaining the characteristic MFI pore projection. Before any theoretical structure models could be built, however, an understanding of the MFI topology and its relative MEL was necessary.

MFI

The MFI topology may be regarded as being built from 5^8-cages (Figure B.1) (i.e. cages bound by eight 5MRs). For the purposes of describing the structures detailed below, these cages can be regarded as possessing 'equatorial' and 'axial' ends as defined in Figure B.1. As a point of reference, units and chains are described with the leftmost cage oriented with its 'equatorial' end to the left.

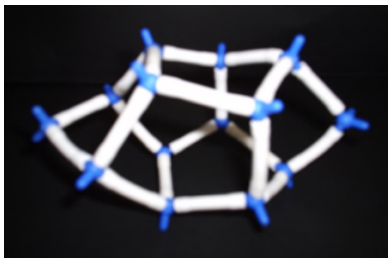
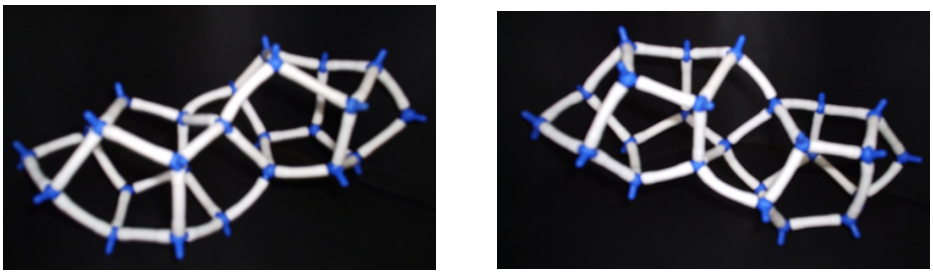


Figure B.1: 5^8-cage, from which all structures discussed below are constructed, with 'axial' and 'equatorial' ends to right and left, respectively.

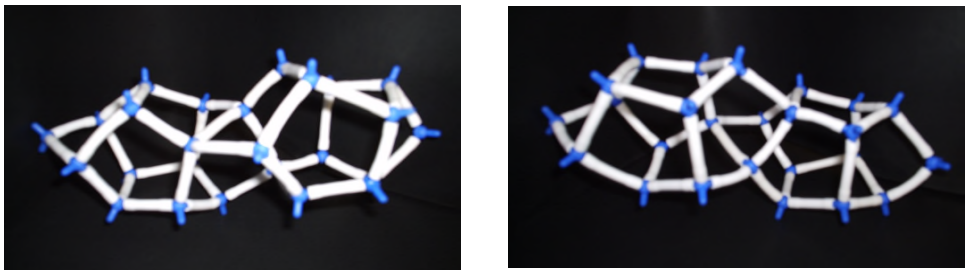
5^8-cages can be fused together in two ways: (1) 'up and back' (denoted UB) (Figure B.2(a)) and (2) 'down and front' (denoted DF) (Figure B.2(b)) - equivalent to (1) rotated 180^o about its long axis.



(a) (b)

Figure B.2: (a) 'Up and back' and (b) 'down and front' arrangements of 5^8-cages.

A further two possibilities are the mirror images of (1) and (2): 'up and front' (UF) (Figure B.3(a)) and 'down and back' (DB) (Figure B.3(b)).



(a) (b)

Figure B.3: (a) 'Up and front' and (b) 'down and back' arrangements of 5^8-cages.

In these ways, chains of 5^8-cages can be constructed. These chains can link to form layers from which an entire framework can be built. MFI is composed of layers that are constructed from two different types of chain (related by a mirror plane): UB, DF, UB, DF…… and DB, UF, DB, UF….. These chains have a sinusoidal character and link across a mirror plane at their closest points to form 10MR openings (Figure B.4). Additional, or 'filler', T-atoms, which do not belong to a 5^8-cage, are introduced to complete the chain connectivity (black atoms in Figure B.4). The resulting layers are stacked in an ABAB fashion where B is created by rotating A by 180^o about the axis perpendicular to the plane of the layer and displacing it by one cage length to the left (Figure B.5). Hence, a centre of inversion relates adjacent planes. The resulting MFI topology possesses a two-dimensional pore system in which straight 10MR channels (Figure B.6) perpendicularly intersect sinusoidal channels (Figure B.7).

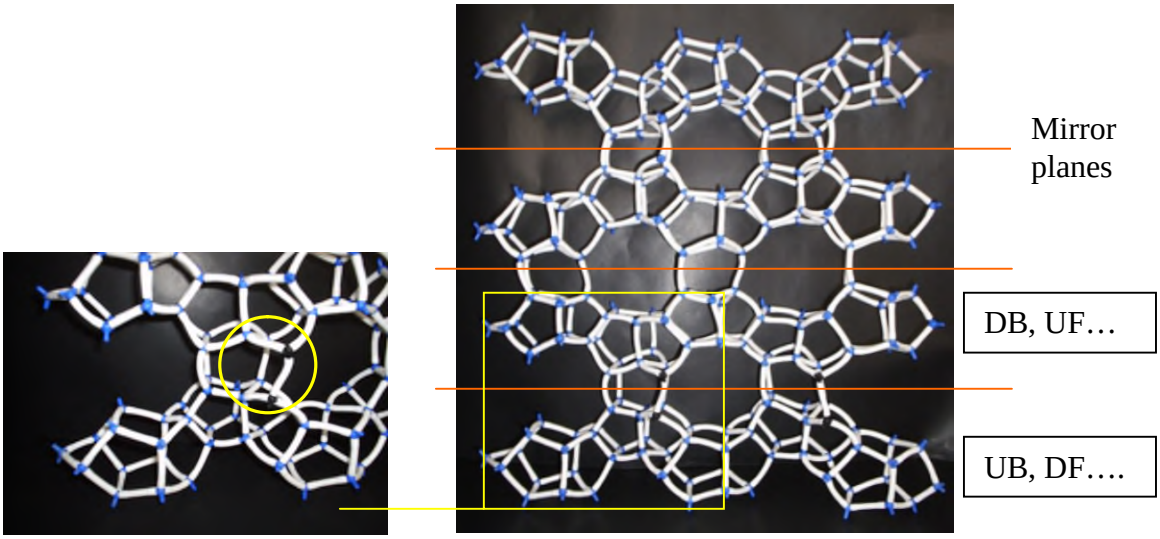


Figure B.4: Structural layer from which the MFI topology is constructed with chain types and mirror planes indicated. Detail of the chain connectivity is shown on the left with 'filler atom' (black) circled.

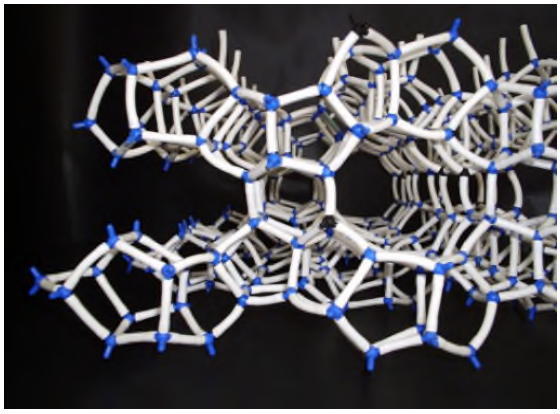


Figure B.5: Edge-on projection of two connected layers in the construction of the MFI topology.

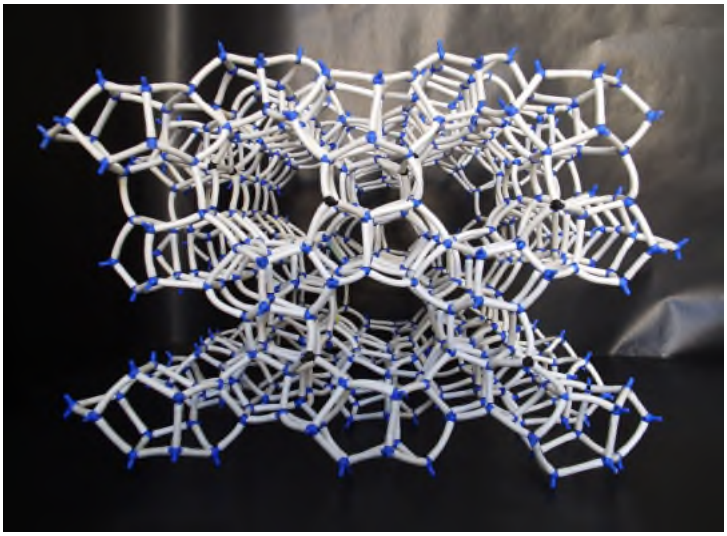


Figure B.6: MFI topology viewed edge-on to the structural layers (along the b-axis) illustrating the straight 10MR channels.

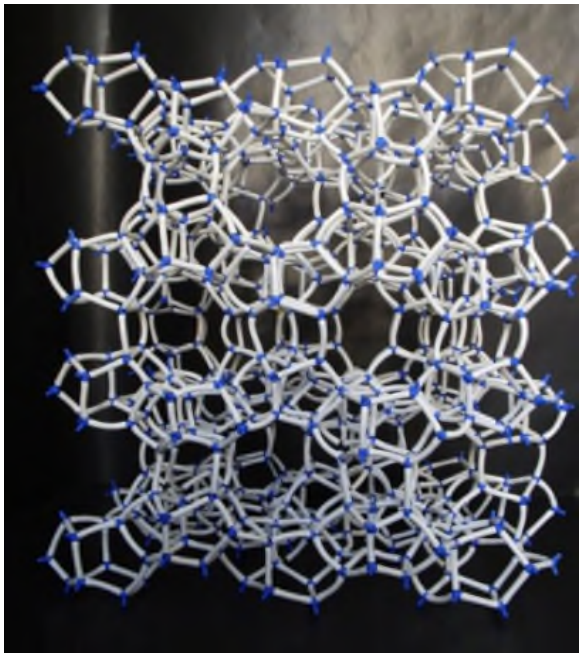


Figure B.7: MFI topology viewed along the path of the sinusoidal channels.

MEL

The MEL topology is constructed from the same layer-type as MFI, but with a mirror plane relating adjacent layers (Figure B.8). In this manner, the sinusoidal channels are 'straightened' and projections along the *a*- and *b*-axes become identical.

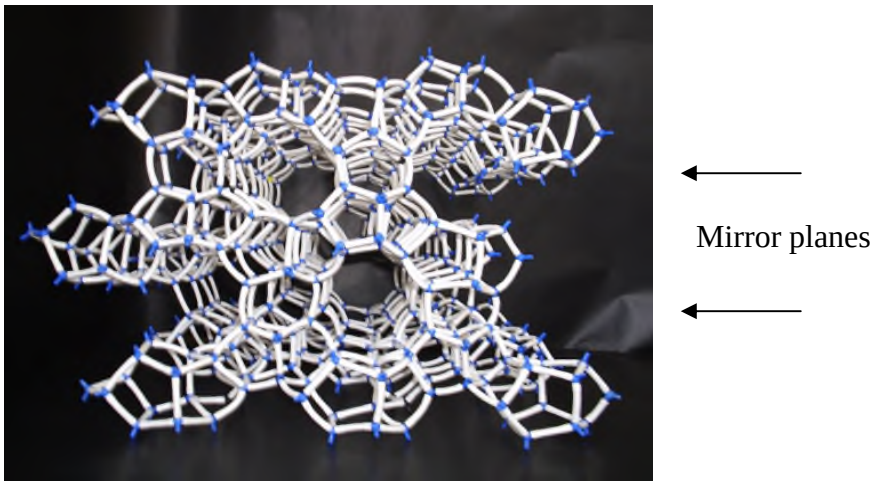


Figure B.8: MEL topology viewed along the a/b-axes illustrating the relationship between adjacent structural layers (horizontal).

It became evident that further variations of the layer-layer relationship would not generate a plausible framework and therefore the search for a possible model for TNU-9 began by re-visiting the chain-building step.

Model 1

Since the observed unit cell for TNU-9 is monoclinic, a chain was constructed with each additional 5^8-cage in a 'down' position – i.e. DF, DB, DF, DB…..(Figure B.9).

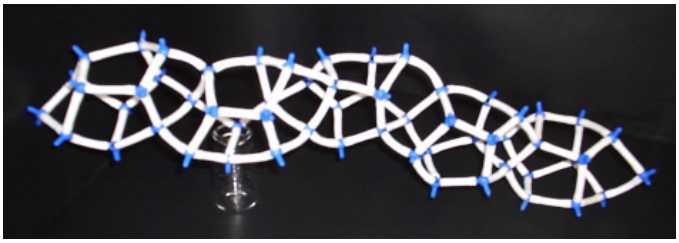


Figure B.9: DF, DB, DF, DB…chain.

Layers were constructed by attaching such a chain to its mirror image across a mirror plane (Figure B.10) (with ‘filler T-atoms included).

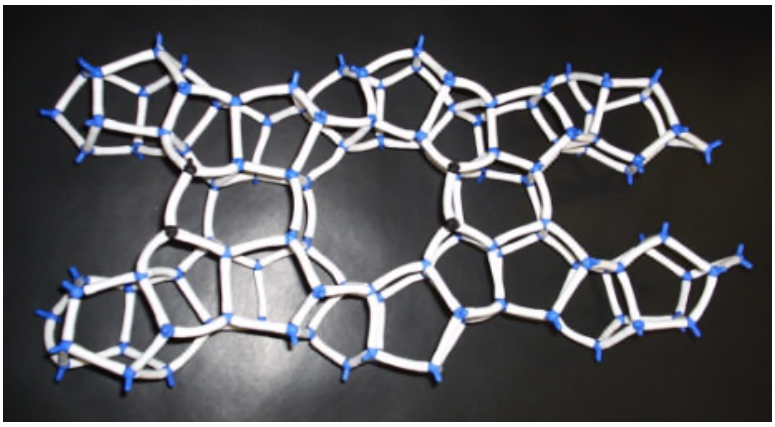


Figure B.10: Construction of a structural layer by the connection of two mirror-related chains. (additional atoms shown black).

Stacking these resulting layers directly on top of each other generated a monoclinic structure with straight 8MR pores running between the layers (Figure B.11) and an MFI-like projection (with straight 10MR channels) along the cell diagonal (Figure B.12). However, the estimated unit cell parameters were a = 14.8Å b = 21.9Å c = 13.9Å β = 140^{o}, with Cm symmetry (TNU-9: a = 28.2219Å, b = 20.0123Å, c = 19.4926Å, β = 92.33^{o}). As a test case, estimated atomic coordinates for Model 1 (measured manually from photographs of the model unit cell) were energy-minimised by Dr Paul Cox at the University of Portsmouth (under constant pressure simulations and in P1 symmetry), and the resulting atomic parameters were used to generate the theoretical powder XRD pattern, is illustrated in Figure B.13.

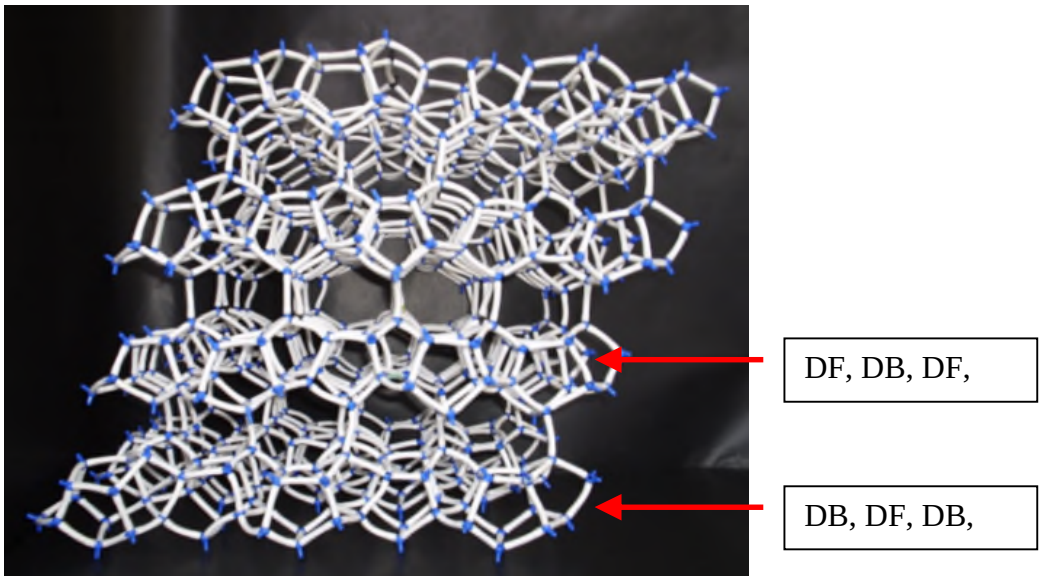


Figure B.11: Model 1 viewed along the b-axis (edge-on to structural layers) illustrating the straight inter-layer 8MR channels.

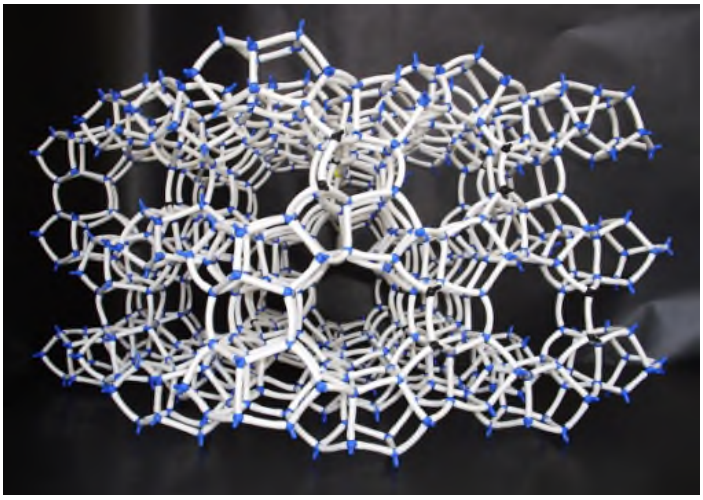


Figure B.12: View of Model 1 along [101] revealing an MFI-like projection with straight 10MR channels.

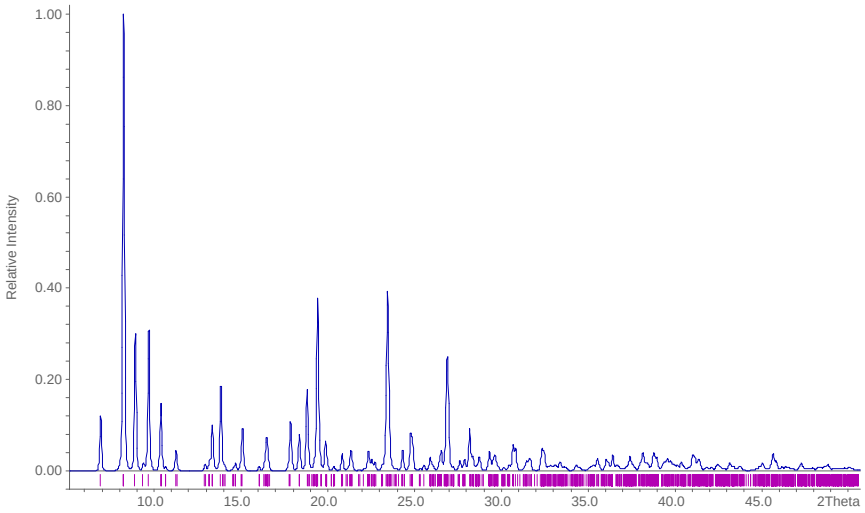


Figure B.13: Theoretical XRD pattern for the energy-minimised framework of Model 1. Energy-minimised cell parameters: a = 13.9651Å, b = 19.8588Å, c = 13.5249Å, α = 90.255°, β = 137.495°, γ = 89.775°.

Model 2

Model 2 was generated from Model 1 by rotating every second layer by 180° about the axis perpendicular to its plane. While the result was to increase the cell dimensions to values more comparable to those desired (a = 21.9Å b = 14.5Å c = 20.23Å), orthorhombic symmetry ($Cmc2_1$) was restored and the MFI-like projection was lost due to the creation of a sinusoidal 10MR pore system (Figure B.14).

Model 3

Model 3 was generated in an attempt to double the repeat between stacked layers in Model 1 and therefore enlarge the unit cell while maintaining monoclinic symmetry. Model 1 was split into *horizontal* layers (i.e. those planes containing 8MRs and parallel to the 10MR channels) and every second layer was flipped 180° about the axis perpendicular to the long axis of its constituent chains. In this manner, mirror planes no longer related adjacent chains in the re-assembled *vertical* layers. Yet although the 8MR channels are lost (consistent with HRTEM images), a doubling between vertical layers was not created.

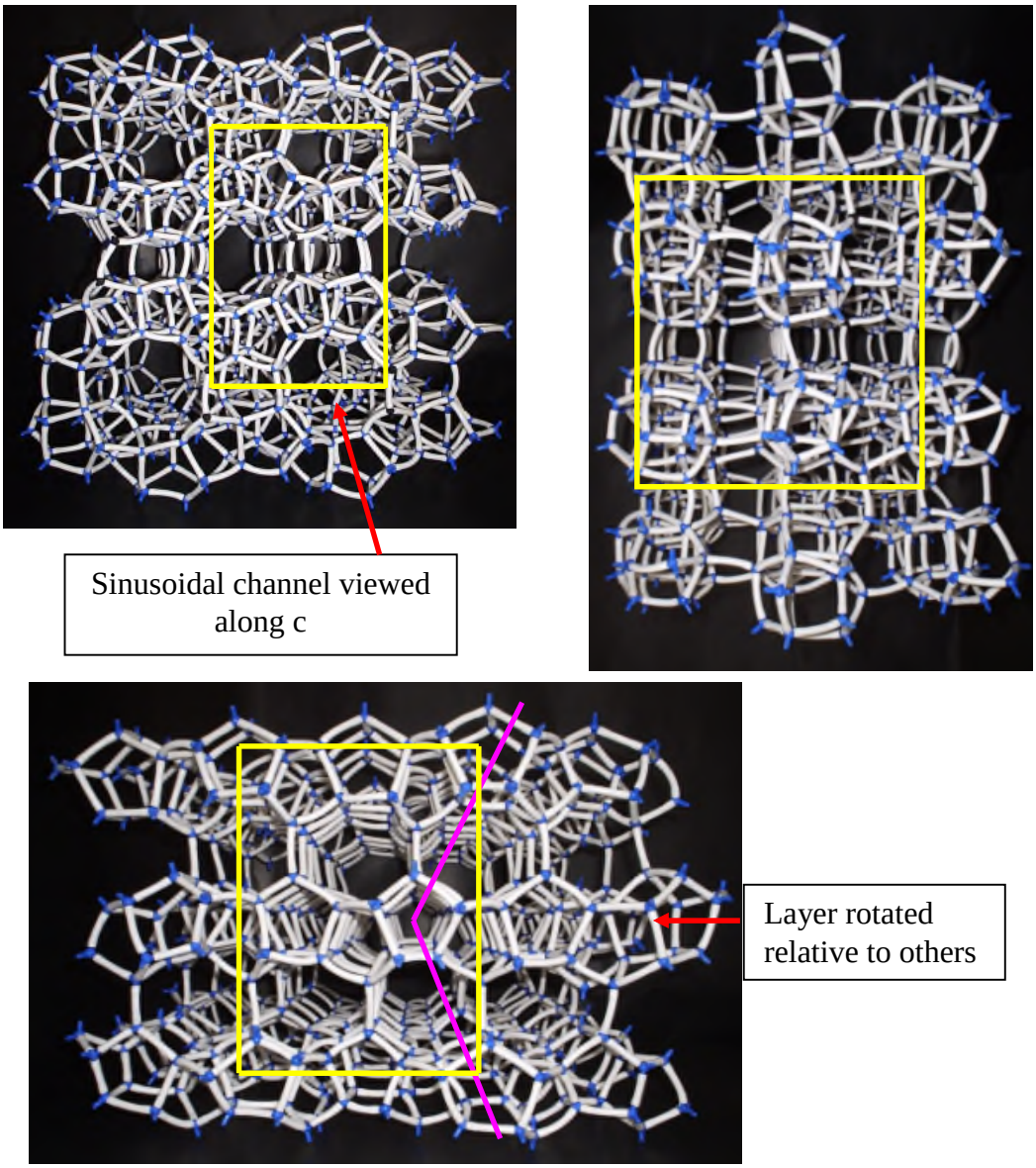


Figure B.14: Model 2 viewed along the c-axis (top left), b-axis (top right) and a-axis (bottom). Unit cell is indicated in yellow and sinusoidal path of the 10MR-channels is indicated by the pink line.

Model 4

This model (Figure B.15) was also generated by altering Model 1. Firstly, Model 1 was split into horizontal layers as in the building of Model 3 above. Every second layer was

flipped 180^{o} about the axis *parallel* to the long axis of its constituent chains. In order to re-connect the horizontal layers and generate an MFI-like projection with straight 10MR channels, the flipped layers were rotated by approximately 45^{o} about the axis perpendicular to their plane. As a consequence, the original (vertical) layer type is lost and the structure must be regarded as being composed of these horizontal layers, whereby every second layer is identical but displaced slightly along the axis parallel to the 10MR channels (Figure B.16). The resulting triclinic unit cell, however, was estimated to be a = 13.98Å, b = 22.50Å, c = 10.50Å, α = 105^{o}, β = 105^{o}, γ = 90^{o}.

Model 5

Similar treatment to that described above can also be given to Model 3.

Further Possibilities

The models described above are generated from the same original chain-type – i.e. DF, DB, DF, DB….. and its mirror-related equivalent. Many other chain-types are also possible, including, for example, UB, DB, UF, DF…. and UB, DB, UF, DB, UB….., all of which may generate an MFI-like projection and 10MR channels. However, variations in the chain composition in this way would act to enlarge the unit cell in the direction parallel to the long axis of the chains and not perpendicular to the plane of the layers as required.

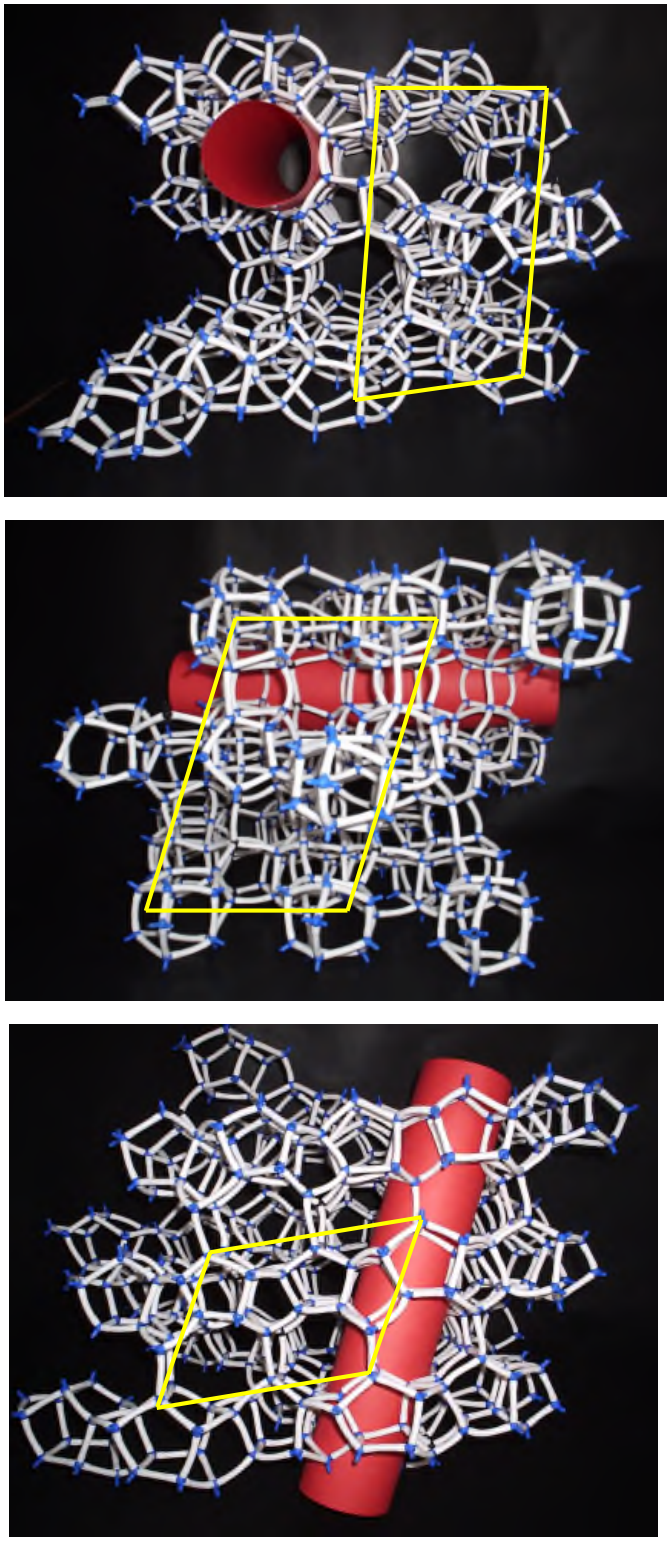


Figure B.15: Projections of Model 4 along the c-axis (top), a-axis (middle) and b-axis (bottom). Unit cell indicated in yellow and one 10MR channel is highlighted in red tube.

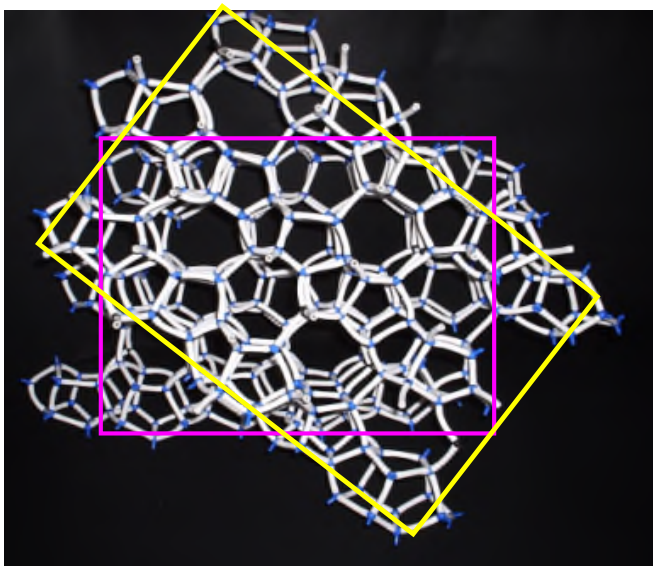


Figure B.16: Model 4 viewed along the b-axis with relationship of adjacent layers indicated in yellow and pink.