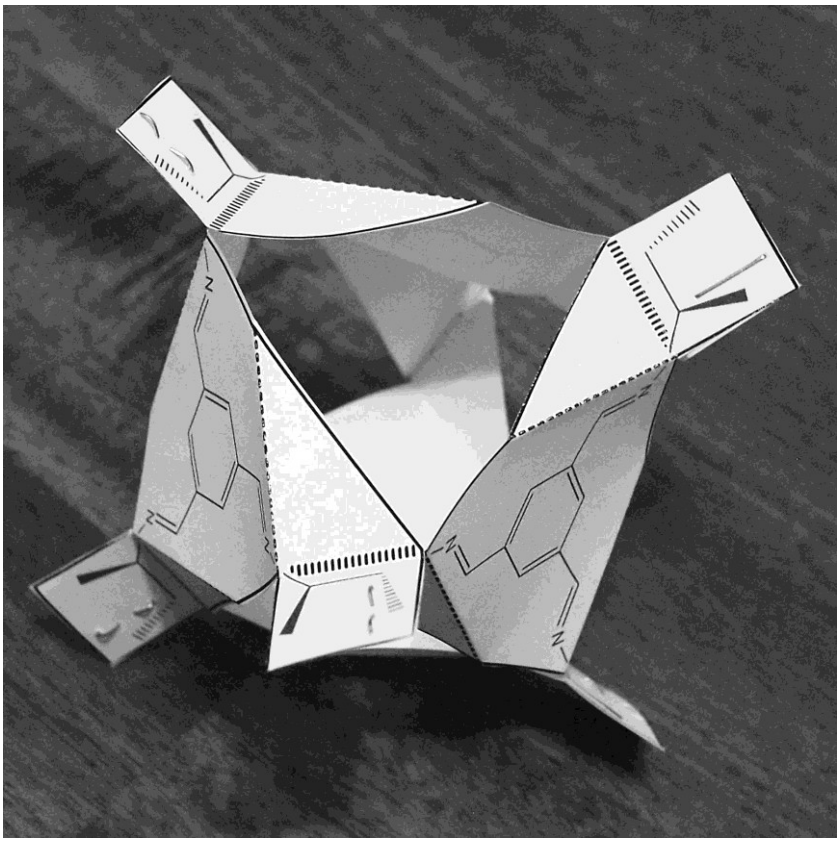
Molecular Cage Origami

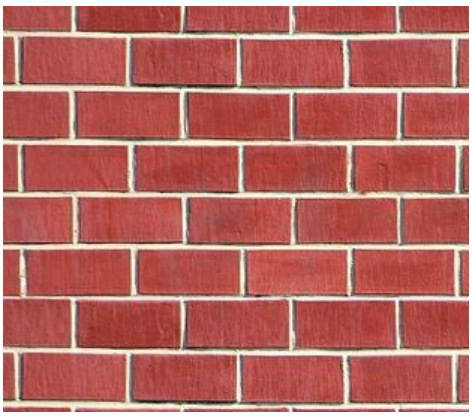
Developed originally by Dr Alexander Steiner, University of Liverpool



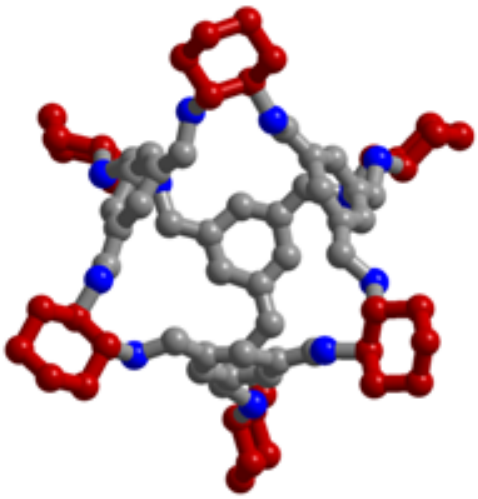
UNIVERSITY OF LIVERPOOL

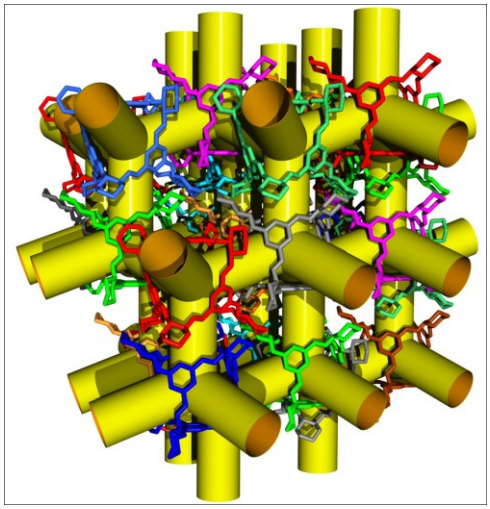
Background

Most molecular crystals pack in a dense, regular fashion, like bricks in a wall.



In 2009, we discovered a method for synthesizing organic molecules that are porous – that is, molecules with a permanent hole in the middle (*Nature Mater.*, **2009**, *8*, 973). These molecules cannot pack efficiently to fill space, and therefore they form solid materials that are porous because they have empty channels running through them.

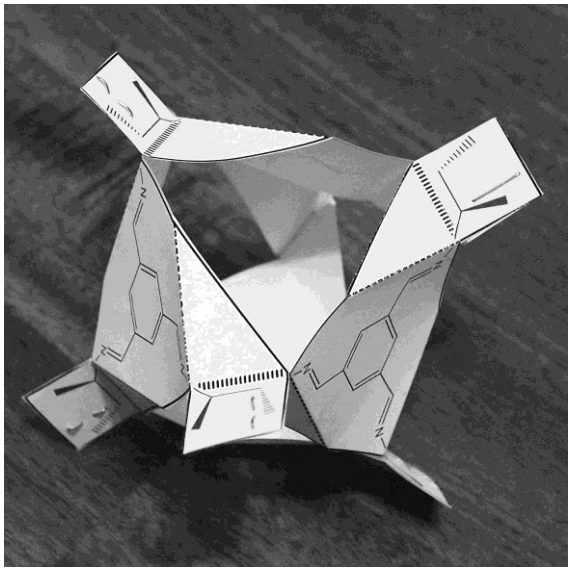




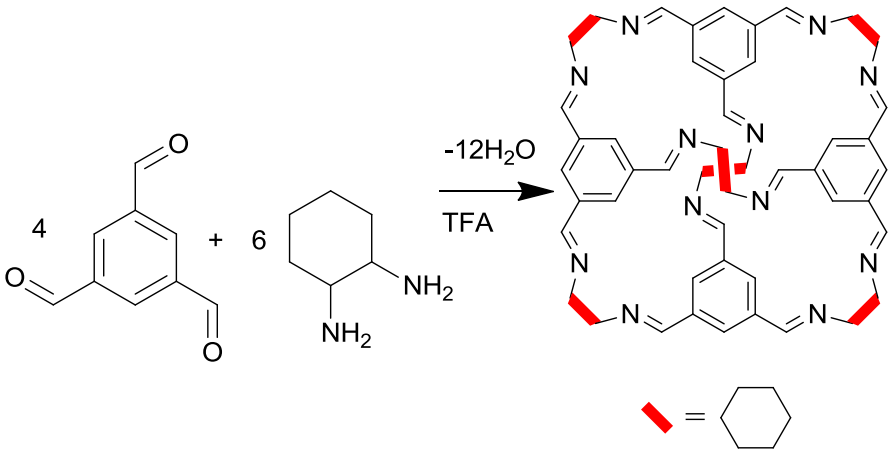
Left: A single 'porous organic cage' molecule

Right: Scheme showing packing of these molecules to form 3-D channels, illustrated here as yellow tubes.

In this document, we show how to create models for these molecules using only paper, scissors, and some glue.



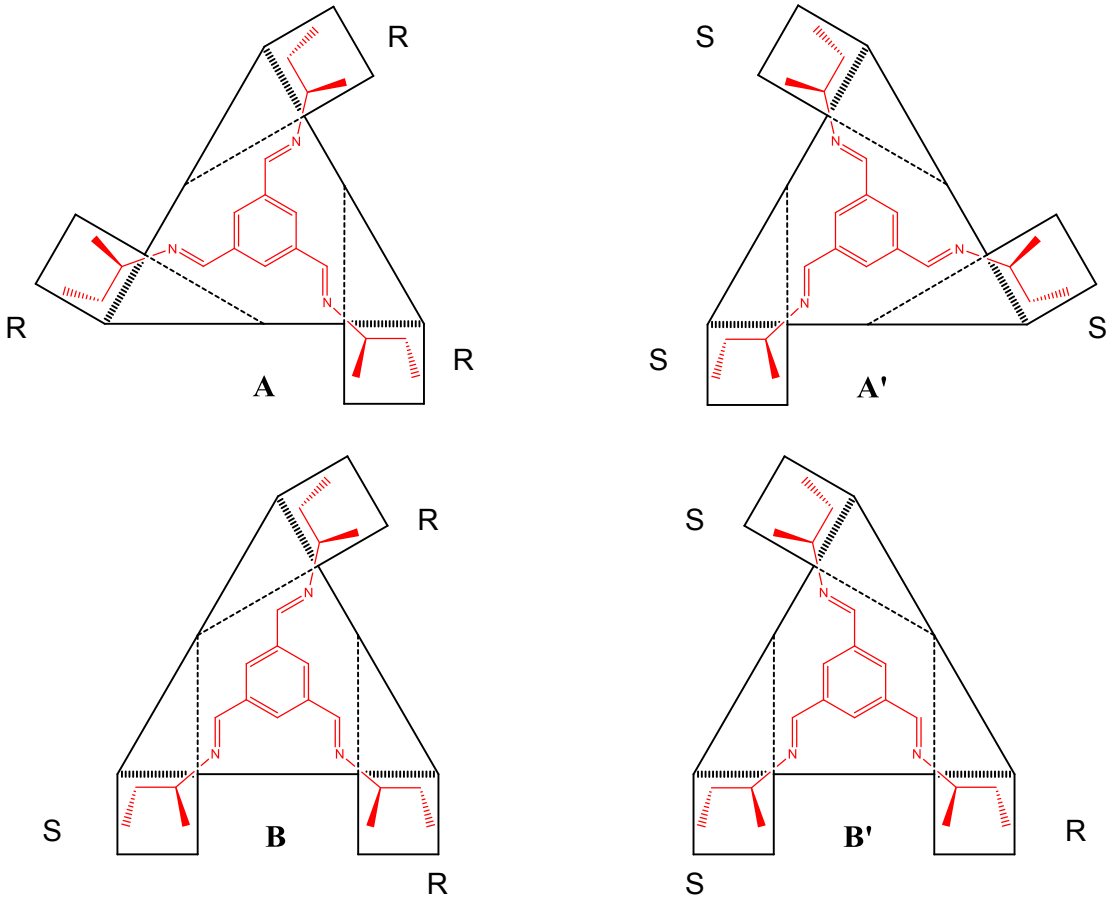
The molecules are synthesized by reaction of an **amine** with an **aldehyde** to form an **imine** cage. The overall reaction can be written as follows:



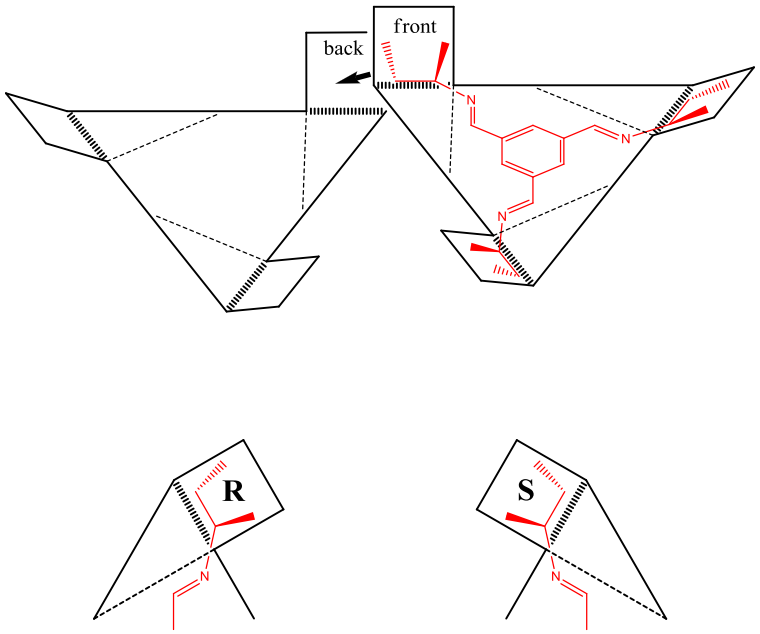
That is four molecules of the aldehyde react with six molecules of the amine to form one cage – that is, each cage is formed from 10 separate parts. This produces 12 molecules of water per cage as a side product, because each C=N imine bond that is formed produces a molecule of water. TFA is trifluoroacetic acid: this is simply a **catalyst** that speeds up the chemical reaction.

Simple Cages

Paper models of these cages can be prepared very easily from four basic shapes **A**, **A'**, **B** and **B'** (below).



To assemble the cages, simply cut out four shapes along the solid black lines and fold along dashed lines (----- = fold into plane; """"" = fold out of plane). (Larger templates are included at the end of this document.) Next, glue or staple the shapes together so that they are joined via the backs of square flaps. Note that only flaps having the same orientation with respect to the main triangular body can be paired up, that is **R**|**R** or **S**|**S**, but not **R**|**S**. The **A** shape might also be labelled **RRR**, the **A'** shape **SSS**, the **B** shape **RRS** and the **B'** shape **RSS**, which makes it easier in terms of finding possible combinations.



The tetrahedral cage that we reported in 2009 is assembled from four equivalent **A** shapes. Its **enantiomer** – that is, its mirror image – can be built from four **A'** shapes.

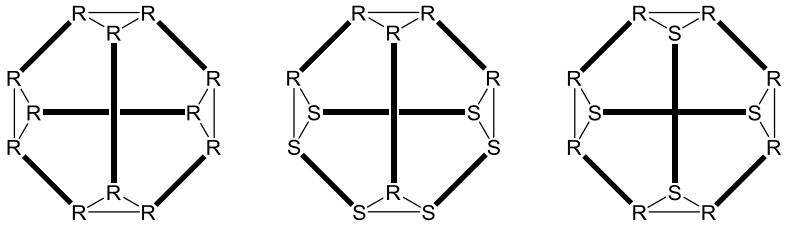
If you build several $\mathbf{A}_4$ and $\mathbf{A'}_4$, it is possible to assess how the cages may pack together in a 3-D crystal structure. For example, does $\mathbf{A}_4$ pack more effectively with itself or its enantiomer, $\mathbf{A'}_4$?

Advanced Cage Construction

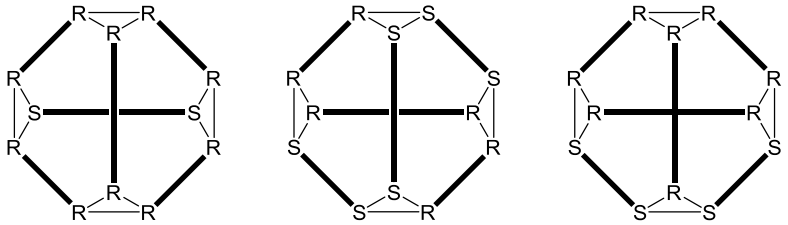
The $\mathbf{A}_4$ and $\mathbf{A'}_4$ models have **tetrahedral symmetry**. Non-tetrahedral cages can also be prepared using the asymmetric shape **B** or its mirror image, **B'**. For example, a C_3 symmetry cage (with a threefold rotation axis) can be built from one **A** shape and three **B'** shapes. Altogether there are six possible conformers plus six enantiomers, which can be made from the combinations listed below. The resulting models are somewhat distorted but free of strain, which suggests

that all six conformers are potential intermediates in the interconversion of enantiomers (see *e.g.*, *Angew. Chem., Int. Ed.*, **2011**, *50*, 749).

Conformer	Point group	Orientation of pairs of flaps	Enantiomer
$\mathbf{A}_4$	T	$(\mathbf{R}\|\mathbf{R})_6$	$\mathbf{A'}_4$
$\mathbf{AB'}_3$	C_3	$(\mathbf{R}\|\mathbf{R})_3(\mathbf{S}\|\mathbf{S})_3$	$\mathbf{A'B}_3$
$\mathbf{B}_4$	D_2	$(\mathbf{R}\|\mathbf{R})_4(\mathbf{S}\|\mathbf{S})_2$	$\mathbf{B'}_4$
$\mathbf{A}_2\mathbf{B}_2$	C_2	$(\mathbf{R}\|\mathbf{R})_5(\mathbf{S}\|\mathbf{S})$	$\mathbf{A'}_2\mathbf{B'}_2$
$\mathbf{B}_2\mathbf{B'}_2$	C_2	$(\mathbf{R}\|\mathbf{R})_3(\mathbf{S}\|\mathbf{S})_3$	$\mathbf{B'}_2\mathbf{B}_2$
$\mathbf{AB}_2\mathbf{B'}$	C_1	$(\mathbf{R}\|\mathbf{R})_4(\mathbf{S}\|\mathbf{S})_2$	$\mathbf{A'B'}_2\mathbf{B}$



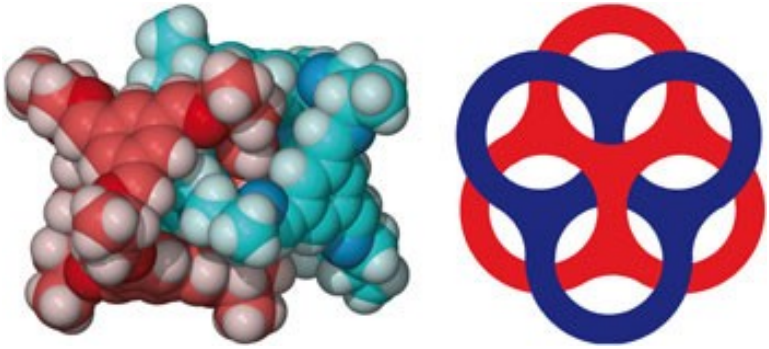
$\mathbf{A}_4$ $\mathbf{AB'}_3$ $\mathbf{B}_4$



$\mathbf{A}_2\mathbf{B}_2$ $\mathbf{B}_2\mathbf{B'}_2$ $\mathbf{AB}_2\mathbf{B'}$

Catenanes

With some skill and dexterity, two cages can be mechanically interlocked. The chemical term for this is a **catenane**.



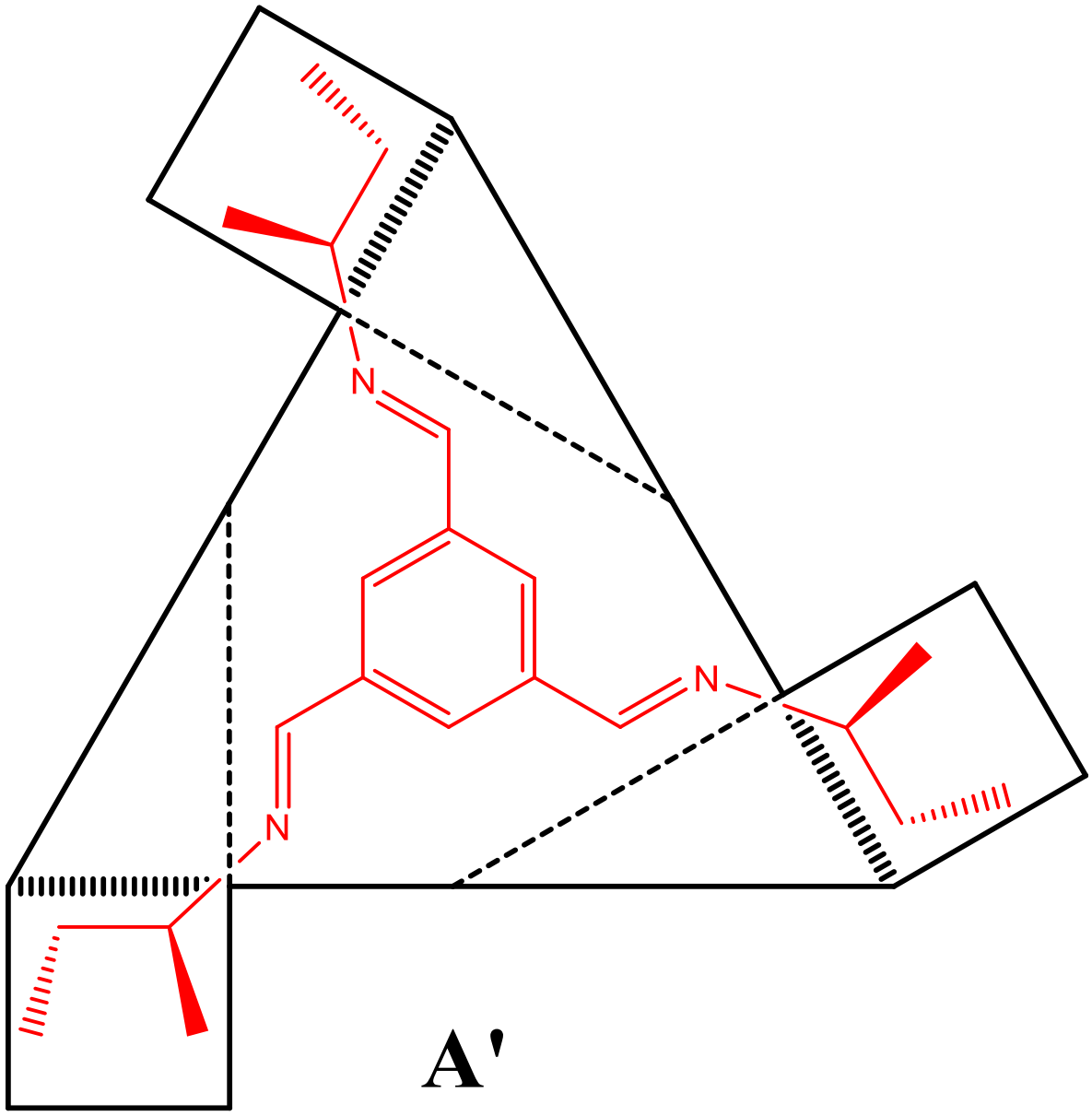
Structure and topological schematic for triply-interpenetrating cage catenane

Paper models for these catenanes demonstrate nicely that the homochiral catenane $(\mathbf{A}_4)_2$ is a better 'fit' than the analogous heterochiral compound $\mathbf{A}_4\mathbf{A'}_4$, as found experimentally (*Nature Chem.*, **2010**, *2*, 750). Surprisingly, just paper, scissors and glue can be used to generate models which tell us something useful about chemical structures!

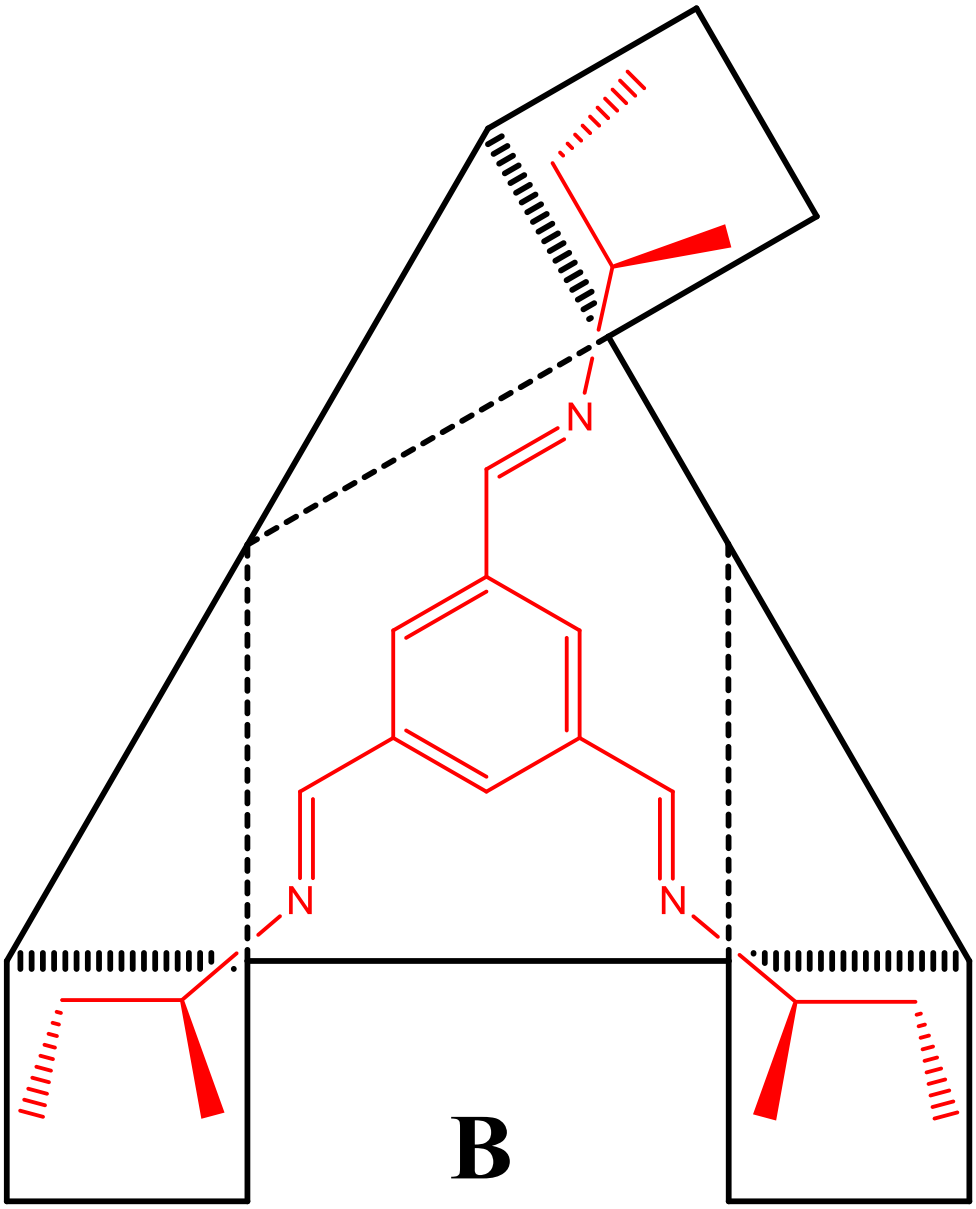
On the following pages (pp. 8–10) there are larger templates which are easier to cut out and work with. Note that the models are much easier to work with if these templates are printed onto stiff paper or thin card.

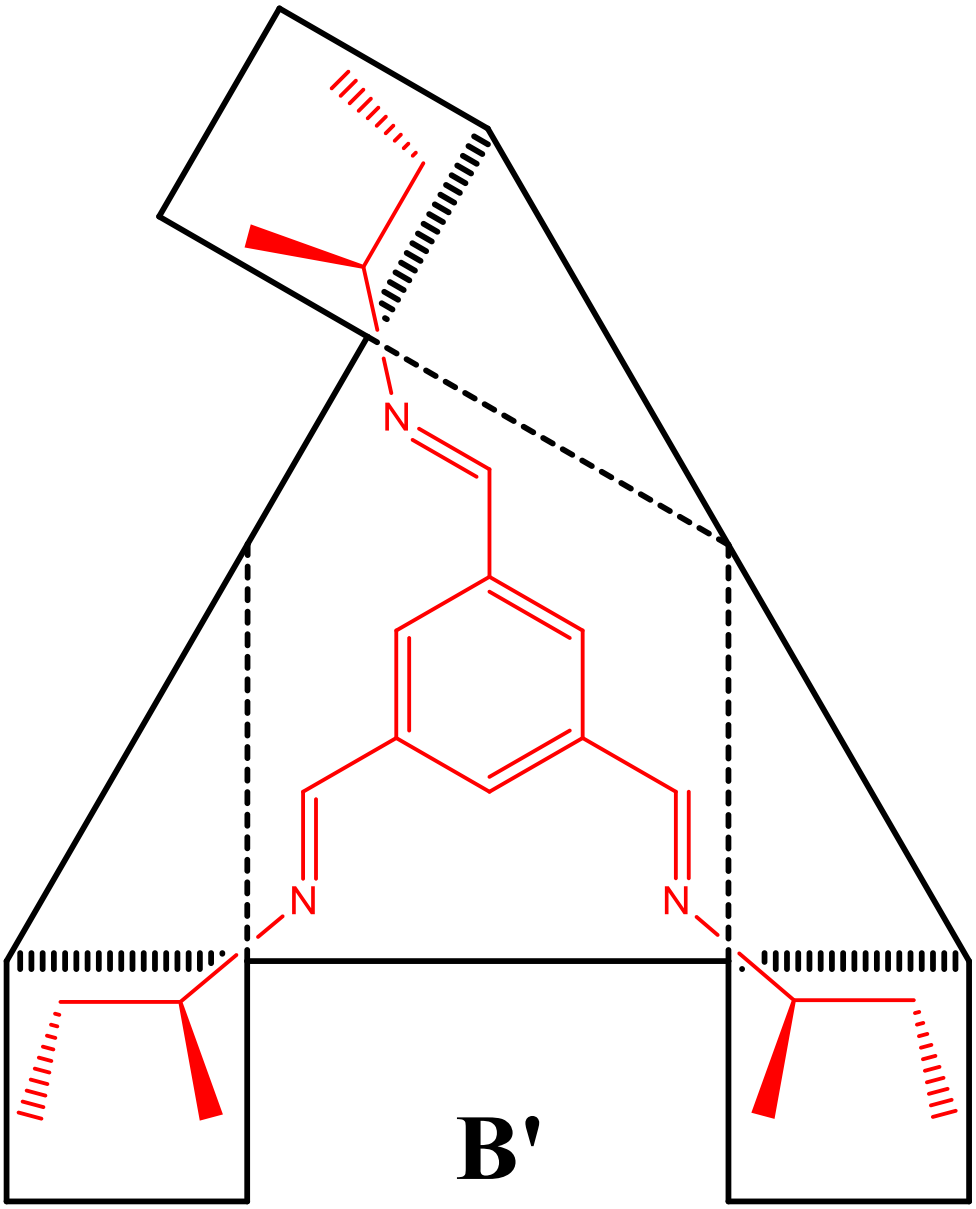
Have fun!

c



A'


N
N
N
B



B'

Exercises

1. Build a tetrahedral $\mathbf{A}_4$ cage and its $\mathbf{A'}_4$ enantiomer. Can you see that these two models are mirror images of each other?

2. Build 5 tetrahedral $\mathbf{A}_4$ cages. With some patience, you should be able to assemble these in a 'window-to-window' packing arrangement to replicate a section of the 3-D pore structure shown on page 2.

3. It is chemically possible to add larger, bulkier functional groups to these cages (*J. Am. Chem. Soc.*, **2011**, *133*, 16566). It is possible to replicate this in paper models, for example by gluing additional shapes to the 'flaps' on the cages. What effect is this likely to have on the potential 3-D packing of the cages? How might the cages pack together as the shapes attached to the flaps get larger and larger?

4 C_3 symmetry cage from one **A** shape and three **B'** shapes. This cage has C_3 symmetry: can you identify the unique threefold rotation axis?

4. Build both a homochiral $(\mathbf{A}_4)_2$ and a heterochiral $(\mathbf{A}_4\mathbf{A'}_4)$ catenane. Which model looks most plausible, bearing in mind that very close contacts between neighbouring atoms are often unfavourable. That is, which catenane fits together most naturally?

5. We challenge you to build paper origami models of other cage-like or macrocyclic molecules in the literature. You will of course need to design your own building blocks, similar to the ones given on pages 8–10… Some literature to start with:

(1) A salicylbisimine cage compound with high surface area and selective CO_2/CH_4 adsorption, Mastalerz, M.; Schneider, M. W.; Oppel, I. M.; Presly, O. *Angew. Chem., Int. Ed.* **2010**, 50, 1046.

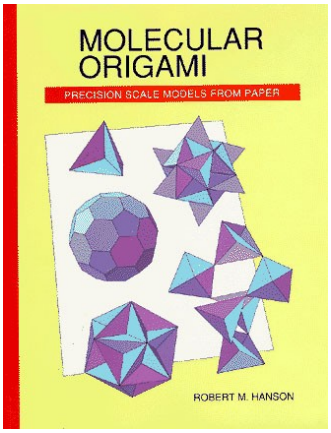
(2) Shape-persistent organic cage compounds by dynamic covalent bond formation, Mastalerz, M. *Angew. Chem.-Int. Edit.* **2010**, *49*, 5042 (and references therein).

(3) Self-assembled $M_{24}L_{48}$ polyhedra and their sharp structural switch upon subtle ligand variation, Sun, Q. F.; Iwasa, J.; Ogawa, D.; Ishido, Y.; Sato, S.; Ozeki, T.; Sei, Y.; Yamaguchi, K.; Fujita, M. *Science* **2010**, *328*, 1144. (Good luck with these ones!!)

We will feature photographs of any particularly impressive models on our website; please e-mail these to: ***aicooper@liv.ac.uk*** *No age restriction for entries…*

Other Resources

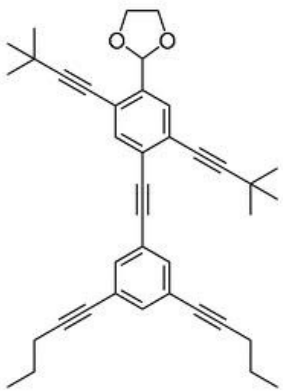
1. **"Molecular Origami"** – a book by Robert M. Hanson (published 1995) giving many more scaled paper molecular models.



2. **DNA "Origami"** – Folding shapes at a different length scale….

P. W. K. Rothemun, *Nature*, **2006**, *440*, 297.

3. "**Nanokids"** – Researchers at Rice University have synthesized molecules that look kind of like people, thus modelling large objects using molecules… http://nanokids.rice.edu/



Acknowledgements

We thank the Engineering & Physical Sciences Research Council (EPSRC) for funding this research (EP/H000925/1).

The Programme Grant in Chemical Synthesis of Transformative Extended Materials focuses on materials with function that extends beyond the molecular sub-unit. Our 10–15 year research vision is the chemical synthesis of advanced functional materials with properties that will challenge contemporary understanding of the physical and chemical behaviour of extended systems, achieved with the precision that is now customary in small molecule chemistry. It is important to realize this vision because the synthesis of new functional materials is of strong societal and economic importance to the UK in priority areas such as energy and healthcare, and because access to materials with unprecedented properties opens up new scientific horizons. Realization of the vision requires strong links to the materials science, condensed matter physics, chemical engineering and life science collaborators who form the Programme Grant (PG) partnership.

The proposal has a single 5-year thematic target: the development of synthetic methodologies for modular materials with "domains" of function.

Theme 1 targets porous materials with incompatible or "contraindicated" chemical functional groups that can deploy flexibly to produce unique molecular separations and catalytic reactivity, producing new paradigms for the efficient use of limited natural resources. The porous cages referred to in this document were synthesized as part of this theme. In Theme 2, optimally controlled interfaces in oxide materials will produce enhanced ionic transport for application in fuel cells and generate contraindicated scientifically challenging physical properties (*e.g.*, ferromagnetism and ferroelectricity in a single material). The properties and functions accessed in Themes 1 and 2 on the molecular scale will be translated into the nano- to meso-scale in Theme 3 by chemical control of the statistical assembly processes which produce nanostructured assemblies.