

3D Printing of a Scalable Molecular Model and Orbital Kit for Organic Chemistry Teaching and Learning

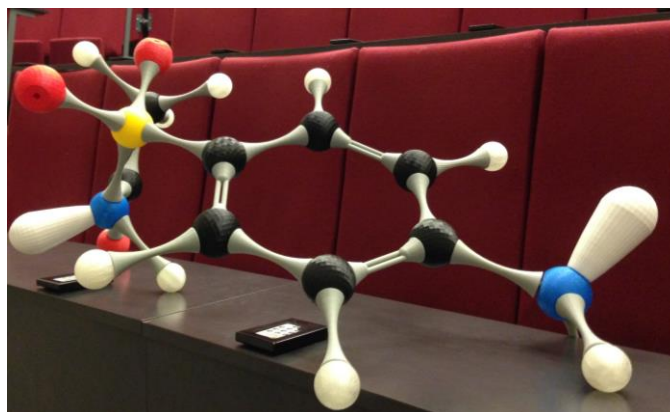
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ABSTRACT

Three-dimensional (3D) chemical models are a well-established learning tool used to enhance the understanding of chemical structures by converting two-dimensional paper or screen outputs into realistic three-dimensional objects. Whilst commercial atom model kits are readily available, there is a surprising lack of large molecular and orbital models that could be used in large spaces. As part of a program investigating the utility of 3D printing in teaching, a modular size-adjustable molecular model and orbital kit was developed and produced using 3D printing and was used to enhance the teaching of stereochemistry, isomerism, hybridization and orbitals.

ABSTRACT GRAPHIC



KEYWORDS

Organic Chemistry, Hands-On Learning/Manipulatives, Alkanes/Cycloalkanes, Alkenes, Chirality/Optical Activity, Conformational Analysis, Drugs/Pharmaceuticals, Stereochemistry, Molecular Modeling.

▪ INTRODUCTION

25 Three-dimensional (3D) models have been an essential kinesthetic pedagogical tool
for educators in chemistry due to their ability to facilitate the visualization of molecules
in three-dimensions.¹⁻³ Due to the difficulty of converting chemical structural
representations of molecules from paper into a 3D image in a student's mind, the need
for clear physical representations is obvious. As a result, the development of molecular
30 models has received considerable attention for the best part of a century, and commercial
models such as Molymod have become widely used by students together with some more
esoteric and innovative compositions.⁴⁻¹⁶ The commercial success of model kits,
particularly with students of organic chemistry, is due to their modular nature; many
molecular models can be assembled, modified and disassembled according to
35 requirements. Unfortunately, due to their small sizes, their usefulness as teaching aids
are limited, especially for demonstration purposes during lectures or seminars in large
teaching spaces. The construction of bigger models for use with a large audience has been
discussed in the literature. However they are often either expensive or lack the flexibility
of a modular kit.¹⁷⁻¹⁹ Alongside the development of molecular models there have also been
40 reports describing the construction of molecular orbital models.²⁰⁻³⁰ However, there is a
comparative lack of either small- or large-scale orbital models in the commercial area,
which is surprising given that students often struggle with the concepts of molecular
orbital theory and its application to organic chemistry.³¹

3D printing, or additive manufacturing, has received much attention in the
45 engineering, scientific and lay communities due to its ability to facilitate the rapid
development of novel prototypes and is quickly becoming a powerful manufacturing
tool.³² In recent years this technique has found numerous applications, and synthetic
chemists have recently applied 3D printing in both research and education.³³⁻³⁸ The
ability to construct complex customized objects with ease and at a very low cost (1 kg of

50 plastic filament currently retails in the region of \$20) has enabled researchers and
educators to tailor teaching aids to their lecture courses. This potential has been realized
in the area of complex inorganic structures that have been 3D printed as well as models
demonstrating abstract concepts in physical and inorganic chemistry.^{10, 39-51}

As educators in organic chemistry will be all too aware, the concepts that often limit
55 the learning and understanding of students are those that require spatial awareness.
Even the most capable students will need to make use of a 3D molecular model in order
to reinforce their knowledge and understanding. In this report the application of 3D
printing in the development of large customized molecular and orbital models is
described. These were used to explain key chemical concepts within the context of a
60 lecture course given to first-year students and complementary 3D printed smaller models
were used in follow-up workshop classes. Descriptions of the various models and their
relative sizes are described in the supporting information, and pre-prepared 3D printing
files are provided free *via* the author's account on Thingiverse and as supporting
information files with this article.⁵²

65 ■ **METHODOLOGY AND APPLICATIONS** **DESIGN AND CONSTRUCTION OF MODELS**

In order to create a chemistry model set, online published chemical structure designs
of models were first investigated. Whilst a 3D model of ethanol on Thingiverse by Rodger
70 proved suitable for one-off small models, it proved unsuitable for larger lecture teaching
models due to the less robust round connectors between atoms and bonds.⁵³ As such,
atom models and bonds were first developed, which it was envisaged could be held
together by means of a semi-rigid clip (Figure 1).⁵⁴ Carbon atoms were designed to be
large enough (62 mm diameter) to be visible from the rear of a large lecture theatre for up
75 to 200 people. Bonds to connect atoms were 104 mm length and were represented as

shown below for clear visualisation of single, double and triple bonds and rotatable bonds (dimensions and construction shown in Supporting Information). A flat surface for connection of the bonds was created by subtracting a negative image of the clips and a smooth surface from a sphere. Using this approach, atoms with sp^3 , sp^2 and sp hybridization (carbon, oxygen, nitrogen), hydrogen atoms, bonds (single, double, triple and rotatable) and clips to join these together were developed and printed with the appropriate colours (Figure 1).

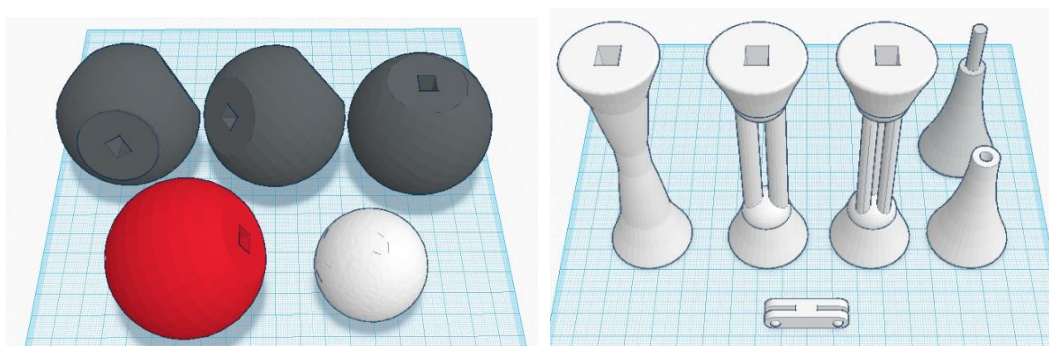


Figure 1. Models of carbon, oxygen, hydrogen, bonds and the clip used to connect these.

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Due to the proposed concept of employing the models for use in large teaching spaces, they needed to be both sturdy, and lightweight at the same time. Fortunately, the software accessible to most FDM printers enables a user to select a level of infill (the amount of material placed in the internal structure of the print) that is fit for the required purpose and hence reduces the print time accordingly. As such, all models were printed at a range of infill percentages in polylactic acid (PLA) or acrylonitrile butadiene styrene (ABS) polymers with the exception of the rotatable bonds, which, due to their delicate nature required a higher level of infill at 30%. The weights, costs, percentage infill and material used for each design are shown in Table 1.

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Table 1. Costs and weights of individual full-size printed modules.

Type	Sub-type	Infill %	Weight g	Color	Material Used	Unit Cost, \$ ^a
Carbon	sp	10	20.27	Black	PLA	0.53
Carbon	sp + 2p	10	20.27	Black	PLA	0.53
Carbon	sp ²	10	20.70	Black	PLA	0.55
Carbon	sp ² + 2p	10	20.70	Black	PLA	0.55
Carbon	sp ³	10	20.92	Black	PLA	0.55
Nitrogen	-	10	20.70	Blue	PLA	0.55
Nitrogen	sp ² + 2p	10	25.49	Blue	PLA	0.67
Oxygen	-	10	20.30	Red	PLA	0.53
Oxygen	+Lone pairs	10	26.13	Red	PLA	0.69
Hydrogen	-	10	9.10	Clear	PLA	0.25
Bond	single	20	10.00	Grey	ABS	0.26
Bond	double	20	9.90	Grey	ABS	0.26
Bond	triple	20	10.20	Grey	ABS	0.27
Bond	rotatable	30	10.20	Grey	ABS	0.27
Lone pair	-	10	56.83	White	ABS	1.49
Lone pair	Pi bond	10	36.94	White	ABS	0.97
Lone pair	Pi bond bridge	10	18.65	White	ABS	0.49
Lone pair	Pi bond infill	5	8.28	White	ABS	0.21
Sigma bond	-	5	34.52	White	ABS	0.91
Clip	-	10	1.10	Green	ABS	0.03

^aThe price per kg in USD is 26.33 with the unit cost being a single object of each unit.

100 During the preparation of atoms, bonds and clips it became evident that different materials were required for different elements as the connectors printed with polylactic acid (PLA) proved too brittle for repeated assembly and disassembly in the models, leading to breakages. Therefore, atoms were printed in either ABS or PLA and bonds and clips in ABS alone.

105 The development of 3D printed orbital models was more challenging as there were scant reports in the literature about their use and few commercial models available. Their development was therefore explored using 3D printing. Sp³ hybrid orbitals were initially designed that would contain lone pairs of electrons for water and ammonia to gauge the

correct size for visualisation (Supporting Information). This took three iterations
110 (Supporting Information) to generate the correct size for the large models for use in
lectures. These were printed in either ABS or PLA and at 10% infill to reduce the weight
of the final object (Figure 2). For simplicity, a single orbital shape was chosen to be used
as a 2p orbital or as an sp^3 , sp^2 or sp hybridized orbital by interchanging with the desired
atom of appropriate geometry. The oxygen atom and nitrogen atom were printed using
115 the same sp^3 model of the carbon atom, but in a different colour.

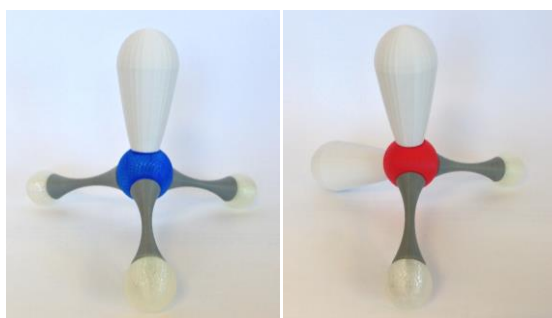
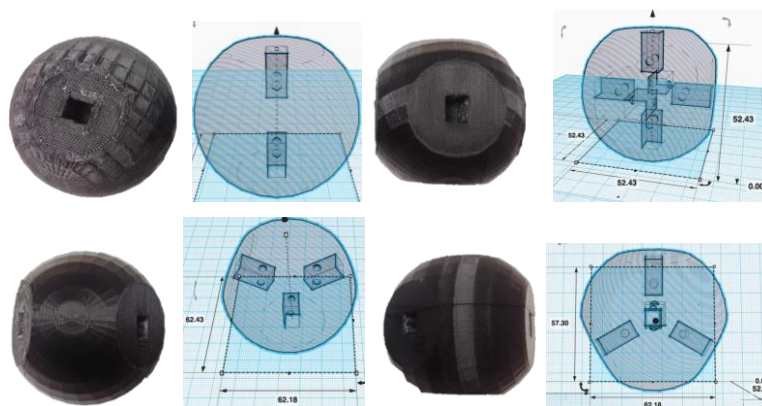


Figure 2. Models of ammonia (left) and water (right) to show the size and scale of the lone pair.

In order to develop carbon atoms with appropriate attachment points for orbitals and
120 pi bonds, a range of atoms was designed and printed (hollow models are shown alongside
for clarity of the design with internal clip points) (Figure 3).



125 Figure 3. Printed (black) and hollow computer models (grey-striped diagram) of carbon atoms of different hybridizations:
 sp (top left), sp with orbital attachment points (top right), sp^2 (lower left) and sp^2 with attachment points for orbitals (lower right).

The second stage of design focused on the correct representation of the bonding orbitals in formaldehyde by firstly constructing a model to show the constituent p orbitals on the oxygen and carbon atoms. These were linked by a 'bridge' to show side-on orbital overlap leading to formation of a pi bond. The 3D-printed 'bridge' between the p orbitals in the formaldehyde model was designed to demonstrate the basis behind the rigid, non-rotatable carbon-oxygen double bond. These were designed via subtraction of one face of the lone pair and extension of this subtracted section into the pi cloud bridge as shown (further details are provided in the Supporting Information) (Figure 4).

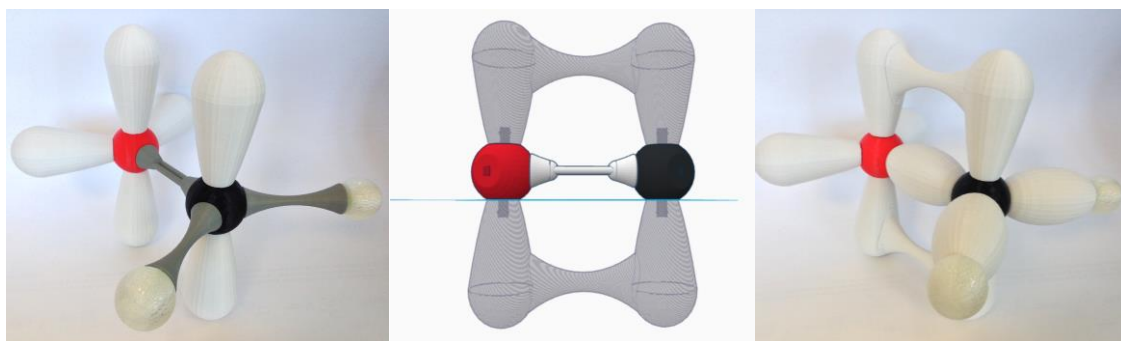


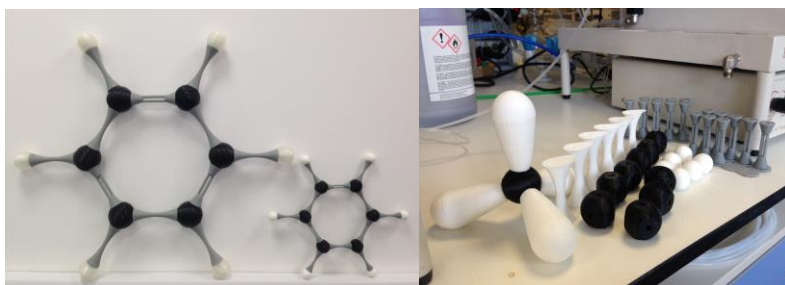
Figure 4. Development of an orbital model of acetone (left). Pi-cloud orbital design model showing the hollow mesh model (centre), and the final model incorporating the pi cloud bridge (right).

Once the models had been printed and evaluated, additional examples were rapidly prepared for workshops where students could benefit from examining and physically interacting with the models. The modular nature of the models allowed a wide range of concepts in organic chemistry to be illustrated as discussed in the following sections.

PRODUCTION OF SMALLER WORKSHOP APPLICABLE MODELS

Due to the facile method of production using 3D printing, smaller-scale workshop-applicable models (for 50 students working in 10 x groups of 5 led by 4 staff members) could easily be prepared by reducing the size of the models at the point of printing using the software on the 3D printers. Models and corresponding bonds were scaled down in the basic software (MakerBot Desktop) by 50% to generate the structures shown, with

150 the larger models shown next to them for comparison. When the clips were printed at 50% scale, they proved too large to use. However, reducing their size further to 47% ensured that they were small enough to connect the atoms together (Figure 5 and Supporting Information).



155 Figure 5. Model of larger-scale benzene against its workshop congener, as well as an illustration of the printing options at 50% scale.

APPLICATIONS

Molecular Models

The initial application focused on the design and production of large, modular 3D
160 molecular models for use in large teaching spaces. These models were designed to explain
the concept of molecular shape to a group size of over 180 students as part of a lecture
course on structure and bonding (Figure 6). These custom-made models helped to
demonstrate fundamental concepts and would have been prohibitively expensive if
externally sourced models had been used. The cost of cyclohexane used in this lecture
165 was around \$13, clearly highlighting the low-cost potential of this approach.

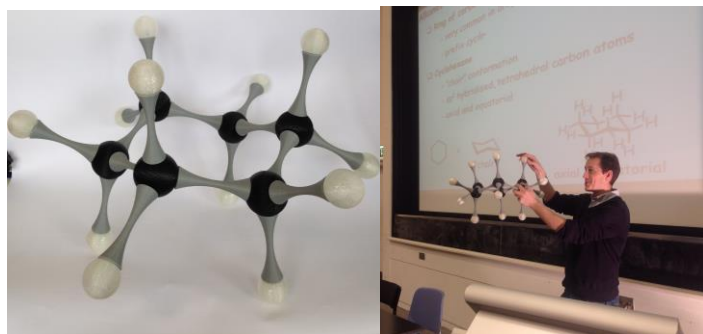


Figure 6. Large-scale models are necessary when presenting to large audiences. In this case a large 3D printed model of cyclohexane (left) is being used to help illustrate its shape and bond angles and to introduce the concept of axial and equatorial orientation of its substituents. Model is fixed in one conformation due to the rigid nature of the clips.

170 **Stereochemistry**

The study of stereochemistry tests the spatial awareness of chemistry students to a greater extent than any other topic and, as such, has been a focus for the effective use and application of molecular models.^{55, 56} This area was therefore an obvious target for this approach to address the fundamentals of geometric isomerism in alkenes and
175 chirality (Figure 7).

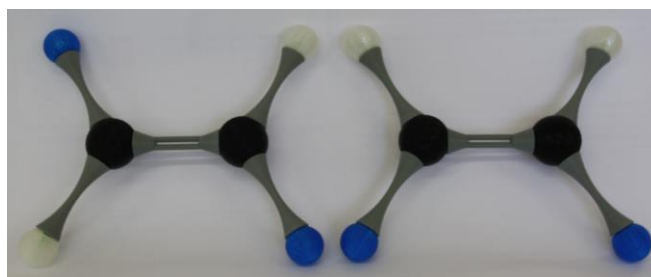


Figure 7. Models of geometric isomers of a simplified alkene showing the *trans*- and *cis*-arrangement of atoms that were prepared for demonstration to large groups of students.

180 There is typically great variability in individual student's innate spatial awareness and this can present difficulties when teaching large groups. Following the discussion of optical and geometric isomerism aided by large 3D printed models during lectures, students were presented with a set of problems in small groups in a workshop setting where mirror image pairs of chiral models were used to aid explanation and the size of
185 each enantiomer can be clearly observed (Figure 8). Students were able to physically manipulate (rotate, align and reorient) the 3D models to help them assign absolute configuration by comparison between molecular structures on paper and 3D models and *vice versa*. It became evident in the workshop that some students were able to grasp the concept by use of these models and, using peer-supported learning, transferred this
190 information to others.

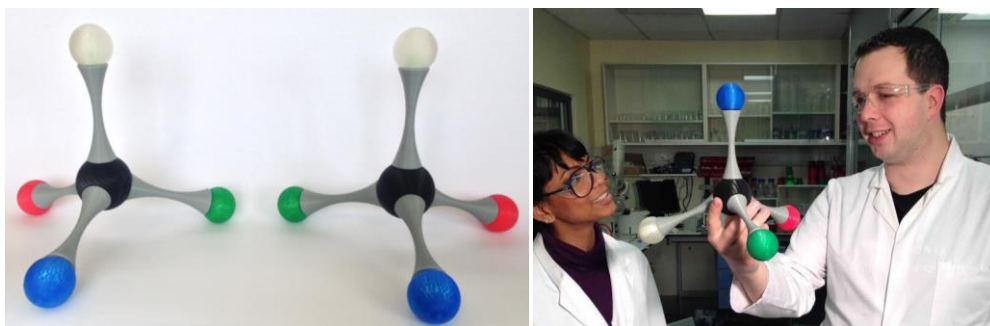


Figure 8. 3D printing has allowed the facile and speedy production of enantiomeric models with which students can interact.

Newman Projections and hybridization

195 A common source of confusion for some organic chemistry students is the relationship between conformation and configuration. This topic has great significance in medicinal chemistry and was therefore particularly pertinent to the students' understanding of drug-target interactions. As bespoke models had been created to illustrate configuration, models were created that would allow students to understand
200 bond rotation.³⁴ A rotatable bond was designed and developed, so that students could familiarize themselves with Newman projections (Figure 9). As mentioned above, it was decided to print the rotatable bond with a higher infill percentage (30%) as it proved to be fairly fragile at lower infill percentages. The eclipsed and staggered forms are shown in Figure 9; by simple manipulation, the interchangeable energy forms can be
205 demonstrated dynamically and are all eminently visible to students. The total cost for this model is less than \$6, highlighting, again, the low-cost nature of this approach.

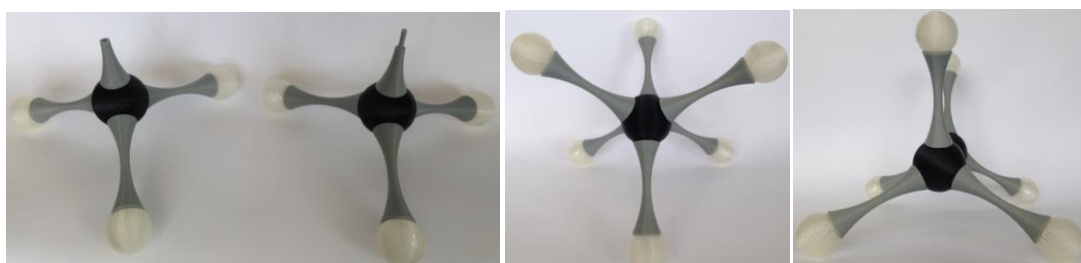
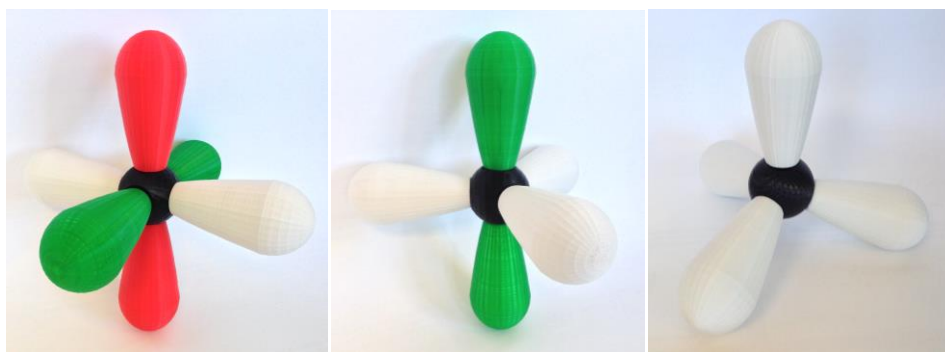


Figure 9. Bespoke rotatable bond to illustrate conformation as exemplified by the staggered and eclipsed forms of ethane.

Hybridization

210 Given the relatively abstract nature of hybridization and its implications to structure and bonding, it was envisaged that the models would have a significant impact on teaching and learning in this area. The relative arrangements of the sp^3 , sp^2 , sp and $2p$ orbitals in different hybridization states were easily constructed and clearly displayed to students in lectures using a combination of lone pairs and carbon atoms from the orbital kit (Figure 10). The formation of sigma bonds from end-to-end orbital overlap, and pi bonds from side-to-side overlap, were demonstrated in the models of ethene and acetylene (Figure 11).



220 Figure 10. sp , sp^2 and sp^3 hybridized carbon atoms were designed for use in the teaching of hybridization and to construct molecular orbital models.

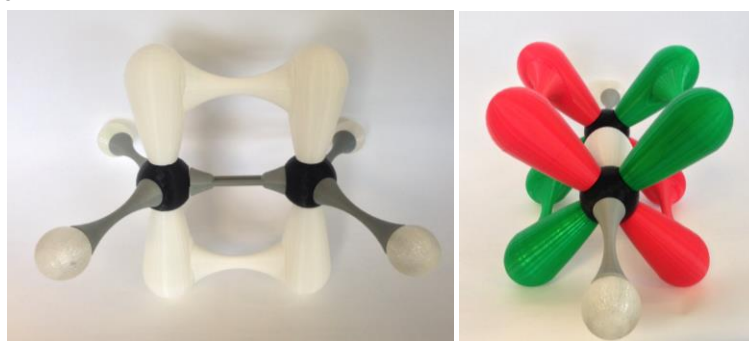


Figure 11. sp^2 and sp hybridized carbon atoms of ethene (left) and acetylene (right) were used to illustrate the orthogonal pi bonds in ethene and acetylene, respectively.

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Aromatic Compounds

As a result of the fact that the models were initially intended for first-year students, the study of aromatic compounds was of particular importance given their prevalence in medicinal chemistry. As the concepts of hybridization and orbital overlap had been reinforced with the use of large-scale models, the introduction and development of aromaticity was a natural progression for this approach. The large size and ease at which models could be put together and disassembled as required was ideal for displaying aromaticity and the clear extended conjugation to large audiences. NMR spectroscopy and electrophilic aromatic substitution reactions also benefited from this approach where the electron cloud of the aromatic ring could be observed. Furthermore, the model of pyridine provided students with an obvious explanation of its basicity with the clear display of the orthogonal lone pair protruding away from the conjugated pi system (Figure 12).

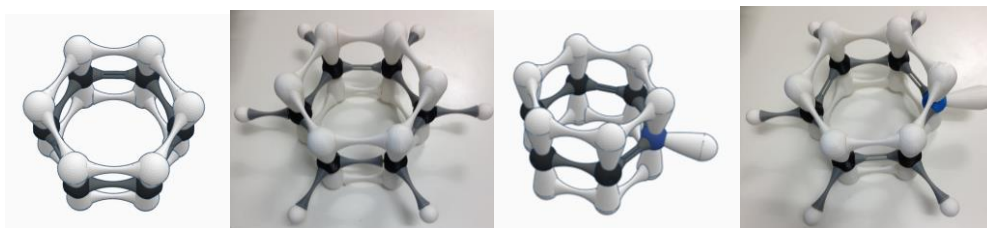


Figure 12. Models of benzene (left) (Tinkercad and printed) and pyridine (right) (Tinkercad and printed) showing the pi cloud of the double bonds and the pi cloud conjugation.

RECEPTION BY STUDENTS

As part of this study, the impact on the students themselves was of particular interest. Anecdotal feedback from undergraduates was extremely positive as they felt better able to understand structural concepts that they had previously found challenging. The ability for students to physically manipulate models to explore rotation, reorientation and view molecules from alternative perspectives in workshops was well-received. An audience response system was used to collect feedback from more than 180 students at the end of the first term of the module. A simple survey found that 72% (130) of students agreed (6%, (11) disagreed) that the models helped with their understanding of structure and bonding

and 79% (149) agreed (6% (11) disagreed) that the use of 3D printed models represented an improvement over 2D images on slides and paper.

CONCLUSIONS

255 3D printing has been used to create scalable, modular molecular and orbital models for use as pedagogical aids in teaching organic chemistry with clear positive feedback from students. The infrastructure to support 3D printing within UCL has also been developed, which has allowed the rapid production of models at a very low cost and reproducible models to illustrate fundamental concepts in stereochemistry, configuration
260 and hybridization have been designed. Further studies into the development of more complex structures will be reported in due course and additional models will be uploaded as they are produced.⁵²

ASSOCIATED CONTENT

265 Supporting Information

Further detailed pictures and descriptions of the molecules, atoms bonds and orbitals are available via the Internet at <http://pubs.acs.org>. 3D .stl files of the models described in this publication are available as a complete zip file.

270 AUTHOR INFORMATION

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