

Molecules in the News.
**A selection in Spring 2017 illustrated with physical model kits of various types
and renditions using software.**

Supplement to "[A comparative review of five brands of molecular model kits. With notes on the educational merits of kits in an age of software.](#)"

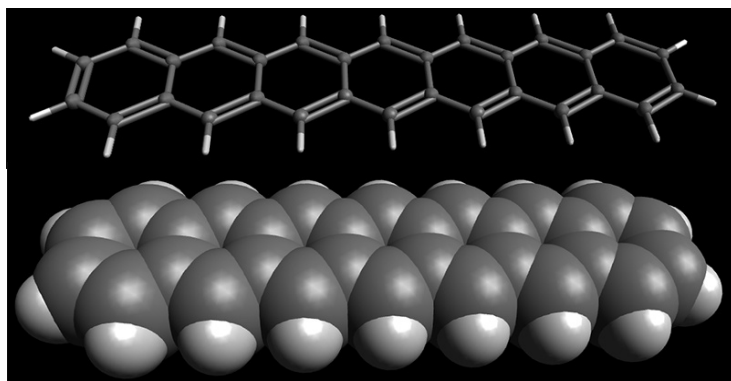
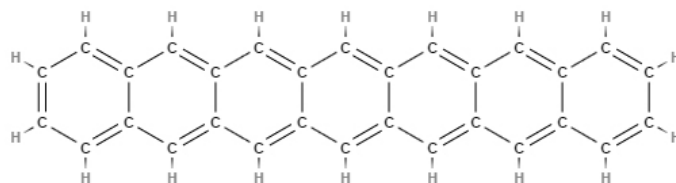
by David Walker, UK

One appealing use of molecular models kits is to make, where possible, physical models of interesting molecules in the news. Below are two specific molecules recently in the news, heptacene and triangulene, represented using one or more of five types of physical kits and are compared with typical software representations. A brief note on the Nobel Prize for Chemistry 2016 awarded to three chemists for their work on molecular machines is also included (to be extended with examples of more models of typical machines). (Scale bar shown on all model images is 10 cm.)

Heptacene *First isolation reported March 2017*

This molecule is the seventh member of the acenes; six membered aromatic carbon rings that are connected linearly. The first three members being benzene, naphthalene and anthracene. Heptacene is a deceptively simple looking molecule compared with the very complex molecules capable of modern organic synthesis but it has resisted until recently attempts to isolate a stable pure solid rather than being stabilised in a solid matrix.

Einholz at the University of Tübingen, Germany with co-workers at this and other institutions, have now reported their successful synthesis of the isolated pure solid. The longer acenes have interesting electronic properties and studying these may suggest uses, the workers' examples include LEDs or solar cells.

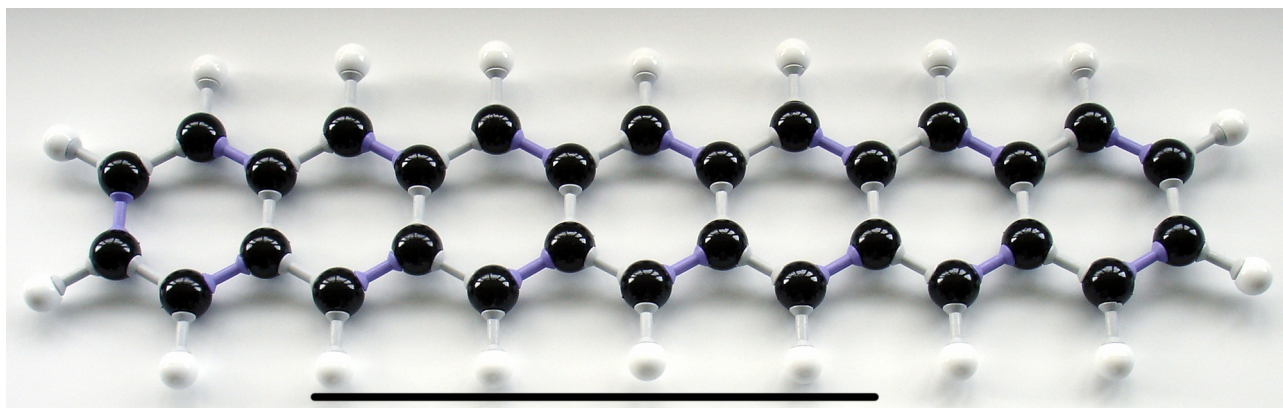


Above. 1) Structural formula, 2) 3D rendering using ball and stick showing the planar structure and 3) van der Waals surface model showing its external form.

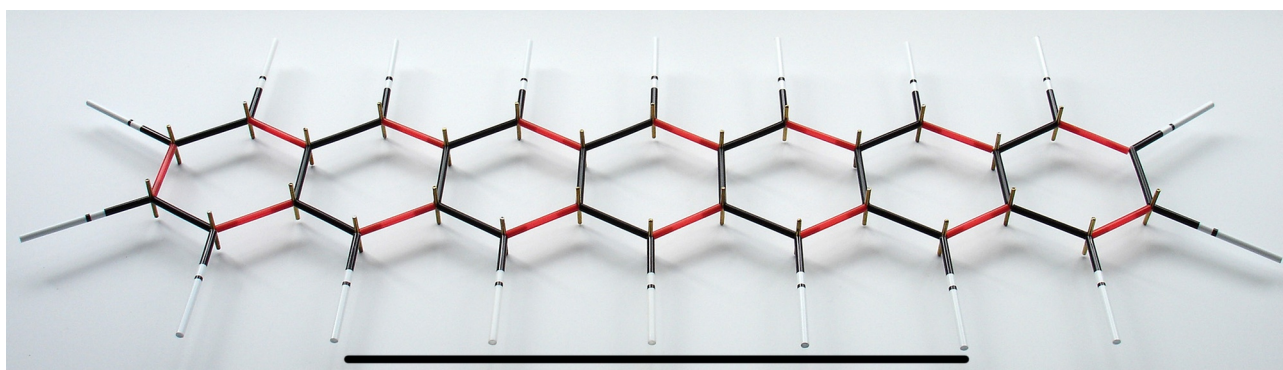
Heptacene is a useful model to illustrate how double bonds can be represented in polycyclic aromatic molecules. Some kits, such as Orbit and Minit, include an option to highlight double bonds with extra white links. Using a contrasting colour for the double bonds e.g. using the purple links included with Molymod kits is another approach (see below). These two methods are preferred as they retain the correct sp^2 atom centres and thus bond angles.

Another option offered by Orbit, Minit and Molymod using the flexible links supplied with tetrahedral carbon centres are not suited for benzene rings; 109.5° bond angles in positions that should be 120° introduce noticeable distortions in the structure. Introducing tetrahedral atom centres into a molecule to form double bonds may also potentially mislead

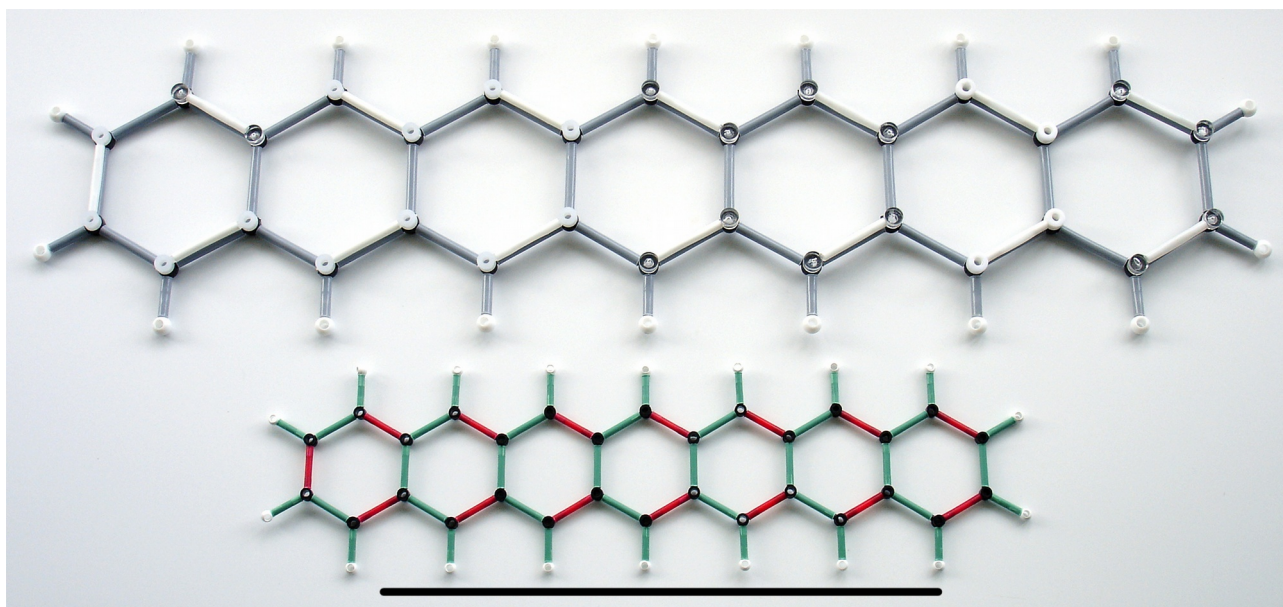
some users; (Ingham remarked on this in her 1988 Ph.D. thesis when interviewing students building models, ref. 1). Using two flexible links arguably works better for isolated double bonds in e.g. aliphatic structures.



Above. Heptacene, Molymod open model using the purple links to highlight double bonds. This retains the correct sp^2 atom centres to give the correct bond angles.



Above. Heptacene, ChemKits model, bar 10 cm. ChemKits does offer a way of showing pi bonding e.g. in aromatic rings (see main article, benzene illustration). This becomes less practical with extensive multiple bonds and highlighting the double bonds in a link of different colour can work well, as shown here. The traditional use of red for oxygen bonds has been put to one side here. As long as the user knows what the bonds represent, there is no potential to mislead.



Above, Heptacene, Orbit and Minit models, bar 10 cm. With the Orbit, the use of white parallel links with pegs supplied to indicate double bonds have been used. For the Minit, a red bond link has been used. Some model systems offer a number of approaches to show multiple bonding.

If desired it is possible with the Orbit and Minit to put white links either side of the single bond to more accurately represent the symmetrical double bonding. This becomes less practical, as here, with polycyclic aromatics.



Above, Heptacene, Molecular Visions model, bar 10 cm. With its dedicated double bond links and rigid construction method holding the molecule planar, this is one of the more successful for large robust models of polycyclic aromatic rings e.g. for demonstration purposes.



Above, Heptacene, Molymod model, bar 10 cm. The short links are used here to represent as a 'semi-space-filling model'. Hydrogens can also be represented by the 'mushroom' or 'Molydome' atoms provided with some kits.

Sources for heptacene

- Ralf Einholz, Treliant Fang, Robert Berger, Peter Grüninger, Andreas Früh, Thomas Chassé, Reinhold F. Fink, and Holger F. Bettinger

J. Am. Chem. Soc., 2017, 139 (12), pp 4435–4442.

["Heptacene: Characterization in Solution, in the Solid State, and in Films"](#)

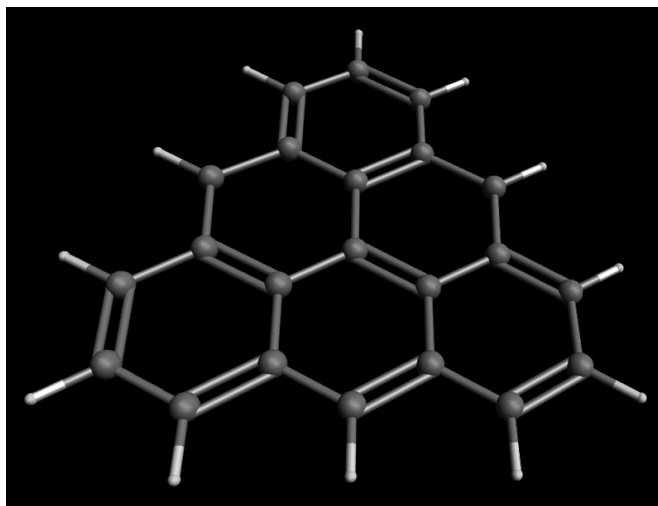
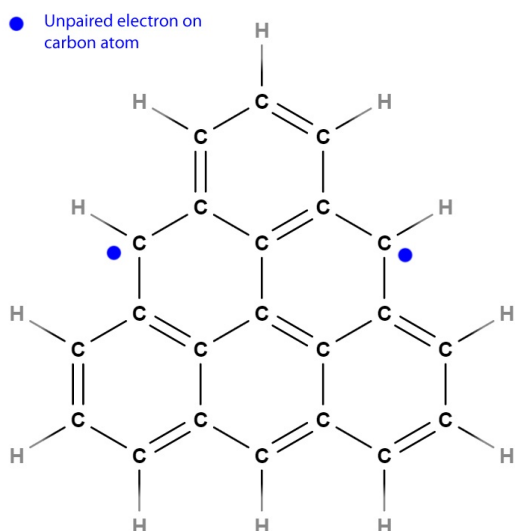
Free access only to affiliates. A free summary is:

- Katrina Krämer, ["Heptacene isolated after 75 years"](#), Chemistry World, 31 March 2017.

The 'enigmatic' and 'elusive' triangulene. First synthesis as discrete molecules February 2017.

The successful synthesis of this molecule by researchers at IBM's labs in Zurich has a number of fascinating aspects which illustrate the amazing manipulations and imaging on the atomic / molecular scale that can be achieved nowadays. Some aspects of the study are summarised below.

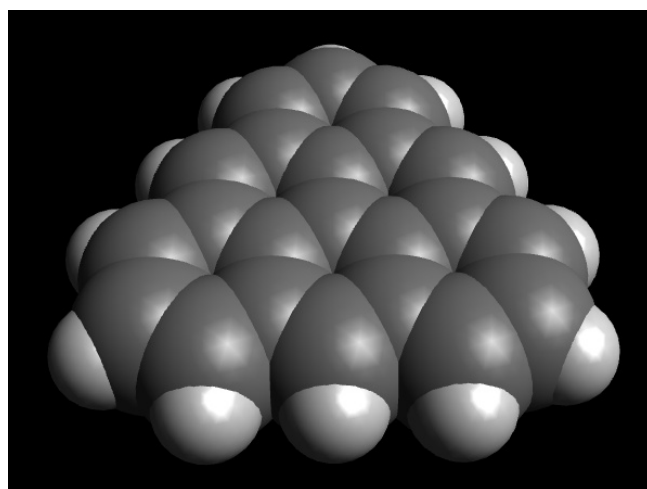
- triangulene has two of its carbon atoms with an unpaired electron on each, which makes it very reactive and thus difficult to synthesise pure (rather than as substituted derivatives) using traditional techniques.
- single molecules were created on selected surfaces (NaCl(100), Cu(111), solid Xe(111)) by manipulating atoms with a 'combined scanning tunnelling microscope / atomic force microscope' (STM / AFM).
- the stable precursor dihydrotriangulene adsorbed on a chosen surface had selected carbon centres exposed to a voltage potential sufficient to remove one hydrogen from each to form triangulene.
- images of single molecules were taken using the same instrument.
- AFM images were taken by placing a single CO molecule on the probe tip to achieve high resolution.
- studies of the electron structure of the molecule, which is essentially a graphene fragment with two unpaired electrons in a triplet ground state, may have importance in fields such as spintronics which exploit the properties of electron spin.



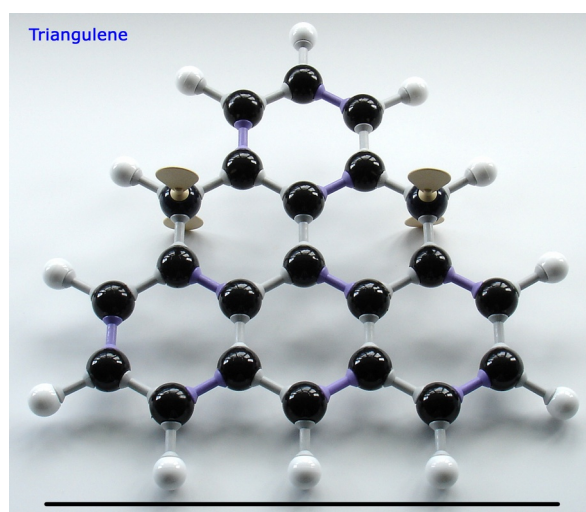
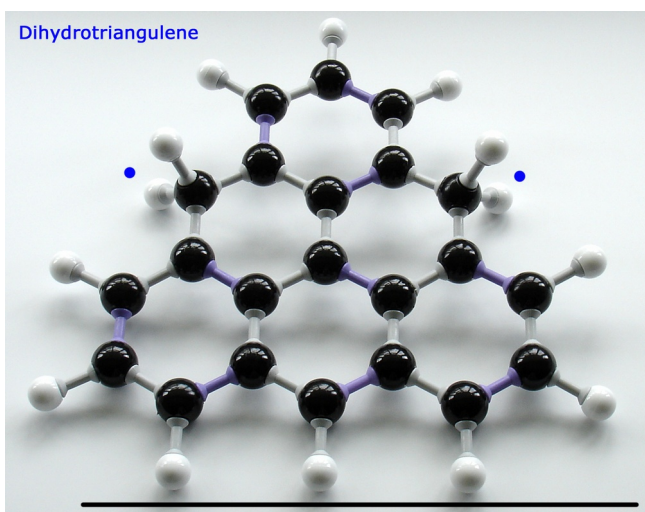
Left above. Structural formula showing the two carbon centres, each with an unpaired electron.

Right above. Ball and stick rendering in software showing the planar molecule.

Right. Rendering in software showing the van der Waals surfaces, a close representation of the true external form of the molecule.



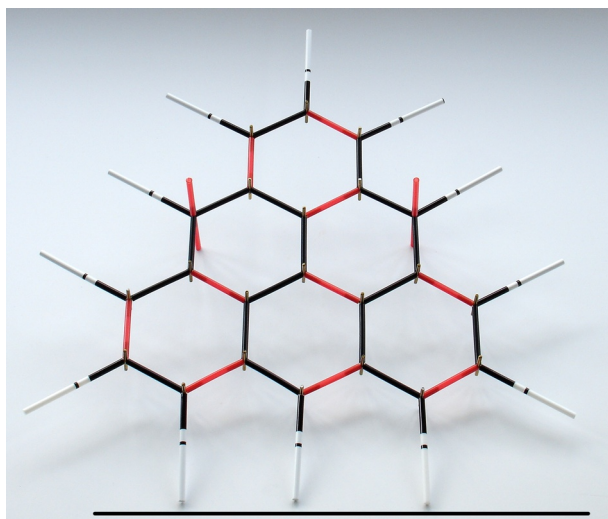
Representing triangulene in physical molecular models. How best to represent the unpaired electrons for each model system may be up to the user, but examples of a model from each kit suggest approaches.



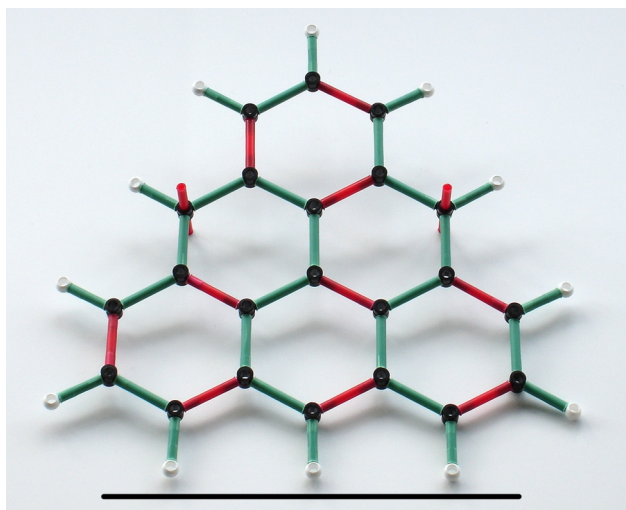
Left above. Molymod. Dihydrotriangulene. This is the stable precursor with two hydrogens at each marked carbon

centre. Isolated molecules were adsorbed onto a selected surface and the carbon centres then exposed to a voltage potential with the ATM / SPM instrument sufficient to dislodge one hydrogen atom from each.

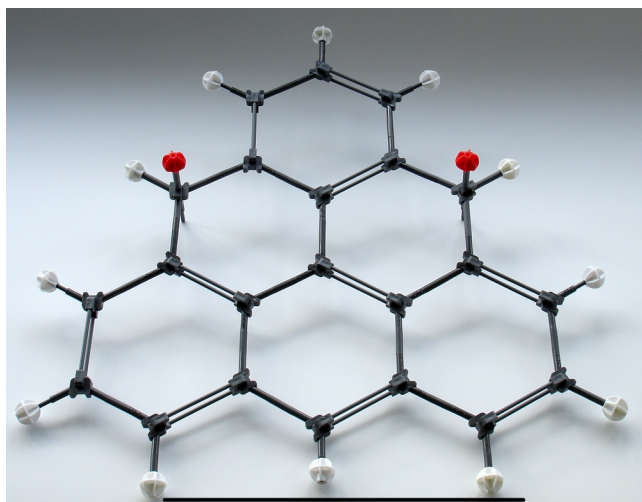
Right above. Molymod. Triangulene. Trigonal sp^2 centres have been used with the supplied lobes. Only one electron occupies each lobe but does correctly show that each is in a π -orbital as noted by the researchers although they are delocalised. Purple links show the double bonds in the rings.



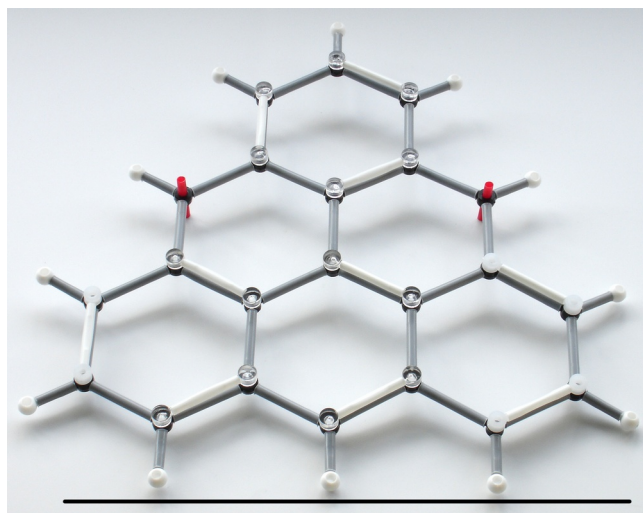
Left above. ChemKits. A trigonal valence cluster has been used with two red bond links to indicate a part occupied p orbital. Red links also show the double bonds in the rings. Molecules made from this kit often seem to me to be particularly aesthetically pleasing.



Right above. Minit. A similar approach to the ChemKits, the holes in each atom centre allow a contrasting coloured (red) link to show unpaired electrons.



Left above. Molecular Visions. Two red atom marker balls have been used with this system to represent the unpaired electron on each of the two carbons and using the dedicated double bond links in the rings. White marker atoms show the hydrogen atoms.



Right. Orbit. Similar to the Minit except white parallel links represent double bonds rather than contrasting coloured single links.

Sources for triangulene All are full free access at time of writing.

- Niko Pavliček, Anish Mistry, Zsolt Majzik, Nikolaj Moll, Gerhard Meyer, David J. Fox and Leo Gross, "[Synthesis and characterization of triangulene](#)", Nature Nanotechnology, Letters, Advance Online Publication, published online February 13th 2017.

- Philip Ball, "[Elusive triangulene created by moving one atom at a time](#)", Nature News, February 13th 2017, vol. 542, issue 7641.

- Manuel Melle-Franco, "[Graphene fragments: When 1+1 is odd](#)", Nature Nanotechnology News and Views, Advance Online Publication, published online February 13th 2017.

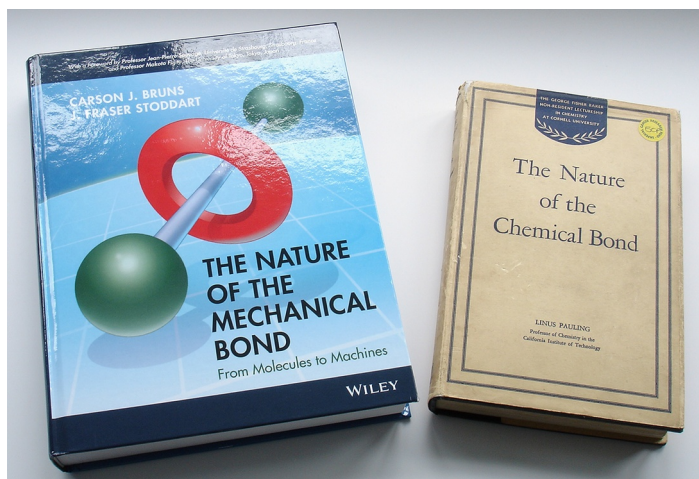
Nobel Prize for Chemistry 2016 – Molecular Machines

'The Nobel Prize for Chemistry in 2016 was awarded jointly to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L Feringa "for the design and synthesis of molecular machines"'. Quote from the Nobel Prize website.

Molecular machines are a fascinating group of molecules developed over the past few decades. A 'major breakthrough' cited was by Sauvage and co-workers in 1983. Each of the award recipients made extensive contributions to the field and key aspects of each of their work are highlighted in the resources. These included advances in synthesis techniques.

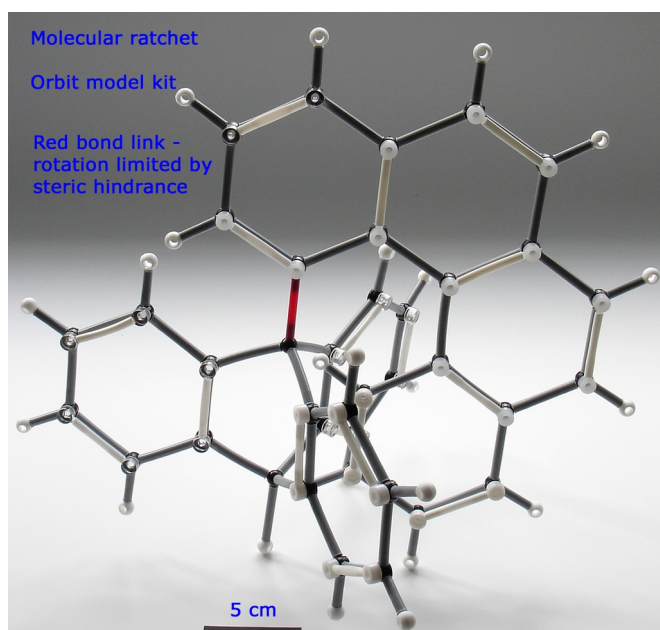
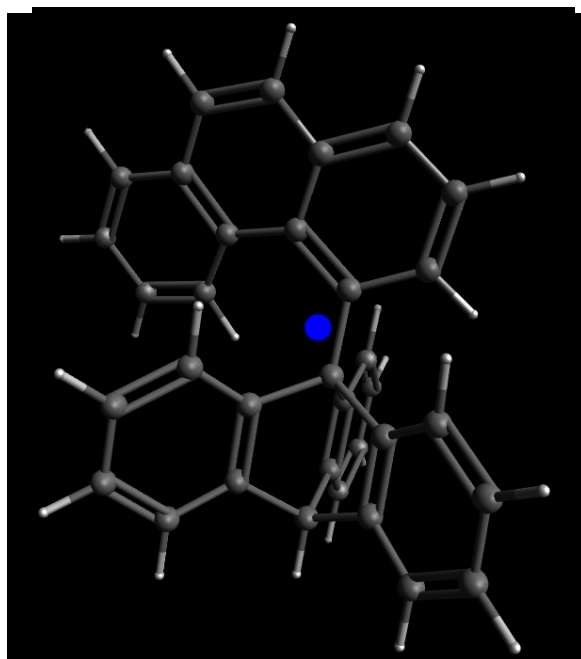
One aspect of such machines is that they often feature a mechanical bond, an unfamiliar term for students like myself studying in the mid 70s being brought up on the more familiar types such as ionic, covalent, dative and hydrogen bonds.

I treated myself to the book 'The Nature of the Mechanical Bond. From Molecules to Machines' by Carson J Bruns and Sir J Fraser Stoddart with superlative graphics, published 2017. Readers familiar with the classic work by Linus Pauling 'The Nature of the Chemical Bond' will appreciate the significance of the title they chose. It's not often that a chemistry book can be devoted to a new type of bond!



Right above. The classic chemistry book by Linus Pauling 'The Nature of the Chemical Bond' first published in 1939 alongside the recent publication 'The Nature of the Mechanical Bond', The authors, Bruns and Stoddart, have in part dedicated their book to the memory of Pauling.

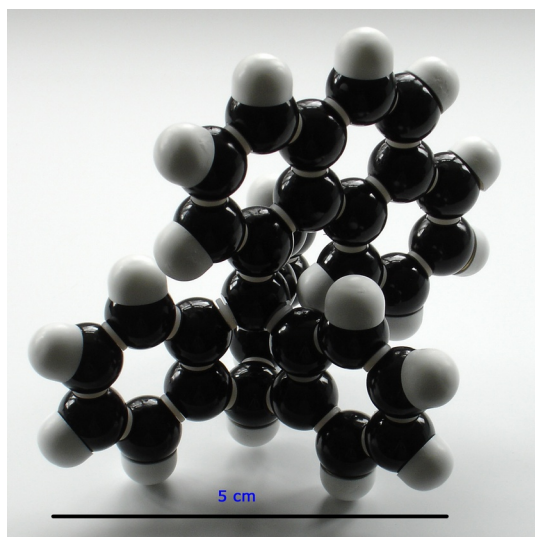
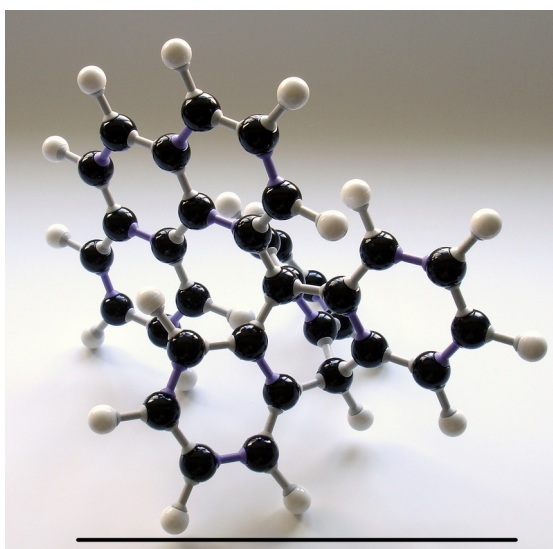
Making models of molecules that have been synthesised which include a mechanical bond and/or are molecular machines is a delightful challenge that I'm currently exploring with the five model kits reviewed. Some are large and the extent to which the kits owned can build examples with atom centres / bonds supplied will be a limitation but a nanocar is planned. To be continued



For the present, illustrated above (software rendered and Orbit model) and below (Molymod) is the molecular ratchet 4-(9-triptycyl)phenanthrene which was synthesized as reported by Kelly and Sestelo ref. 2. The upper three membered ring phenanthrene is connected by a single bond highlighted to the lower triptycene group. Rotation about this single bond is restricted by steric hindrance of the two groups.

From their proton NMR studies of the molecule up to 160 °C, the researchers were able to extrapolate and calculated that the barrier to rotation may be overcome at 220 °C. So the molecule would behave as a temperature controlled molecular ratchet.

A wide variety of molecular machines have been synthesized and/or postulated of mechanical analogues and which include ratchets, tweezers, motors, nano vehicles such as a nanocar, lifts, switches and logic gates.



Above, the same molecular ratchet 4-(9-triptycyl)phenanthrene using Molymod.

Left - medium links to give an open ball and stick model,,

Right - short links with Molydomes for hydrogens to give a semi-space-filling model.

Sources for Nobel Prize for Chemistry 2016 All are full free access at time of writing on the [Nobel Prize website page](#) devoted to the award with links to their resources below.

'The Nobel Prize in Chemistry 2016', Press Release dated 5 October 2016.

'How molecules became machines', Popular Science Background.

'Molecular Machines', Scientific Background dated 5 October 2016.

Additional references

1) Angela N Ingham, "Models in Chemical Education: An Investigation into their Uses", PhD thesis, Dept. of Educational Studies, University of Surrey, December 1988, page 8. Freely available as a downloadable Acrobat file at <http://epubs.surrey.ac.uk/771366/1/234561.pdf>

2) T Ross Kelly and José Pérez Sestelo, 'Rotary motion in single-molecule machines', in *'Structure and Bonding. Molecular Machines and Motors*, vol. 99, Springer-Verlag, 2001, p.36ff. Volume Editor Professor Jean-Pierre Sauvage.

Acknowledgements

Most software derived 3D images used the Open Source software [Avogadro version 1.2.0](#) with thanks to the developers for making available this excellent software, offering features from the beginner to advanced worker: See: Marcus D Hanwell, Donald E Curtis, David C Lonie, Tim Vandermeersch, Eva Zurek and Geoffrey R Hutchison; "Avogadro: An advanced semantic chemical editor, visualization, and analysis platform" [Journal of Cheminformatics](#) 2012, 4:17. (Open Access paper.)

Structural 2D formula and some 3D images were drawn using Herman Bergwerf's excellent 'Open-Source Project' [MolView](#). This also has a routine to check a molecule's structure on databases before presenting a 2D structural

drawing as the 3D molecule.

Contact author David Walker, email, micscape AT ntlworld DOT com.

(Email in anti-spam format, remove spaces, replace capitals with equivalent character and copy / paste to email software.)

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