Chemistry Chat -Focusing on the Elements-

Molecular Regular Polygons

Kentaro Sato

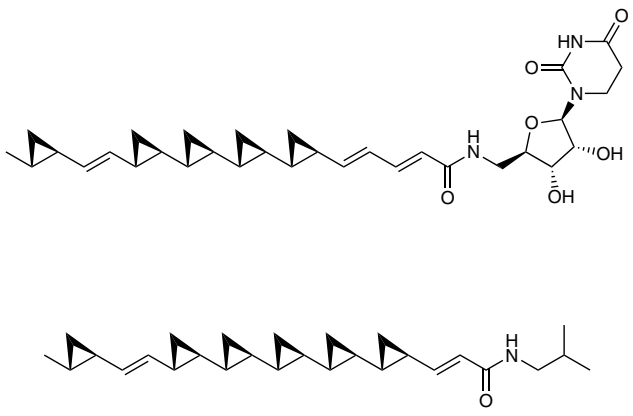
The hexagonal molecule of benzene composed of six carbon and six hydrogen atoms is one of the most beautiful structures in organic chemistry. Commonly known as the "turtle shell," the structure is regarded as a symbol of the field. The shape was born from the balance between the attractive and the repulsive atomic forces and is a reflection of the fundamental laws of nature.

The structure of organic molecules follows simple rules of atomic connectivity and there are some very impressive polygonal examples besides benzene. In this article, let us put a spotlight on carbon-based equilateral polygonal molecular structures.

Regular Triangles

The smallest cyclic molecules made of three carbon atoms, called cyclopropanes, are of course triangular. As a single unsubstituted compound, cyclopropane is a gas with a boiling point of -33 degrees Celsius. It was once used as an inhalation anesthetic for the sedating property, but is no longer used because of the flammability and the potential explosiveness.

Cyclopropane units are sometimes found as part of the structures of natural products such as terpenes. Among them, the two compounds that stand out are FR900848 and U-106305, both of which were discovered by pharmaceutical companies as drug candidates. As you can see, they feature a uniquely repetitive array of cyclopropane units. It is interesting to note that these two compounds that share this distinctive substructure were isolated from completely different organisms and also have completely different biological activities.



FR900848 (top), U-106305 (bottom)

It is a shame that these compounds have been called only by these alphabetical and numerical codes, as is always the case in pharmaceutical industry. However, the former compound has been named “jawsamycin” recently. Not surprisingly, the naming compares the alignment of triangles to the shark jaw.

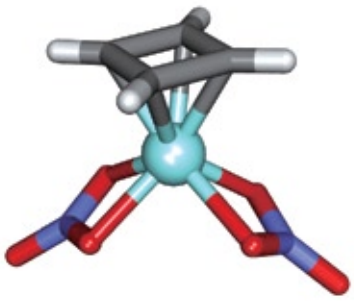
Squares

Introductory organic chemistry textbooks teach that four-membered ring and bigger cycloalkanes cannot have a planar conformation because of the bond angles. Annulenes, which are cyclic compounds composed of alternating single and double bonds, can take planar shapes but do not easily become equilateral polygons except for benzene.

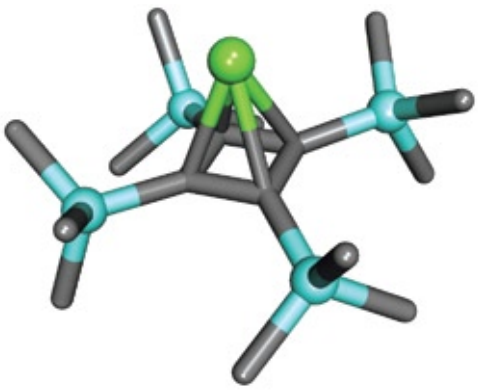
[4]Annulene, also known as cyclobutadiene, is highly strained and electronically antiaromatic with its 4π system. These properties make the molecule extremely unstable and its isolation as a pure form impossible. Based on spectroscopic analysis, it has been shown that the four carbon-carbon bonds of cyclobutadiene are not all equivalent and the structure is actually rectangular.

However, cyclobutadiene can be the ligand of organometallic complexes with metals such as iron. In these cases, the four-membered ring accepts a pair of electrons from the metal to complete the 6π aromatic system. In the iron complexes, it is known that all of the carbon-carbon bonds become equivalent and cyclobutadiene coordinates as a square.

In 2013, a compound called pyramidane was synthesized by V. Y. Lee and Akira Sekiguchi and the structure was determined by X-ray analysis. The molecule’s shape is literally pyramidal, with its structure composed of germanium or tin atom positioned at the apex and the four carbon atoms forming the square base. Each of the four carbon atoms is bonded to a trimethylsilyl group that protects the sensitive complex against decomposition. What an absolutely amazing creation!



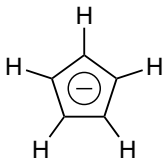
An example of cyclobutadiene organometallic complex



Pyramidane

Regular Pentagons

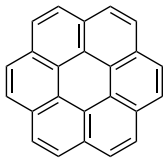
As for equilateral five-membered ring compounds, cyclopentadienyl anion is well-known. The cyclopentadienyl anion formed by the deprotonation of cyclopentadiene is a 6π electronic system that shows aromatic character. The five carbon atoms are equivalent and the molecule has a shape of regular pentagon. When it binds to transition metals, the resulting compounds are generally called metallocenes. Metallocenes are familiar compounds to us today, but their early discoveries were so impactful that they triggered the emergence of a new genre called organometallic chemistry.



Cyclopentadienyl anion

Regular Hexagons

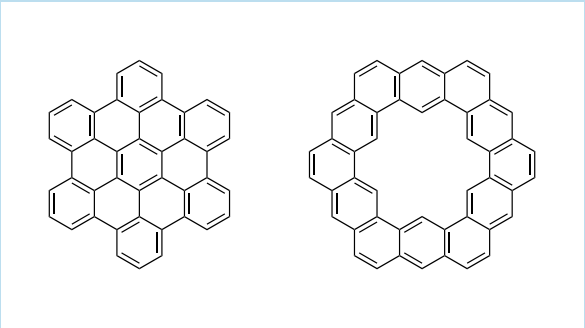
As mentioned in the beginning, benzene is a symbolic compound possessing regular hexagonal structure. There are a number of compounds in which several benzene rings are fused to form a larger hexagonal structure as a whole. The compound consisting of seven fused benzene rings is called coronene after the corona of the Sun.



Coronene

Coronene is found in coal tar and also known to form during petroleum cracking processes. Interestingly, the mineral ore called Karpatite produced in places like Ukraine contains coronene as its main constituent.

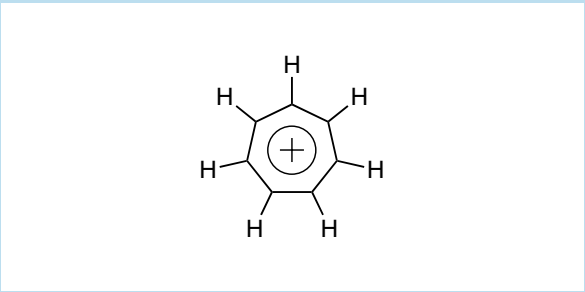
Hexabenzocoronene, which is coronene plus six additional fused benzene units, is considered a trendy material in recent nanotechnology research. Kekulene, which you could call "the benzene made of benzenes," was synthesized in 1978 for the first time. Needless to say, this macrocyclic aromatic compound was named after August Kekulé, the German chemist who proposed the six-memebered ring structure of benzene.



Hexabenzocoronene (Left), Kekulene (Right)

Regular Heptagons

We have so far seen four-, five-, and six-membered ring examples with 6π electronic system, so let us move on to analogous seven-membered rings. The chemical species called tropylium cation ($C_7H_7^+$) is the most famous one, which is synthesized from cycloheptatriene (by Lewis acidic treatment, for example).

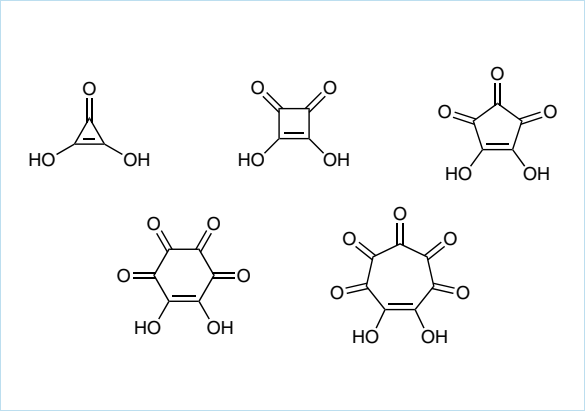


Tropylium cation

Carbon-based seven-membered ring structure attracts a special interest in the field of recent nano-carbon science. The infinite extension of fused six-membered rings would result in a large flat structure known as graphene. On the other hand, when both five- and six-membered rings are available, the carbon atoms tend to form round and finite structures such as fullerene.

When seven-membered rings are also available, the resulting nano-scale structures tend to adopt bent and curled shapes. For example, nanotubes containing seven-membered rings can have bent and branched substructures. In terms of the application of carbon materials to electronic devices and other nano-scale materials, the ability to incorporate seven-membered rings may become a key factor.

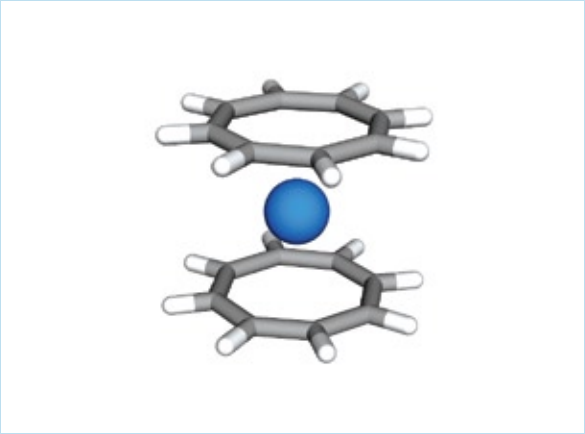
Let us look through compounds of the slightly different family. As shown below, oxo-carbon acids with the ring sizes from three to seven are known. Upon releasing two protons, these compounds become regular polygonal structures by delocalizing the charges. Because the dianions are stabilized by aromaticity, these oxo-acids show exceptionally strong acidities for compounds only made of C, H, and O.



Oxo-carbon acids

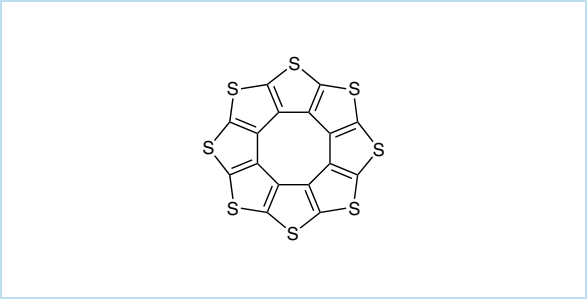
Regular Octagons

Cyclooctatetraene ([8]annulene) does not assume flat conformation unlike benzene and related aromatic compounds. The flat structure would be an 8π antiaromatic system, therefore the boat-shape becomes a more stable structure. However, the dianion formed by treatment with reducing agents is a 10π aromatic system that can exist as a flat regular octagon. Also, in some organometallic complexes containing cyclooctatetraene, the ligand is known to coordinate with the metal center as a flat regular octagon.



Uranocene [$U(C_8H_8)_2$]

In 2006, a neutral compound containing equilateral octagonal structure was synthesized. This compound composed of eight fused thiophene units looked like sunflower, so it was named “sulflower” by combining sulfur and flower.

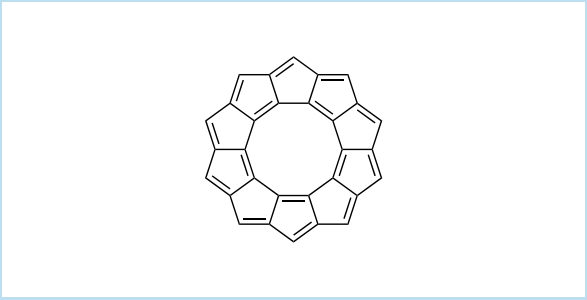


Sulflower

Regular Decagons and Beyond

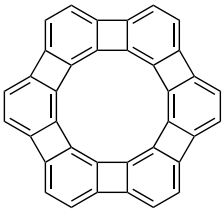
One could think of regular polygonal molecules larger than eight, but those would be unlikely to exist as flat molecules considering that the ideal bond angle of sp^2 carbon is 120 degrees. One possibility is to make them as an inner structure by surrounding it with small ring units like sulflower.

For instance, there is a structure called [10.5]coronene, which consists of five-membered rings positioned on each side of a decagon. This structure has been of great theoretical interest for a long time but its synthesis has yet to be achieved.



[10.5]Coronene

One could also imagine a structure like the one shown below, which has six- and four-membered rings placed alternately on the sides of a dodecagon. This type of compounds composed of fused benzene and cyclopentadiene rings (known as [N]phenylenes) are widely known, but this particular compound has never been synthesized. It has been difficult because both the inner and outer rings (12π and 24π, respectively) are antiaromatic. For this reason, this molecule has a fitting nickname "antikekulene."



Antikekulene

Seeing the gallery of these structures reminds us that symmetry is an important keyword in the world of molecules. Revisiting familiar organic compounds with geometric point of view can be refreshingly eye-opening and possibly gives you unexpected hints for your research.

Introduction of the author :

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[Brief career history] He was born in Ibaraki, Japan, in 1970. 1995 M. Sc. Graduate School of Science and Engineering, Tokyo Institute of Technology. 1995-2007 Researcher in a pharmaceutical company. 2008-Present Freelance science writer. 2009-2012 Project assistant professor of the graduate school of Science, the University of Tokyo.
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