

Classroom



In this section of *Resonance*, we invite readers to pose questions likely to be raised in a classroom situation. We may suggest strategies for dealing with them, or invite responses, or both. “Classroom” is equally a forum for raising broader issues and sharing personal experiences and viewpoints on matters related to teaching and learning science.

The Story of Hexamethylbenzene Proving that Benzene is Flat and Symmetric

Benzene is a special molecule. There is hardly any other molecule that has captured the imagination of generations of chemists. It was isolated first in 1825 by Michael Faraday but took more than 100 years before the actual structure was nailed down. This article intends to highlight one crucial discovery: the actual determination of the crystal structure of hexamethylbenzene which solved the riddle about the structure of benzene conclusively.

Probably the most well-known milestone in terms of chemistry lore, was the proposal by Kekulé in 1865 that benzene was a cyclic structure with alternate double bond and single bond. The readers are referred to the May 2001 issue of *Resonance* where the life and work of Kekulé is discussed. As discussed by Nagendrappa in his article titled ‘Benzene and its isomers: How many structures can we draw for C_6H_6 ?’, one can write 328 isomers (including stereoisomers) for benzene. *Table 1* lists the possible types of structures.

So, even if we consider the proposal of Kekulé that benzene consists of alternate single and double bonds in a monocyclic ring, there are still quite a few possible structures. As shown in

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Table 1. Possible isomers of benzene.

Category	Number of Isomers
Acyclic	17
Monocyclic	71
Bicyclic	134
Tricyclic	87
Tetracyclic	19

Figure 1. Various plausible structures of benzene sharing alternate single and double bonds within a single ring (monocyclic form).

A. Planar ring (in D_{3h} symmetry).

B. Boat structure.

C. Chair structure.

D. Twisted structure.

E. Envelope structure.

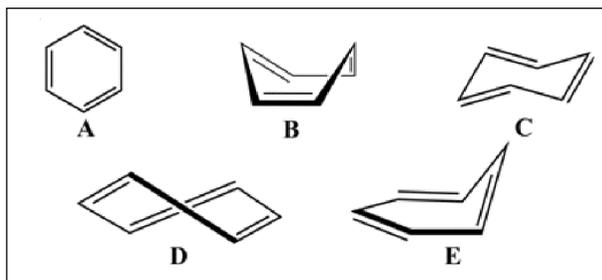


Figure 1, the six-membered rings can be flat, puckered (chair or boat like), twisted or envelope like.

Secondly, one was not sure if benzene contained three distinct (localized) double bonds or the three double bonds were evenly distributed over all the six carbon atoms. These two questions remained unanswered till Kathleen Lonsdale (Box 1), a

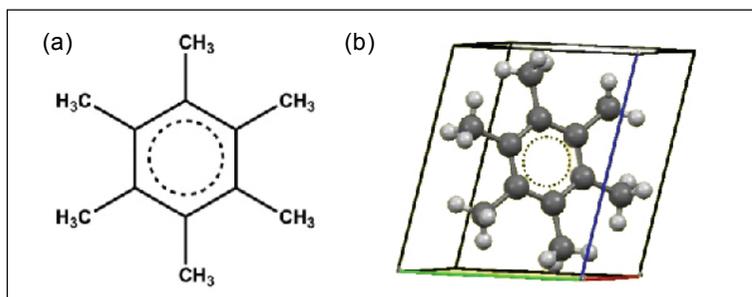
Box 1. Kathleen Lonsdale (1903–1971)

Kathleen Lonsdale née Yardley, FRS, an Irish crystallographer was the first woman tenured professor at University College London, the first woman president of the British Association of Advancement of Science and also the International Union of Crystallography. In 1956, she was named Dame of the British Empire. Lonsdale was elected as one of the first two women Fellows of the Royal Society in 1945. Lonsdale obtained her bachelor's degree in physics at age 19, in 1922. She set up her independent crystallography laboratory in the physics department at Leeds University from where she solved the structure for hexamethylbenzene in 1928 (just 6 years after her undergraduate degree!).

A pacifist for life, she served a month in prison in World War II for her refusal to register for civil defense duties, or pay a fine. Lonsdale died of cancer in 1971 probably due to prolonged exposure to X-rays. *Lonsdaleite*, a polymorphic form of diamond is named in her honour.



Image courtesy: BBC UK, URL: <http://ichef.bbci.co.uk/images/ic/640x360/p01lcxtp.jpg>

**Figure 2.**

(a) Structure of hexamethylbenzene

(b) Crystal structure of hexamethylbenzene (CCDC Refcode: CSD-HMBENZ04).

crystallographer solved the structure of hexamethylbenzene in 1928. Hexamethylbenzene, where each carbon atom of the benzene ring is linked with a methyl ($-\text{CH}_3$) group, crystallizes in such a way that each unit cell has only one molecule (*Figure 2*). The reason is that the methyl groups shield the aromatic rings from each other thereby negating the possibility of C(aromatic)-H... π interactions between the rings which leads to a herringbone-type packing pattern typical in many aromatic systems including benzene. A herringbone-type packing typically leads to more than one molecule per unit cell which would make investigation of the nature of the double bonds inside the aromatic rings difficult. So, hexamethylbenzene was the ‘cleanest’ system that could answer if the three double bonds in the benzene ring were localized or not.

From the intensity patterns of reflection of X-rays in hexamethylbenzene, Lonsdale concluded that the six-membered ring was flat and formed a regular hexagon. The proposition of Kekulé with three localized double bonds in benzene was disproved and one could clearly ‘see’ that benzene was flat and hexagonal. This of course meant that the electrons were evenly distributed over all the six carbon atoms. This 1928 experiment quickly formed the basis of a series of works including the Hückel molecular orbital theory which provides a foundation for our understanding of the reactivity and electron spectra of a wide class of aromatic molecules.

Suggested Reading

- [1] E Wilson, Hexamethylbenzene, 100 years of X-Ray Crystallography, *Chemical and Engineering News*, p.34, August 11, 2014.
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