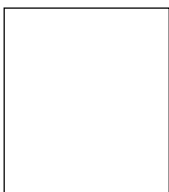


# On Benzene and Aromaticity

## History and Some Folklore

***M V Bhatt***



**M V Bhatt** hails from Sringeri, Karnataka. Like many others of his generation, he was drawn to a career of science after hearing a talk by C V Raman. **M V Bhatt** was in the Department of Organic Chemistry, IISc for over three decades, where he carried out research in synthetic and physical organic chemistry with distinction.

**Several interesting historical details about the structure of benzene and the concept of aromaticity are provided.**

Organic Chemistry is a mature science, with its set of principles and practices, goals and methodologies, heroes and history, and of course, some folklore. It is important that students are given a flavour of all of these in the classroom and not just presented with dry facts. The development of the field over the last two centuries should be placed often in a historical context. The impact of some of the advances in the subject on society at large is a particularly relevant topic for information and discussion. The manner in which several puzzles were resolved using intuition, deduction and simple experimentation also need to be retold. The creativity of scientists has an appeal that transcends the subject.

Chemistry of aromatic compounds provides ample opportunities for the teacher to cover many of the above aspects. One can move from almost trivial questions to those that require deep analysis. For example, one could consider the origin of the name 'benzene' and then of the term 'aromaticity'. It would be of interest to describe how Kekulé arrived at the structure of benzene, the difficulties posed by the proposal, their resolution through subsequent experimental and theoretical work, etc. The discussion of the topic can be rounded off with representative examples of the impact of aromatic chemistry on society.

The name 'benzene' has a curious origin. The main island of the Indonesian archipelago is named Java (which means grain (barley) in Sanskrit). Incense from this island was an article of commerce from prehistoric times. It made its entry to Europe



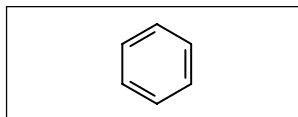
through the Arabian gateway, Morocco, and the Italian ports. The name 'Leban Javi' (incense from Java in Arabic) got changed to 'Le Benjamin', and 'gum benjamin' and later 'gum benzoin' in the Italian ports. *Tincture benzoin* used to figure in British Pharmacopia till recently. In 1834 the German chemist Mitscherlich isolated an odourless white crystalline acid from gum benzoin. He heated it with soda lime and obtained a colourless liquid with no characteristic odour. He named it 'benzin'. The editor of the journal to which the work was communicated insisted on using the name 'benzol'. To this day, this name is retained in Germany to describe 'benzene' (incidentally, 'benzin' in German stands for petrol). Michael Faraday had already isolated the same compound from liquified illuminating gas in 1825. Since the suffix 'ol' is used to denote alcohols, benzol may be mistaken to have a hydroxy group. Hence the name 'benzene' was preferred in English.

The way the structure of benzene was derived is another interesting story. Many students have the mistaken belief that chemical structures were correctly worked out only after modern instrumentation and analytical tools became available. It may come as a surprise that by 1910, structures were formulated for more than 200,000 unique organic compounds! Even with the advent of powerful physical tools like infrared, Raman, and nuclear magnetic resonance spectroscopic methods and X-ray crystallography, an overwhelming majority of these structural proposals did not need revision. (Of course, this is not to belittle the technical advances. They certainly have made the task of structure determination easier and more reliable and have reduced the drudgery of the effort). Recounting the achievements of chemists of earlier generations who had none of the modern technical tools at their disposal is an excellent source of inspiration for students.

August Kekulé's name is mentioned in the folklore of chemistry, for some right and for some wrong reasons. The claim that he arrived at the cyclic structure by daydreaming in a bus is now

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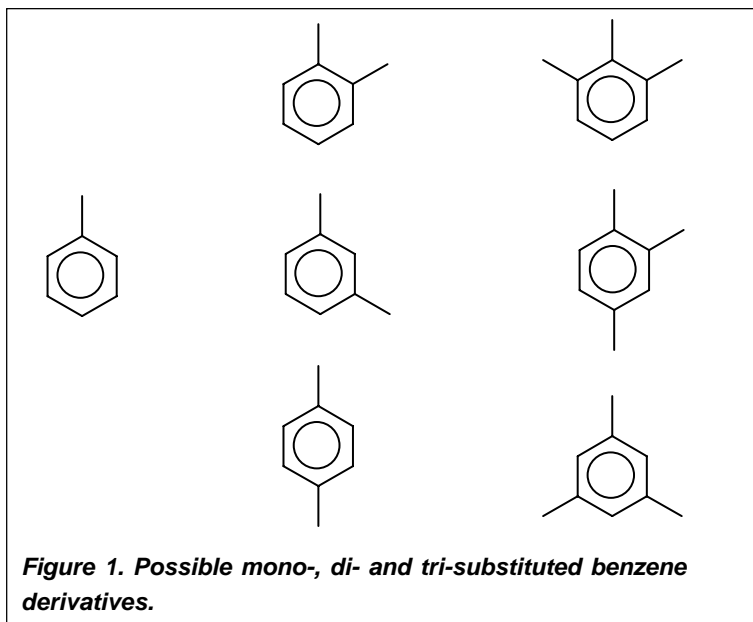
**Structure 1.**

seriously doubted. But there is no doubt about the brilliance of his proposals that all aromatic compounds contained benzene as a common 'nucleus' and that the structure of benzene was a hexagon with three double bonds (*Structure 1*).

In order to appreciate these remarkable predictions, we have to remind ourselves of what was known and what remained unknown in the middle part of the previous century. The discovery of the electron was far away. Even the idea that molecules could have well defined structures which are amenable to experimental verification appeared highly speculative to many eminent chemists. However, it was recognised that atoms had characteristic valencies. Kekulé and others had worked out the valency of carbon to be four. The question now was to assign a structure for a combination of six carbon atoms and six hydrogen atoms satisfying the valence requirements of all the atoms and which was consistent with all available chemical data on benzene. One can think of several acyclic and a few cyclic structures. What were the crucial experiments carried out by Kekulé and his school to prove the cyclic structure of benzene?

Kekulé recognised the implications of symmetry in the structure which he proposed. He decided to make many derivatives of benzene through substitution reactions. Even before he got interested in the benzene problem, there were some well characterised monosubstituted benzene derivatives in the chemical literature. Aniline (from Sanskrit *nila*) had been obtained from natural indigo, and as stated earlier, benzoic acid from gum benzoin. Replacement of any of the six hydrogen atoms of benzene resulted in a single mono-substituted derivative. This meant most alternative structural formulations were ruled out in one bold stroke. Further substitution gave no more than three isomers for disubstituted derivatives, what is now termed *ortho*-, *meta*- and *para* isomers. In the case of trisubstituted derivatives, again no more than three isomers could be isolated. All these findings are consistent with the monocyclic form as the only acceptable structure (*Figure 1*).

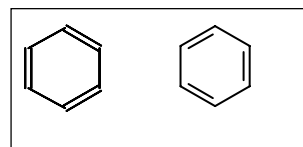




There were of course some objections. With an alternating set of single and double bonds, there ought to be two isomeric forms for the ortho-disubstituted derivatives (*structures 2 and 3*).

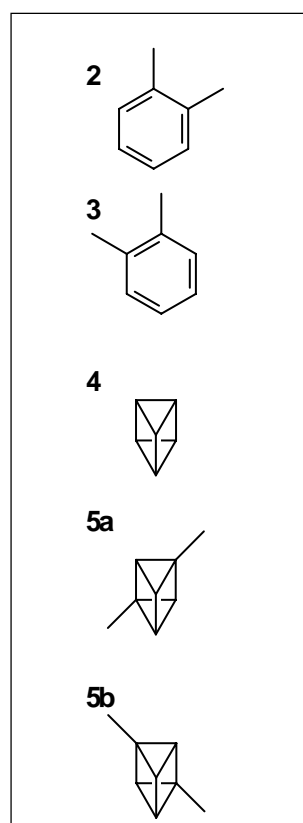
Kekulé got around the difficulty by suggesting that two possible structures of benzene with alternating single and double bonds rapidly oscillate in time to produce a structure of hexagonal symmetry (*Figure 2*).

There was another problem. Ladenburg argued that a prism (*structure 4*) would yield the same number of isomers on substitution as the monocyclic form (*Figure 3*). The flaw in this argument was pointed out by van't Hoff, probably the first chemist to recognise that molecules were not always flat. By invoking his tetrahedral model for the valencies of carbon, he showed that one of the disubstituted prismane derivatives must be optically active. That is, it must have two non-superimposable mirror images (*structures 5a and 5b*). Since such enantiomeric forms had not been isolated, the planar monocyclic Kekulé structure must be correct.

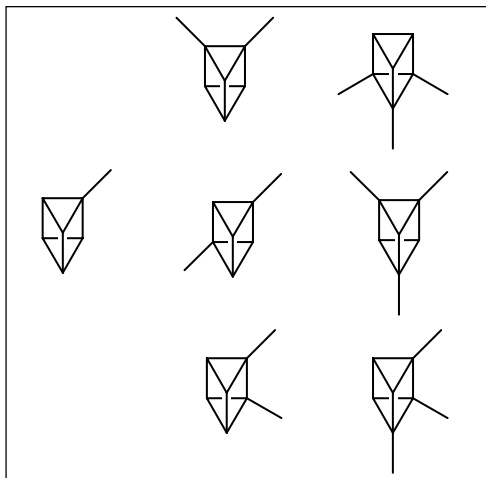


**Figure 2. Two Kekulé structures 'in oscillation' to produce a single structure with hexagonal symmetry.**

#### Structures 2–5.



**Figure 3. Possible mono-, di-, and tri-substituted prismane derivatives.**



<sup>1</sup> See J Chandrasekhar, *Resonance*, Vol.1, No.2, 80–83, 1996. for a discussion of a few isomers of benzene.

During the past fifty years, many isomers of benzene or their substituted analogues have been prepared and characterised by an array of physical methods. Needless to say, these isomers are different from benzene in every way. Importantly, they decompose on their own or under mild conditions.<sup>1</sup>

Although the cyclic structure for benzene was accepted, the nature and directionality of the bonds (valence) continued to bother chemists. Even Kekulé's students, including Adolf von Baeyer (famous for his Strain Theory, among other contributions), tried to come up with alternative proposals. They were generally unsuccessful. The first reasonable description of bonding in benzene became possible only after the discovery of the electron, the idea of the electron pair bond by Lewis, its quantum mechanical formulation by Heitler and London, and its extension to conjugated systems by Pauling. The molecular orbital theory of Mulliken and its application to conjugated systems by Hückel provide an elegant and simple approach to the problem. The latter's work provides an easy general definition of aromaticity. In spite of these advances, the intricate question of what precisely constitutes aromaticity is still being debated in research journals. But, at least one definition is definitely wrong. The concept has nothing to do with smell. While some textbooks still claim that aromatic molecules got their name from their



aroma, most of them do not have a characteristic smell.

Kekulé's work led to rapid developments in all of organic chemistry and especially in the study of aromatic systems. Many fairly complex molecules, particularly natural and synthetic dyes, could be made with great control in the laboratory. Baeyer, for example, passionately pursued the synthesis of indigo<sup>2</sup>. (Interestingly, in 1888, he became 'so fatigued from indigo research and so disgusted with it' that he turned to the study of simpler molecules like acetylenes, from which emerged the Strain Theory!). The sodamide process for the manufacture of indigo was worked out in 1901. By the next decade, the German company *Badische Anilin and Soda Fabrik* (BASF) was ready to spend the equivalent of 5 million US dollars for the production of synthetic indigo. This destroyed the Indian monopoly for the natural dye, held for two and a half millenia, in just five years. The consequence for the farmers of a remote district in Bihar, who were being compelled to cultivate indigo plants by colonial rulers, was disastrous. With none to understand their plight, one of the farmers enlisted the help of a humanist who had made a name for himself fighting for just causes under trying conditions in South Africa. The appeal fell on sympathetic ears. A historic non-violent struggle to obtain relief for the hapless farmers followed. It drew national attention to the peaceful method of protest and fundamentally altered the course of the movement for Indian independence. Yes, we are talking about a person named M K Gandhi and the historic Champaran struggle. Who could have imagined that the synthesis of indigo in a German laboratory would catalyse the emergence of a Mahatma?

<sup>2</sup> See S Ranganathan, *Resonance*, Vol.1, No.8, 22–27, 1996 for a discussion of the synthesis of indigo.

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The centenary of Kekulé's structural proposal was celebrated in both West Germany (Federal Republic of Germany) and East Germany (German Democratic Republic) through commemorative stamps.

