
Benzene and its Isomers

How many Structures can we Draw for C_6H_6 ?

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An important epoch in the growth of chemistry in general and organic chemistry in particular is the period between 1825 when benzene was isolated and 1865 when its correct structure was proposed. Significant initial strides were made during these years in finding new organic reactions and searching for methods to draw molecular structures.

For an average chemist the molecular formula C_6H_6 instantly brings benzene to mind. Benzene is one of the most basic structural units of thousands of the so-called aromatic compounds, which include dyes, drugs, polymers and many more types of compounds that are very useful for our existence and progress. The whole gamut of the chemistry of aromatic compounds, which forms a large part of organic chemistry, is based on the properties and reactions of benzene. Compared to our present vast knowledge of extremely complex structures of thousands of organic compounds, the structure of benzene now appears ridiculously simple, but it had taken nearly half a century of effort by some of the greatest ever scientists to arrive at it correctly.

Benzene was discovered by Michael Faraday in the year 1825 as part of an assignment given by a gas company. The gas obtained by thermal decomposition of whale oil used to be stored in cylinders under pressure for illuminating streetlights. Faraday succeeded in isolating benzene by distillation and crystallization of the light mobile oil left behind in the gas cylinders. He was also able to determine its quantitative composition and vapour density from which he gave its empirical formula as C_2H , as the atomic weight of carbon at that time was taken to be 6. Mitscherlich obtained benzene in 1834 by dry distillation of benzoic acid with lime, and established its formula correctly as C_6H_6 , because of better understanding of the

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atomic weights and availability of improved analytical methods.

At this time the concept of writing structural formulae for organic compounds had not yet been developed, though serious attempts were being made. Fruitful initial steps in this direction were taken around 1852 by Frankland and later in 1855 by Kolbe. But proper foundation for drawing the structures of organic molecules was laid by Couper and Kekule independently in 1858. They showed that most of the aliphatic compounds known at that time could be represented by planar structures indicating the interrelationship of atoms. (The tetrahedral structure for carbon was proposed by van't Hoff and LeBel much later, in 1874.) On the other hand, the structure of benzene, and therefore the structures of aromatic compounds in general, eluded the efforts of even the best chemists of that time in giving it a meaningful form, because the formula C_6H_6 indicated unsaturation of the type in acetylene, C_2H_2 , and benzene exhibited no reactivity that is characteristic of the unsaturated compounds, which was rather confusing and incomprehensible.

In 1862, Loschmidt started writing a sort of ring structure for benzene with a circle symbolizing the six carbons to which were sticking six smaller circles representing the six hydrogen atoms. Though this was a remarkable attempt to visualize benzene molecule in the form of a ring, it fell far short of giving the true picture of the molecule that would indicate proper bonding relationships of the atoms.

Later, in 1865 Kekule proposed, as is well known now, the hexagonal structure for benzene with the six corners being occupied by six carbon atoms bonded to each other by alternating single and double bonds and to one hydrogen each. Kekule argued in his final paper on this subject published in 1872 that though one could write two such structures, which are now called the Kekule structures, in reality they are indistinguishable and the true structure is an average of the two. During the last century, every possible physical method has been employed to 'look into' the benzene molecule and each one has supported the claim of Kekule.

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Isomers which can be represented by the molecular formula $(CH)_n$, where n is an even number, are known as valence isomers.

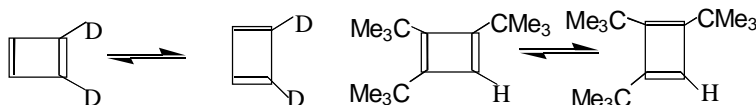
Soon after Kekule announced his structure for benzene in 1865, many others jumped onto the bandwagon. They found the Kekule model to be inadequate in explaining the properties of benzene, especially its failure to behave as an unsaturated compound. Most of these other proposed structures were essentially born out of 'tinkering' with the Kekule construction and directed towards remedying the problem posed by the presence of double bonds and will not be considered here. However, two structures, the so-called 'Dewar benzene' proposed by Stadeler (1868) and Wichelhaus (1869), and the 'prism structure' proposed by Ladenburg (1869) are worth noting. Though Dewar benzene and the prism form were considered as alternative structures for benzene then, now it is common knowledge that each of them is an isomer of benzene and is an independent molecule in its own right. Looking back at that period, it is quite surprising that no other reasonable cyclic structures conforming to the formula C_6H_6 were offered, especially when one realizes that it is possible to write nearly 330 (vide infra) isomeric structures, out of which about 310 are cyclic*. Note that all these structures fulfill the basic valency requirement of carbon (4) and hydrogen (1), but many of them are too strained or unreasonable to have any chance of existence even under the most favourable conditions. It is obvious that none of them, except the Kekule structure, would adequately explain the properties of benzene.

If a restriction is imposed such that each of the six carbons is attached to one hydrogen, the formula would then be $(CH)_6$, as distinct from C_6H_6 , and the number of isomers will be drastically reduced to only five (or six if the last structure of the tetracyclic set is included), which include Dewar benzene and prismane*. Such isomers which can be represented by the molecular formula $(CH)_n$, where n is an even number, are known as valence isomers. In this sense the two Kekule structures are valence isomers, if the double and the single bonds in them are localized and frozen. However, the actual structure of benzene is different, with the bond order between any two carbon atoms in the molecule being identical to that between any other two. An important distinction between a resonance structure or canonical form and a valence isomer is that the





latter has a finite possibility of independent existence as a compound while the former does not. It may be noted with interest in this context that the extremely unstable cyclobutadiene, an antiaromatic compound, does exist in two rectangular valence tautomeric forms, e.g.,



Such examples are unknown in the case of benzene derivatives.

One can write 217* basic isomeric skeletal structures that possess the molecular formula C_6H_6 . If the diastereomers and enantiomers are taken into account, the total number of isomers will add to 328. Among these, 17 are acyclic (2 of them are diastereomers), 71 are monocyclic (10 diastereomers and enantiomers), 134 are bicyclic (52 diastereomers and enantiomers), 87 are tricyclic (42 diastereomers and enantiomers) and 19 are tetracyclic (5 diastereomers and enantiomers) structures. Although all the structures formally satisfy the valency requirements of carbon (4) and hydrogen (1), it is evident that many of the isomers are highly strained. Acetylenic centers as well as allenic and higher cumulenes prefer a linear geometry. Forcing them in cyclic structures would lead to significant strain. Bicyclic structures do not easily accommodate double bonds at bridgehead positions (Bredt's rule). Many of the polycyclic isomers clearly violate this requirement. A few of the polycyclic forms have 'inverted' carbon atoms, with the four valencies pointing to one hemisphere. Since tetracoordinate carbon atoms strongly prefer a tetrahedral arrangement, serious distortions lead to instability. As a result, out of the entire set of possibilities, only about 80 have the structural features that would give them sufficient chance to exist if prepared under suitable conditions. However, less than 40 are known to date. The most stable of them all or indeed one of the very stable organic compounds is, of course, benzene.

The 217 basic isomeric topological structures of the formula C_6H_6 are given in the poster* and are classified as acyclic, monocyclic,

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etc. The molecules that can exist as diastereomers and/or enantiomers are indicated below them by appropriate symbols (E, Z, R and S). They include the six valence isomers also, and five of them are listed separately in the poster again, because of the interest they have stimulated during and after Kekule's period and have engaged the attention of synthetic organic chemists even in recent times.

None of the isomers, except benzene, has much practical application. Yet the fascination of both synthetic and theoretical chemists for the isomers of benzene is so great that even after about 140 years history of benzene structure, the organic chemist is taking up even today the challenging task of synthesizing the difficult C_6H_6 molecules for purely academic reasons.

* All the 217 structures are given in the form of a poster with this issue of *Resonance*.

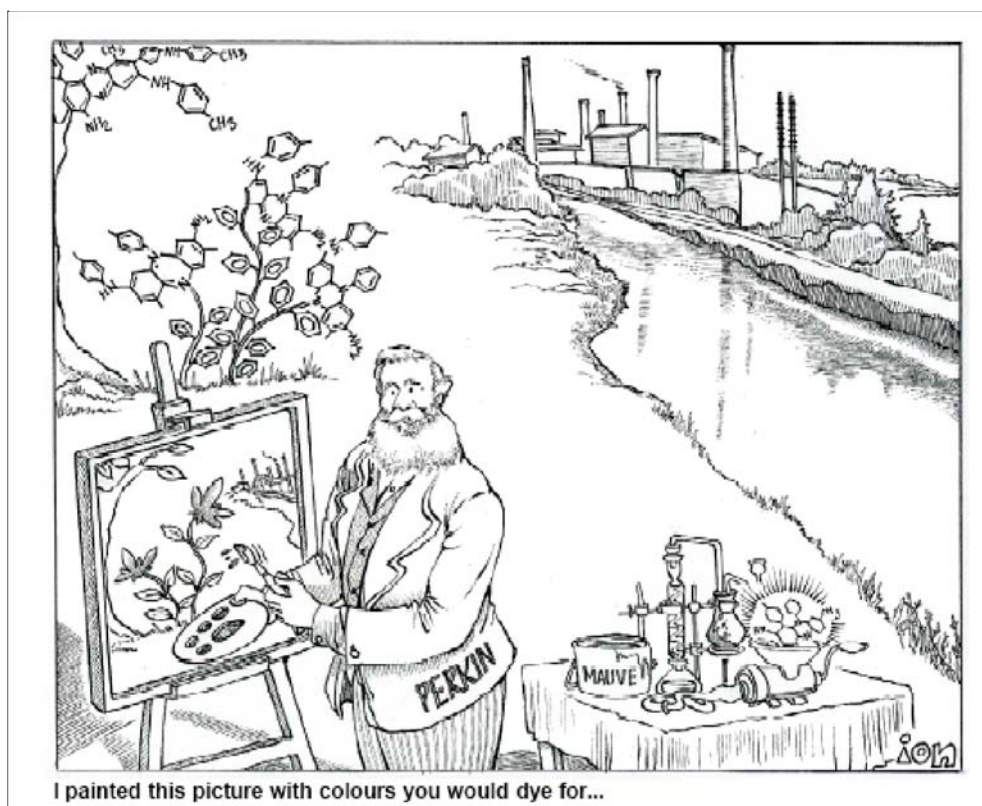
Suggested Reading

- [1] W Baker and D H Rouvray, Para-Bond or "Dewar" Benzene?, *J. Chem. Educ.*, 55, 645, 1978.
- [2] H Bock, Fundamentals of Silicon Chemistry: Molecular States of Silicon-containing Compounds, *Angew. Chem. Int. Ed. Engl.*, 28, 1627, 1989.
- [3] W C Shakespeare and R P Johnson, Two New Highly Strained C_6H_6 Isomers, *J. Am. Chem. Soc.*, 112, 8578, 1990.
- [4] J H Potgieter, The Diverse Nature of the C_6H_6 Molecule, *J. Chem. Educ.*, 68, 280, 1991.
- [5] I Gutman and J H Potgieter, Isomers of Benzene, *J. Chem. Educ.*, 71, 222, 1994.

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Benzene and its Isomers

In the May 2001 issue of *Resonance* the article with this title was subtitled, "How many structures can we draw for C_6H_6 ?" The 217 structures set out in the poster are basic framework structures drawn according to valency rules. If one takes into consideration the enantiomeric, geometric and other stereoisomeric forms, wherever possible, the total number of isomers would increase significantly. For instance, *trans, trans, trans*-1,3,5-cyclohexatriene (all-*trans*-benzene), Dewar benzene with *trans* ring junction or the two double bonds with *cis, trans* or *trans, trans* configuration etc. are in principle conceivable isomeric structures. But they would be so distorted that it would be difficult even to draw them! The basic frameworks turn out to be only 217 as listed here.

(Note: The bond angle around *sp* hybridized (acetylenic and allenic) carbon in acyclic compounds and exocyclic substituent in mono- and bi-cyclic structures is 180 degrees (i.e. linear). In the poster this angle is shown as bent for reasons of convenience in drawing them and aesthetics. When the triple bond or allene is part of a ring system, the linearity cannot obviously be maintained.)



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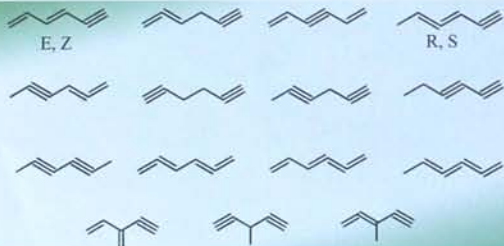
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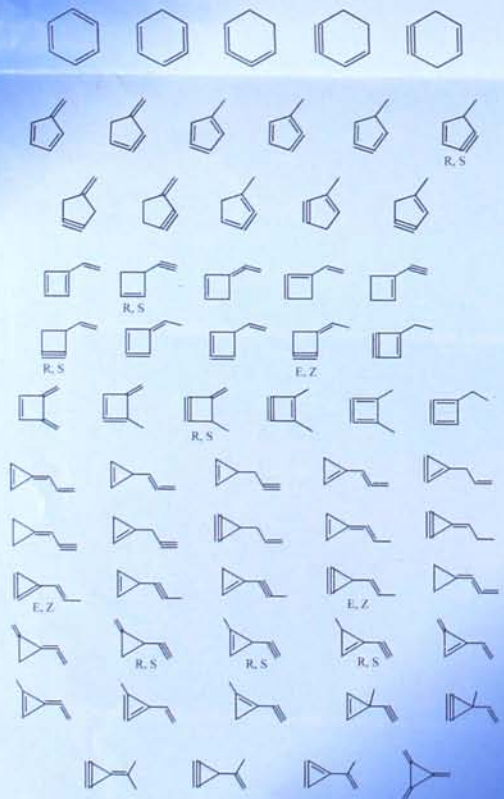
In the table below are given the valence isomers of benzene (for definition and explanation see the article, Benzene and its Isomers, *Resonance*, Vol. 6, No. 5, pp. 74-78, 2001). A few properties that are listed here give an idea of how different and interesting such isomers could be. These structures can be found among the 217 structures given in this poster.

Structure	Name	Source	Properties
	Benzene	Petroleum, coal tar, trimerization of acetylene, natural products, etc.	Colourless liquid, b.p.80°C; m.p.5.5°C. Stable. Has relatively pleasant odour. (Carcinogenic). Industrially a very important compound.
	Dewar benzene; Bicyclo[2.2.0]hex-2,5-diene	van Tamelen and Pappas (1963)	Unstable, $t_{1/2}$ = 2 days. Rearranges to benzene. (Stable in pyridine soln).
	Benzvalene; Tricyclo[3.1.0.0 ^{2,4}]hex-3-ene	Wiltzsch and others (1967) Katz and others (1971)	Stable in solution. Explosive in pure state. Foul smelling.
	Prismane; Tetracyclo[3.1.0.0 ^{1,4} .0 ^{2,3}]hexane	Katz and Acton (1973)	Odourless liquid. Explosive. Stable at RT in toluene, at 90°C isomerizes to benzene, $t_{1/2}$ = 11 hours.
	Bicyclopropenyl (2,2); (3'-cycloprop-1-enyl)-3-cycloprop-1-ene	Billups and Haley (1989)	Stable below 10°C, above that, decomposes to an unknown solid.

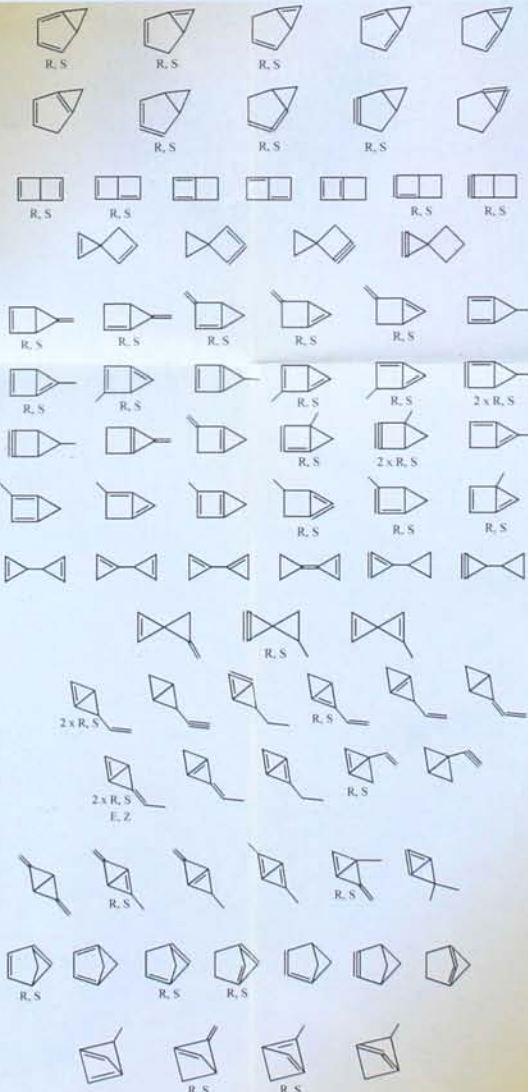
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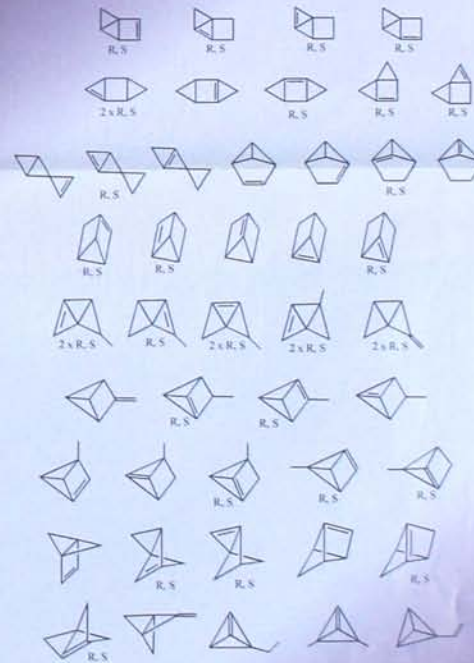
MONOCYCLIC



BICYCLIC



TRICYCLIC



TETRACYCLIC

