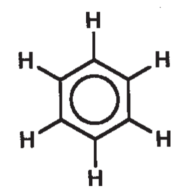
Molecule of the Month

Isomers of Benzene – Still Pursuing Dreams

J Chandrasekhar

J Chandrasekhar is at the Department of Organic Chemistry of the Indian Institute of Science, Bangalore.

Three new monocyclic C_6H_6 isomers which are highly strained have been made in recent years.



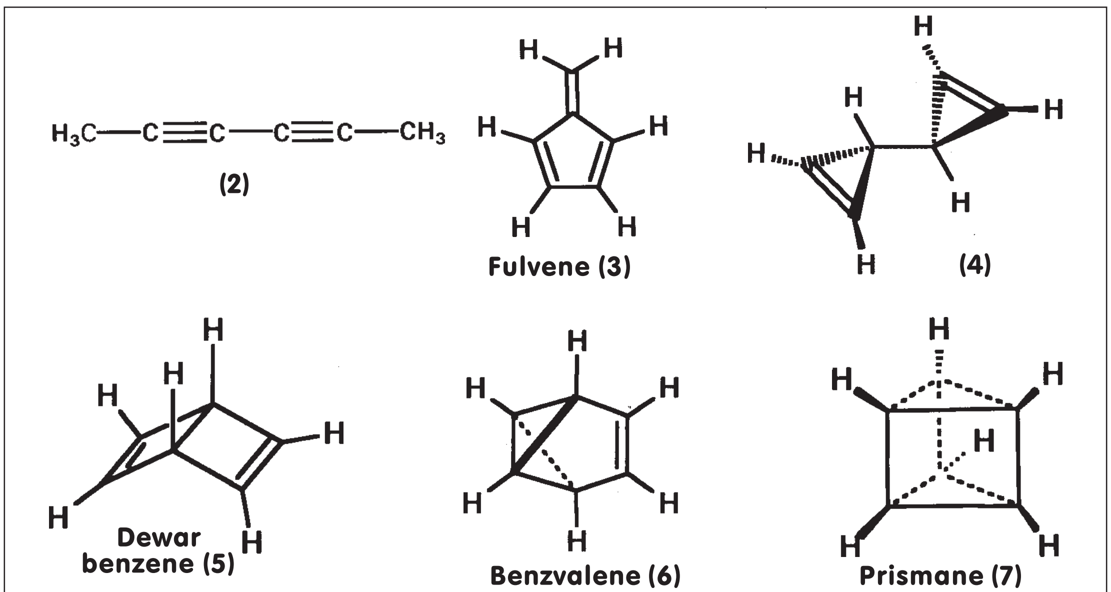
(1)

Figure 1 Kekulé structure of benzene shown with delocalised π electrons.

Michael Faraday opened up a new chapter in chemistry when he isolated benzene from the distillate of coal tar. The deceptively simple molecule with the formula C_6H_6 has triggered many experiments and theoretical proposals. The correct ring structure, shown in **1** (see *Figure 1*), was assigned by Kekulé after his celebrated dream of a snake attempting to swallow its tail. Some chemistry historians are debunking this bit about the dream. But it may be too late; fact or fable, it is now part of chemistry folklore.

How many isomers are possible for C_6H_6, using the known rules about hydrocarbons? Many acyclic structures, such as dimethylbutadiene (**2**), readily come to mind. A large number of substituted 3-, 4- or 5- membered rings are also possible. Fulvene (**3**)

Figure 2 Some experimentally known C_6H_6 isomers.



is a famous example. Two 3-membered rings can also be connected to form C_6H_6, as in isomer **4**. Among bicyclic structures, Dewar benzene (**5**) is well known. (Can you think of others?) It was first proposed as a bonding model for benzene. Later, an independent isomeric structure, with a non-planar geometry was made. A more complex ring fusion is involved in benzvalene (**6**). This strained molecule has also been successfully synthesized. More rings can be added until we reach the highly symmetrical structure, **7**, appropriately called prismane. This isomer was obtained as one of the products by photolysing Dewar benzene. Octahedrane (**8**) would have been a beautiful structure, but the valency of carbon does not permit this form.

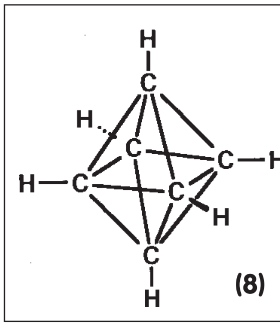

(8)

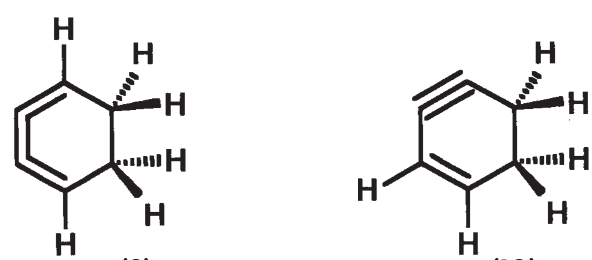
***Figure 3** An impossible structure for C_6H_6.*

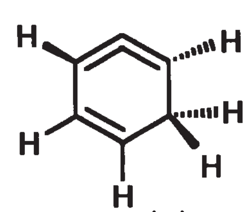
After all the isomeric structures are written down, the final count turns out to be 217! Only a small fraction of these have been made so far.

Consider only those isomers which have a 6-membered ring. Enamoured as we are by the symmetry and aromaticity of benzene, many of us would not even dream of an alternative to **1**. But, believe it or not, a *chemist* named William Shakespeare has proven the existence of two such isomers.

What are these 'Shakespeare benzenes'? The correct chemical names are 1,2,3-cyclohexatriene (**9**) and cyclohexen-3-yne (**10**). The former has three double bonds in a row (a butatriene unit), while the latter has a triple bond and a double bond. The central atoms of the

***Figure 4** New monocyclic isobenzenes.*


(9) (10)
Shakespeare benzenes


(11)
Christl benzenes

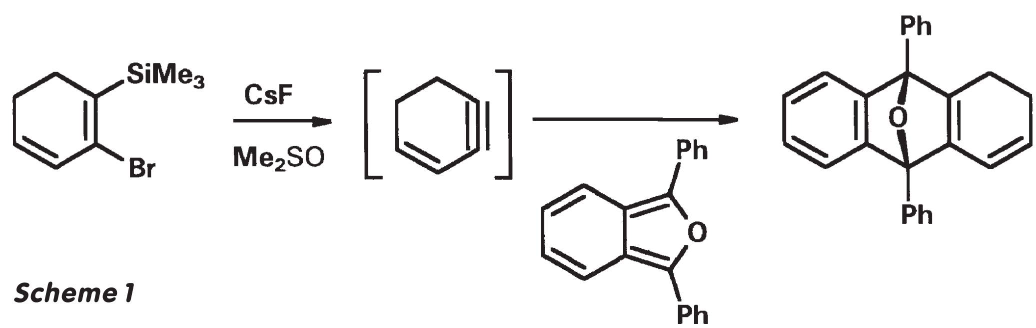
butatriene unit and the atoms forming the triple bond prefer linear geometry ('sp' hybridisation). This is impossible in a 6-membered ring. Hence, both molecules are highly strained, besides lacking aromatic stabilisation.

The isomers **9** and **10** were made using standard methods for making butatrienes and enynes, respectively, from appropriate 6-membered ring precursors. In view of their high strain, the isobenzenes could not be isolated and characterised. However, the formation of these species was proven by trapping them as cycloadducts with a reactive furan (see *Schemes 1, 2*).

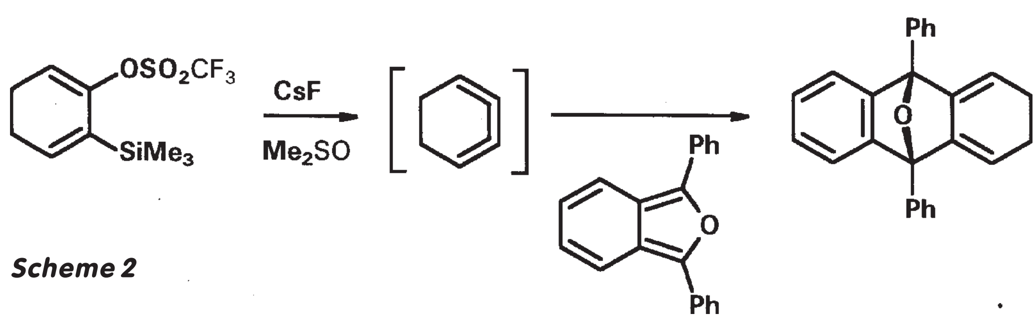
***Scheme 1** Experimental route to the preparation and trapping of cyclohexeneyne.*

***Scheme 2** Experimental route to the preparation and trapping of 1,2,3-cyclohexatriene.*

Spurred by this success, another isobenzene was created by a German chemist Christl. This new structure, 1,2,4-cyclohexatriene (**11**), has an allene unit and a double bond constrained in a 6-membered ring. Allenes do not like to be planar. Part of the strain

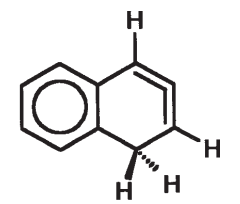


Scheme 1



Scheme 2

can be relieved by the hydrogen atoms bending out-of-plane. However, the molecule is expected to have considerable diradical character. The formation of **11**, following successive elimination reactions from a suitable precursor, could be confirmed only by means of a chemical trapping experiment (see *Scheme 3*).



(12)

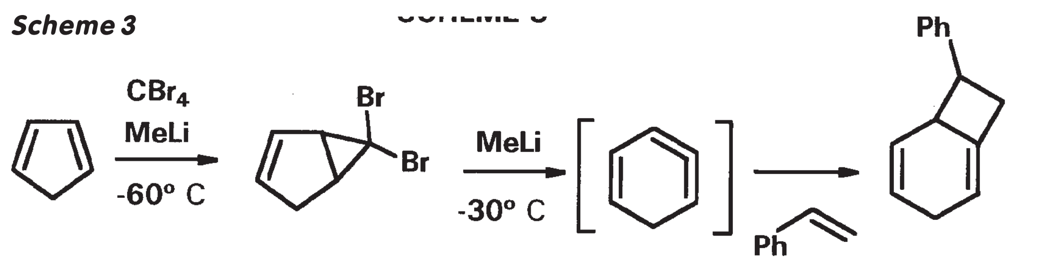
***Figure 5** Christl napthalene.*

We may expect more such work, especially aimed at the more strained forms, to complete the tally of benzene isomers. But surely the search has to end at 217? More likely, it won't. Benzene is only the first member of the aromatic series of compounds. There is the question of similar isomers for naphthalene, anthracene, etc. Christl has already considered and prepared his isomeric version of naphthalene (**12**). Further, if we are prepared to introduce enormous strain in the molecule, we should also consider the possibility of high energy isomers in which the valency restrictions are partially removed. As pointed out by another William Shakespeare:

"There are more things in heaven and earth, Horatio, than are dreamt of in your philosophy".

***Scheme 3** Reaction sequence used to prove the existence of 1,2,4-cyclohexatriene.*

Scheme 3



Did you know? ... When lead is bombarded by neutrons for a long time, it rearranges itself internally and becomes so elastic that a bell made of it might chime as resonantly as bells cast from the best bronze.

Address for correspondence
J Chandrasekhar
Department of
Organic Chemistry,
Indian Institute of Science,
Bangalore 560 012, India.