

Benzene and its evidence

During a drug induced daze in 1858, Friedrich Kekule stumbled on his theory of the benzene structure and it seemed a simple solution to the mind boggling molecule of Mr 78. He proposed that six carbon atoms were joined by a ring of alternating double bonds and single bonds. Each carbon atom in benzene was bonded to a hydrogen atom and this was otherwise referred to as a "cyclohexatri-1,3,5-ene" structure. Kekule went on to conclude that these alternating bonds constantly oscillated so that benzene was actually made up of two rings with different alternative carbon-carbon bonds, which were on opposite sides of equilibrium. Yet, this posed problems as the theoretical properties of Kekule's crazy compound were completely contradictory to the observed properties.

These properties included:

- the chemical bonding properties
- the shape
- the stability

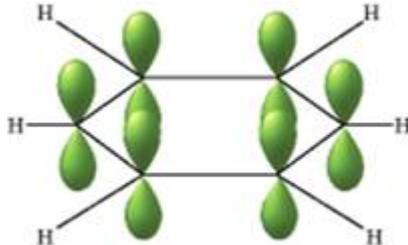


Fig. 2 The modern theory of overlapping p-orbitals

However, over 150 years later, with an abundance of more modern analytical techniques (and significantly less opium in our systems!), we can prove that each carbon atom in benzene has a p-orbital of completely delocalized electrons. This overlap, giving rise to a planar structure, although Kekule's cyclic structure laid the foundations for modern chemists, it was actually incorrect. Rather than two oscillating structures, we now know that benzene does have two different structures but these coexist as an intermediate with a lower energy than either of the two. None of the contributor structures are observed in benzene's actual electron structure – a theory which is known as "resonance hybridisation". But how did the boffins prove this?

Kekule's big mistake was his idea of alternating double and single carbon-carbon bonds, which would suggest that bonds in benzene were of different lengths. Single carbon-carbon bonds are known to be 0.154 nm long while double bonds are much shorter at 0.133nm. However, when benzene is cooled it crystallises and x-ray diffraction can be used to measure the bond lengths, which in benzene are all found to be 0.139nm. Therefore, Kekule's proposal of alternating single and double bonds is impossible.

In X-ray diffraction, X-rays meet a crystal, they interact with electrons and they are then scattered. The distribution of electron charge in a crystal molecule can be determined from the pattern of scattered rays. An X-ray examination of benzene can be carried out and may produce a complicated pattern of different intensity reflections. From this, an electron density contour map can be obtained, which, in the past, was extremely difficult to plot but is far easier today due to modern computing equipment. Peaks can be drawn into the map of the molecule and in benzene's case a symmetrical hexagonal shape carbon-carbon bonds can be seen. What is important is that all six of these bonds appear to be the same length. Hydrogen atoms are observed less clearly in an electron density map due to their weaker X-ray scattering.

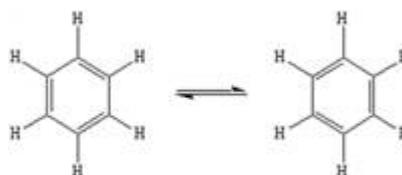


Fig. 3 Kekule's idea of oscillating structures

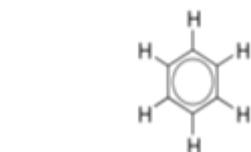
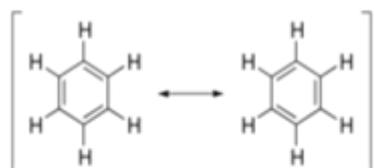


Fig. 4 The accepted theory of resonance

In 1928, Kathleen Lonsdale used this technique to identify Kekule's hexagonal shaped benzene structure as being correct. However, conversely she found a clear difference in length between aromatic carbon-carbon bonds and ordinary aliphatic carbon-carbon bonds, which disregarded Kekule's idea of alternating single and double carbon-carbon bonds.

Another issue for scientists of the 20th century was that Kekule's model meant that the benzene ring, like all other molecules, had a centre of symmetry. Yet, by means of long wave spectroscopy, this is contradicted. Within long wave spectroscopy there are two spectrums - useful in this case – infra-red absorption and the Raman scattering spectrum. The first of these, infra red light, can be directed at any molecule causing a surge of electrons and a periodic variation in the dipole. If the molecule already has a naturally occurring vibration in its sequence of bonds, and if the light

waves have a complementary frequency to this oscillation, the light waves will strongly stimulate the vibrations in the molecule. This will release energy, which will be displayed as bands of the absorption spectrum and are symmetric. The second involves ultra-violet or near visible light, which usually sets up a constant rapid dipole variation when directed at a molecule. This radiates a scattered secondary ray of the same frequency as the incident ray. However, molecules with a periodic variation in electric elasticity will fluctuate in their amplitude of radiation, hence recording a steady beat in the Raman spectra, which is asymmetric. Of course, in some special cases, molecules have to be awkward and over complicate things by excluding waves in either of these spectrum – for example carbon dioxide due to the "selection rule". However, the average molecule shows each vibration in no more and no less than one of the two spectra. Therefore, all of them are proven to have a centre of symmetry ... except benzene.

Benzene actually has waves in both of these spectra with old records showing up to twelve different frequencies of incident rays from benzene appearing in both the Raman spectrum and the infrared spectrum. This means that Kekule's regular hexagonal structure is wrong as benzene does not appear to have a centre of symmetry. Between 1938 and 1939, in the Bakerian Lecture, which was published from the Royal Society of London, Christopher Kelk Ingold described how he and his team extended this idea using comparisons with deuterium (heavy hydrogen) isotopes of benzene. When long wave spectroscopy analysis was carried out on heavy benzene and benzene, although waves in one spectrum were at different frequencies to the other, the coexisting waves in both the Raman spectrum and the infrared spectrum remained the same. Therefore, waves appearing on both spectra of a benzene molecule were not simply different waves with the

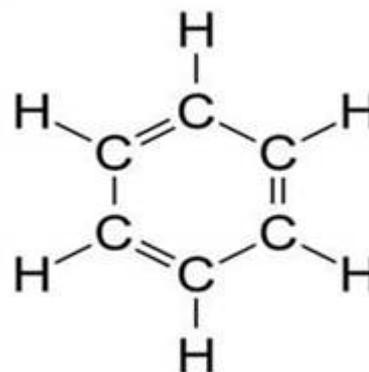


Fig. 1 Kekule's proposed structure of alternating single and double bonds

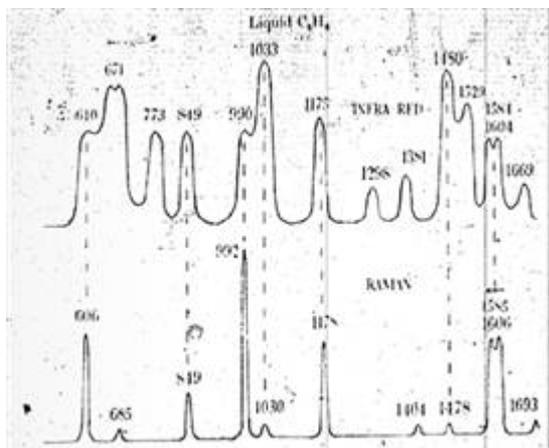


Fig. 5 A comparison of the Raman spectrum and the infrared spectrum in BENZENE, where identical waves can occur in both spectra

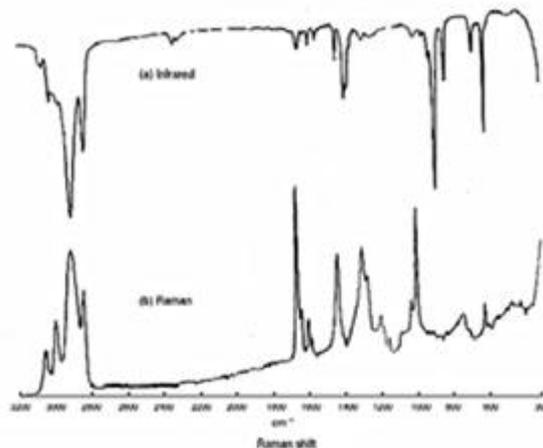


Fig. 6 A comparison of the Raman spectrum and the infrared spectrum in WATER with a centre of symmetry

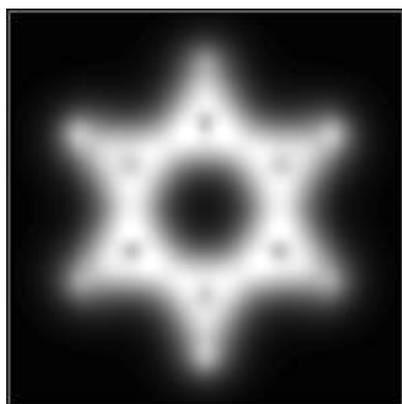


Fig. 7 Electron density map of benzene

same frequency that were indistinguishable; they were actually the same wave. The reason for benzene's lack of symmetry was further investigated using liquid benzene and it was concluded that the overlapping vibrations and intermolecular forces distorted the equilibrium of benzene's two resonance structures, which destroys the centre of symmetry. It is important to question the stability of benzene in Kekule's structure too, because when benzene hydrogenation is observed, the actual enthalpy energy released is far less than what is expected. The hypothetical value for the hydrogenation of benzene, based on Kekule's structure, can be easily worked out on a calculator, safely behind your desk using Hess' Law. Remember that the enthalpy of a reaction is independent of the route that's followed, provided the products and reactants are the same. Therefore, we can add together the known enthalpy of formations for the bonds broken in cyclohexa-1, 2, 3-

triene (Kekule's version of the benzene electron arrangement) and the bonds in three hydrogen molecules. The resulting cyclohexane molecule's enthalpy of formation is then subtracted from the energy released when bonds were broken to give the theoretical enthalpy of hydrogenation for benzene. In this process -359.2KJ/mol is calculated as the enthalpy of hydrogenation. Alternatively we can measure the actual hydrogenation enthalpy of benzene by reacting benzene with hydrogen in the presence of a transition metal catalyst. Calorimetry then reveals the true hydrogenation enthalpy of benzene to be -208.5KJ/mol. The difference between the observed and the expected enthalpy of formation is known as the resonance energy or delocalisation energy. Because of the relatively large delocalisation energy it is suggested that benzene is a stable, delocalised molecule, unlike the unstable Kekule structure. Therefore, scientists now think that there must be an equal spread of electrons around the molecule, giving rise to the overlapping orbitals of electrons in benzene.

Due to benzene's high delocalisation energy, we can explain why benzene does not easily undergo electrophilic substitution reactions with bromine. Normally, it would be expected for an unsaturated hydrocarbon like benzene to turn bromine water brown, indicating the presence of double carbon-carbon bonds. However, this is not the case as no single carbon atom has enough electron density to polarise a non-polar molecule, such as bromine. In addition, while it is possible for benzene to react in the presence of an aluminium chloride catalyst with chlorine, only one monosubstituted and three disubstituted chlorobenzene molecules are produced. As a result, we can confirm that benzene does not have alternating single and double carbon-carbon bonds.

A further process that can be used to prove that Kekule had the right idea with his hexagonal structure of benzene is electron diffraction. This was discovered at around the same time as X-ray diffraction. It involves "zapping" a molecule in the gas phase with an electron beam under low pressure. Atoms in the molecule scatter the rays and, by substituting into a series of complex equations, doing some number crunching and then measuring angles, an electron diffraction pattern can be produced. When this method is extended to benzene, it provides evidence that there are four possible distances between a carbon atom and a hydrogen atom within a molecule and three separate interatomic distances between carbon atoms. Scientists can draw a molecule of benzene to support Kekule's hexagonal structure based upon the information in benzene's electron diffraction pattern, despite shredding to pieces the rest of Kekule's structure!

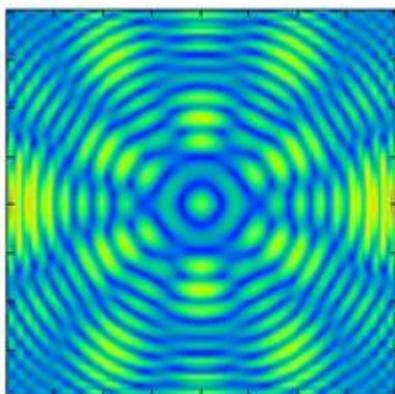


Fig. 9 An electron diffraction pattern of benzene

To conclude, while Kekule may have got his alternating bond theory in benzene wrong, he certainly laid the foundation for scientists such as Kathleen Lonsdale. If Newton stood on the shoulders of giants, then Kekule was most certainly a giant for others to stand on – even if we do give him and his theory a kick now and then with modern analytical techniques! To conclude, scientist August Wilhelm von Hofmann summed up the Kekule structure perfectly: "I would trade all my experimental works for the single idea of the benzene theory."

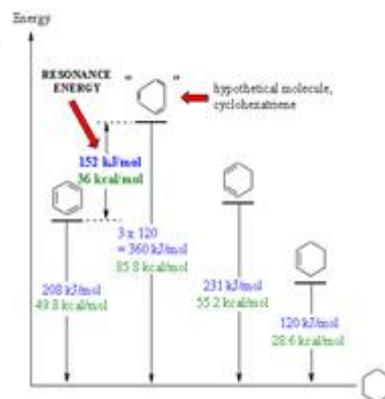


Fig. 8 Diagram showing the enthalpy of hydrogenation and delocalised (resonance) energy for benzene

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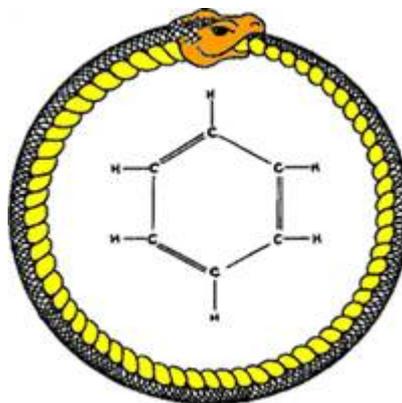


Fig. 10 The dream of whirling snakes, of the structure of benzene