1. Introduction

1.1. Aromatic character. Benzene was discovered in 1825 by Faraday; he obtained it from the condensate of a compressed illuminating gas which had been prepared by decomposing whale oil at red heat. In 1834 Mitscherlich found that the same hydrocarbon can be prepared from benzoic acid by dry distillation with lime, and he showed that it has the formula C_6H_6. A. W. Hofmann and C. B. Mansfield discovered benzene in coal tar in 1845, but it was not until 1848 that Mansfield isolated relatively pure benzene from this source. Mansfield carried out the distillations in a glass retort with the thermometer in the liquid, and he wrote:

'It has been, perhaps, the tedium of the methods necessary to effect a separation of mixed hydrocarbons from each other, which has deterred experienced chemists from devoting their time to disentangling the oils here treated of: and, perhaps, to have conducted the innumerable distillations necessary for this purpose in a laboratory imperfectly furnished with gas and other conveniences, would have been a task too laborious to have been persisted in.'

Faraday named his compound 'bicarburet of hydrogen'. Mitscherlich named it 'benzin'; but Liebig criticized this name as implying a relationship to strychnine and quinine and recommended 'benzol' (German, öl, oil). In 1837 A. Laurent suggested the name 'pheno' from the Greek 'I bear light' in recognition of the discovery of the hydrocarbon by Faraday in an illuminating gas. The name 'benzol' became established in Germany, but in England and France the name was eventually changed to 'benzene' to avoid confusion with the systematic names of alcohols. Laurent's suggestion was never adopted for the hydrocarbon itself, but 'phenyl' has long been used to designate the C_6H_5 group.

Many benzene derivatives had been discovered long before the isolation of benzene itself. Benzoic acid was obtained from gum benzoin as early as the sixteenth century; and benzaldehyde (oil of bitter almonds), cymene (oil of carraway), and toluene (balsam of Tolu) have also been known for a very long time. The coal gas industry was developed in England during the first half of the nineteenth century. Coal tar was a troublesome by-product, but the successful isolation of benzene and of some benzene derivatives soon suggested possible uses for the material. Coal tar soon became the most important source of benzene and its derivatives.

Kekulé called benzene and its derivatives 'aromatic compounds' because of their characteristic odour. A special name was justified because it had become evident that benzene and its derivatives possess rather special properties, and contain a higher proportion of carbon than the fatty compounds. Benzene has the formula C_6H_6, but the saturated aliphatic compound with the same number of carbon atoms has the formula C_6H_{14}. On the other hand, benzene and its derivatives are not highly unsaturated substances, but are characterized by their remarkable stability. Benzene itself can be prepared by the high-temperature decarboxylation of benzoic acid, by distilling phenol with zinc dust, and even by passing acetylene through a red-hot tube.

In his classical papers on the constitution of aromatic compounds, August Kekulé (1865, 1866) proposed the well-known cyclic structure for benzene, and he suggested that the peculiar properties of the aromatic compounds are dependent on the properties of this ring system. Kekulé therefore equated the terms 'aromatic' and 'benzenoid', and this view persisted for many years.

The peculiar properties of benzene and of its derivatives led to the use of the expression 'aromatic character'. Aromatic character cannot be rigidly defined, but can be illustrated by the following observations:

(i) A characteristic property of benzene is its thermal stability, and its ease of formation by pyrolytic methods.

(ii) Reagents such as nitric acid, sulphuric acid, and bromine, attack benzene under suitable conditions to give substitution products rather than addition products.

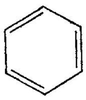
(iii) Benzene is remarkably resistant to oxidation: it is not oxidized by cold alkaline permanganate or by nitric acid, for example.

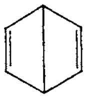
(iv) The properties of substituted benzenes are often different from those of analogous aliphatic compounds. Aniline is less basic than aliphatic amines, and it reacts with nitrous acid in the presence of hydrochloric acid to form benzene diazonium chloride. Phenol is a stronger acid than the alcohols. Benzoic acid is a stronger acid than acetic acid. Halo-benzenes are much less reactive than aliphatic halogen compounds.

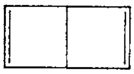
1.2. The structural formula of benzene. The problem of providing an adequate structural formula for benzene engaged the minds of chemists for many years. In 1865 Kekulé published his paper entitled *Sur la constitution des substances aromatiques* in which he suggested that the six atoms of carbon form a closed chain. In another paper published in the same year he used a regular hexagon formula in which the six carbon atoms were labelled by the letters *a–f*. The familiar hexagon formula with alternate single and double bonds was first used in a paper published in 1869 (Kekulé, 1869).

Kekulé showed that all disubstitution products must exist in three isomeric modifications, that there are only three isomers of the general formula $C_6H_3X_3$, and that there are six of the formula $C_6H_3X_2Y$. He was also able to explain the nature of the homologues of benzene and the essential difference between substitution in the nucleus and substitution in a side chain.

Although very successful in explaining the number and nature of the various substitution derivatives, Kekulé's cyclohexatriene formula (I) has always been regarded as only partly satisfactory: it is very difficult to explain the stability of benzene if it is assumed to have three ethylenic double bonds. From this point of view the structure (II) generally attributed to Dewar is even less satisfactory, for it requires a long *para* bond. It is of interest that a compound (III) akin to 'Dewar benzene' has been synthesized (van Tamelen & Pappas, 1963), and substituted derivatives have also been reported.


(I)
Kekulé


(II)
Dewar


(III)

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Excerpt
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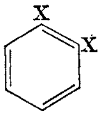
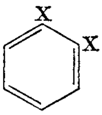
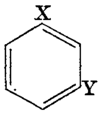
One of the most serious objections to the Kekulé structure (I) was pointed out by Ladenburg. If the structure of benzene really involves alternate double and single bonds, then *ortho*-disubstituted derivatives should exist in two isomeric modifications (IV) and (V). Moreover, when the two groups are different, there should also be two isomeric *meta* derivatives (VI) and (VII). As such isomers were, and are, unknown, some modification of the Kekulé structure appeared to be necessary. Victor Meyer suggested that the differences between such isomers might be so slight as to escape detection; but Kekulé further proposed that benzene has a kind of dynamic structure in which each carbon–carbon bond oscillates between a single and double bond. In other attempts to solve the benzene problem, Ladenburg tried to interpret its peculiar stability by picturing the molecule as a triangular prism (VIII); but this suggestion is only of historical interest for as well as being incapable of correctly representing relationships amongst benzene derivatives the prism structure is in conflict with the established planarity of benzene.



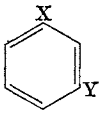
(IV)



(V)

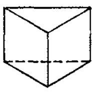


(VI)

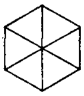


(VII)

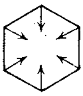
Claus also abandoned the use of double bonds and proposed a formula (IX) having three *para* bonds. In this structure, each carbon atom is supposed to be linked to three others, two in the *ortho* and one in the *para* position, so that *ortho–para* direction in substitution reactions would not be unexpected. In spite of the fact that such a structure does not offer a satisfactory explanation for the stability of benzene, it received considerable support at the time.



(VIII)
Ladenburg



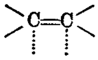
(IX)
Claus



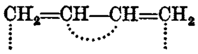
(X)
Armstrong–
Baeyer

Armstrong attempted to overcome the difficulty of the six unused valencies in benzene in another way (X). He suggested that 'the remaining six (valencies) react upon each other,—acting towards a centre as it were, so that the "affinity" may be said to be uniformly and symmetrically distributed'. Baeyer put forward a similar interpretation. These structures can hardly be seriously considered, for the hypothetical bonds directed towards the centre of the ring have no real meaning in terms of the modern electronic theory. The Armstrong–Baeyer formulation was little more than a pictorial representation of the fact that the problem of the fourth valency remained unsolved.

Of all the structures proposed for benzene that of Thiele (1899) is probably the nearest approach to the modern view. Thiele supposed that the reactivity of an olefinic linkage is due to incomplete saturation of the affinities of doubly-bound carbon atoms, which may be assumed to have partial valencies, represented by dotted lines. In conjugated compounds the partial valencies of adjacent carbon atoms linked by a single bond were supposed to neutralize each other with a resulting accumulation of partial valency at the ends of the conjugated system. According to Thiele, benzene is a conjugated system of double bonds *par excellence*, all the partial valencies being neutralized, as in (XI).



Isolated double bond

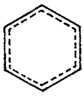


$CH_2{=}CH{-}CH{=}CH_2$

Conjugated system

As the theory of conjugated systems developed, this formula was modified, and the fully symmetrical structure (XII) of J. J. Thomson, involving real fractions of covalent bonds, came into use.

(XI)
Thiele



(XII)
Thomson

1.3. The application of physical methods to the benzene problem.

X-ray and electron diffraction experiments. The structure of benzene has been established beyond doubt by the application of two types of physical method: X-ray and electron diffraction, and infrared spectroscopy.

In X-ray diffraction and in electron diffraction experiments, a picture of the molecule under investigation is built up by recombining the waves which it scatters. The electron diffraction method is most easily applied to gases and to volatile substances, and the X-ray method to crystalline compounds. In particular, the diffraction method lends itself to the accurate determination of interatomic distances, or bond lengths. By these means it has been possible to determine the normal covalent radii for a large number of atoms (Pauling, 1960). It was found, however, that the C—C bond length is not a constant, but varies considerably with the nature of the linkage. In diamond, and in the saturated aliphatic compounds, the C—C bond length has been found to be near 1·54 Å; in ethylene, the C═C double-bond length is about 1·34 Å; and in acetylene, the C≡C triple-bond length is 1·20 Å. In non-conjugated compounds these lengths are found to be virtually constant; but in conjugated compounds considerable variations have been observed, the formal double and triple bonds in such compounds being longer than normal and the formal single bonds being shorter than normal.

The C—C bond length in benzene, and in benzene derivatives, has been determined both by electron diffraction and X-ray diffraction experiments to be near 1·39 Å. For example, analysis of the X-ray diffraction pattern of crystals of hexamethylbenzene gave a value of 1·39 Å for the length of the aromatic C—C bonds; and the length of the bonds linking each methyl group to the annular carbon atoms was found to be 1·53 Å. Following electron diffraction experiments with benzene vapour, Pauling & Brockway (1934) were unable to confirm that all the C—C bonds are identical, but at least the results were consistent with a picture of benzene having sides of length 1·39 Å.

The crystal structure of benzene at −3° has also been determined by X-ray diffraction, using detailed three-dimensional analysis (fig. 1.1). The benzene molecule was found to be a regular planar hexagon with C—C bond lengths of 1·392 Å. This value is in good agreement with the bond length (1·397 ± 0·001 Å) determined by electron diffraction of benzene vapour (Bastiansen, 1957).

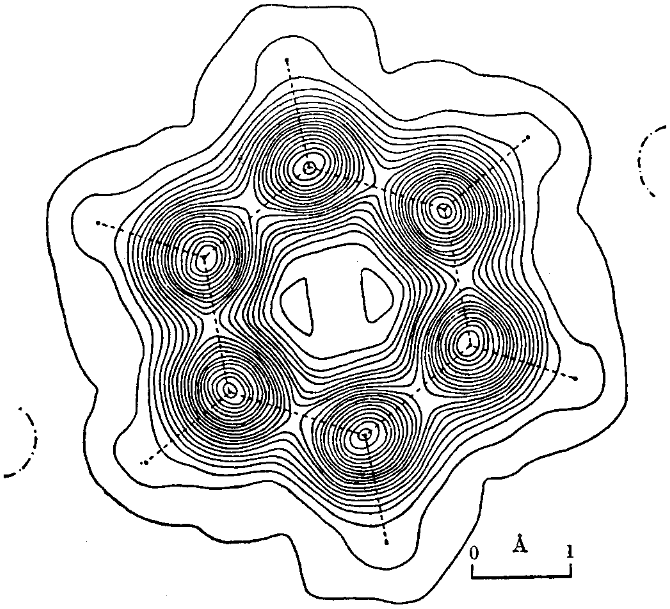


Fig. 1.1. Electron density in the plane of the benzene ring; contour interval 0·25e/Å^3 (from Cox, Cruickshank & Smith, 1958).

The physical evidence of electron diffraction and of X-ray diffraction therefore indicates that benzene has a regular planar hexagonal structure of side 1·39 Å.

Infrared spectroscopy. The application of spectroscopy to the study of the structure of benzene depends on the fact that a change from a lower to a higher energy state is accompanied by absorption of light, and a change from a higher to a lower energy state by emission of light. The frequency of the light emitted or absorbed is determined by the magnitude of the energy change involved, and is given by the equation

$$\Delta E = E_2 - E_1 = h\nu = \frac{hc}{\lambda},$$

where ΔE is the difference in energy between the two energy levels (E_2 and E_1), ν is the frequency of light absorbed or emitted, h is Planck's constant, and c is the velocity of light. Changes in rotational energy are associated with frequencies in the far infra-

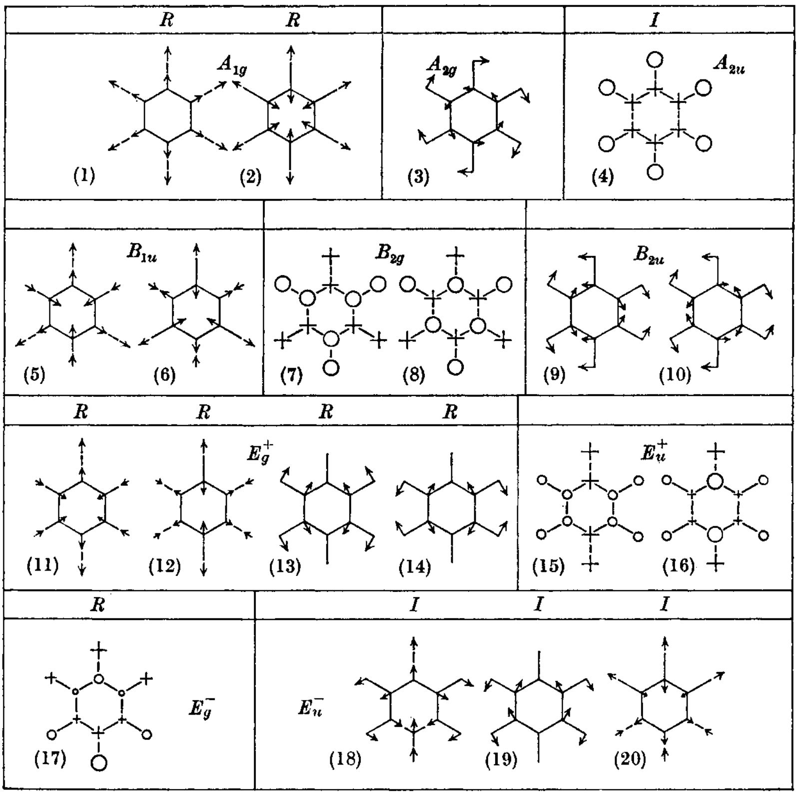


Fig. 1.2. Twenty fundamental vibrational forms of benzene (from Ingold, 1938).

red region; electronic transitions are associated with light in the ultraviolet and visible regions; and the vibration frequencies of molecules are in the infrared region.

Ingold (1938) has pointed out that if benzene has a planar, regular hexagonal structure it must have twenty fundamental vibrations, as illustrated in the accompanying diagrams (fig. 1.2). The arrows indicate motions in the plane of the ring, and the noughts and crosses motions perpendicular to the plane. Through a study of the spectral characteristics of benzene and of its deuterated analogues it was found possible to assign all the vibrational forms of the model to particular frequency bands in the spectra.

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Only those vibrations which are associated with an oscillation of dipole moment are recorded in the infrared absorption spectra. The planar, regular hexagonal model for benzene has four such vibration forms (labelled I), and four fundamental absorption bands were observed in the infrared absorption spectrum of benzene vapour. Similarly, only those normal vibrations can appear as fundamentals in the Raman spectra which involve an oscillation of molecular polarizability. The model requires seven such vibrational forms, and seven fundamental bands were observed.

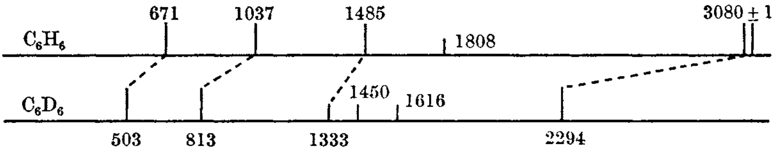

Fig. 1.3. Correlation of fundamentals in the infrared spectra of C_6H_6 and C_6D_6 (from Ingold, 1938).

The assignment of each band to a particular vibrational form was achieved by comparison of the spectrum of benzene with that of hexadeuterobenzene, C_6D_6; for the sole effect of the substitution of deuterium for hydrogen is to alter the *mass* and hence the vibration frequency (fig. 1.3). As the ratio of the masses was known, the frequency shifts for a given model were calculated, and the comparison of these calculated frequency shifts with those observed served the double purpose of assisting in or confirming the identification of the normal vibrations and of testing the model. Clearly the model which always gives the correct relations is proved.

The low-frequency band, 671 cm^{-1} in the infrared absorption spectrum of C_6H_6, and the 503 cm^{-1} band in C_6D_6 have been identified with the vibrational form in which the six hydrogen atoms together move perpendicularly to the plane of the ring (no. 4, fig. 1.2). Similarly, the lines at 849 cm^{-1} in the Raman spectrum of C_6H_6 and at 661 cm^{-1} in that of C_6D_6 have been assigned to the vibrational form in which the plane of the hydrogen atoms rocks over the plane of the carbon ring about an axis common to both planes (no. 17, fig. 1.2). The highest frequency line at 3062 cm^{-1} in the Raman spectrum of C_6H_6, and at 2292 cm^{-1} in C_6D_6, is the breathing vibration of the hydrogen atoms (no. 2, fig. 1.2). The frequency shift is large because almost all the motion is in the hydrogen (or deuterium) atom, whose mass changes in the ratio 1:2.

In this way eleven of the twenty vibrational forms of the model were investigated. The other vibrational forms are not recorded in either the infrared or the Raman spectra, and it was necessary to attack the problem in other ways. One method involved a study of the fluorescence (emission) spectra, and a second method involved the investigation of the Raman and infrared spectra of benzenes in which only some of the hydrogen atoms are replaced by deuterium. In this way, chosen elements of symmetry can be destroyed, thus enabling additional vibrational forms to appear in the spectra.

The pure rotational Raman spectra of benzene and benzene-d_6 have also been examined (Stoicheff, 1954). On the assumption that the molecule has a planar hexagonal structure, and that the interatomic distances are the same in both molecules, the C—C bond length was found to be 1·3973 ± 0·0010 Å, and the C—H distance 1·084 ± 0·006 Å. Finally, an investigation of the rotational Raman spectra of symmetrical benzene-d_3 gave a C—C bond length of 1·397 Å and a C—H bond length of 1·084 Å (Langseth & Stoicheff, 1956).

The successful conclusion of all this work has established the structure of benzene beyond all doubt. It is a plane regular hexagon of side 1·39 Å, and all the C—C bonds are entirely equivalent.

1.4. The application of wave mechanics. The electronic configuration of carbon in the ground state is $(1s)^2\,(2s)^2\,(2p_x)^1\,(2p_y)^1$. This configuration, with two unpaired electrons, corresponds to bivalency and it is, of course, well known that carbon rarely forms compounds in this way. The characteristic quadrivalent state can only be achieved if there are four unpaired electrons and Pauling (1931) described how this can be achieved by a process of exciting one of the $2s$ electrons into the empty $2p_z$ orbital, followed by hybridization.

When the four orbitals, $2s$, $2p_x$, $2p_y$, $2p_z$ are hybridized, the overlapping in phase occurs in such a way that four new orbitals are formed, all at angles of 109° 28′ to one another. This is termed tetrahedral hydridization, and the contours of ψ for such sp^3 orbitals can be drawn (fig. 1.4).