The change in concentration of the acid was found to affect the potential exactly as predicted.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 87]

THE DYNAMIC MODEL OF THE CHEMICAL BOND AND ITS APPLICATION TO THE STRUCTURE OF BENZENE

BY LINUS PAULING[1]

RECEIVED SEPTEMBER 14, 1925 PUBLISHED MAY 5, 1926

Introduction

The continued success of the Bohr atom has led all physicists except the most cautious to attribute a certain reality to the physical concept underlying the theory; namely, that the atom is composed of electrons rotating in stable orbits about the positive nucleus. The determination of these stable orbits can be made, in those cases that are simple enough to permit mathematical treatment, by the application of the principles of the quantum theory, thus verifying the correctness of the dynamic atom, since the quantum theory has been widely used in the explanation of the most varied phenomena. Hence, in attempting to explain the chemical properties of substances on the basis of the structure of the atom it would seem desirable to assume the Bohr theory to be true, and to make only those changes and additions which are necessary and logical extensions of the theory. This was the procedure followed by Knorr,[2] who first suggested and supported the idea that in non-ionized molecules electrons are in motion in orbits about two atomic nuclei. Further evidence in support of Knorr's views has since become available.

The study of the structures of crystals has also provided valuable information regarding the nature of the chemical bond. In this paper the arguments in favor of the dynamic models of molecules are reviewed and crystal structure evidence is presented to show that in molecules or ions, atoms may have stable electronic arrangements other than those of the noble gases. Electronic structures of benzene and other aromatic compounds based on these conceptions are then suggested and briefly discussed.

The Electron-Orbit-Sharing Theory of Chemical Bonding

The Pairing of Electrons.—Lewis[3,4] has shown that electrons have a strong tendency to pair. In terms of the Bohr atom the pairing of elec-

---

[1] National Research Fellow.

[2] Knorr, *Z. anorg. allgem. Chem.*, **129**, 109 (1923).

[3] Lewis, THIS JOURNAL, **38**, 762 (1916).

[4] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, **1923**, p. 79.

trons must be interpreted to mean that two electron orbits form a stable group, through the action of some unexplained force, perhaps magnetic as suggested by Lewis. Furthermore, other electron configurations are characterized by enhanced stability, in particular those of the noble gases. Thus, helium possesses two electrons, composing the K shell; neon, two K electrons and eight L electrons; argon, two K electrons, eight L electrons and eight M electrons. This tendency to form stable configurations may be due to a residuum of the force which causes the pairing of electrons.

The Electrostatic Bond and the Shared Electron Bond.—The classification of substances as polar and non-polar is not of fundamental importance with respect to the nature of the chemical bond. For example, water is commonly classed as polar and methane as non-polar; but there is every reason to believe that the oxygen-hydrogen bond is closely similar to the carbon-hydrogen bond. For this reason it is here proposed to classify substances as ionic compounds and molecular compounds. In an ionic compound the valence bond is the result of the transfer of an electron from one atom to another and the electrically charged ions are then held together by electrostatic attraction.[3,5] In a molecular compound the valence bond results from the sharing of electron pairs by two atomic nuclei. Lewis, who originally proposed the sharing of electrons by two atomic nuclei, at first considered the electrons to be at rest or undergoing small oscillations or rotations about equilibrium positions between the nuclei; more recently he remarked that his proposal is not incompatible with the idea that the electrons are moving in large orbits. Knorr has specifically discussed a dynamic model in which the electrons are in rotation in orbits including the two nuclei.

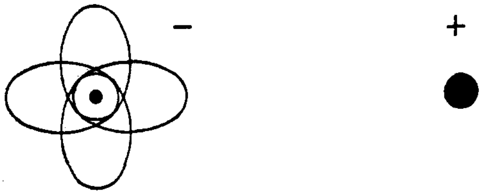


Fig. 1.—Diagrammatic representation of a compound with undeformed ions.

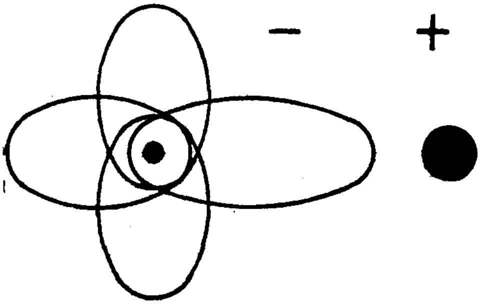


Fig. 2.—Representation of a compound in which electron orbits in the anion are deformed by the field of the cation.

Ionic Compounds.—The properties of ionic compounds in solution are well explained by the assumption that electrons are completely trans-

---

[5] Kossel, *Ann. Physik*, 49, 229 (1916).

ferred from one atom to another.[6] Observed properties of crystals of these substances have also been shown, notably by Born, to be in agreement with this conception. The ions do not, however, act as rigid bodies but are capable of deformation.[7] The electrons of the anion are attracted by the cation, and their orbits are displaced towards the cation; this causes an increase in the force between the two ions. Fig. 1 represents diagrammatically a compound whose ions exert only a small deforming influence on each other, and Fig. 2 one in which this influence is large.

Non-Polar Bonds with Hydrogen.—In a molecule of hydrogen chloride the proton (or hydrogen nucleus) because of its positive charge is attracted by two electrons rotating in their paired orbits, and in consequence of its small size assumes a position within these orbits, which are then no longer ellipses described about one nucleus, but include two nuclei. According to this idea the molecule of hydrogen chloride does not consist of a positively charged proton attached to the surface of the chlorine ion, as indicated by the usual picture $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\mathrm{H}$, but instead resembles an argon atom with one pair of its electron orbits enlarged and including the proton.

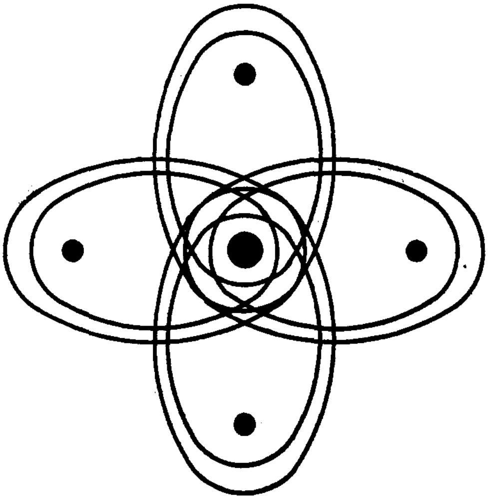
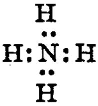


Fig. 3.—The dynamic model of the ammonium ion. The four pairs of electron orbits are directed approximately towards the corners of a regular tetrahedron.

Similarly, on this basis the ammonium ion would resemble in electron arrangement a neon atom in which a proton has been introduced inside of each pair of L electron orbits, expanding them until they are of about the size of the M orbits in argon (as shown in Fig. 3). This ion would then be closely similar to the potassium ion, which has the argon structure; thus Knorr's dynamic model leads to an explanation of the similarity in the physical and the chemical properties of salts of the two ions. On the other hand, the static or nearly static model of the ammonium ion,  $\mathrm{H}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}:\mathrm{H}$, is characterized by having on the periphery of the ion four

---

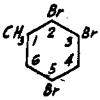
[6] See, for example, Lewis, Ref. 4; Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920).

[7] Fajans, *Naturwissenschaften*, **11**, 165 (1923).

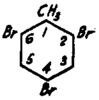
positively charged protons; so that from the outside this ion does not at all resemble a potassium ion, $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{K}}:$, which is surrounded by a sheath of electrons.

Since in these hydrides the proton has been taken within the electron-orbits of the other atom, the resulting group will act as a single atom. Indeed, Grimm[8] has been led to the formulation of the following displacement law, analogous to the radioactive displacement laws: "An atom not more than four places to the left of a noble gas in the periodic system changes on adding 1, 2, 3 or 4 hydrogen atoms in such a way as to form a pseudo-atom similar to the atom in the group 1, 2, 3 or 4 places to the right." Thus NH is similar to O, NH_2 to F, NH_3 to Ne and NH_4 to Na. By similar it is meant that the atoms and pseudo-atoms have the same valence and number of external electrons, but in general different sizes. This law was supported by the consideration of a number of properties: the mole-refraction, Van der Waals' b, the kinetic diameter σ, interatomic distances in crystals, isomorphism and morphotropy of crystals and formation of solid solutions, and ionization-potentials; in the case of pseudo-atoms with no electric moment consideration was also given to heat of vaporization, boiling point, and Van der Waals' a.

As an illustration of these arguments we will consider only isomorphism and solid-solution formation. Crystals are isomorphous in case the atom groups of which they are composed are so similar in shape as to permit the construction of similar crystals. Solid solutions are formed by the replacement of one atom or atom group by another, which must be similar in size and shape. The isomorphism of the salts of ammonium with those of potassium and rubidium[9] requires these ions to have similar external appearances corresponding to the dynamic structure assigned the ammonium ion. The oxonium ion, OH_3^+, would be assigned a similar structure, making understandable the complete isomorphism of crystals of perchloric acid monohydrate, $HClO_4 . H_2O$, and of ammonium perchlorate, NH_4ClO_4, as shown by X-ray examination[10] and by their formation of a complete series of solid solutions. The similarity in shape of bromine atoms and methyl groups likewise explains the complete isomorphism of the 1, 2, 3, 5 and 1, 2, 4, 6 tribromotoluenes;[11] for their molecules would have similar shapes, since they both have one or the other of these substituents in the same positions, as is seen from their formulas



and



---

[8] Grimm, *Z. Elektrochem.*, **31**, 474 (1925).

[9] Tutton, *Proc. Roy. Soc.*, **79A**, 370 (1907).

[10] Volmer, *Ann.*, **440**, 200 (1924).

[11] Jaeger, *Z. Krist. Mineralog.*, **38**, 555 (1904); **39**, 170 (1904); **40**, 357 (1905).

In the case of such very large molecules, however, the argument is less certain, for a considerable change in one atom would have only a small effect on the shape of the entire molecule.

The Single Shared Bond in General.—The single shared bond between two atoms is interpreted in general as consisting always of two electrons in orbits including the nuclei of both atoms. Since the orbits about a nucleus are directed in position, the bond is also directed. Diamond consists of carbon atoms, each of which has two K electrons and the orbits of two other electrons shared with each of the four atoms surrounding it tetrahedrally. The ionic substance sphalerite, ZnS, on the other hand, while possessing a similar atomic arrangement, is pictured as consisting of ions not connected by shared orbits. On this view, then, there is a sharp demarcation between ionic and molecular compounds; a gradual transition is not conceivable, unless a dynamic equilibrium between two forms is postulated to explain transition cases.[12]

The preceding discussion shows that introducing a proton into L orbits increases their size. Since a satisfactory mathematical treatment of even the simplest cases of orbits about two nuclei is lacking, no definite size and shape can be assigned these shared orbits; I suggest that for convenience orbits obtained by introducing another nucleus into the L shell be called λ orbits, into the M shell μ orbits, and so on for the other shells.

The structures assigned by this theory to chain and ring compounds containing single bonds are obvious. It is evident that a mechanism for the phenomenon of "electron displacement"[3,13] along the chain, as differentiated from purely electrostatic action through space, is at hand in the form of variations of the screening constant.[14] This point will be further discussed in a paper by H. J. Lucas.

Double and Triple Bonds.—Double and triple bonds may involve the sharing of four or six electron orbits by two atom nuclei, or the sharing of two electrons and the consequent deficiency in electron shells of one or both atoms.[15] In the first case unsaturation results from the mutual

---

[12] Knorr believes that a gradual transition might occur by gradually increasing the force exerted by the cation on the electrons of the anion, until finally the orbits included the cation nucleus. But it would seem that two distinct cases are still present; one in which the orbits include one nucleus, the other in which they include two. In solutions of acids a dynamic equilibrium is present between the un-ionized acid HA and the ions A^- and H_3O^+. The oxygen-hydrogen bonds in H_3O^+ are shared bonds, as is the A-hydrogen bond. If at equilibrium only a very small amount of HA is present, the acid is strong; while if only a very small amount of H_3O^+ is present, the acid is weak; and transition acids are intermediate.

[13] Lucas and Jameson, THIS JOURNAL, **46**, 2478 (1924).

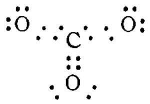
[14] Sommerfeld, "Atomic Structure and Spectral Lines," translated by Brose, E. P., Dutton and Co., New York, **1923**, p. 501.

[15] Lewis, Ref. 4, p. 88; *Chem. Rev.*, **1**, 231 (1924).

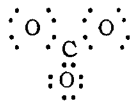
repulsion of the two pairs of electrons in their orbits about the two nuclei, and in the second case from the deficiency in the shells.

Stable Electron Configurations.—The carbon atom usually has the tetrahedral electron arrangement which it possesses in diamond; it is then the carbon atom of Van't Hoff and Le Bel. X-ray investigation has verified the existence of the tetrahedral carbon atom in hexamethylene tetramine,[16] $C_6H_{12}N_4$. Other atoms with small kernels also ordinarily assume a tetrahedral arrangement of eight electron orbits in pairs. However, the carbon atom is not always tetrahedral; in crystals of pentaerythritol, $C(CH_2OH)_4$, X-ray examination[17] has shown that the four carbon atoms attached to the central atom *lie in one plane.*

At times, moreover, the arrangement of six electron-orbits becomes stable. The study with X-rays of calcite and related crystals[18] has shown that the carbonate ion, $CO_3^=$, has a three-fold symmetry axis; moreover, the four atoms lie in the same plane, the carbon atom being surrounded by the three oxygen atoms. If we represent by two dots pairs of electron orbits, reasonable arrangements of the twenty-four electrons other than K electrons are



(1), and



(2)

These structures have both been suggested before in order to explain the X-ray evidence, the second structure by Latimer and Rodebush[19] and the first by Huggins.[20] We shall be able to make a choice between them, using the dynamic model, by a consideration of the tendency of a kernel to hold electron orbits. This tendency depends upon the charge of the kernel; fluorine, with a kernel charge of seven, would have a very strong tendency to hold eight electrons, and would share them with reluctance; oxygen, with a kernel charge of six, would attract electrons much more strongly than carbon, with a charge of four.[21] Thus we see that

---

[16] Dickinson and Raymond, This Journal, **45,** 22 (1923).

[17] Mark and Weissenberg, *Z. Physik,* **17,** 301 (1923). Huggins and Hendricks, This Journal, **48,** 164 (1926).

[18] See, for instance, Wyckoff, *Am. J. Sci.,* **50,** 317 (1920).

[19] Ref. 6, p. 1429.

[20] Huggins, This Journal, **44,** 1841 (1922).

[21] The tendency to form hydrogen bonds depends on the force with which the electrons are attracted by the atomic nuclei. Hydrogen ordinarily has two shared electrons, as in the hydrides discussed above. In the hydrides of the very electropositive metals, such as calcium and lithium, it has two unshared electrons, forming a negative hydrogen ion, H^-. In some cases, first noticed by Huggins, it shares four electron orbits, two with one atom and two with another and thus acts as a bond, for example, in the acid fluoride ion, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$. The singly charged proton should be satisfied with two shared orbits, except when the other kernel has such a large charge as to hold

the first structure of the carbonate ion cannot be correct, for it gives the oxygen atoms only four unshared and four shared electrons, and the carbon atom twelve shared electrons.[22] We may, therefore, accept the second structure, in which the carbon atom possesses three pairs of electron-orbits with their major axes in one plane and 120° apart.

The nitrate ion has the same structure as the carbonate ion, for the crystal structure of sodium nitrate is closely similar to that of calcite. Moreover, the similarity of the trigonal crystal nordenskiöldine, $CaSn(BO_3)_2$, with the rhombohedral angle 102° 58′, and the trigonal crystal dolomite, $CaMg(CO_3)_2$, with this angle equal to 102° 53′, shows with only a small uncertainty that the borate ion, $BO_3^{=}$, has this structure also. Only elements with small kernel charges, such as boron, carbon and nitrogen, would be expected to form stable arrangements with six electron-orbits; and boron, with a kernel charge of three, should have greater tendency to do so than carbon, and carbon greater than nitrogen.

The crystal structure of graphite has finally been determined satisfactorily.[23,24] The atoms are arranged in layers separated by a large distance, 3.40 Å., the atoms ineach layer being coplanar, and only 1.42 Å. apart. The very small value of the coefficient of expansion in the plane of these layers,[25] compared with the much larger value normal to the plane, suggests that the atoms, which are arranged at the corners of close-packed hexagons, are connected by electron orbits as shown in Fig. 4, these orbits having the same positions as those about a carbon atom in the carbonate ion. The remaining electrons, one per atom, are, as shown by the high conductivity of graphite, similar to the valence electrons in metals and indeterminate in position. In this figure and the following ones the larger

the shared electrons very tightly. Accordingly, highly charged kernels should show the greatest tendency to form hydrogen bonds, in agreement with observation, for fluorine (HF_2^-, H_6F_6) is most active in this respect, oxygen (H_4O_2) less active, and nitrogen (NH_4OH) still less.

Some atoms other than hydrogen seem to be able to hold a shell containing only two shared electrons. Both the mercurous and mercuric ions are colorless, although a mercury atom with a charge of one would contain an odd number of electrons, and hence be colored. [See Bichowsky, THIS JOURNAL, **40,** 500 (1918)]. Moreover, in solution and in crystals the mercurous ion is doubled, and exists as the dimercurous ion $(Hg_2)^{++}$. [Havighurst, *Am. J. Sci.,* **10,** 15 (1925)]. These facts are all explained by the assumption that the dimercurous ion has the structure $(Hg^{++}:Hg^{++})^{++}$. The kernels of the two atoms are just as in the mercuric ion, and are doubly charged; and in addition there are two electrons in an outer shell binding the kernels together. The resultant ion accordingly has a charge of plus two.

[22] The arguments used in reaching this conclusion may be based on Postulate 3 of Langmuir, *Science,* **54,** 59 (1921).

[23] Hassel and Mark, *Z. Physik,* **25,** 317 (1924); these authors state that Ewald has prepared Laue photographs which verify this structure.

[24] Bernal, *Proc. Roy. Soc.,* **106A,** 749 (1924).

[25] Backhurst, *Proc. Roy. Soc.,* **102A,** 340 (1922).

black circles represent carbon nuclei with their two K electrons and the smaller black circles (not shown in Fig. 4) protons or hydrogen nuclei; the double curves drawn through (or near) the nuclei represent orbits in which a pair of electrons are rotating around the two nuclei which the curves connect (or enclose).

According to our suggested electronic structure of graphite a crystal of this substance consists of a pile of layer-molecules, the atoms in each layer being connected by bonds just like the carbon-carbon bonds in organic compounds; in a crystal of diamond there is only one molecule, for all of the atoms are connected by such bonds.

It may be mentioned at this point that the ease of formation of aromatic compounds such as mellitic acid from graphite suggests that the structure of benzene is similar to that of graphite. This argument was used in favor of a puckered arrangement of the atoms in the benzene ring at the time when such an arrangement was assigned to graphite;[26] the same argument evidently now supports a plane benzene ring.

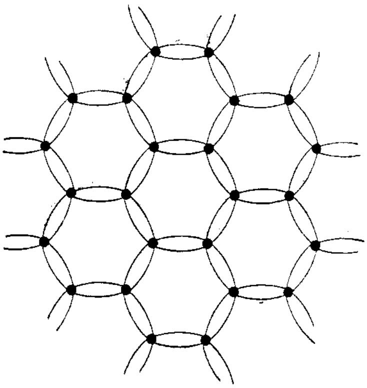


Fig. 4.—The atomic and suggested electronic arrangement of a graphite crystal in one layer, parallel to (0001).

The Structure of Aromatic Compounds

Benzene.—A consideration of the application to aromatic compounds of the electronic models of ions and molecules discussed in the earlier sections of this paper has led us to propose the structure for benzene represented diagrammatically in Fig. 5. All six carbon atoms and all six hydrogen atoms are in the same plane, at the corners of two similar regular hexagons. Each carbon atom is connected by pairs of λ electron orbits to the two adjacent carbon atoms and to one proton, the angles between pairs of orbits being 120°. The λ shells of the carbon atoms are then as in the carbonate ion and in graphite. Furthermore, there are two electrons in orbits including each carbon atom and the one directly across the ring. These orbits are twice as long as the λ orbits: I propose then that they be designated μ orbits, for they can hardly be assigned to the λ shell.

The unusual stability of aromatic compounds as compared with ordinary unsaturated compounds is to be attributed to the stability of this group of six crossed μ orbits. It is probable that this stability is the result of an effect similar to that responsible for the stability of the neon and

[26] See, for example, Huggins, This Journal, **45**, 264 (1923).

argon arrangements. On partial reduction to dihydro and tetrahydro derivatives ordinary unsaturated compounds are formed, the μ orbits being destroyed; this is in agreement with the chemical investigations of Baeyer and the thermochemical work of Stohmann.[27]

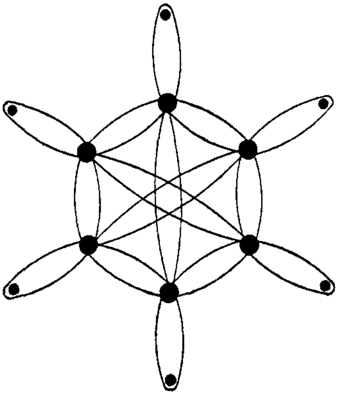


Fig. 5.—The suggested structure of the benzene molecule.

The symmetry of this benzene ring is that of point group D_{6h}, the highest possible other than that of cubic point groups. Accordingly all of the mono-substituted and all of the *ortho*-di-substituted derivatives should be identical, in agreement with the failure to find any such isomers.

It will be noticed that there is a direct connection from each carbon atom to the one directly opposite, that is, to the *para* atom, but no direct connection to the *meta* atoms. *The structure proposed accordingly provides a mechanism whereby a substituent group is able to influence the para position directly.* This property sharply differentiates this structure from nearly all those previously proposed, such as the centric formula of Armstrong and Baeyer, in which the fourth bond of each carbon atom is directed towards the center of the ring, and the structure of Huggins,[28] in which six electrons occupy fixed positions in the center of the ring. The only exception is the benzene ring of Claus, which is similar to that proposed in that there are direct bonds across the ring. This satisfactory structure, which was proposed by Claus long before modern atomic structure conceptions were developed, is now shown to have a plausible justification from electronic viewpoints, by employing Knorr's hypothesis of the chemical bond and abandoning the tradition that carbon atoms have necessarily a tetrahedral arrangement of their valences.

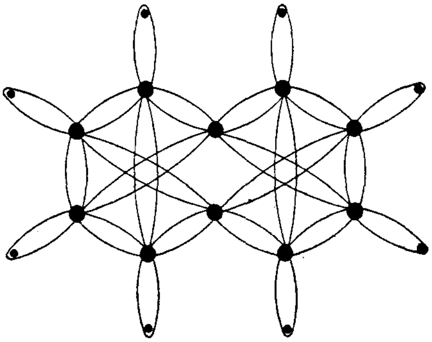


Fig. 6.—The structure of the naphthalene molecule.

Naphthalene.—The electronic structure assigned to naphthalene, $C_{10}H_8$, is shown in Fig. 6. The stable groups of μ orbits are also present here.

---

[27] See Henrich, "Theories of Organic Chemistry," translated by Johnson and Hahn, Wiley, New York, **1922**, p. 24.

[28] Huggins, This Journal, **44**, 1607 (1922).

The lack of direct connection between carbon atoms 9 and 10 throws a strain on the 1–4 and 5–8 bonds. This is probably responsible for the reactivity of these positions; as shown by the fact that naphthalene is more easily reduced than benzene, the addition occurring first in the 1–4 (or 5–8) positions.

Anthracene.—The structure of anthracene, $C_{14}H_{10}$, is shown in Fig. 7. The atoms are coplanar. The lack of 11–12 and of 13–14 bonds throws a great strain on the 5–10 bond, and smaller strains on the 1–4 and 6–9 bonds, explaining the reactivity of the 5 and 10 carbon atoms.

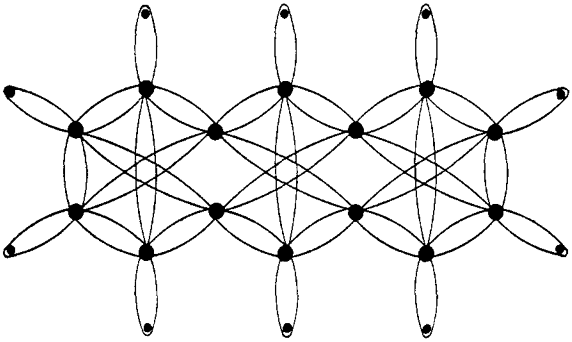


Fig. 7.—The structure of the anthracene molecule.

It will be noticed that a direct bond is provided between carbon atoms 5 and 10, in agreement with chemical evidence, such as its formation by the Friedel and Crafts synthesis from benzene and acetylene tetrabromide. The formation of acridine from formyl diphenylamine further supports this conclusion.

The Dimensions of the Molecules.—The nearest coplanar carbon atoms in graphite are 1.42 Å. apart. Possibly the μ electrons in benzene decrease this distance slightly, but it can be accepted as approximately the carbon-carbon distance around the benzene hexagon. Assuming that the λ orbits connecting a carbon atom and a proton are about the same size as those connecting two carbon atoms, the benzene molecule can then be assigned a diameter of about 6 Å. Similarly, the naphthalene molecule, described in the next section, would have a width of about 6 Å. and a length of about 8.5 Å., and the anthracene molecule the same width and a length of about 11 Å.

In the diagrammatic representations of the proposed structures the electron orbits are pictured in the plane of the atomic nuclei. It seems probable, however, that the planes of the orbits are perpendicular to the plane of the nuclei. The thickness of molecules of benzene, naphthalene and anthracene would then depend on the minor axes of the electron orbits. These minor axes are probably about 2 or 2.5 Å.; the repulsion of electron orbits could then keep adjacent molecules about 3 Å. apart, as is indicated by experimental measurements.

W. H. and W. L. Bragg have investigated with X-rays crystals of naphthalene and anthracene.[29] From their limited experimental data they concluded that a molecule of naphthalene occupies a parallelepiped with dimensions 3.0 × 6.0 × 8.7 Å., and a molecule of anthracene one with dimensions 3.0 × 6.1 × 11.2 Å. These values are in good agreement with those predicted above. Further verification of the predicted values is given by the kinetic theory measurements of Mack,[30] whose data for benzene are in good agreement with a molecule 3.0 Å. thick and 6.0 Å. in diameter, and for naphthalene and anthracene with molecules of the sizes found by the Braggs.

Summary

A natural extension of the Bohr theory had led earlier investigators to the hypothesis that the shared-electron valence bond consists in the rotating of a pair of electrons in orbits about the nuclei of the two bonded atoms. This fundamental idea is now extended in proposing the following electronic structure of the benzene molecule. The six carbon atoms and six hydrogen atoms lie in the same plane at the corners of two concentric regular hexagons. Each carbon atom is connected by two shared bonds of the type just described with the two adjacent carbon nuclei and by a third such bond with a hydrogen nucleus, the distribution of these bonds being similar to that about the carbon atoms in the carbonate ion and in

---

[29] W. H. and W. L. Bragg, "X-Rays and Crystal Structure," 4th edition, G. Bell and Sons, London, **1924**, p. 233. These authors, basing their arguments on an incorrect determination of the crystal structure of graphite, in which the carbon atoms were staggered instead of lying in one plane, suggested structures for benzene and other aromatic compounds in which the carbon atoms were staggered. These suggested structures were not supported by any experimental evidence, however, other than the incorrectly interpreted data on graphite.

The structure which we have suggested for naphthalene has the point-group symmetry V_h, and so has three planes of symmetry and three two-fold axes, as well as a center of symmetry. This is in disagreement with the statement of the Braggs (p. 253) that the naphthalene molecule has a center of symmetry but no plane of symmetry or symmetry axis. Their statement is, however, incorrect, and is not borne out by their data (note the statement concerning point-group symmetry in the next paragraph).

When sufficient X-ray data from crystalline benzene have been obtained, the structure suggested in this paper can be further tested. Inasmuch as the point-group symmetry of the molecule is held to be D_{6h}, it might be thought that the crystals could not have such low symmetry as that of the orthorhombic system. There is, however, no reason for this belief; for a molecule, while required to possess at least the symmetry of its position in the crystal, may have the further symmetry of any point-group containing the point-group of its position in the crystal as a sub-group. Thus a knowledge of the space-group symmetry of a crystal may give the *minimum* symmetry possessed by the molecules of the substance, but cannot give their *maximum* symmetry.

[30] Mack, THIS JOURNAL, **47**, 2468 (1925).

graphite. Furthermore, each carbon atom is connected with the carbon atom directly opposite by its fourth bond consisting of two electrons rotating in long orbits about the two nuclei of these atoms. The six crossed orbits form a stable arrangement, accounting for the stability of the benzene ring. Similar electronic structures are proposed for naphthalene and anthracene.

In support of the proposed structures the evidence concerning this dynamic model of the shared bond is summarized. Crystal structure evidence is also advanced to show that the carbon atom does not always have four electron pairs arranged about it tetrahedrally, but may have other stable electronic arrangements, notably one with three electron pairs.

The properties of benzene, naphthalene and anthracene, in particular the sizes of their molecules, are discussed with reference to the proposed structures.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE SIR WILLIAM RAMSAY LABORATORIES OF PHYSICAL AND INORGANIC CHEMISTRY, UNIVERSITY COLLEGE]

AN APPARATUS FOR THE ANALYSIS OF SMALL AMOUNTS OF VAPOR WHEN PRESENT IN PERMANENT GASES

BY IVAN ROY MCHAFFIE

RECEIVED SEPTEMBER 28, 1925 PUBLISHED MAY 5, 1926

The apparatus to be described was constructed to measure very small amounts of water vapor present in air but might well be employed for other vapors and other gases.

It is essentially a device for measuring the mass of very small amounts of water (0.5 mg.) with an accuracy of 1 in 1000. The construction of the apparatus is shown in Fig. 1. One limb of a U-tube, A, which has a capacity of approximately 30 cc., is joined to a tap B and the other limb is connected with glass tubing to a mercury manometer G. A glass tube 78 cm. long is sealed to the bottom of the manometer and the other end is sealed to a mercury air trap H which is joined to a mercury reservoir with a length of rubber tubing. A McLeod gage is sealed to the side of the manometer at D. A two-way tap is placed at C. E is connected to mercury diffusion pumps; F to an aspirator bottle or other means of measuring the volume of gas passed through the apparatus. A glass scale calibrated to 0.01 mm. is mounted behind the manometer tube. The volume of A to the tip of a ground-glass pointer in the manometer tube is accurately measured.

As it is necessary in making a measurement to heat the apparatus to a temperature of 40° with a very low pressure in A, the tap B (as used by Professor F. G. Keyes) was constructed so that it would remain firmly seated as the tap grease softened. The small end of the barrel is closed by