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BOND CHARACTER, BOND ORDER AND THE QUADRIVALENCY OF CARBON

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Abstract—When the chemical bond is treated as a resultant without specific reference to its exact nature, a consistent interpretation of the relationship between the various types of carbon–carbon bonds is possible. The terms bond character, bond order and quadrivalency are considered in the light of this interpretation. It is emphasised that the chemical bond must be regarded as a vector quantity involving both direction and magnitude factors.

THE idea of the chemical bond lies at the root of our knowledge of the structure of molecules and without it the science of organic chemistry could hardly have developed. Saturation and unsaturation, the tetrahedral disposition of the bonds of carbon and many other accepted principles of molecular structure are all developments from the primitive bond theory. It was inevitable, when something was learnt about the inner structure of atoms, that the electronic nature of chemical bonds should be discovered and the stage set for more detailed investigations into their exact make-up. A host of physical and mathematical methods and many interpretations of the results obtained have been brought to bear on the problem. The consequent, rapidly advancing branch of knowledge consists of established facts, constantly changing techniques and numerous exploratory theories all inter-connected in an increasingly complex pattern.

What will be said here deals with a small chapter of this large and expanding science and uses as its basis the measurements of bond lengths, bond angles and bond energies recorded in the literature. An attempt is made to rationalise the relation between the old and the new points of view on chemical binding and molecular structure. There is no intention of trying to make a critical review of the present state of knowledge, even in a restricted field.

Whatever else the old-fashioned chemical bond may be, it must be regarded as a resultant of many contributing factors concerned with nuclear and electronic attractions, repulsions and movements. It is represented as a straight line joining what are considered to be the mean positions of the nuclei of the atoms linked by it. It is, therefore to be characterised by its length (i.e. the internuclear distance) and its direction. The length is a function of the bond energy, but it must be pointed out that scientists are not unanimous as to what the term bond energy means. In this discussion the values worked out by Pauling[1] and called by him "empirical" will be used.

There is another fundamental matter involved, namely, the quadrivalency of carbon. It may seem obvious that, taking hydrogen as univalent and knowing that methane has the composition CH_4, the valency of carbon must necessarily be four.

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[1] L. Pauling, *Nature of the Chemical Bond* (2nd Ed.) pp. 53 and 131. Cornell University Press, New York (1945).

The simple addition, however, of four univalent bonds to make a total valency of four leaves out of consideration the directions of the bonds and this omission, as we shall see later, may give rise to misleading conclusions.

The particular aspect of "bond science" to be dealt with first is the classification of bonds according to "character" or "order". This assumes considerable importance in connection with the C,C bonds in benzene, graphite and conjugated systems.

When the symmetry of the benzene ring, its planarity and the equality in length of its C,C bonds are considered in the light of the older ideas of valency, it is natural to conclude that the bonds are half-way between double and single bonds in "character." Pauling and Brockway[2] used this terminology in discussions on the presumed resonance of benzene and allied structures. Their equation

$$d = 1{\cdot}54 - 0{\cdot}20[3x/(2x+1)]$$

connects double-bond character x with observed bond length d. It is the algebraic expression of a graph obtained by plotting four assumed bond characters (0 for a single bond, 1/3 for a graphite bond, 1/2 for a benzene bond and 1 for a double bond) against the corresponding observed bond lengths. Two things about this equation must be noticed: (*a*) it depends mainly on the two characters assumed for the C,C bonds in benzene and graphite, and (*b*) it has no reference to the triple bond. It implies that each carbon in benzene can be regarded as having a single bond linking it with hydrogen and two "one-and-a-half" bonds linking it with neighbouring carbons. The simple addition of these values to make a total of four satisfies the classical requirement of the quadrivalency of carbon.

A different approach to the quantitative definition of a chemical bond can be made by assuming that the "orders" of the bonds usually classified as single, double and triple are actually 1, 2 and 3, respectively. It is then possible to evolve an equation connecting observed bond lengths with these "orders" and at the same time to provide a means of assigning an "order" to any bond whose observed length diverges from those accepted as normal for single, double and triple bonds. From time to time many such equations have been put forward. That particularly considered here depends on the fact that the inverse squares of the bond lengths of single, double and triple C,C bonds form, within a reasonable margin of error, an arithmetic series. On this basis, Gordy[3] framed the equation $N = aR_x^{-2} - b$, in which R_x is the observed length of the bond and N its order, a and b being constants. With a suitable selection of constants, this equation is widely applicable. A better version of it, especially for C,C bonds, is:

$$N = (R_x^{-2} - k)/(R_1^{-2} - k)$$

which replaces the two constants a and b by one, k; R_1 is the length of the single bond. The numerical value of k for C,C bonds is 0·281; this is very close to the value of $\frac{2}{3}R_1^{-2}$, namely 0·279. Substituting k by $\frac{2}{3}R_1^{-2}$ and simplifying, we arrive at the expression[4] $N = (3R_1^2/R_x^2) - 2$. In this simple equation we have the means of assigning a numerical value to the order of a C,C bond of any observed length, R_x. Applying it to the benzene bonds of length 1·397 Å, we arrive at the order 1·67; for

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[2] L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.* **59**, 1235 (1937).

[3] W. Gordy, *J. Chem. Phys.* **15**, 305 (1947).

[4] J. C. Earl, *Chem. & Ind.* 173 (1955).

the graphite bonds of length 1·42 Å, we get the order 1·55. These values are in surprisingly close agreement with those resulting from molecular-orbital calculations by Coulson,[5] namely, 1·67 and 1·53. It must be noted, however, that a simple summation of the orders of the bonds pertaining to any one carbon does not give a total of four. For the carbons in benzene we have 1·67 for each of the C,C bonds and 1 for the C,H bond, making a total of 4·34. In graphite, each carbon is linked to three of its neighbours by bonds of order 1·55, giving a total of 4·65. This matter will be discussed in more detail later.

At this point the question of relating bond energy to bond length must be taken up. Pauling,[1] by calculations based on the known energy changes involved in the formation of saturated hydrocarbons, assigned to the C,H bond the energy of 87·3 kcal and to the C,C bonds, 58·6 for the single bond, 100 for the double bond and 123 for the triple bond. These energy values can be correlated with the observed lengths of the bonds by plotting a curve of energy against order and working out the corresponding algebraic equation. When this is done, the equation $E = 130{\cdot}9 - 8(4 - N)^2$ is obtained.[6] The numerical value of N is available by the procedure already described; E is the bond energy. When the equation is applied to the C,C bonds of benzene, the value of 87·5 kcal is obtained for their energy.

This value of 87·5 kcal lies very close to the 87·3 kcal of the C,H bond. The agreement may be fortuitous, but it seems likely that it has important significance. There is a considerable body of evidence that the three bonds of each carbon atom in benzene are symmetrically disposed about it in one plane. In other words, their directions are at 120° to one another. If, at the same time, their energies are equal, one would expect that the arrangement would show unusual stability. A similar, symmetrical distribution of energy is involved in the structure of methane, but there it is three-dimensional as opposed to the two-dimensional distribution imposed by the planarity of the benzene molecule. A further suggestive result has been obtained by studying the distribution of energy about the carbons in the hypothetical structure for benzene containing alternate single and double bonds in the ring, commonly called the Kekulé structure, although Kekulé's original idea involved both the possible structures of this type. It is shown in a recent note[7] that the total energy involved at each carbon is the same as that in the "regular" structure, but it is unsymmetrically distributed.

One is now in a position to assign a more definite meaning to the ideas of double-bond character (p) and bond order (N). It is significant that for benzene C,C bonds the relation:

$$p = (N \cos 120^\circ / \cos 109^\circ 28') - 2$$

holds. In other words, the bond-character terminology does not take into account the divergence of the bond angles in benzene (120°) from the tetrahedral angle (109° 28′). A similar consideration has to be taken into account when looking at the apparent discrepancy between the result of the simple addition of the orders of the bonds of any carbon atom and the value of four accepted as the valency of carbon. For the carbons in benzene we have $2 \times [(1{\cdot}67 \cos 120^\circ / \cos 109^\circ 28') - 1]$ for the two C,C bonds and 1 for the C,H bond; this adds up to the required total of four. Similarly

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[5] C. A. Coulson, *Proc. Roy. Soc.* A **169**, 413 (1939).
[6] J. C. Earl, *Chem. & Ind.* 1520 (1955).
[7] J. C. Earl, *Tetrahedron* **2**, 355 (1958).

for the three C,C bonds in graphite of order 1·55, we have $3 \times [(1{\cdot}55 \cos 120^\circ/\cos 109^\circ 28') - 1] = 4$.

One conclusion to be drawn with certainty from the above discussion is that chemical bonds, i.e. the resultants of the wide variety of forces that operate in the regions between the nuclei of atoms in a molecule, must be considered always as vector quantities. They cannot be submitted to any form of quantitative calculation without taking account of both their direction and energy. Where the regular tetrahedral distribution in carbon compounds is not interfered with by ring formation or other form of restraint, the direction component may not make itself evident, but, nevertheless, it has its part.