

THE TETRAHEDRAL CARBON ATOM AND THE STRUCTURE OF DIAMOND*

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1. INTRODUCTION

My address to the Academy this year concerns itself with the element carbon and its chemical behaviour. The importance of this subject hardly needs to be stressed. Indeed, the amazing power which the atoms of carbon display of combining with themselves and with other atoms to form an immense variety of distinct compounds is one of the marvels of nature. It is perhaps part of the secret of life itself.

The science of chemistry made a great step forwards when it was realised that the structure of a chemical molecule can only be properly described in terms of the configuration in three-dimensional space of the atoms of which it is composed. This approach to chemical problems made its debut in the year 1874 when Van't Hoff put forward his famous hypothesis of the tetrahedral carbon atom. What that description of the carbon atom really signifies, the physical and chemical evidence on which our belief in its validity is based and the explanation of the chemical behaviour of carbon in terms of the ultimate structure of its atoms are the topics which we shall proceed to consider. The ideas which emerge from the discussion will then be applied to an elucidation of the crystal structure of diamond and the explanation of the properties of that remarkable substance.

2. THE FOUR VALENCES OF CARBON

The simplest molecules exhibiting the disposition in space of the valences of the carbon atom are those in which an atom of carbon combines with four similar atoms or similar groups of atoms. This situation exists, for example, in the cases of methane (CH_4), deuteromethane (CD_4), carbon tetrafluoride (CF_4), carbon tetrachloride (CCl_4), carbon tetrabromide (CBr_4), tetramethyl methane [$\text{C}(\text{CH}_3)_4$] and so forth. In all these cases, the atoms or atomic groups which combine with the carbon atom are found to be disposed in space with perfect tetrahedral symmetry round it. This is most convincingly shown by the study of the vibration spectra of these molecules.

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A molecule composed of five atoms would in general exhibit nine modes of free vibration. On the other hand, the five-atom groups listed above exhibit only four fundamental frequencies of vibration. Such a reduction would follow as a necessary consequence of the molecule possessing perfect tetrahedral symmetry. It is therefore to be regarded as demonstrating that the atoms in these molecules are located at the vertices of a regular tetrahedron with the carbon atom itself at its centre.

The vibration spectra of molecules in which an atom of carbon combines with three atoms of one kind and a fourth of a different kind show that in every such case, they have six fundamental vibration frequencies and no more. As examples of this behaviour may be listed the molecules of DCH_3 , HCD_3 , HCF_3 , FCH_3 , HCCl_3 , DCCl_3 , FCCl_3 , ClCH_3 , ClCD_3 , BrCH_3 , BrCD_3 and ICH_3 . Dynamical theory shows that a five-atom group possessing a triad axis of symmetry would exhibit only six distinct frequencies instead of nine. The observed facts are thus a clear proof that the molecules listed do possess such a symmetry. On the other hand, molecules containing carbon combining with two atoms of one kind and two atoms of another kind should exhibit all the nine modes of vibration, and this is in agreement with experience.

The symmetry of form of the molecules in each of the cases referred to above can also be inferred from the numbers respectively of polarised and depolarised lines observed as frequency shifts in the spectra of light-scattering. Here again, the experimental facts confirm the tetrahedral character of the atomic grouping around the central carbon atom.

Studies on the vibration spectra of various molecules of the kind quoted above also furnish us with a convincing proof of the non-existence of the several isomers which may be expected to be forthcoming if the four valences of carbon were not equivalent. For, the vibration frequencies of the molecules would be influenced by the atomic configurations and each isomer would therefore have its own set of vibration frequencies. As the characteristic frequencies reveal themselves as well-defined lines in the spectrum, multiplication of the number of observed frequencies would follow as a consequence of the existence of more than one form of the molecule. As no such effect is observed in the numerous cases which have been studied, we are justified in inferring that such isomers do not exist.

A question of great importance which arises in regard to molecules in which an atom of carbon is joined to four others which are not all the same is whether their joins with it make equal angles with each other as is

to be expected if the valences were directed along the axes of a regular tetrahedron. This question can only be answered if methods for precise determination of the atomic configurations were available. Two such methods have been employed for the determination of the atomic configurations in molecules, namely, X-ray diffraction and electron diffraction. Both of these methods involve recondite theoretical considerations besides complicated calculations. The results derived from them must therefore be considered as subject to some measure of uncertainty and this has to be borne in mind in assessing the significance of the reported results. Pauling, in his book '*On the Nature of the Chemical Bond*' (Second Edition, 1940, Table 14-I) gives a list of sixteen carbon compounds of varying degrees of complexity whose molecular structure has been investigated by electron diffraction methods. The table of results gives the bond angle subtended at the carbon atom for eight different species of bonds, namely, C-C-C, C-C-Cl, C-C-Br, F-C-F, Cl-C-Cl, Br-C-Br, F-C-Cl and N-C-N. In five of these cases, namely, C-C-Br, C-C-Cl, F-C-F, F-C-Cl and N-C-N the angles are indistinguishable from the tetrahedral angle of $109^{\circ} 28'$, while in the three other cases, namely, Cl-C-Cl, C-C-C and Br-C-Br the reported bond angles exceed the tetrahedral angles by a degree or two; but this difference cannot be regarded as significant since the reported experimental uncertainties are of the same order of magnitude.

We may sum up the conclusions which may be legitimately drawn from the facts of experiment cited above as follows: *When an atom of carbon combines with four others, the four valences are directed along the four axes of a regular tetrahedron but are otherwise indistinguishable from each other.*

3. THE ATOMIC STRUCTURE OF CARBON

The interpretation which has to be placed on the results stated above becomes clear when we take note of the position of carbon in a list of the chemical elements arranged in the order of atomic numbers, that is to say, according to the magnitude of charge on the nucleus of the atom or the number of the electrons outside the nucleus. In such a list, the chemically inert gas helium occupies the second position, and the chemically inert neon occupies the tenth, while carbon with its six electrons occupies a position midway between them. Likewise, silicon which in several respects exhibits a chemical behaviour similar to carbon and has fourteen electrons stands midway between the inert gases neon and argon which have respectively ten and eighteen electrons outside their atomic nuclei. This is an example of the periodicity in chemical behaviour which makes itself evident when the elements are listed in the order of their atomic numbers. Such periodicity

finds its explanation in certain general features manifested in the building up of the atoms, *viz.*, the arrangement of the extra-nuclear electrons in a series of shells denoted respectively as K, L, M, etc. When the K shell is complete with its two electrons, we have the inert gas helium; when the L shell is also complete with its eight additional electrons, we have the inert gas neon; when a further eight electrons have been put into the M shell, we have the inert gas argon. Thus it is clear that the quadrivalence of carbon arises from the fact that it has four electrons in the L shell, just half the full quota of eight electrons needed to complete that shell. Further, since the valences are directed along the four axes of a regular tetrahedron, we are evidently concerned here with a state of the atom in which the four electrons in the L shell by reason of their interactions with each other and with the force field of the charged core of the atom constitute a system which is electrically neutral but exhibits perfect tetrahedral symmetry. This system may therefore be rightly designated as the tetrahedral carbon atom. It can combine with four other atoms or groups of atoms to form molecules, but does not depart sensibly from its tetrahedral symmetry of structure as the result of such combination.

We have now to ask ourselves what precisely are the circumstances which favour the formation of the tetrahedral quartet of electrons referred to above. It is well known that helium, neon and argon besides being chemically inert are also diamagnetic in their behaviour. The explanation given for the latter circumstance is that in the building up of the electronic clouds, the magnetic moments arising from the inherent spins of the electrons as well as those, if any, arising from their orbital movements around the nucleus mutually cancel each other out. The same circumstance is also responsible for the chemical inertness of these gases. For this to happen in the L shell of an atom we require eight electrons, but since there are only four present in the L shell of carbon, the same situation cannot arise in its case. But the question does arise as to how the angular momenta associated with the orbital motion and the inherent spins of the four electrons are disposed. If the configuration resulting from the mutual interactions of the four electrons is to possess full tetrahedral symmetry, it is clearly necessary that the resultant angular momenta associated with each of the four electrons considered individually should be equal and that further, these momenta should set themselves respectively along the four axes of a regular tetrahedron. The total angular momentum of the quartet and hence also its magnetic moment would vanish in these circumstances, and hence *the quartet of electrons must be considered as diamagnetic. But it would not*

be chemically inert since the cancellation is a result of the tetrahedral setting of the individual angular momenta and not of their internal pairing off.

An interesting consequence of the foregoing ideas should be here referred to. The angular momentum of an electron and hence also the magnetic moment associated with it is a vector and hence must be regarded as having both a direction and a sign. As already remarked, the directions in the present case are along the four axes of a regular tetrahedron, and if the quartet is to possess tetrahedral symmetry, all the four vectors concerned should have the same sense. Hence, they should all be directed either outwards or inwards from the core of the atom. Thus we have two distinct possible states of the tetrahedral carbon atom which we might designate as the α and the β states respectively. These do not differ from each other except in the sense of the angular momenta of the individual electrons, these being directed respectively outwards or inwards from the charged core of the atom in the two cases.

4. THE CRYSTAL STRUCTURE OF DIAMOND

Diamond furnishes a perfect illustration of Van't Hoff's hypothesis of the tetrahedral carbon atom. For, X-ray analysis discloses its structure to consist of two sets of carbon atoms, each carbon atom in one set being chemically linked with perfect tetrahedral symmetry to four carbon atoms belonging to the other set and *vice versa*. The joins of the carbon atom in each set with the four others in the second set are all parallel to each other and to the four body-diagonals of a cube. Hence diamond exhibits the symmetry belonging to a crystal of the cubic class. Considering this situation in the light of the remarks made in the preceding section, it follows that diamond is a crystal whose properties would not be uniquely decided by the crystal structure alone as determined by the methods of X-ray analysis. Diamond consists of two interpenetrating lattices of carbon atoms. In an ideal crystal all the atoms belonging to one lattice should be the same, but as there are two possible types of tetrahedral carbon atom, it follows that an ideal diamond may belong to any one of four types, namely, $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$. There is no reason to expect that these four types of diamond would exhibit any significant differences in such properties as lattice spacings, or the energy of formation, or the atomic vibration frequencies and so forth. But we should expect observable differences of a less obvious kind arising from the fact that the $\alpha\alpha$ and $\beta\beta$ types of diamond would possess a perfect octahedral symmetry in their crystal structure, whereas the two other types $\alpha\beta$ and $\beta\alpha$ would exhibit only the lower or tetrahedral symmetry.

Thus our present approach to the basic problems of organic chemistry leads to a natural and intelligible explanation of the fact that some diamonds exhibit infra-red absorption in the region of wave-lengths about 8μ including the characteristic lattice frequencies of vibration, while other diamonds do not exhibit this absorption. The diamonds which exhibit such absorption are those whose structure is of the $\alpha\beta$ or $\beta\alpha$ type, while those that do not are those whose structure is of the $\alpha\alpha$ or $\beta\beta$ type. Considerations of the same nature would also account for the differences exhibited by diamond in respect of other properties including especially the presence or absence of absorption of light in the near ultra-violet, which as is well known accompany the presence or absence of infra-red absorption in the 8μ region. We shall not enter into these questions here in detail but shall content ourselves with making two further remarks. The difference between the diamonds exhibiting octahedral and tetrahedral symmetry respectively cannot be expected to manifest itself in any difference in piezo-electric behaviour. The other remark is to recall the fact long known to mineralogists that the external forms of the diamond crystals found in nature more often than not indicate the lower or tetrahedral symmetry instead of the higher or octahedral one. This fact ceases to be surprising in the light of the considerations set forth above.

5. THE THEORY OF HYBRID BOND ORBITALS

We cannot avoid making some reference here to the attempts that have been made to explain the directed valences of the carbon atom in terms of ideas based on the Schrodinger solution of the wave-equation for the hydrogen atom. The theory of hybrid bond orbitals, as it is called, can be summarised as follows: The solution of the hydrogen problem by the Schrodinger method yields a series of solutions (s , p , d , etc.) which indicate the possible distributions of electron density around the nucleus. The wave-function s indicates a distribution of electron density spherically symmetrical round the nucleus, where there are three wave-functions denoted by p_x , p_y and p_z respectively which represent density distributions whose maximum extensions are respectively along the x , y and z axes in both directions. All these wave-functions represent the same energy and hence it is possible to construct linear combinations of them so as to produce new wave-functions which are orthogonal to each other. By giving equal weights to the wave-functions p_x , p_y and p_z but different signs in different cases and adding the s wave-function, it is possible to obtain four wave-functions which are tetrahedrally symmetric with respect to the nucleus.

The four orbitals thus derived are put forward as a representation of the directed valences of a carbon atom.

Several criticisms of a fundamental nature regarding the theory thus briefly summarised may be put forward. The first objection is that we are not concerned here with a hydrogen atom having a single electron but with a carbon atom having two inner and four outer electrons; the interactions of these with each other and with the atomic nucleus are of the very essence of the problem but they are left out of consideration in the theory. A second objection is that the theory does not explicitly consider the spin of the electrons, though they play a fundamental role in the theory of atomic structure. Apart from these difficulties, one is also confronted with the fact that we have an infinite number of possible sp^3 hybrids and the question may well be asked why the particular set which gives four orbitals indicative of a tetrahedral orientation of the valences should be chosen out of them all. The fundamental feature of the quadrivalence of carbon is that the tetrahedral disposition of the valences is maintained even when the four atoms with which the combination occurs differ from each other enormously, as for example, hydrogen, carbon, nitrogen, fluorine, bromine, chlorine and iodine—to mention no others. *It is this circumstance which indicates that the determining factor which gives rise to the tetrahedral configuration of the valences is not the energy of formation of the bond or bonds, but is an inherent property of the carbon atom itself.* In other words, it is to be found in the mutual interactions between the quartet of electrons which compel them to set themselves in a uniquely determined tetrahedral configuration.

6. SUMMARY

The experimental evidence derived from the study of the vibration spectra of molecules and of their electron diffraction patterns shows unequivocally that the four valences directed outwards from a carbon atom are parallel to the four axes of a regular tetrahedron. That this disposition is maintained even when the four atoms combining with the carbon atom differ enormously from each other indicates that we are concerned here with an intrinsic property of the carbon atom, namely, that the quartet of electrons in the L shell as a result of their mutual interactions can set themselves so as to constitute a structure possessing perfect tetrahedral symmetry. Such a structure would be diamagnetic but not chemically inert, since the individual angular momenta cancel out as a result of the tetrahedral setting and not as a consequence of the internal pairing off as in the inert gas molecules.

It follows from these considerations that there are two possible states of the carbon atom and hence also four possible forms of diamond, which may be designated as $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$ and $\beta\beta$ respectively. The first and the last would have true octahedral symmetry, while the second and the third would have the lower or tetrahedral symmetry. The differences in physical behaviour exhibited by even ideal diamonds in various respects, including especially their infra-red absorption spectra, thus receive a natural and intelligible explanation.