THE STRUCTURE AND PROPERTIES OF GRAPHITE AND BORON NITRIDE

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For more than 40 years the structure shown in Figures 1b and 2b has been almost universally accepted for the graphite crystal. This structure, involving hexagonal layers of carbon atoms, with repetition after two layers, was reported by Hull\(^1\) in 1917. He described the layers of carbon atoms as puckered; during the next few years other investigators showed that the layers are not puckered, but are planar.\(^2\) A rhomboedral form of graphite is also observed.\(^3\) Its structure is the same as that of ordinary graphite, except that there is repetition after three layers, rather than two. Rhomboedral graphite is less stable than ordinary graphite; on treatment with acid or on heating, the layers shift into the two-layer sequence.\(^4\)

Most of the properties of graphite have seemed to be accounted for in a satisfactory way by the hexagonal two-layer structure, but some observations that disagree have been reported. Lukesh\(^5,6\) found that X-ray diffraction patterns of some single crystals of graphite show the unit of structure to be larger than that reported, and to have lower symmetry, perhaps orthorhombic rather than hexagonal. Hoerni and Weigle\(^7\) also found that electron diffraction patterns of small single crystals of graphite show diffraction maxima that cannot be accounted for by the accepted structure. These observations led to the proposal that the double bonds between adjacent carbon atoms in a layer do not resonate equally among all of the positions, to give bond order 4/3 to every carbon-carbon bond, but instead are concentrated to a larger extent in certain of the positions.

A highly significant observation has been recently reported by Lynch and Drickamer.\(^8\) They found that

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\(^1\)Hull, W. H., 1917.

\(^2\)Lukesh, E. G., 1946.

\(^3\)Pauling, L., 1958.

\(^4\)Hoerni, M. S., and Weigle, J. D., 1960.

\(^5\)Lukesh, E. G., 1946.

\(^6\)Lukesh, E. G., 1946.

\(^7\)Lukesh, E. G., 1946.

\(^8\)Lukesh, E. G., 1946.
at low pressures the compressibility of graphite in the basal plane (compressing the carbon-carbon bonds) is much greater than that of diamond; whereas because of the stronger bonds in graphite than in diamond, it would be expected to be less. (The compressions were measured by observing the changes in the lattice constants, as shown by the X-ray diffraction patterns.) Moreover, although the compressibility of diamond remains constant to over 250 kb, that of graphite in the basal plane decreases with increasing pressure, becoming essentially constant for pressures higher than 200 kb. The high-pressure compressibility in the basal plane is about one third that of diamond, as would be expected from the smaller bond lengths. Lynch and Drickamer, in reporting these observations (and similar behavior for boron nitride), say that it seems necessary to invoke some phenomenon such as puckering and subsequent stiffening of the rings to account for the large change in compressibility in the basal plane. An alternative explanation, involving some concentration of the double bonds in certain positions in the hexagonal layers of graphite, is suggested in the following paragraphs, in which there is developed a general structure theory of graphite and graphitic carbons.

The Structure of a Layer of Carbon Atoms.—In a graphite layer each carbon atom has three neighboring atoms, at the distance (which may be an average distance) 1.421 Å, as given by the observed lattice constant \(a = 2.461\) Å for both hexagonal and rhombohedral graphite. Each carbon atom forms two single bonds and one double bond. The double bond has usually been assumed to resonate equally among the three positions, leading to bond number \(4/3\) and hexagonal symmetry, as indicated in Figure 1b. The other extreme structure is the quinoid structure, shown in Figure 1a, in which each carbon atom forms one bond that has a large amount and two bonds with smaller amounts of double-bond character. Another quinoid structure, Figure 1c, was suggested earlier\(^6\) to account for the observed X-ray and electron diffraction patterns. More complex structures may also be devised, for example, benzene rings connected to one another by conjugating single bonds.

It is not easy to make a reliable prediction about the relative stability of these structures. The simple valence-bond theory\(^4\) gives 0.24 \(J\) for the conjugation energy per conjugating single bond (that is, per carbon atom for the quinoid structure), 0.254 \(J\) for conjugated benzene rings, 0.260 \(J\) for conjugated naphthalene residues, and about 0.27 \(J\) per carbon atom for complete resonance. With the resonance integral \(J\) equal to 32 kcal/mole, the calculated resonance energy ranges from 7.7 kcal/mole to 8.6 kcal/mole, with maximum stability for the symmetric structure, as found by Anno and Coulson\(^9\) through a detailed quantum-mechanical calculation.\(^11\)

The Stacking of Graphite Layers.—In natural graphite, both hexagonal and rhombohedral, the layers are 3.354 Å apart. Larger values of the interlayer spacing have been reported for graphitic carbons, many in the region 3.44 ± 0.01 Å, and it was shown by Franklin\(^12\) that intermediate values are averages of the values 3.354 Å for orientated layers and 3.44 Å for disorientated layers. Several arguments, especially that based on the observed compressibility in the basal plane, have led me to the conclusion that the smaller interlayer spacing is shown by layers with the quinoid structure (Fig. 1a), and the larger one by layers with complete resonance (Fig. 1b).

With the quinoid structure, two thirds of the bonds are expected to have length
about 1.453 Å (15% double-bond character) and one third to have length about 1.357 Å (70%). The bond angles are expected to have the values 112°, 124°, and 124°. With the sequence of layers ABAB⋯ the unit of structure has orthorhombic symmetry, with \( a = 2.409 \text{ Å}, \ b = 4.339 \text{ Å}, \ c = 6.708 \text{ Å}, \) 4C at \( 0 \ u \ 0, \ 1/2 \ 1/2 + u \ 0, \ 0 \ \bar{u} \ 1/2 \) \( 1/2 \ - u \ 1/2, \) and 4C at \( 0 \ v \ 0, \) etc., with \( v = u + 0.315. \) The value of \( u \) is small; it is suggested below that it is about 0.05.

The advantage of the quinoid structure over the complete-resonance structure is that it permits the better packing of the superimposed layers and consequent decrease in the interlayer spacing and increased stabilization through van der Waals attraction between the layers. For the complete-resonance structure we may represent the mid-points of the bonds by circles, as in Figure 2b; these are the regions where the bonding electrons extend above and below the nuclear plane. There is no especially good way of packing these bulges; in the graphite structure the bulges of adjacent layers are separated by 0.72 Å in projection in the basal plane. For the quinoid structure, on the other hand, one third of the bulges are large (the circles at the mid-points of the bonds with large double-bond character, Fig. 2a) and two thirds are very small, and the large bulges are in the positions corresponding to optimal packing, with separation of about 1.3 Å in projection in the basal plane. Accordingly, it is reasonable to assign the observed interlayer spacing 3.354 Å to the quinoid layers and 3.44 Å to the complete-resonance layers.

The energy of van der Waals attraction of the layers can be calculated by the London equation

\[
E = \frac{3\alpha^2 I}{4r^6}
\]

for two atoms with electric polarizability \( \alpha \) and effective excitation energy \( I \) the distance \( r \) apart. Its value, for \( I = 14 \text{ eV} \) and \( R = 4\pi Na/3 = 3.27 \text{ cm}^3 \) (from the observed molar refraction of benzene corrected for the hydrogen atoms, \( R = 1.10 \)), is found by integration over the layers to amount to \(-244 \text{ s}^{-4} \text{ kcal/mole, with} s \text{ the interplanar spacing in Å. The values} -1.93 \text{ kcal/mole for} s = 3.354 \text{ Å}
\)

and \(-1.74 \text{ kcal/mole for} s = 3.44 \text{ Å show stabilization of the well-packed quinoid structure by 0.19 kcal/mole. Additional stabilization of the quinoid structure is provided by its smaller bond-angle strain and bond-compression strain.}

The Compressibility of Graphite.—It was pointed out by Waser and Pauling\(^{14}\) that for many crystalline elements of a row in the periodic table a linear relation holds between the reciprocal of the cube root of the force constant and the interatomic distance. This relation is similar to the one discovered by Badger for diatomic gas molecules.\(^{15}\) For some elements, however, the force constant was observed to be smaller than the value expected on the basis of these regularities; that is, the compressibility for these elements was found to be larger than expected. The hexagonal metals zinc and cadmium constitute examples of one sort. These metals have structures formally equivalent to hexagonal closest packing, but with a large value of the axial ratio \( c/a; \) in consequence, the bonds between the atoms in one hexagonal layer and those in the layers above and below are longer than the bonds within the layer (by 0.25 Å for zinc and 0.30 Å for cadmium). The observed compressibility of these metals along the \( c \) axis is about 5 times the value expected from the bond lengths. The difference in bond lengths in the hexagonal layers...
and between the layers in zinc and cadmium has been interpreted as indicating that the valence of these metals is not divided equally among the 12 bonds about an atom, but is concentrated in the bonds in the hexagonal layer, with these bonds having bond number 0.5 and the others having bond number 0.2. The explanation proposed for the high compressibility along the $c$ axis is that when the crystal is compressed, and the bonds between layers are shortened, the bond number of these bonds increases and that of the bonds in the layers decreases.

A similar explanation can be advanced for the observed very large initial compressibility of graphite in the basal plane. It is that pressure not only compresses the bonds but also causes a change in electronic structure of the layers, from the quinoid structure to the complete-resonance structure, with a decrease of 0.007 Å in the average bond length. This decrease is the result of the curvature of the curve giving the bond length as a function of the amount of double-bond character.16

The large compression (reaching 14%) of graphite at the pressures used by Lynch and Drickamer requires that the change in size of the unit cell be taken into consideration in the evaluation of the force constants of the bonds. This can be done by using a corrected pressure, $P' = P ac/a0c0$. In Figure 3 the observed values of $a/a0$ are plotted against this corrected pressure. The straight line that is drawn in the figure has the slope corresponding to the compressibility $0.32 \times 10^{-13}$ cm$^2$/dyne, which is the value calculated for carbon-carbon bond length 1.42 Å by the equation of Waser and Pauling,14 corresponding to the Hooke's law constant $1.80 \times 10^6$ dyne/cm for the bonds (the value for the Hooke's law constant for the bonds in diamond is $0.61 \times 10^6$ dyne/cm). The agreement of this slope with the last two high-pressure measurements of Lynch and Drickamer suggests that at pressures above 139 kbar the layers of carbon atoms in graphite have assumed the hexagonal structure usually attributed to them, with all bonds having equal length, rather than a puckered structure suggested as a possibility by Lynch and Drickamer.

An expected sort of twinning of the orthorhombic crystals is that in which there is rotation around the $c$ axis, so that the staggered rows of alternating single and
double bonds of one layer fit in between the rows for the superimposed layer, but the a and b axes for one layer are rotated by $122^\circ$ from that of the other, as calculated from the values $a = 2.409$ Å and $b = 4.339$ Å, given above (angle $122^\circ$ between [110] and [110]). Lukesh$^4$ reported that many specimens of natural graphite (nearly 50% of those found in clear calcite in Low Township, Quebec) show a doubling of the X-ray diffraction pattern corresponding to two crystals with a common c axis and mutual rotation by about $2.5^\circ$ about this axis.

Multiple twinning of this sort could produce single crystals with hexagonal face development and hexagonal diffraction patterns.$^{17}$

The interlayer spacing for the rotated layers presumably has the value 3.44 Å reported by Franklin$^{12}$ as occurring, together with the normal spacing 3.354 Å, in graphitizing carbons.

Turbostratic graphite consists of graphite layers superimposed with great disorder.$^{18}$ The interlayer spacing is large, ranging from 3.44 Å to 3.70 Å. The argument given above about stabilization of the quinoid structure by the packing of layers leads to the conclusion that the layers of turbostratic graphite have the complete-resonance structure, with all bonds equal in length. Such a difference in structure of the layers in ordinary graphite and turbostratic graphite provides a simple explanation of the difference in the observed values of the magnetic susceptibility with field parallel to the c axis, $-22 \times 10^{-6}$ emu/gm and $-34 \times 10^{-6}$ emu/gm, respectively,$^{19}$ at room temperature ($-28 \times 10^{-6}$ emu/gm for ordinary graphite at 100° K). The bonds with unequal lengths provide more resistance to the induced electric currents responsible for the large diamagnetic anisotropy than those with equal lengths.$^{20}$ The observed susceptibility at room temperature corresponds for ordinary graphite to ring currents involving 300 carbon atoms in a layer (diameter 31 Å), and for turbostratic graphite to 450 carbon atoms (diameter 39 Å).

**Boron Nitride.**—The stable form of boron nitride is a soft white crystalline substance resembling graphite in cleavage, but with much smaller electric conductivity and diamagnetic anisotropy. Its structure involves hexagonal layers similar to those of graphite, with bond length 1.446 Å; boron atoms and nitrogen atoms alternate in the layer. The layers are superimposed in such a way that each atom of one kind is directly above and below an atom of the other kind in the adjacent layers.$^{21}$ The interlayer spacing is 3.331 Å. There is no evidence for packing of the graphite type, either ABAB... or ABCABC... etc.

The observed bond length indicates resonance between the structures

\[
\begin{align*}
B & \equiv N \\
B^+ & \equiv N^-
\end{align*}
\]

We may assume the boron-nitrogen bond lengths to be equal to the corresponding carbon-carbon bond lengths. The observed bond length 1.446 Å leads, with use of equation (7-3) of reference 13, to 22 per cent double-bond character for each bond in the hexagonal layer. This amount of double-bond character is reasonable, in that it makes the boron atoms and nitrogen atoms electrically neutral if the amount of ionic character of the bonds is 18 per cent, which is close to the value 22 per cent corresponding to the difference in electronegativity of boron and nitrogen.$^{22}$

The electronic structure of the layer may accordingly be described as involving about 50 per cent retention of an unshared electron pair (essentially 2s$^2$) by the
nitrogen atom. The major electron bulges of the layer are accordingly not midway along the bonds, as in graphite, but on the nitrogen atoms. The sequence of layers in hexagonal boron nitride (AAA · · · , with boron and nitrogen atoms interchanged in alternate layers) corresponds to hexagonal packing of these bulges.

Lynch and Drickamer\(^6\) reported that the compressibility in the basal plane of hexagonal boron nitride, like that of graphite, is abnormally large. The explanation given above for the large compressibility of graphite cannot be extended to boron nitride because of the difference in the structures of the two substances. Instead, we suggest a different change in structure caused by increase in pressure: the increase in amount of double-bond character from 22 per cent to 33\(\frac{1}{2}\) per cent, with decrease of 0.03 Å in the bond length.

**Summary.**—Graphite and hexagonal boron nitride have been reported to have large compressibility in the basal plane, about 10 times as great as calculated from the empirical equation relating the force constant of bonds to the bond length. The suggested explanation is that compression causes a change in the nature of the bonds: for graphite, a change from a quinoid structure, with one third of the bonds having most of the double-bond character, to the complete-resonance structure, with every bond having one third double-bond character; and for boron nitride (in which the bonds are between atoms with different electronegativity) an increase from 22 per cent toward 33\(\frac{1}{2}\) per cent double-bond character for each bond. The proposed structures are shown to be compatible with some of the properties of the substances.

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11 Anno and Coulson were led to make their calculation by the observations reported in refs. 5, 6, and 7 and the fact that the absorption frequencies of the conjugated polyenes can be explained only by the assumption of incomplete resonance, even in very long chains (Kuhn, H., *J. Chem. Phys.*, **17**, 1198 (1949); Dewar, M. J. S., *J. Chem. Soc.*, **1952**, 3544 (1952); Huzinaga, S., and T. Hasino, *Progr. Theoret. Phys.*, **18**, 649 (1957).)
11 These values are 0.010 Å less than those given by equation (7-3) of Pauling, L., *The Nature of the Chemical Bond* (New York: Cornell University Press, 1960).
16 Pauling, L., L. O. Brockway, and J. Y. Beach, *J. Am. Chem. Soc.*, 57, 2705 (1935). The value of this decrease given by equation (7-3) of ref. 13 is 0.0077 Å.
21 Tables 3–10 of ref. 13. A similar discussion can be given the metastable form of boron nitride, which has the sphalerite structure, with bond length 1.565 Å (Wentworth, R. H., Jr., *J. Chem. Phys.*, 26, 956 (1957)). This bond length corresponds to bond number 0.923 (equation (7-7) of ref. 13), and to electroneutrality for 19 per cent ionic character of the bonds.