

energies. The nuclear phenomena which we study in the laboratory are mostly man-made. Hence the natural place of nuclear processes would be the center of stars, where they are essential for energy production and element formation. It is symbolic for the ever-increasing scope of science that in our nuclear research we have recreated a world of phenomena here on earth whose natural place is outside of our abode.

THE ARCHITECTURE OF MOLECULES

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Molecular architecture may be said to have originated in 1874, when J. H. van't Hoff and J. A. le Bel independently formulated the brilliant postulate that the four valence bonds of the carbon atom are directed approximately toward the corners of a regular tetrahedron. It was extended into inorganic chemistry in 1893, when A. Werner suggested that in many inorganic complexes six atoms are arranged at the corners of a regular octahedron about a central atom, and that other geometrical structures are represented by other complexes. However, the present-day subject of molecular architecture, involving the precise discussion of the structure of molecules and crystals in terms of interatomic distances and bond angles, is a product of the last half century. It began in 1913, when W. H. Bragg and W. L. Bragg reported the determination of the arrangement of atoms of sodium and chlorine in the sodium chloride crystal and the evaluation of the distance between the centers of the atoms by the newly discovered method of analysis of the X-ray diffraction pattern. During the last 50 years the precise structures of thousands of crystals and molecules have been determined by the methods of X-ray diffraction, electron diffraction, and molecular spectroscopy, with the aid of other techniques, such as the determination of entropy values.

The structures of many crystals and molecules can be conveniently described by reference to the five regular polyhedra—the tetrahedron, the octahedron, the cube, the icosahedron, and the pentagonal dodecahedron. Thus the crystal beryllium oxide has a structure involving tetrahedral coordination: each beryllium atom has as its nearest neighbors four oxygen atoms, which surround it at the corners of a regular tetrahedron. In the sodium chloride crystal each atom of one kind is surrounded by six atoms of the other kind, which lie at the corners of a regular octahedron, and in the cesium chloride crystal each atom of one kind is surrounded by eight atoms of the other kind, at the corners of a cube.

The classical structure theory of organic chemistry was developed in the years following 1874 on the basis of the postulate of the tetrahedral carbon atom, which accounted for the existence of enantiomeric pairs of organic substances, with the power of rotating the plane of polarization of light by equal amounts in opposite directions. The tetrahedral character of the carbon atom was then verified in a striking way in 1914 by W. H. Bragg and W. L. Bragg, when they determined the structure of diamond and found that each carbon atom in the diamond crystal is

surrounded by four other carbon atoms at the corners of a regular tetrahedron. I continue to be astounded that during the 40-year period between 1874, when the postulate of the tetrahedral carbon atom was proposed, and 1914, when the Braggs reported their determination of the structure of diamond, no scientist had described this tetrahedral arrangement of atoms and suggested that it might represent the structure of diamond. An English investigator, W. Barlow,¹ had in 1883 described several ways that seemed reasonable to him for packing atoms together in crystals, and had correctly assigned one of them to sodium chloride, another to cesium chloride, and others to certain cubic and hexagonal metals. Barlow and his collaborator Pope assigned diamond also to a close-packed arrangement, with ligancy 12, rather than 4, for the carbon atom. Their failure to discover the diamond arrangement may have resulted from their lack of confidence in the postulate of the tetrahedral carbon atom.

In the molecule of methane, CH_4 , the four hydrogen atoms lie close to the corners of a regular tetrahedron, and the bond angles HCH have the value $109^\circ 28'$ characteristic of a regular tetrahedron. In order to account qualitatively for the optical activity of a molecule in which the four atoms attached to the carbon atom are different, such as fluorochlorobromomethane, HCFClBr , it is not necessary to assume that the bonds are directed toward the corners of a regular tetrahedron, but only that the four atoms attached to the carbon atom not lie in a plane with the carbon atom. Many experimental studies of the structure of molecules of this sort have been carried out since 1930, and it has in fact been found that the tetrahedral carbon atom is nearly regular, with the bond angles equal to the tetrahedral angle $109^\circ 28'$ to within better than 3° , in most molecules.

During the period from 1916 to 1930 it was customary for chemists, following the lead of Gilbert Newton Lewis, to describe atoms other than carbon, such as the oxygen atom in the water molecule, as tetrahedral: the oxygen atom was described as having four electron pairs in its outer shell—two unshared pairs and two pairs involved in forming the bonds to the hydrogen atoms—and the four pairs were assumed to be located at tetrahedron corners. In 1930 J. C. Slater² pointed out that the quantum-mechanical theory of the electronic structure of molecules suggests that the bond angle should be approximately 90° . He assigned one of the unshared pairs of electrons to the $2s$ orbital of the oxygen atom, which has a lower energy value than the $2p$ orbital. The bonding electrons of the oxygen atom are then described as occupying bond orbitals that are largely $2p$ in character, and Slater pointed out that these $2p$ orbitals have their maximum values in directions in space at 90° to one another, and that the bond angle should accordingly be approximately 90° . In the water molecule the HOH bond angle is 104.5° , and in H_2S , H_2Se , and H_2Te the bond angles lie between 92° and 90° .

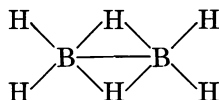
The theory of the tetrahedral carbon atom leads to the description of two carbon atoms that form a double bond with one another as two tetrahedra sharing a common edge. If the tetrahedra were regular, the value of the angle between a single bond and the double bond would be $125^\circ 16'$. Many experimental values for this angle lie in the range 124° to 126° ; for example, the value of the $\text{C}=\text{C}=\text{C}$ angle in propylene, $\text{H}_3\text{C}-\text{CH}=\text{CH}_2$, is $124^\circ 45' \pm 20'$. Ethylene, $\text{H}_2\text{C}=\text{CH}_2$, is an exception; the observed value for the angle $\text{H}-\text{C}=\text{C}$ in this molecule is $121^\circ 20'$. The corresponding angle for an atom with an unshared electron pair, such as the

nitrogen atom in nitrosyl chloride, $\text{Cl}-\ddot{\text{N}}=\ddot{\text{O}}:$, is smaller in value, usually about 113° .

A useful refinement of chemical structure theory was made in 1937 by Kemp and Pitzer,³ who discovered that the rotation of the two ends of a molecule that are connected to one another by a carbon-carbon single bond is not free, but is restricted, with the potential hump (for ethane) approximately 3 kcal/mole. The stable configuration of the ethane molecule and related molecules is the one in which the bonds are staggered, rather than eclipsed. This structural feature has been found to have great value in the interpretation and prediction of thermodynamic properties of substances, as well as their spatial configurations.

An interesting development during the last few years has been the recognition of the importance of the icosahedron and pentagonal dodecahedron in molecular architecture. The icosahedron has been found to play an important part in the structure of many electron-deficient substances, including metals and alloys.

In the discussion of the electronic structure of many molecules and crystals, it is found that each of the stable orbitals in each atom is occupied by an unshared electron pair or by the electrons involved in a bond. For example, in the methane molecule each hydrogen atom uses its sole stable orbital, the 1s orbital, in forming a bond with the carbon atom; and the carbon atom uses its four stable outer orbitals, the four tetrahedral orbitals formed by hybridization of the 2s orbital and the three 2p orbitals, in the formation of the four bonds to the hydrogen atoms. In the water molecule the four orbitals of the oxygen atom are used for formation of two bonds and for occupancy by two unshared electron pairs. In each of these molecules the number of electrons available is great enough to permit utilization of all of the stable orbitals in this way. In borane, BH_3 , on the other hand, there are only three electron pairs (aside from the pair of 1s electrons of the boron atom), so that the four stable orbitals of the boron atom cannot all be occupied. In fact, borane exists as the dimer, B_2H_6 , rather than as the monomer, BH_3 . The structure of B_2H_6 , diborane, as determined experimentally, can be represented by the diagram



The boron atom has as its near neighbors four hydrogen atoms and the other boron atom: its ligancy is 5. Two of the hydrogen atoms, the bridging hydrogen atoms, have ligancy 2, rather than the normal value 1. The diborane molecule is called an electron-deficient molecule, because the number of valence electrons is less than the number of stable orbitals that might be used in bond formation. In diborane, as in other electron-deficient substances, the ligancy of the atoms is not only greater than the number of valence electrons, but even greater than the number of stable orbitals.

The structure of one of the more complex boranes, decaborane, $\text{B}_{10}\text{H}_{14}$, was determined by Kasper, Lucht, and Harker⁴ in 1950. This structure, shown in Figure 1, is closely related to the icosahedron (see Fig. 5a). The 10 boron atoms occupy 10 of the 12 corners of a nearly regular icosahedron. Ten of the hydrogen atoms lie at the corners of a larger icosahedron, each being bonded to one boron atom. The other four hydrogen atoms are bridging hydrogen atoms, each with

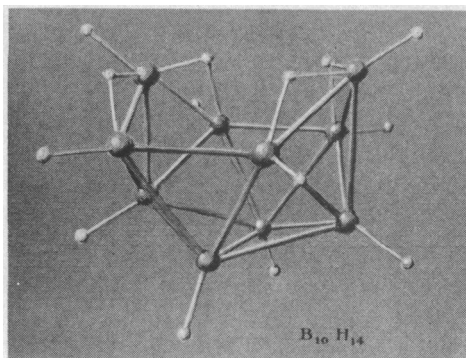


FIG. 1.—The structure of decaborane. The 10 boron atoms, represented by the larger spheres, lie at 10 of the 12 corners of an approximately regular icosahedron. There are 4 bridging hydrogen atoms and 10 nonbridging hydrogen atoms.

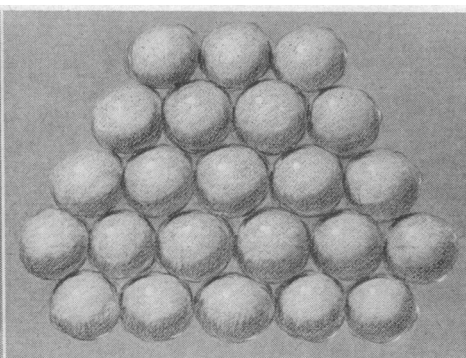


FIG. 2.—A portion of a close-packed layer of spherical atoms.

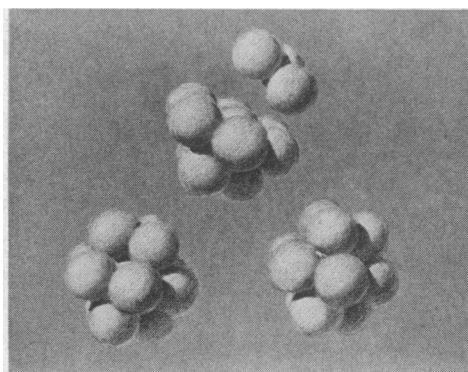


FIG. 3.—The coordination of 12 spherical atoms about a central one, as found in cubic closest packing (*lower left*) and hexagonal closest packing (*lower right*).

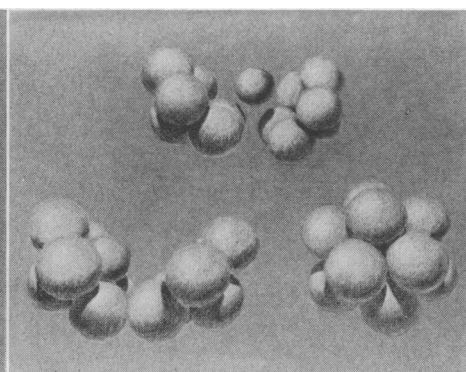


FIG. 4.—The coordination of 12 spherical atoms about a central atom with 10% smaller diameter. The 12 larger atoms lie at the corners of a regular icosahedron. This is the closest-possible packing of 12 equivalent atoms about a central atom.

ligancy 2. Each of the boron atoms has ligancy 6. The positions of the bridging hydrogen atoms may be described by saying that each of the two corners of the icosahedron that are not occupied by boron atoms is split between two hydrogen atoms. The observed bond lengths in the icosahedral framework have approximately the values expected for half-bonds, that is, for bonds involving electron occupancy half as great as for a shared-electron-pair bond.

Structure determinations have been made for several other complex boranes, and most of them have been found to be related to the icosahedron. Much of the recent work in this field has been carried out by W. N. Lipscomb and his collaborators. An especially interesting structure is that of the $B_{12}H_{12}^-$ ion, in the crystal $K_2B_{12}H_{12}$; this ion is found to have the boron atoms at the corners of a nearly regular icosahedron, with a hydrogen atom attached to each boron atom.⁵

Metals and intermetallic compounds are electron-deficient substances, with the number of valence electrons per atom less than the number of stable orbitals.

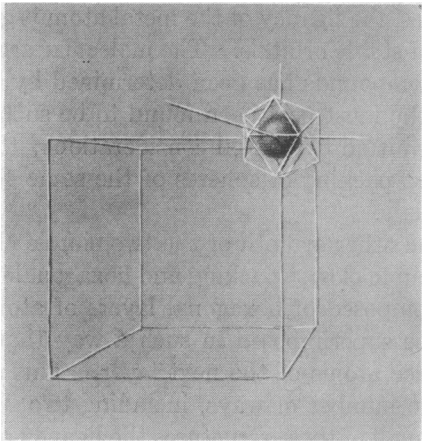
As with other electron-deficient substances, the ligancy of the metal atom is greater than the number of valence electrons or of stable orbitals. The molecular architecture of many metals and intermetallic compounds has been determined by X-ray diffraction, and the structures have for the most part been found to be such as to correspond to the maximum ligancy permitted by spatial considerations; that is, the structures can be described as closest packing of spheres of the same size or, in the case of unlike atoms, of different sizes.

Most metals crystallize with one or the other or both of the two simple closest-packed structures described by Barlow, cubic closest packing and hexagonal closest packing. Each of these structures is composed of hexagonal layers of atoms, as shown in Figure 2. These layers can be superimposed in such a way that each atom in one layer is in contact with three atoms of the next layer. This superposition can be carried out in an infinite number of ways, including two in each of which the atoms are all equivalent. In all of these structures the ligancy of each atom is 12. The arrangement of the 12 atoms around the central atom to which they are ligated is shown in Figure 3—for cubic closest packing at the lower left and for hexagonal closest packing at the lower right. The coordination polyhedron in each case has six triangular faces and four square faces.

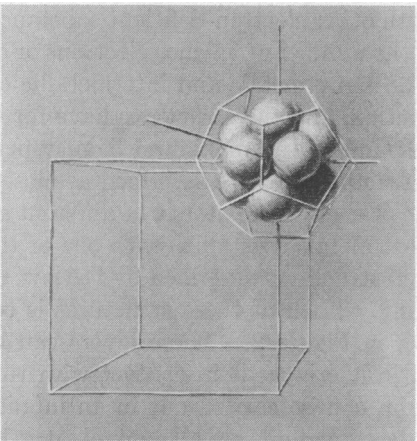
Although cubic closest packing and hexagonal closest packing (and the more complex ways of superimposing the hexagonal layers) represent the ways of packing spheres of equal size to obtain the maximum density, the complexes shown in Figure 3 do not provide the most closely packed arrangement of 12 equivalent spherical atoms around a central atom. The smallest complex of 12 equivalent spherical atoms around a central atom is shown in Figure 4. In this complex the central atom is 10 per cent smaller than the 12 surrounding atoms, and the 12 atoms lie at the corners of a regular icosahedron.

It has been found by experiment that many intermetallic compounds have structures involving the centered icosahedron. Most of these structures are very complicated. It might be thought that the high symmetry of the icosahedron would permit it to be present in crystals with simple structure, but the symmetry elements of the icosahedron (15 twofold axes, 10 threefold axes, and 6 fivefold axes, as well as planes of symmetry) are not especially helpful in crystallization, because crystals cannot have fivefold axes of symmetry.

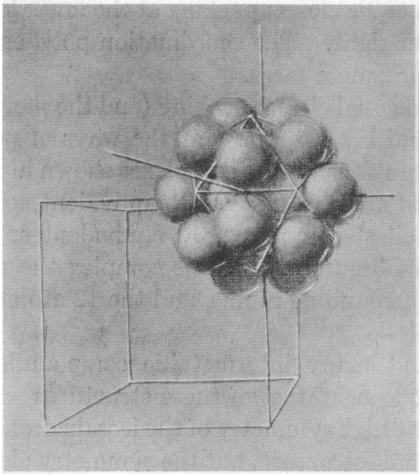
The intermetallic compound $\text{Mg}_{32}(\text{Zn}, \text{Al})_{49}$ may be described as an example of an electron-deficient substance in which each atom forms the largest number of bonds with adjacent atoms permitted by the relative atomic sizes. The atoms of magnesium are somewhat larger than those of zinc and aluminum, permitting icosahedral coordination. The structure of the crystal seems to be based upon the principle that each coordination polyhedron is a triangular polyhedron—all of its faces are triangles. In Figure 5a a single (small) atom is indicated at the corner of the unit cube, with an icosahedron outlined about it. The 12 larger atoms occupying the corners of the icosahedron are shown in Figure 5b. The pentagonal dodecahedron that is sketched about the complex has its corners at the positions out from the centers of the triangular faces of the icosahedron. The 20 atoms occupying these positions are shown in Figure 5c, and a larger icosahedron is sketched in. When the 12 atoms of this larger icosahedron are introduced, the outer shell of the complex involves 32 atoms, lying at the corners of a rhombic triacontahedron. Con-



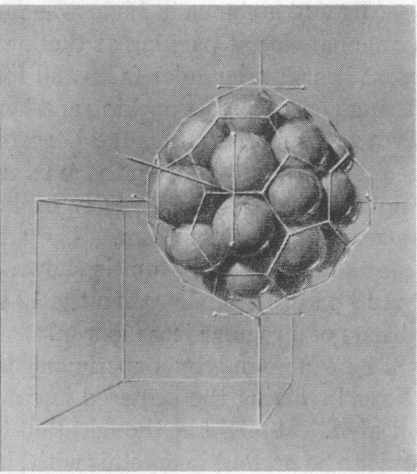
(a)



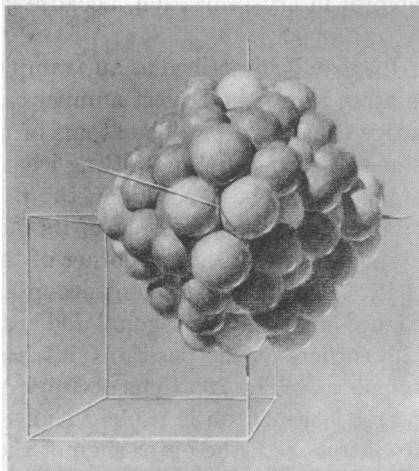
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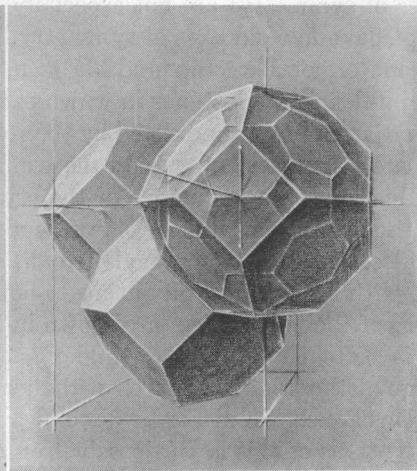
(c)



(d)



(e)



(f)



tinued application of the structural principle leads to the shell of 72 atoms shown in Figures 5*d* and *e*—60 atoms at the corners of a truncated icosahedron, and 12 additional atoms out from the centers of 12 of the 20 hexagonal faces of the truncated icosahedron. These large complexes, with their centers at the corners and the centers of the unit cube, are then condensed together in the way shown in Figure 5*f*. Each of the 72 outer atoms in the outermost shell of each complex is shared between two complexes, so that each outer shell contributes 36 atoms per lattice point, which with the inner shells of 45 atoms gives 81 atoms per lattice point, a total of 162 in the unit cube.

Some even more complex structures have been determined recently. The most striking one is that of the cubic crystal with approximate formula NaCd_2 , for which the structure determination was made by S. Samson.⁶ This crystal has 1192 atoms in the cubic unit of structure. Each atom is closely surrounded by 12, 13, 14, 15, or 16 ligands; 528 of the 1192 atoms are at the centers of icosahedra.

Among the most interesting problems of science are those of the structure and properties of substances of biological importance. In this branch of molecular architecture, which has been developing rapidly during recent years, a structural feature called the hydrogen bond is of great importance.

The hydrogen bond was discovered by Latimer and Rodebush⁷ in 1920. It is a bond by a hydrogen atom between two electronegative atoms. Sometimes, as in the hydrogen difluoride ion, $[\text{FHF}]^-$, the hydrogen atom lies midway between the two electronegative atoms, but usually it is attached more strongly to one than to the other. For example, in a crystal of ordinary ice each water molecule is attached to four other water molecules, which surround it in an approximately tetrahedral arrangement, by four hydrogen bonds, with two of the hydrogen atoms at 1.00 Å and the other two (which are strongly bonded to the other oxygen atoms) at 1.76 Å, the oxygen-oxygen distance being 2.76 Å. Determinations of the crystal structure of amino acids and simple peptides carried out during a period of years beginning in 1938, especially by R. B. Corey⁸ and his collaborators, showed that the molecules of these substances, which are closely related to proteins, attach themselves to one another by forming hydrogen bonds between the nitrogen atom and the oxygen atom of peptide groups, with $\text{N}-\text{H} \cdots \text{O}$ distance about 2.90 Å, and also showed that the peptide group is essentially planar. This knowledge led to the formulation of the alpha helix, a configuration of polypeptide chains that has been found to be present in many proteins. The great developments in the field of protein structure that have been carried out during recent years by J. C. Kendrew and M. Perutz, who have used X-ray diffraction to make nearly complete structure determinations of

Fig. 5—The body-centered cubic structure of 162 atoms in the unit cube of the intermetallic compound $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$. (a) An atom at a lattice point is represented as at the center of a regular icosahedron, which is outlined. (b) The corners of the outlined pentagonal dodecahedron lie out from the centers of the 20 triangular faces of the icosahedral shell of 12 atoms. (c) An icosahedron is shown with its corners out from the centers of the pentagonal faces of the dodecahedron. (d) The completed shell of 32 atoms is indicated. The truncated icosahedron has its 60 corners out from the centers of the triangular half-faces of the rhombic triacontahedron, and 12 other atomic positions are shown, out from the centers of the hexagonal faces of the truncated icosahedron. (e) The complex of atoms about a lattice point has 72 atoms in its outer shell, and 45 in the inner shells. The atoms of the outer shell lie on the faces of a cubo-octahedron. (f) The complexes shown in (e) share the atoms of their outer shells when they are arranged about the points of a body-centered cubic lattice, as indicated here.

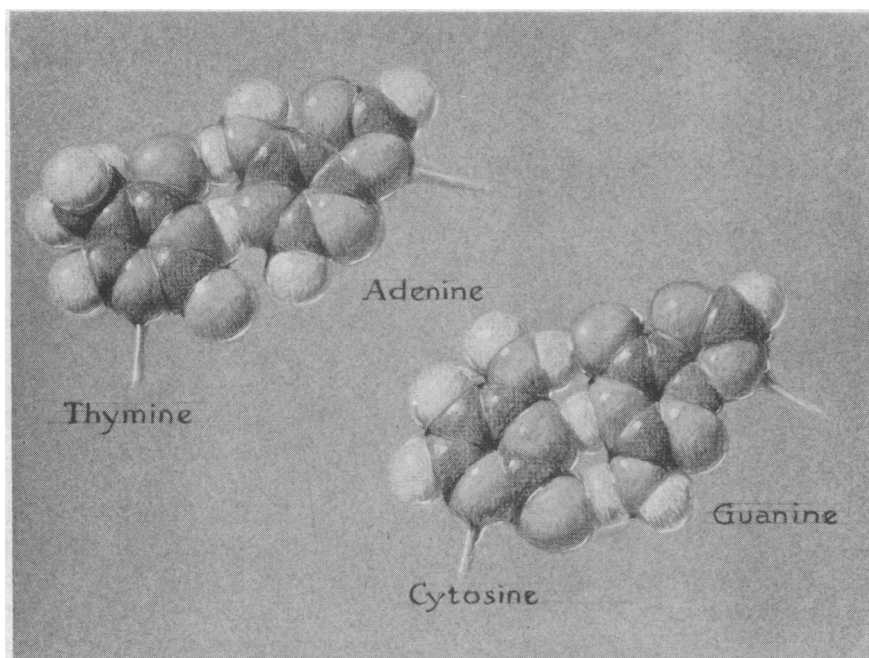


FIG. 6.—The structure of the thymine-adenine pair, forming two hydrogen bonds, and the cytosine-guanine pair, forming three hydrogen bonds, as postulated in the Watson-Crick theory of DNA.

crystals of the globular proteins myoglobin and hemoglobin, cannot be described adequately in a brief review of molecular architecture.

The importance of the hydrogen bond in determining the structures and properties of the nucleic acids was recognized by J. D. Watson and F. H. Crick when they made their great contribution to science in formulating their helical structure for deoxyribonucleic acid.⁹ This structure involves a detailed complementariness of two intertwined polynucleotide chains. The complementariness results from the formation of hydrogen bonds between a pyrimidine residue in one chain and a purine residue in the other chain, for each pair of nucleotides in the chains. The pairs are thymine-adenine and cytosine-guanine, with the first pair forming two hydrogen bonds and the second pair three, as shown in Figure 6.¹⁰ The simplicity of the explanation of the self-duplicating property of DNA that is provided by the Watson-Crick structure gives a basis for hope that additional studies in the field of the molecular architecture of living organisms will lead ultimately to a thorough and satisfying understanding of all of the phenomena of life.

* Contribution no. 3090.

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⁶ Samson, S., *Nature*, **195**, 259 (1962).

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⁹ Watson, J. D., and F. H. Crick, *Nature*, **171**, 737, 964 (1953).

¹⁰ Pauling, L., and R. B. Corey, *Arch. Biochem. Biophys.*, **65**, 164 (1956).