[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

THE SPACING OF NON-POLAR MOLECULES IN CRYSTAL LATTICES. THE ATOMIC DOMAIN OF HYDROGEN. A NEW FEATURE OF STRUCTURE OF THE BENZENE RING

BY EDWARD MACK, JR.[1]

Our knowledge of the structure of the crystal lattices of organic compounds is gradually increasing. But the progress is dishearteningly slow, due, of course, to the very great difficulties inherent in the problem. Several score of organic crystals have been subjected to x-ray analysis. In by far the larger number of these cases the analysis has not been rigorous enough to do more than tell us the dimensions of the unit cell and define the space group, if indeed it tells us as much as this. In only a very few cases has the more intimate structure been indicated, the orientation of the molecules with respect to the crystal axes and the arrangement and spacing of the atoms within the molecule.[2] One of the most disappointing features of the present technique of x-ray analysis is its inability to locate the hydrogen atoms. Most organic molecules contain a larger population of hydrogen than of any other kind of atom, and as a rule the hydrogen atoms, because of their single valence bond, occur at the ends or on the exterior surface of the molecule. As a consequence, x-ray analysis of an organic crystal generally presents us with a picture of a three-dimensional array of molecules hung in empty space, with large gaps between neighbor molecules, a picture more like that of a gas than of a solid. A question which immediately comes to mind is whether such intervening spaces can be filled up, by attachment of the missing hydrogen atoms on the proper chemical bonds, so that neighbor molecules then interlock. The present paper undertakes, in part, to answer this question.

In "A Note on the Crystalline Structure of Certain Aromatic Compounds," Sir William Bragg[3] remarks "when cell dimensions and space

[1] Guggenheim Memorial Fellow, 1929.

[2] For an excellent critical review of this field up to about the end of the year 1930, see "Crystal Structures of Organic Compounds" by Sterling B. Hendricks, *Chem. Rev.*, **7**, 431 (1930).

[3] Bragg, *Z. Krist.*, **66**, 24 (1927).

group have been determined the really difficult and the more fascinating problem still remains in finding the distribution of the atoms in space." In the present, although undoubtedly only temporary, default of x-ray intensity methods in determining the lattice positions of atoms in most of these aromatic molecules, the present author wishes to advance a stereochemical solution of some of these three-dimensional picture puzzles. The solution is based on the theory that the benzene ring is the flat graphite ring, a contention strongly supported[4] by the rigorous analysis which Mrs. Lonsdale has made of the structure of crystalline hexamethyl-benzene.[5] From a stereochemical consideration of the probable structures of these aromatic crystals, we shall be able to draw some consistent conclusions regarding the size of the hydrogen atom, and shall also be led to the proposal of a new feature of structure for the benzene ring, based, as will be seen, on empirical evidence.

To begin with, before we proceed to a consideration of the size of the hydrogen atom and of the possibility of interlocking between neighbor lattice molecules, it would be well to define clearly just what we intend the expression "size of an atom" to mean.

Definition of Radius of Atomic Domain

The size of an atom, or molecule, will depend on the nature of the experimental probe which is used in its exploration. An atom which appears to be of a certain size under one set of conditions may present itself quite differently in another situation. Thus, for example, has arisen the well-recognized distinction between the "gas kinetic radius" and the "crystal radius" of an atom. Such a difference is not only to be expected on theoretical grounds, but is fully supported by a comparison of atom sizes actually obtained under different experimental conditions. The meaning of the expression "the size of an atom" is therefore ambiguous, unless the circumstances of the determination are defined. In the present paper we are interested in the size of hydrogen atoms under the conditions existing in the crystal lattice. This means that we are concerned with the size which the hydrogen atom (on a molecule) possesses in collision with hydrogen atoms on the surfaces of neighbor molecules, as a result of thermal motions which these molecules are undergoing, generally vibration, although sometimes also rotation.[6]

[4] Since the manuscript of this article was submitted for publication, two other papers have appeared which indicate that the benzene ring is really the flat graphite ring: "An X-ray Analysis of the Structure of Hexachloro benzene, etc.," Mrs. Lonsdale, *Proc. Roy. Soc.* (London), **A133**, 536 (1931); and "The Molecular Association, The Apparent Symmetry of the Benzene Ring, etc.," Hendricks and Hilbert, THIS JOURNAL, **53**, 4280 (1931).

[5] Mrs. Lonsdale, *Proc. Roy. Soc.* (London), **A123**, 494 (1929).

[6] Pauling, *Phys. Rev.*, **36**, 430 (1930).

Gas Kinetic Radius.—We may attempt to represent the geometrical factors of a typical gas collision by Fig. 1. H represents a hydrogen atom bonded chemically to a carbon atom C, which in turn is connected to the other atoms in the molecule of which it is a part. The distance between the two nuclei C–H is about 1.08 Å. This may be calculated from the moment of inertia 5.17×10^{-40} for methane.[7]

About the same value, 1.08 Å., is also readily calculated from the smallest moment of inertia found by Patty and Neilsen[8] for formaldehyde, namely, about 2.7×10^{-40} for the rotation of the molecule $_H^H{>}C{=}O$ about the horizontal axis.
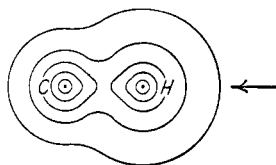

Fig. 1.

This distance of separation of the nuclei of the two atoms is likely to remain approximately the same for methane molecules in the solid, liquid and gaseous states, and over a considerable temperature range, because of the difficulty of exciting vibration along the C–H bond, and this distance is also likely to hold for a hydrogen bonded to aliphatic carbon in *any* organic molecule.

In accordance with the somewhat vague picture fostered at the present moment by the quantum mechanics, the two electrons of the electron pair which holds the two nuclei together, one electron supplied by the hydrogen and the other by the carbon, one electron with a right-handed and the other with a left-handed spin, are circulating around both nuclei, throughout both atomic domains, but spending a large share of their time, because of the eccentricity of the virtual orbits, between the two nuclei. The distribution of the electron density in such a system possibly resembles somewhat that calculated by London[9] for the hydrogen molecule, and may be represented by the contour lines shown in Fig. 1. The positions of these contours given in the present figure are not to be considered the true ones, which must wait upon the actual calculation, but as merely indications of the fact that the electron density is greatest near the central portions of the system, and from there grades off exponentially toward the outer regions of the atomic domain. In a certain sense, then, the atomic domain of the hydrogen may be said to extend out from the nucleus to a very large distance, indeed to an infinitely large distance.

Now, when another molecule approaches from the direction indicated by the arrow, presenting one of its hydrogen atoms so that collision will occur with Hydrogen Atom H of Fig. 1, the two approaching hydrogen atoms first interact to develop an attractive force, the so-called van der Waals force. As the approaching hydrogen atom is carried deeper into

[7] Dickinson, Dillon and Rasetti, *Phys. Rev.*, **34**, 582 (1929).

[8] Patty and Neilsen, preliminary report in the Am. Physical Society Program Bulletin for the Cleveland Meeting, **5**, 24 (1930).

[9] London, *Z. Physik*, **46**, 455 (1928).

the contours of Atom H, a mutual repulsive force begins to make itself effective. Rebound will finally set in, and the visitor atom will be driven elastically back out of the reach of the field of Atom H. Thus we may define the gas kinetic radius by dividing the distance of closest approach of the two hydrogen nuclei (one of which is shown in Fig. 1) by 2, and, taking this distance as radius, circumscribe two virtually hard spherical shells about the two nuclei, so that the two shells touch at the mid-distance. The depth of penetration, and hence the atomic domain radius, will depend on the violence of the impact blow; the radius would be expected to *become smaller as the temperature increases*, and in general will be smaller for a gaseous collision than for a solid or liquid.

Crystal Radius.—In a crystal the momentum of the approaching hydrogen atom is the momentum of the molecule to which it is rigidly attached, and the motion of the molecule is a vibration of the molecule as a whole about an average position within the lattice. As the approaching molecule moves out of its average position to approach Atom H, the blow against Atom H is very greatly softened because an attractive force seated in a neighbor molecule on the other side of the vibrating molecule slows it down, in the same way that a pendulum is slowed down after it passes through the bottom of its swing. In a gaseous collision, on the other hand, there is no source of attraction to hold the approaching molecule in check, and its blow of impact is delivered in full force. An organic crystal which is warmed up through a considerable temperature range suffers an expansion of its lattice to accommodate the increasing amplitude of the thermal vibration of the molecules with more free space or co-volume, and even as fairly low temperatures it is to be supposed that some free space will exist. It is therefore to be expected that the crystal radius, in contrast with the gas kinetic radius, will *increase with increasing temperature*.

Figure 2 diagrams the situation. A and B represent the framework of two lattice molecules vibrating about their average positions. When the two hydrogen atoms H_A and H_B move far enough toward each other, due to the motion of A and B, to which the hydrogen atoms are attached, repulsive forces cause them, and consequently also A and B, to retreat. On the other hand, when the molecules A and B recede beyond their average positions, the hydrogen atoms are pulled back together by attractive forces. We may define the crystal radius as half of the *average distance* between the hydrogen nuclei.[10] This definition of atomic domain radius in crystals will also hold approximately for the domain radius of atoms on the

[10] If this picture of the spacing of molecules in a lattice is pushed to its logical conclusion, it is to be noted that over the whole temperature range in which the lattice is stable, even at the absolute zero (because of the zero-point energy), the molecules will never occupy true equilibrium positions, that is, positions at which the repulsive and attractive forces balance, but will be occupying average positions. In the average positions the hydrogen atoms will be attracting one another.

surface of a liquid molecule.   To adopt such a definition of atomic domain in the case of two vibrating neighbor molecules in a crystal lattice is, of course, begging the question of the space gaps between neighbor molecules which we have set out to answer, unless the particular size of hydrogen atom domain which is employed can be justified independently or unless the particular size which will explain the spacing of this molecule along one crystal axis will also account for the spacings along all other axes of the same crystal and along all axes of all other crystals in which the H . . . . H contact is involved.

The electron density contours of the hydrogen atoms of Fig. 2 may be thought of as being compressed on approach, and as expanding on recession, like two balloon surfaces always in contact; or they may be thought of as undergoing a penetration into one another, as shown in the figure.   In the present paper we fortunately need not concern ourselves with this precise mechanism, or with the origin and mechanism of the attractive and repulsive forces, since *the intention is to approach the prob-*

Fig. 2.

lem in a purely empirical manner, to determine whether the spacing of organic molecules in crystal lattices can be explained in terms of atom domains of constant size in the same way that the spacing in inorganic crystals is at present accounted for in terms of ion domains of substantially constant radii.
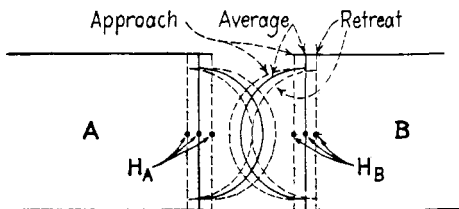
It is extremely convenient to describe the positions and spacings of the molecules with respect to one another by means of drawings and three-dimensional lattice models.   For this purpose it is almost essential to repre-sent the outer regions of the atom domain as a hard surface, and, since there is good reason for believing that the atom domain possesses approxi-mately spherical symmetry, we shall employ a hard spherical surface.   To call an atom a hard sphere is, admittedly, using a figure of speech.   But if we recognize that it is figurative language, no harm is done and much advantage is gained in the simplicity and usefulness of the conception for the purposes of model building.

It is now possible to proceed with the estimation of the actual size of the hydrogen atom domain.   It will be done first for a gaseous molecule, and then it will be shown that a reasonable extrapolation to a larger size will give a hydrogen atom crystal domain which will account consistently for the spacings of organic molecules in a crystal lattice.   To complete the argument it would be desirable to compute the radius of the hydrogen atom domain on liquid molecules; but the difficulty of knowing the precise packing of the molecules in the liquid state and of allowing for the free

space arising from the probably more or less chaotic orientation of the molecules, seems to make the computation impossible in most cases. The situation of oriented molecules in the monomolecular oil film may eventually afford the opportunity of making such a computation, but at present our ignorance of the nature of the lateral packing and interlocking of the hydrocarbon chains does not encourage the attempt.

Empirical Estimation of Gas Kinetic Radius for Hydrogen.—The radius of the atomic domain of hydrogen bonded to carbon in a gaseous molecule may be obtained probably more easily from methane than from anything else. Rankine and Smith[11] have found from viscosity measurements, and by calculation with Chapman's equation, that the collision area of methane is 7.72 sq. Å. In so far as the Sutherland model is not valid, and to the extent to which Rankine and Smith's value is not reliable because of the small temperature range of the viscosity measurements (only from 17 to 100°), our own calculation of the atomic domain will be in error. The value is probably substantially correct, and at any rate is good enough for our present needs.

In a gaseous encounter with another like molecule, a molecule of methane probably presents itself as a sphere of revolution. The reasons for believing that this is so are as follows.

From the principle of the equipartition of energy the energy, E, of rotation of the methane molecule about a single axis is $1/2\ kT$, where k is the Boltzmann constant and T the absolute temperature. If, at let us say 25°, we assume that the equilibrium partition of energy is attained, $E = 2.04 \times 10^{-14}$ ergs. From the equation $\nu = \sqrt{2E/I}/2\pi$, where I is the moment of inertia, the frequency of spin ν may be calculated to be about 1.42×10^{12} r. p. s., and the time for one complete revolution to be about 7×10^{-13} seconds. Since both colliding molecules may be thought of as spinning simultaneously about four three-fold symmetry axes, or about three rectangular axes, and, furthermore, since the molecule would only have to execute about one-sixth of a revolution, it would behave effectively as a sphere if allowed a time not less than about 0.2×10^{-13} seconds. During such a time interval the translatory velocity of the bombarding molecule would carry it through a distance on the average of only about 0.14 Å.

If we further neglect any possible acceleration of velocity as the two molecules approach each other,[12] due to the attractive van der Waals forces, and any possible orientation as they get into one another's field, it is not likely that the approaching molecule would be able to penetrate appreciably into the spherical envelope of the molecule undergoing attack in regions where the hydrogen atoms do not happen to be at the instant of impact.

[11] Rankine and Smith, *Phil. Mag.*, **42**, 615 (1921).

[12] Herzfeld and Smallwood, Taylor's "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, 1931, Chapt. IV, Vol. I, p. 241.

It therefore seems difficult to escape the conclusion that the spinning molecule is able to guard its envelope of revolution against invasion, and that it will present itself almost as a total sphere (Fig. 3). If this is true, the collision area of such a sphere would be Rankine's value of 7.72 sq. Å., with a radius of 1.57 Å. Since the distance from the carbon nucleus to a hydrogen nucleus is 1.08 Å., the radius of the atomic domain of hydrogen beyond the nucleus would be about 0.50 Å. (0.49 Å.). This is the minimum size: it may be slightly larger, to an amount depending on the extent to which the methane molecule behaves as a partial rather than a total sphere of revolution.[13]
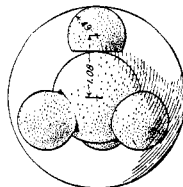
Fig. 3.

Empirical Crystal Radius for Hydrogen.—In view of what has already been said it is now reasonable to expect to find the crystal radius for hydrogen atom domain to be very much larger than the gas kinetic radius. Such an increase in domain size in passing from the gaseous through the liquid to the solid state is very likely to be a perfectly general behavior, characteristic of all atoms. For example, Natta and Nasini have recently shown that the xenon atom,[14] crystallizing in a face-centered cubic lattice, has a radius of 2.18 Å., whereas the gas kinetic radius[15] is 1.70 Å. For krypton the radius in the crystal is reported to be 1.98 Å.[16] and 2.04 Å.,[15] in a face-centered cubic lattice, while the radius in the gas is about 1.55 Å. For argon the respective crystal and gas radii are 1.92 Å.[17] and about 1.44 Å.[18] Approximately the same ratio holds for neon, and the same effect can be readily demonstrated for chlorine, bromine, iodine and other atoms.

Thus it will be noted that the crystal domain radius is larger than the gas kinetic radius by a factor of about $4/3$ or $5/4$ for the rare gases; the factor is 2 or more for hydrogen in the C–H group, for in the following sections the crystal lattice data indicate hydrogen atom domain radii of about 1.165 Å. (at about $-195°$) and 1.29 Å. (at room temperature), as compared with about 0.50 Å. for the gas kinetic radius. The hydrogen radius would seem to depend to some extent on the nature of the atom to which it is bonded. For example in crystalline H_2 (hexagonal close-packed and assuming rotating molecules) it is necessary to assign a value of about 1.5 Å. to the radius. In the present paper, however, we are interested only in hydrogen bonded to carbon. It is to be noted also that the crystal radius of hydrogen may be reduced by rotational rubbing.

[13] The problem of collision between rotating molecules has been treated by Pidduck, *Proc. Roy. Soc.* (London), **A101**, 101 (1922); and by Chapman and Hainsworth, *Phil. Mag.*, **48**, 593 (1924).

[14] Natta and Nasini, *Nature*, **125**, 457 (1930).

[15] Nasini and Rossi, *Gazz. chim. ital.*, **58**, 433 (1928).

[16] Keesom and Mooy, *Nature*, **125**, 889 (1930).

[17] Simon and Simson, *Z. Physik*, **25**, 160 (1924).

[18] Rankine and Smith, *Phil. Mag.*, **42**, 601 (1921).

Crystalline Methane.—Mooy, whose results are undoubtedly more reliable than those of McLennan and Plummer,[19] has recently shown by x-ray[20] examination of methane at liquid nitrogen temperature that the molecules are cubic close-packed in a unit cell of 5.88 Å. edge length. Pauling, basing his argument in part on heat capacity data, has demon-
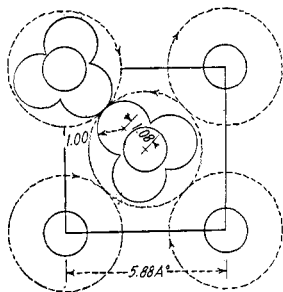

Fig. 4.

strated that the methane molecules are almost certainly rotating in the lattice above 20°K. (−253°). These effective spheres of revolution, without points of strong attraction for their neighbors, would be expected to pack together, as they do, in a face-centered cubic lattice, just as do the spherically symmetrical argon, krypton and xenon atoms.

The x-ray analysis shows, of course, the positions of the carbon atoms only. The space gaps may be filled up so that the spheres of revolution osculate in the lattice, as shown diagrammatically in Fig. 4, by attaching hydrogen atoms to the carbon atoms at tetrahedral angles, with a C–H internuclear distance of 1.08 Å., and a hydrogen atom domain of radius 1.002 Å. This radius, probably reduced to the given size by rotational rubbing against neighbor molecules, would be expected to be somewhat larger if the molecules were not rotating. Perhaps some "cog-wheel" rotation occurs.

Crystalline Ethane.—Mark and Pohland[21] have made an x-ray examination of crystalline ethane, using the powder photograph method, also at liquid nitrogen temperature (−195°), and report the hexagonal structure shown in Fig. 5. (This figure is similar to one given in Hendricks' review.) The carbon atom pairs in the figure are the C–C atoms of the C_2H_6 molecule. Now, if hydrogen atoms of size a little larger than that in methane, namely, with atomic domain radius of 1.165 Å., are attached to the carbon atoms at

Fig. 5.

tetrahedral angles and with C–H internuclear distance of 1.08 Å., the space gaps are all filled up, so that the *hard spherical surfaces of the hydrogen atom domains of neighbor molecules just kiss*, on the supposition that the molecules
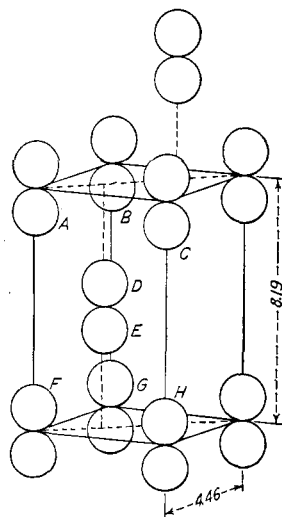
[19] McLennan and Plummer, *Phil. Mag.*, **7**, 761 (1929).

[20] Mooy, Dissertation, *Nature*, **127**, 707 (1931); *Proc. Acad. Sci. (Amsterdam)*, **34**, 550 (1931).

[21] Mark and Pohland, *Z. Krist.*, **62**, 103 (1925).

are not rotating.   Figure 6, which is a photograph of a three-dimensional model made to scale, shows the manner of the interlocking.   This hydrogen atom size accounts exactly not only for the horizontal edge length of the unit cell, 4.46 Å., but also for the vertical height, 8.19 Å.   The hexagonal symmetry of the lattice is most beautifully accounted for in terms of the inter-locking of the molecules, which themselves possess hexagonal symmetry, as is clearly to be seen from the photograph of the model, and also from Fig. 7, which
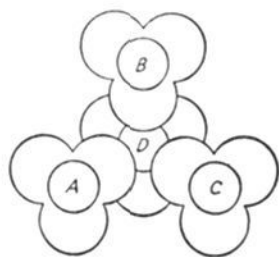

Fig. 6.

presents a view from above. Every ethane molecule in the body of the lattice makes six double contacts with its six immediate neighbors, contacts which resemble the meshing of teeth in gears.

Fig. 7.

It is of course possible that the molecules are rotat-ing in the lattice about their own vertical axes.   The hydrogen domain radius would then be about 0.96 Å., approximately the same as in methane, and is to be thought of as reduced to this size from 1.165 Å. by rotational rubbing.   Possibly the rotation is more or less of a "cog-wheel" type.   On the whole perhaps the non-rotating molecule solu-tion is more satisfying, but both solutions seem possible stereochemically, and the question of whether the molecules are really spinning or not below the melting point of crystalline ethane will have to be determined by some independent method.

Crystalline Hexamethylene-tetramine, $(CH_2)_6N_4$.—Figure 8 is the well-known diagram of the ar-rangement and spacing of the hexa-methylenetetramine molecules in the body-centered cubic lattice, worked out by x-ray analysis by Dickinson[22] and Raymond. Inspec-tion of the figure shows the large space gaps between neighbor mole-cules. The spacing of the molecules

Fig 8.

is determined by contact between the missing hydrogen atoms along the cube edges.   Such a contact is illustrated in Fig. 8 by the insertion of Hy-drogen Atoms, a, b, c, d to complete the two methylene groups.   (The carbon atoms are represented by the solid black circles.)

[22] Dickinson and Raymond, THIS JOURNAL, **45**, 22 (1923); and Mark, Z. *physik. Chem.*, **107**, 181 (1923).
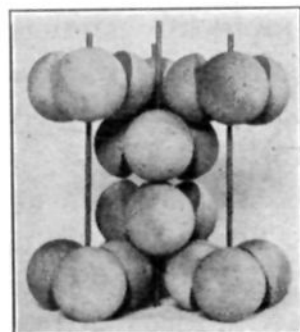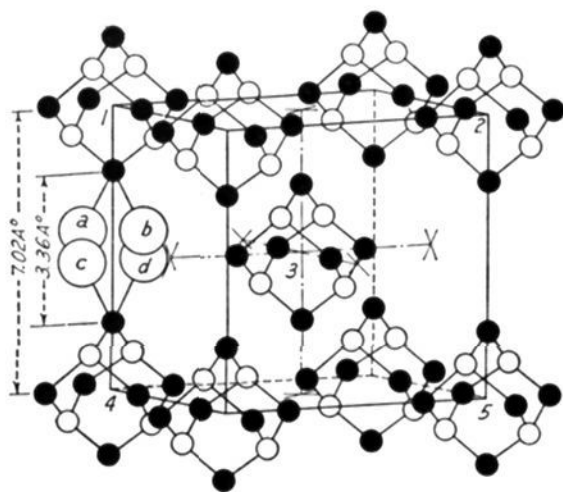
If hydrogen atoms of crystal radius 1.29 Å. and with C–H internuclear distance of 1.08 Å. are now attached to the carbon atoms, distant 3.36 Å. from one another, the unit cube edge 7.02 Å. is precisely accounted for. The radius 1.29 Å. may be thought of as being assumed *ad hoc* or as derived empirically; but this same radius will now account extraordinarily satisfactorily for the spacings along all axes of all other crystals (where H .... H contacts are involved and at room temperature) so far studied by the author. This is the radius which will be used in the stereochemical solutions of aromatic molecule lattices in the following pages.

The molecules also contact along the cube diagonals. Figure 9 is a diagonal plane section through the cube from one edge to the edge opposite; two of the cube diagonals lie in this plane, running from 1 to 5 and from 2 to 4, in the figure. The carbon atoms, diameter 1.54 Å., are represented by

Fig. 9.

the solid black circles, the nitrogen atoms by the systems of concentric rings and the hydrogen atoms by the large single circles. Hydrogen Atom A of Molecule 3 (the middle molecule) kisses the nitrogen atom of Molecule 4 in the plane of the paper; and Hydrogen Atom B, which is somewhat forward of A, and a third hydrogen atom lying directly behind B, and deeper than A into the plane 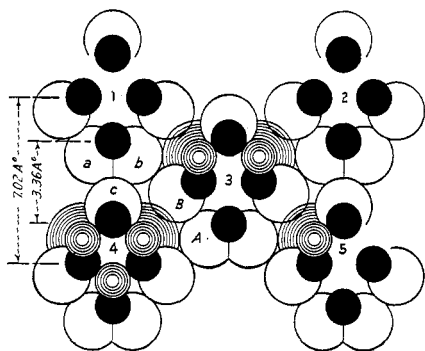of the paper, both also kiss the nitrogen atom. *Thus the domain of the nitrogen atom on Molecule 4 rests in a nest of three hydrogen atoms belonging to the neighbor Molecule 3, with the triplicate contact centering along the cube diagonal.*

The radius of the nitrogen atom domain which will permit contacts of this sort is about 1.5 Å. A nitrogen atom, with five valence electrons, uses only three in bonding itself chemically to the three carbon atoms to which it is linked in the hexamethylenetetramine molecule, and accordingly is left with a residuum of two unshared electrons. It is entirely reasonable to suppose that these two electrons will form an atomic "bulge" or projecting domain considerably larger than the hydrogen atom domain. More quantitatively, 1.5 Å. is about the domain radius size which one would expect the nitrogen atom to possess, in view of the fact, already noted, that atoms in general will exhibit a larger domain in crystals than in gases, and in view of the further fact that in order to account for the collision area of the gaseous ammonia molecule, 6.40 sq. Å. (reported by Rankine),[23] on the assumption that the molecule has a tetrahedral shape,

[23] Rankine, *Phil. Mag.*, **42**, 613 (1921).

nitrogen atom at the top and the three hydrogen atoms at the base, with a moment of inertia of 2.78×10^{-40} (reported by Robertson and Fox),[24] it is necessary to assign the nitrogen atom domain a radius size of about 1.2 Å. in the gaseous state.   The ratio 1.5:1.2 for the crystal and gas radii is about the same as for the rare gases.

Hence it seems very probable that every molecule in the lattice partakes in eight such contacts, as illustrated by Molecule 3 in Fig. 9, two contacts along every one of the four diagonals of the unit cell.   The spacing and symmetry of the lattice are thus accounted for in a most satisfactory manner, both along the cube edges and diagonals of the unit cell, in terms of the dimensions and symmetry of the molecule.

A Proposed New Feature of Structure for the Benzene Ring.—In spite of the large number of proposals of benzene molecule structure that have been made in classical organic chemistry and the more recent accretions to the list, the disposition of the fourth bond of the carbon atoms is still a baffling problem.   x-Ray analysis is beginning to indicate quite clearly, as has already been noted on a previous page, that the unsaturated benzene "ring" is indeed a six-carbon atom ring and that the ring is flat, like the graphite ring rather than the "puckered" ring of diamond, although the saturated cyclohexane ring may be puckered as in diamond or as in the camphor molecule.

Not long ago Pauling made a most interesting suggestion that the fourth electron of every carbon atom is circulating,[25] in so-called μ-orbits, across the flat ring and around the carbon atom nucleus in the para position, thus forming chemical bonds connecting the para carbon atoms; but in a more recent paper he[26] suggests the possibility that every carbon atom is connected to one neighbor carbon by two single bonds and to the other by a double bond, and explains away the susceptibility to chemical addition, which is to be expected from such an unsaturated structure, by supposing that there is oscillation of the double bonds from one position to another, a supposition which in terms of the quantum mechanics would probably lead to chemical stability.   At any rate it now appears, in apparent default of decisive chemical evidence to render judgment among the claims of the various benzene structure theories, that we may not be unduly optimistic to hope for an early solution of the difficulty either by means of x-ray intensity measurements, or even perhaps at the hands of the quantum mechanics.

But, in the meantime, whatever the answer to the question of fourth bond disposition may eventually be, it would seem abundantly clear that the unsaturation of the benzene ring manifests itself in the form of a pro-

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[24] Robertson and Fox, *Proc. Roy. Soc.* (London), **A120**, 189 (1928).

[25] Pauling, THIS JOURNAL, **48**, 1132 (1926).

[26] Pauling, *ibid.*, **53**, 1367 (1931).

tuberance or "bulge," extending out perpendicularly from each face of the flat ring. This idea may be said to be strongly supported by empirical evidence. As the idea developed in the author's mind it was at first supposed that the bulge might take the form of a crater-like elevation protruding above and below the carbon ring; then that the bulge might be cone-like, with the summits above and below the center of the ring; but finally that it must take the form of hemispherical domes, with a dome on each face of the ring. This dome is to be thought of as an electron domain, analogous to the domain of the hydrogen atom and the nitrogen atom, already discussed in preceding pages. The space occupied by this dome domain is guarded more or less against invasion by approaching atoms and molecules depending on the violence of the impact below. The best evidence for the existence of the dome arises from the possibility of explaining quite satisfactorily the observed manner of the spacing and packing of aromatic molecules in crystal lattices, if such a dome is assumed to be present, and the apparent difficulty of so doing without the dome.

In the present paper, while we are primarily interested only in the empirical evidence supporting the idea of the presence of the dome, it may be noted, in passing, that a seemingly sound theoretical justification for the idea is to be found in Pauling's first proposal of benzene ring structure. His virtual electronic μ-orbits, encircling para carbon atoms, would be expected to repel one another, and to flare out symmetrically from both faces of the ring to give effectively two hemispherical domes.

Now we may proceed to the proposed stereochemical solutions of graphite, anthracene and naphthalene, benzene and hexamethylbenzene; then some additional arguments for the presence of the benzene dome will be presented.

Structure of Graphite.—x-Ray analysis has now shown without doubt that the carbon atoms of graphite are arranged in flat hexagonal rings in flat layers, in contrast to the puckered layers of diamond. These flat layers are superimposed above one another, but are separated from one another at a surprisingly large distance[27] (3.40 Å.), a structure for which it has hitherto been difficult to find a satisfactory explanation. Such a large distance between these molecule layers certainly strongly suggests the presence of protuberances perpendicular to the flat layers, that is, to the faces of the hexagonal rings. It is these protuberances which hold the layers apart at the observed spacing.

Figure 10 shows the nature of the suggested structure. Every hexagonal graphite ring possesses a hemispherical dome on each of its two faces, with a dome domain radius, measured from the mid-point of the ring, of about 1.84 Å. This dome radius is considerably smaller in graphite than

[27] Hassel and Mark, *Z. Physik*, **25**, 317 (1924); Bernal, *Proc. Roy. Soc.* (London), **A106**, 749 (1924).

in benzene, as will be seen later, because in the graphite structure every carbon atom is a part of three different rings, and must share its fourth electron among three different domes. Thus every graphite ring can claim only two electrons for the formation of its two domes, whereas benzene builds its two domes from six electrons. A dome in one layer fits into a nest of three domes in the adjacent superimposed layer, and this relative arrangement of superimposed layers explains exactly the relationship deduced from x-ray analysis. In the observed arrangement a six-carbon hexagon in one layer is so placed that three of its carbons (all in meta positions with respect to one another) lie directly above and below carbon atoms in adjacent horizontal layers, and the other three carbons (also in *meta positions*) lie directly above and below the centers of rings in adjacent layers. Furthermore, while the carbon atoms within a flat layer are held together by chemical bonds, the interlayer forces, by vi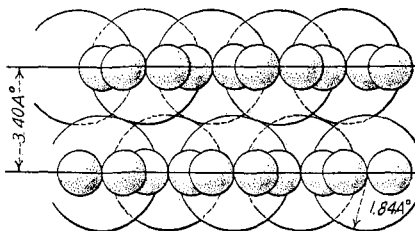rtue of the contacting between the electron domain domes, are merely van der Waals forces. Hence these layers would be expected to be susceptible to slippage and gliding with respect to one another, in a manner which accords with the facts.

Fig. 10.

Anthracene and Naphthalene.—In Sir William Bragg's[28] original examination of crystals of naphthalene and anthracene, and even in Robertson's more recent analysis,[29] it was supposed that the carbon rings in the two molecules were puckered diamond rings. But, still more recently, in a letter to *Nature*, Banerjee[30] presents what is undoubtedly just about the correct solution of these crystal structures, and his analysis shows that the carbon rings are flat, and further differs from the solutions of Bragg and Robertson in placing the flat faces of the molecules more nearly in the *bc* than in the *ac* planes. In the same number of *Nature* Robertson admits the essential correctness of Banerjee's conclusions and also presents reasons based on unpublished work of his own and of Bragg in further support of these conclusions. Banerjee was apparently able to make his successful analysis because of the work of Bhagavantum on the magnetic anisotropic properties of naphthalene. Bhagavantum,[31] taking advantage of the peculiarly strong magnetic susceptibility of the benzene ring in a direction perpendicular to its flat face, suspended small crystals from silk fibers in a strong magnetic field, and from the position assumed by the

[28] Bragg, *Proc. Phys. Soc.* (London), **34**, 1, 33 (1921); **35**, 3, 167 (1923).
[29] Robertson, *Proc. Roy. Soc.* (London), **A125**, 542 (1929).
[30] Banerjee, *Nature*, **125**, 456 (1930).
[31] Bhagavantum, *Proc. Roy. Soc.* (London), **A124**, 545 (1929).

crystals in the field deduced the placement of the naphthalene and anthracene molecules with respect to the crystal axes of the lattice. With this much of a guide to the probable parameters of the individual carbon atoms, Banerjee very cleverly obtained a good match between calculated and observed x-ray intensities, thus establishing an extremely probable structure.

According to Banerjee, "the correct positions of the molecules are obtained by first placing them along the bc planes, then rotating them through 25° about the c axis (the two molecules in the unit cell being rotated in opposite directions), and then rotating them about b axes through 12 and 9° for naphthalene and anthracene, respectively." This statement together with the cell dimensions and space group will be taken as the basis of our stereochemical solution.

Since the molecules of any lattice normally arrange themselves so that the maximum number of contacts between atoms attracting one another with van der Waals forces is obtained, and the minimum possible potential energy achieved, we should expect the molecules of anthracene, for example, to pack together face to face, with the ten hydrogen atoms of one molecule contacting with the ten of a neighbor molecule. But since the presence of the dome-like protuberance on the faces of the rings prevents as close a packing as this, just as it does in the case of graphite, the molecules have to be content with the next closest possible packing, which would seem undoubtedly to be the one described by Banerjee.
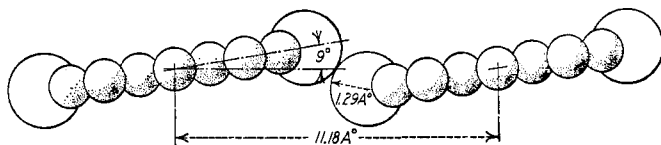

Fig. 11.

The dimensions of the anthracene monoclinic unit cell are: $a = 8.58$, $b = 6.02$, $c = 11.18$ Å., $\beta = 125°$. The space group is C_{2h}^5. Let us consider Fig. 11, where two anthracene molecules (with the domes temporarily omitted) are inclined to the c axis at an angle of 9°, in accordance with the specifications of Banerjee. The distance between molecule centers is 11.18 Å. (length of c axis). The three rings of the anthracene molecule are graphite rings with carbon atom diameters of 1.42 Å. The hydrogen atoms are placed in the plane of the rings, with a C–H internuclear distance of 1.02 Å. This distance is reduced from 1.08 Å., the H-*aliphatic* C internuclear distance, to correspond with the analogous reduction observed from aliphatic C-*aliphatic* C (1.54 Å.) to aliphatic C-*aromatic* C (1.48 Å.). It cannot be in error by more than a few hundredths of an Ångström unit, and probably is just about right. In the figure there are contacts between

two end hydrogen atoms of one molecule and two of the other, although the second hydrogen atoms are hidden directly behind those shown in the drawing. With the molecules in the position shown, the hydrogen domain radius which just gives contact is 1.29 Å. In *naphthalene*, the c axis length is 8.68 Å., and when these two molecules, shorter than anthracene, are set along the c axis, with their centers at this distance apart, and with their end hydrogen atoms (radius 1.29 Å.) just kissing, the angle of inclination of the molecules to the c axis is 12°, which accords beautifully with Banerjee's requirement.

It is indeed difficult to represent clearly in two-dimensional drawings the details of these fairly complicated three-dimensional models. In Fig. 12, where we look into the ab face of the anthracene unit cell, we may avoid some confusion of lines by looking directly into the ends of the molecules rather than perpendicularly into the face. Such a view foreshortens the a axis, reducing it from 8.58 to 7.71 Å. In this figure the five molecules Nos. 1, 2, 3, 4, 5, the centers of which lie in the nearer ab face, have their carbon atoms shaded; the others, Nos. 6, 7, etc., which lie in the farther ab face, are unshaded. It will be noted that Molecules 1 and 2 (at the top) as well as Molecules 4 and 5 (at the bottom) are inclined at angles of 25° to the bc plane, and that when their centers are spaced 6.02 Å. apart, their three
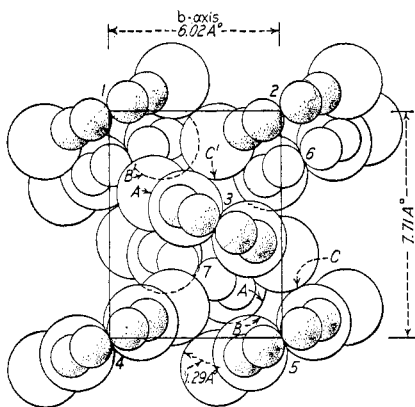

Fig. 12.

outlying side hydrogen atoms (two of which are hidden in the drawing directly behind the first) all just contact with three of a neighbor molecule, when the hydrogen domain radius is 1.29 Å. Molecule 3, which is located a little to the right of the face center, is rotated 25° clockwise, in contrast with the counter-clockwise rotation of Molecules 1, 2, 4 and 5. Of the three outlying hydrogen atoms on the lower right-hand side of Molecule 3, the one farthest to the front rides on the upper right-hand end hydrogen atom (farthest to the front) on Molecule 5, as shown at C. A similar contact in the next layer above is shown at C'. All three of these hydrogen atoms of Molecule 3 also ride on the domes of Molecule 5, although the domes are not drawn in Fig. 12. But the manner in which the side hydro-gen atoms (not shown in Fig. 12) of Molecule 7 ride up on the domes of Molecule 8, which lies below Molecule 5, is clearly indicated in Fig. 13, which gives a view looking into the ac face. The size of the domes on anthracene is small enough to permit Molecule 7 to slip far enough to the

left (in Fig. 13) and far enough to the front (in Fig. 12) to let Hydrogen Atom A of Molecule 7 ride up on top of Hydrogen Atom. B of Molecule 5. The same sort of contact occurs between Molecules 7 and 4 (Fig. 12). These hydrogen–hydrogen, and hydrogen–dome contacts between the oppositely inclined layers, repeated over and over again from layer to layer, account very satisfactorily for the observed spacings along the a axis. The angle β (125°) between the a and c axes is also quite exactly explained in terms of the contacts described.

The dimensions of the unit cell of naphthalene are: $a = 8.34$, $b = 5.98$, $c = 8.68$ Å., $\beta = 122°44'$. The arrangement of the molecules in the cell is almost identically the same as in anthracene. We have already accounted for the spacing along the c axis. The smaller a axis in naphthalene
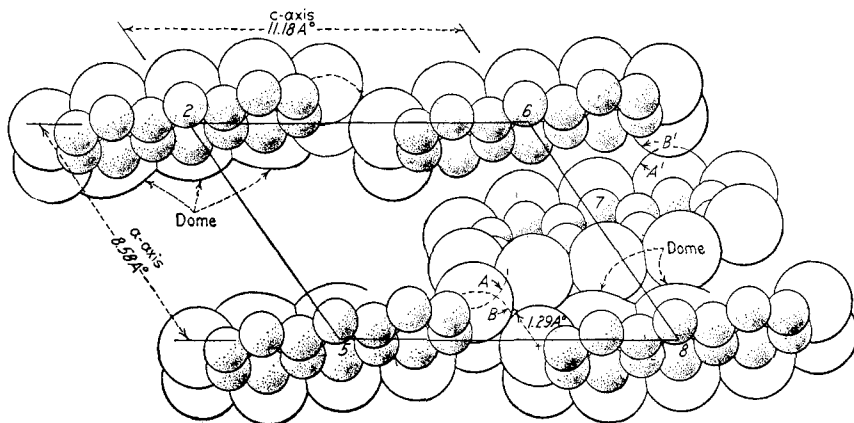

Fig. 13.

as compared with anthracene is to be attributed to the presence of a larger dome size at the two extremities of the naphthalene molecule as compared with anthracene. The domes over the middle ring of anthracene are distinctly small, probably not much larger than the graphite dome. At the extremities of the anthracene molecule the dome size becomes larger because there the fourth electrons do not have to be shared between the domes of an adjacent ring. To put the matter in most general terms, without attempting to give a detailed description of the exact size and shape of these domes, we may observe that in naphthalene we have ten electrons to distribute through the domes over two rings, whereas in anthracene we have only fourteen electrons to distribute over three rings. It is to be expected, then, that the dome size at the two extremities of the anthracene molecule would be appreciably smaller than in naphthalene. This larger dome in naphthalene prevents Molecule 7 (Fig. 13) from slipping quite as far to the left as it does in anthracene, and hence gives a smaller value of the angle β; and prevents Atom A from riding quite as high up

on Atom B (Figs. 12 and 13), and hence also reduces slightly the length of the a axis in the case of naphthalene. The b axes are almost exactly the same in the two crystals, but it is likely that the slightly different arrangement of the molecules in naphthalene results in tipping the molecules with respect to the bc plane (Fig. 12) slightly more than in the case of anthracene, enough to reduce the b axis from 6.02 to 5.98 Å.

It may be of interest to note that essentially the same stereochemical solution can be obtained, as far as spacing along the c axis is concerned, by employing the puckered diamond ring. However, along the b and a axes the staggering of the hydrogen atoms above and below the plane of the puckered ring is such that no consistent contacting between hydrogen atoms occurs. If the nature of the packing here suggested is accepted as correct, then the stereochemical argument strongly favors a graphite instead of a diamond ring.

Benzene.—Eastman,[32] Broomé,[33] Mark[34] and Cox[35] have subjected crystalline benzene to x-ray examination. All of the analyses agree roughly as to the orthorhombic cell dimensions. Probably Cox's results, obtained with crystals at $-22°$, are most reliable; $a = 7.44$, $b = 9.65$, $c = 6.81$, 4 molecules per unit cell and space group Q_h^{15}.

The stereochemical solution is shown in Fig. 14, looking into the ac face. The five shaded molecules, with their centers lying in the plane of the ac face, form a part of an end-centered lattice. At the opposite end of the cell, in the farther ac face, lying directly behind the shaded molecules of Fig. 14, is an exactly similar stack of molecules. In between these two lies a third similar stack, connecting the two together, but displaced in the lattice. In Fig. 14, the four unshaded molecules belong to this middle stack. On these unshaded molecules the domes have

Fig. 14.

been omitted to avoid some confusion of line. This middle stack of molecules nestles into the nearer stack of the ac face and also into the farther stack, in such a way as to determine the length of the b axis (shown in Fig. 15) as well as the lengths of the a and c axes (Fig. 14). The details of this "nestling-in" are as follows. The farther end hydrogen atom of Molecule S', in the lower right-hand corner of the cell (Fig. 14), supports the nearer
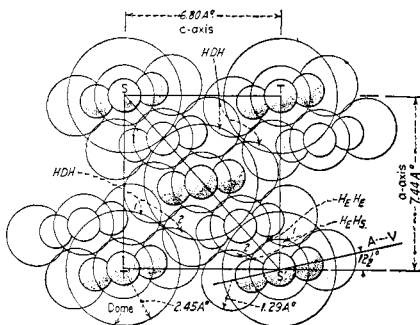
[32] Eastman, THIS JOURNAL, **46**, 917 (1924).

[33] Broomé, *Physik. Z.*, **24**, 124 (1923); *Z. Kryst.*, **62**, 325 (1925).

[34] Mark, *Ber.*, **57**, 826 (1924).

[35] Cox, *Nature*, **122**, 401 (1928).

end hydrogen atom of a molecule in the middle stack, as shown at H_EH_E. This type of contact is repeated over and over again from layer to layer up through the diagonal plane S'S. Also the farther end hydrogen of Molecule S' contacts perfectly with the nearer side hydrogen atom of the middle stack molecule as shown at H_EH_S, Arrow 1; and the nearer end hydrogen of the middle stack molecule contacts perfectly with the farther side hydrogen of Molecule S', as shown at H_EH_S, Arrow 2. In order to make these H_EH_S contacts perfect it is necessary to suppose that the benzene molecules are all tipped at an angle of $12^1/_2°$ to the bc plane, and they have been so drawn in Fig. 14. The H_EH_E and H_EH_S contacts are also illustrated in Fig. 15.

It is interesting to note that, when the molecules (Fig. 14) are tipped $12^1/_2°$ as just described, the two side hydrogen atoms on the left-hand side of the middle molecule of the nearer ac face (shaded) make a perfect con-

Fig. 15.

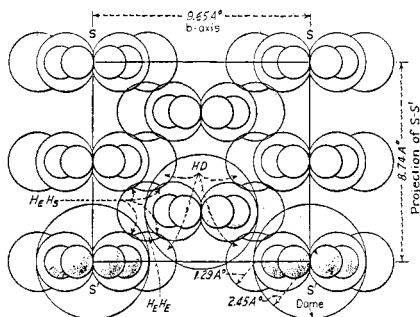tact with the dome of Molecule T', if the dome is assigned a radius of 2.45 Å., as shown at HDH, Arrow 1. And similarly the right-hand side hydrogen atoms of Molecule T contact perfectly with the dome of the molecule at the center of the face, as shown at HDH, Arrow 2. Thus these HDH, H_EH_E and H_EH_S contacts explain the spacings along the a and c axes. It will be noted that the side hydrogen atoms (radius 1.29 Å.) of Molecule S' do not contact with the side hydrogen atoms of Molecule T' along the horizontal axis, as was the case in naphthalene and anthracene.

In Fig. 15 we are looking into the ab face, but in order to simplify the drawing we are not looking normally into the face but into the Section SS' (see Fig. 14), into the plane of the molecules themselves, that is, along the line A . . . . V (see Fig. 14), at an angle $12^1/_2°$ to the bc planes. This stereochemical solution accounts for the symmetry and all of the dimensions of the unit cell down to the last hundredth of an Ångström unit. The only further ad hoc assumption that must be made, except for the radius 2.45 Å. for the dome, is that the dome is very slightly deformable near the carbon atoms of the benzene ring, so that the end hydrogen atoms of neighbor molecules can penetrate a little into the spherical domain, as shown at HD in Fig. 15. Such a penetration is quite reasonable, since the hydrogens enter between the carbons, and can be thought of as slipping in between the ridges of Pauling's μ-orbits.

In concluding our discussion of the benzene lattice it may be pointed out that the stereochemical solution suggested here gives four molecules

per unit cell, strongest reflections for the 111 plane (as observed by Cox) and space group Q_h^{15} with the four molecules of the middle stack (Fig. 14) displaced somewhat, however, out of the face centers. As in the cases of naphthalene and anthracene, the puckered ring does not yield a satisfactory solution.

Hexamethylbenzene, $C_6(CH_3)_6$.—Mrs. Lonsdale's analysis[4] of the triclinic crystal hexamethylbenzene demonstrates the general features of structure shown in Fig. 16. This diagram gives a view looking into the ab face of a unit cell, where the a and b axes are inclined to one another at an angle of 119°34'. In this face the four corners are occupied by benzene hexagonal plane rings, made up of carbon atoms of diameter 1.42 Å., and in the figure numbered 1, 2, 3, 4, 5, 6. Attached to these at carbon bond
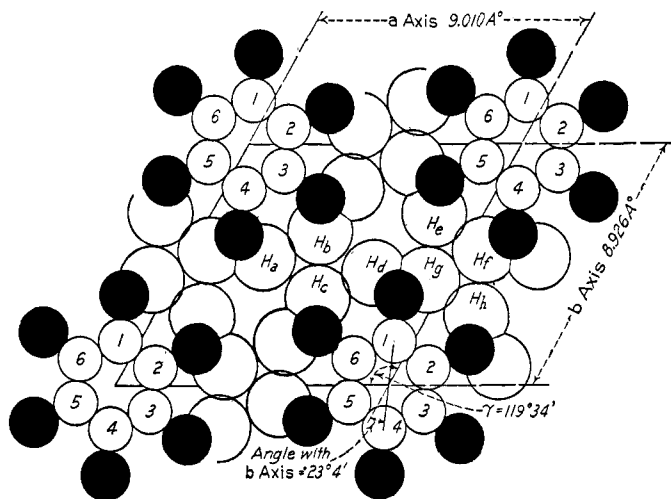

Fig. 16.

angles of 120° are the aliphatic carbon atoms (solid black circles) of diameter 1.54 Å., co-planar with the aromatic ring. The presence of large space gaps between the carbon atom clusters is evident from the figure. The question which we wish to have answered is: Can these gaps be filled up by attachment of the missing hydrogen atoms?

Regarding the methyl group Mrs. Lonsdale herself makes the following remarks. "In scattering power it is heavily weighted at the end nearer to the benzene ring by its carbon atom, which appears to retain its own electronic system more or less unchanged. . . . In fact the methyl group acts toward x-rays like an electronic shuttlecock, whereas single atoms behave rather like tennis balls. . . . Possibly if the exact shape and orientation of the methyl groups could be determined the problem of the crystal system would resolve itself into a question of the most convenient packing. . . . .

The easy distortion of the crystals by slipping about the crystallographic axes may be caused by the rolling of methyl groups upon one another."

Following out Mrs. Lonsdale's suggestion, one may now attach the missing hydrogen atoms of the methyl groups with the C–H internuclear distance 1.08 Å., as we have done in the case of the preceding *aliphatic* bonds. We must bear in mind, at this point, that Pauling has shown that the methyl groups in hexamethylbenzene are probably rotating,[6] at room temperature. With a hydrogen atom domain of 1.29 Å. radius no rotation could occur because of the interference of neighboring methyl groups (ortho positions) on the benzene ring, unless the violence of the rotation were sufficiently great to compress the atomic domains. This is probably just what happens. The collisions between the hydrogen atoms of rapidly rotating adjacent methyl groups resemble in many respects gaseous collisions. The momentum of the approaching hydrogen atoms would easily carry them rather deeply into one another's domain, probably without altering appreciably the nature of the rotation, thus allowing one methyl ring of revolution to roll against another. At the same time, the bumping of these rotating methyl groups against one another would be expected to produce a little bond bending, and in the supplementary stereochemical solution which we are offering here to account for the spacings actually observed by x-ray analysis, we are making the very reasonable assumption that the hydrogens of a methyl group, while maintaining their distance of 1.08 Å. from the carbon atom, are pushed together slightly, or, stated more exactly, that the normal tetrahedral angle (109°28′) between the line connecting a hydrogen atom to the aliphatic carbon and the line connecting the aliphatic to the aromatic carbon is distorted to an angle of about 125°.

In Fig. 10 the positions which the hydrogen atoms in the ring of revolution would occupy in the plane of the paper are shown. The rubbing of a methyl ring against a ring of *another molecule* would also be expected to reduce the atomic domain radius of the hydrogen atoms to some extent, and in the diagram the radius has been taken as 1.06 Å., reduced to this extent from 1.29 Å. by the impact of rotational collision. The reduction of the size of the hydrogen domain by rubbing between methyl groups on the *same* molecule is even more than this, to an extent illustrated in the drawing by the overlapping of Hydrogen Atoms H_c and H_d, H_g and H_h, etc.

The nature of the contact between methyl groups on vicinal molecules is clearly shown. Along the *b* axis, Methyl Group 1 makes a double contact with Methyl Groups 4 and 5 of the neighboring molecule, Hydrogen Atom H_g with Hydrogen Atoms H_e and H_f. Methyl Group 4 makes a double contact with Methyls 1 and 2.

We may now observe the lattice by looking perpendicularly into the *bc* face, Fig. 17. Since the 1–4 axis of the molecule is inclined 23°4′ to the

b axis (Fig. 16), we shall not be looking directly into Methyl Group 3, but shall be viewing it somewhat obliquely. It is extremely difficult to make the nature of the contacts, viewed in this direction, as obvious in a plane drawing as it is in a three-dimensional model of the lattice. But with
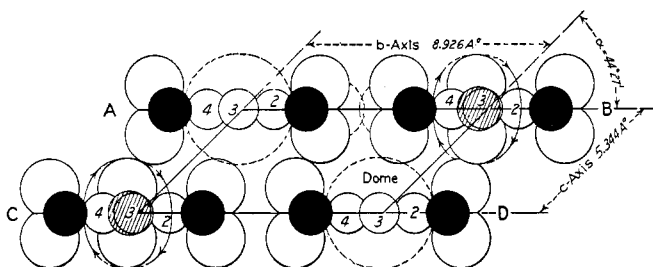

Fig. 17.

the aid of Fig. 17 and with the following list of the observed contacts, the general type of packing can be made fairly clear.

Upper layer   Lower layer

Methyl group 1 rolls on Methyl group 5
Methyl group 2 rolls on Methyl group 4
Methyl group 3 rolls on Methyl group 2
Methyl group 4 rolls on Methyl group 3 and Dome
Methyl group 5 rolls on Methyl group 6 and Dome
Methyl group 6 rolls on Methyl group 1

In these contacts made between molecules in the upper and lower layers, the hydrogen atom exhibits a domain radius approximately the same as in the *ab* plane, namely, 1.06 Å. Because of the presence of, and size of, the dome over the center of every benzene ring the molecules cannot pile directly over one another, center over center, and this is the reason, no doubt, why the crystal is not monoclinic or hexagonal. The lattice is triclinic because of the manner in which the Molecule A (Fig. 17) in the upper layer bridges the Molecules C and D in the lower layer.

In Fig. 16 it will be observed that the contacting between the spinning methyl groups of neighbor molecules along the *a* axis is almost, but not quite, the same as along the *b* axis, as indeed is to be expected from the slightly different lengths of the *a* and *b* axes. Dr. Pauling has very kindly suggested that this different spacing is controlled by the nature of the superposition of *ab* layers on one another. This is very probably the case. The spacing of the molecules in the *bc* stacks or nets is determined both by the rolling contact between methyl groups on vicinal molecules and by the nature of the bridging between layers, as already described. The different stacks of molecules along the *a* axes (Fig. 16) must then fit into one another as best they can. While the contacts along the *a* axes are good, and resemble quite closely those along the *b* axes, the contacts near the center of

the *ab* face are not so good. Here Atom H_b makes a single contact with Atom H_c, and Atom H_d just fails to touch Atom H_b, and H_a similarly fails to kiss H_c, or at least the interaction is looser than in the other contacts.

On the whole, this stereochemical solution for hexamethylbenzene has required more *ad hoc* assumptions than for the other crystals reported in this paper. But it must also be remembered that its structure is much more complicated than any of the others. In a later paper solutions of diphenyl, phenanthrene, indigo, *p*-dichloro-, dibromo- and di-iodobenzene, will be presented. In fact no crystal so far studied by this stereochemical method has failed to yield a reasonable and consistent result. With a little more experience in matching the stereochemical solution against the x-ray analysis, and with a more complete knowledge of the domain radii of oxygen and nitrogen and other atoms, it is probably not too much to hope that we shall be able to predict, accurately, the structural details of unit cells of organic crystals without x-ray analysis, simply from crystallographic and density data. At the very least, such a stereochemical approach should become an important aid, like Bhagavantum's studies on magnetic susceptibility, in determination of the parameters of the individual atoms in the skeletal organic molecules of the lattice.

Other Arguments for the Benzene Dome

In addition to the empirical crystallographic evidence already presented, we may marshal some further arguments in support of the postulate of the presence of an electronic dome domain over the face of the benzene ring.

1. **Collision Area of the Gaseous Molecule.**—Nasini and Lowry[36] have reported a collision area of 19.0 sq. Å. for the benzene molecule, determined by gaseous viscosity measurements. The satisfactory correspondence which one can obtain between collision areas of molecules in general and the collision areas predicted from a shadow-graphic treatment of probable models made to scale,[37] would seem to warrant an extension of this method of approach to the problem of gaining a decision among various disputed spatial configurations of organic molecules.

In the present case, a model of benzene made to scale (1 inch = 1 Å.) from a graphite ring, with six attached hydrogen atoms of *gas kinetic* radius about 0.63 Å. (taken as 0.63 instead of 0.50 Å. because probably *two* hydrogen atoms on each molecule on the average partake in the collision),[38] with a C–H internuclear distance of 1.02 Å., and with due consideration of the spins of the gaseous molecule gives a shadow area of

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[36] Nasini and Lowry, *Proc. Roy. Soc.* (London), **A123**, 686, 692 (1929).

[37] Melaven and Mack, THIS JOURNAL, **54**, 888 (1932).

[38] Adam, *Proc. Roy. Soc.* (London), **A103**, 676 (1923); Adam, Berry and Taylor, *ibid.*, **A117**, 532 (1928).

just 16.0 sq. inches. This average area is much too small, and suggests strongly that the benzene molecule must certainly possess some structural feature which causes it to present a much larger target to molecular bombardment. When a hard-surfaced spherical dome is attached to each face of the ring, with a *gas kinetic* dome radius of about 2.0 Å. (reduced 20% from the crystal dome radius of 2.45 Å. by analogy with the similar reduction suffered by the rare gas atoms), the collision area comes out to be about 18.6. This is very good correspondence with the result of Nasini and Lowry. The argument is reasonable, and its force cannot be ignored.

2. **Oil Films.**—Adam[38] and his students, in their study of oil films made up of long chain molecules attached to polar heads which were phenol groups, with the molecules probably oriented vertically in the water surface, have found a surface area of 24.0 sq. Å. for every benzene ring in the condensed film, on the assumption, of course, that the OH group plays no part in the spacing. Since this film is re-ported to be a *solid* film, it would be very plausible to suppose that the packing resembles that of the end-centered lattice in the *ac* face of crystalline benzene, Fig. 14. The nature of the close-packing which we here propose for this film is illus-trated in Fig. 18. The hydrogen atom dimensions (1.29 Å.) and the dome dimensions (2.45 Å.) are here exactly the same as in Fig. 14. It will be remembered that the lengths of the *a* and *c* axes in Fig. 14 are de-

Fig. 18.

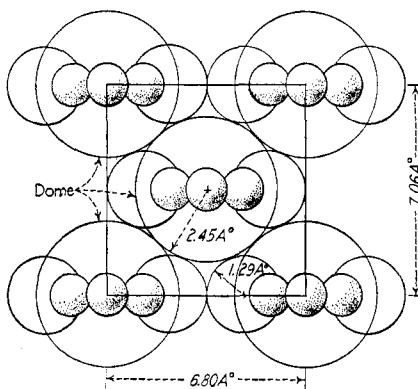termined by the nestling in of the middle stack of benzene molecules. Here, in Fig. 18, the domes would be expected to pack together tightly, allowing the setting up of the system of perfect contacts between hydrogen and hydrogen, dome and dome, and dome and hydrogen pairs, shown in Fig. 18.

The author has considered various other possible packings, involving the hydrocarbon chains as well as the benzene rings, but cannot find any arrangement that is nearly as quantitatively satisfactory as this one. The film area of this unit rectangle, which contains two molecules, is exactly 48.0 sq. Å., giving 24.0 sq. Å. per molecule. The possibility of this arrangement and spacing depends, of course, on the presence of the dome. This argument for the presence of the dome would therefore seem to carry considerable force.

3. **x-Ray Examination of Liquid Aromatics.**—Stewart[39] has deduced from his x-ray examination of liquid benzene and other liquid aromatics

[39] Stewart, *Chem. Rev.*, **6**, 495 (1929).

some spacings of the order 4.7 Å., which he supposed to correspond with the thickness of the rings as they are packed together in the liquid state. But, as Adam[40] points out, it is difficult to account for such a large spacing in terms of the ordinary conception of benzene molecule structure. Such spacings can, quite evidently, be satisfactorily explained with the aid of the dome.

4. Molecular Domain Due to Unsaturation.—In general it is to be expected that unsaturation such as that of the benzene ring, or of a double bond, or of a triple bond, will manifest itself as a geometrically symmetrical bulge more or less impenetrable by approaching atoms and molecules. For example, Titani[41] has calculated from his gaseous viscosity measurements the collision areas (he expresses the results in terms of radii) of 10.63, 10.29 and 10.63 sq. Å., respectively, for molecules of ethane, ethylene and acetylene. These results obviously indicate, even when the spins are taken into consideration, that ethylene and acetylene, which in spite of their smaller number of hydrogen atoms and smaller internuclear C–C distances present about the same target area in collision as ethane, acquire considerable domain by virtue of their unsaturation. Very likely the acquired bulge is produced by the repulsion of the bonding electrons.[42]

In addition to the arguments given above, mention may be made of a curious x-ray diffraction effect which Raman observed when working with graphite.[43] It seems likely that this effect, as well as the peculiar magnetic[44] properties of the aromatic ring, may be related to the dome.[45]

And now, at the end, if it may be granted that the empirical evidence presented here constitutes a reasonably good case for the existence of the dome, there are certain implications which follow from the presence of the dome on the aromatic ring. For example, it becomes possible to make a

[40] Adam, "The Physics and Chemistry of Surfaces," Oxford University Press, 1930, p. 106.

[41] Titani, *Bull. Chem. Soc. Japan*, **4**, 277 (1929); **5**, 98 (1930).

[42] In this general connection it is possible to marshal the arguments of the Sugden parachor and the various treatments of liquid molecular volume to show the probability of a bulge on the benzene ring due to unsaturation. We shall, however, refrain from so doing because of the well-founded suspicion that such arguments, based on an application of the additive principle to skeletal organic molecules, are likely to be extremely misleading.

[43] Raman, *Nature*, **124**, 53 (1929).

[44] Raman, *ibid.*, **123**, 945 (1929); Ehrenfest, *Physica*, **5**, 388 (1925).

[45] Since the present manuscript was submitted for publication, Mrs. Lonsdale has published a paper (Ref. 4) in which she gives a map of electron density contours for hexachlorobenzene. It is exceedingly interesting to note that she does find a considerable electron density over the face of the benzene ring, and it seems quite possible to interpret the density distribution as being that which one would expect for a dome. There is a question, however, as to what interpretation can be put on the curious figure-8 shape of the contours over the center of the ring, if indeed the resolution of the analytical method is powerful enough to establish the form definitely.

calculation of the compressibility of graphite, and also of the compressibility of the single-layer phenol films studied by Adam. The working out of the Crum–Brown rule and its modifications is probably in part a matter of the steric hindrance of the dome. The benzene molecule is inert chemically because it is sheathed in the fairly impenetrable electron cloud of the dome. When a foreign atom or group does manage to displace a hydrogen atom under the dome-deforming influence of such a thing as a catalytic surface, for example, then the electrical character of the substituent itself, when it has entered the ring, will play a controlling role in the precise nature of the resulting distortion of the dome, and the resultant guarding and unguarding of the various positions around the ring. A detailed consideration of conclusions to which some of these implications lead must be left for a future paper.

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Summary

The problem of the space gaps between molecules in organic crystals and the interlocking of the molecules in the lattice is stated, and the question of whether the molecular spacing can be accounted for by contact between out-lying hydrogen atoms is considered.

The "size of atomic domain" is defined for the purposes of the problem, and the actual sizes of the hydrogen domain radius in the gaseous and crystalline states are derived empirically.

In terms of a probable hydrogen atom size the spacings of the molecules and the symmetry of the lattice are explained for crystalline methane, ethane and hexamethylenetetramine.

From a consideration of some aromatic crystal lattices there emerges a proposed new feature of structure of the benzene ring, namely, *a dome-shaped electronic domain protruding symmetrically from both faces of the flat hexagonal ring*. In terms of this dome a stereochemical solution of the spacing of the layers in crystalline graphite is offered, and in terms of the dome and a constant hydrogen crystal radius of 1.29 Å. explanations are offered of the lattice symmetry and molecular spacing of anthracene, naphthalene and benzene. An attempt is also made to give a stereochemical solution of the structure of the hexamethylbenzene lattice.

Further arguments are presented for believing in the existence of the dome, including the empirical evidence of collision area, oil films, x-ray examination of liquid aromatics and molecular volume.

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