sively and assumed that atomization accompanies or follows ionization, a triatomic molecule of hydrogen being formed from the combination of the free atoms with the neighboring H_2 molecules.

It is interesting to note that the active hydrogen is produced in all cases under circumstances analogous to those in which ozone is produced. The analogy is evident from the work of Burt and Edgar.[1] The analogy is still further shown in the work on the evolution of active hydrogen in the decomposition of metallic hydrides by water, which is almost finished by the author. Work on the production of active hydrogen in the process of evolution of hydrogen in an absorbed condition from palladium and platinum is being carried on.

It is a pleasure to thank Y. Narasimham, Professor of Chemistry, in the Maharajah's College, Vizianagaram, for the interest he has taken in this work.

I am greatly indebted to Dr. G. L. Wendt, formerly of the University of Chicago, for the great interest he has taken in me and my work.

Vizianagaram, South India

[Contribution from the Chemical Laboratory of the University of California]

THE STRUCTURE OF BENZENE[1]

By Maurice L. Huggins[2]

Received July 11, 1922

The Structure and Dimensions of Graphite

The Disposition of Atomic Centers.—The structure of graphite has been studied by means of X-rays by Hull[3] and by Debye and Scherrer.[4] These investigators agree that the atomic centers are in layers of hexagons, as shown in Fig. 1. The relative intensities obtained by Hull from some of the "pyramid" planes indicate that each layer is "puckered" as in diamond, the nuclei being alternately in one or the other of two parallel planes (above and below the plane of the paper, in the figure). Debye and Scherrer give no evidence for or against such puckering, for they obtained no reflections from planes closer together than 0.815 Å., and it is only the reflections from such planes which can furnish evidence in regard to alternations of this type.

[1] This paper is an abridgment of a thesis presented by the author in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Much of the subject matter was presented at a meeting of the California Section of the American Chemical Society held in conjunction with the annual meeting of the Pacific Division of the American Association for the Advancement of Science at Berkeley on August 5, 1921. A short note on the subject has appeared in *Science*, **55**, 679 (1922).

[2] Du Pont Fellow in Chemistry, **1921–1922.**

[3] Hull, *Phys. Rev.*, [2] **10**, 692 (1917).

[4] Debye and Scherrer, *Physik. Z.*, **18**, 294 (1917).

Debye and Scherrer arrange the layers over each other as indicated in Figs. 2*a* and 2*b*. With puckered layers this is the same *marshaling* as in diamond. The hexagons are a little smaller, the distance between the two planes of atomic centers in each layer is slightly less, and that between adjacent planes in different layers is considerably greater in graphite, however.

Hull states that the structure which "fits the experimental data best of all that have been tried" is that represented by Figs. 2*a* and 3.

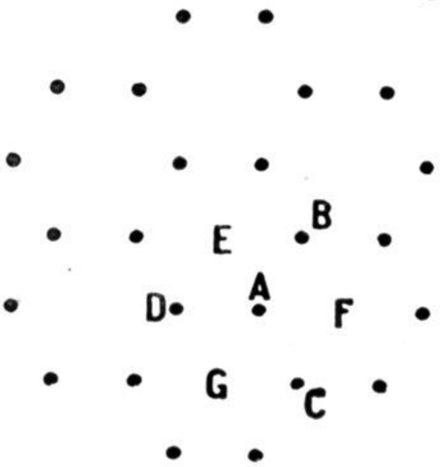

Fig. 1.—Arrangement of atomic centers in each layer in graphite.

The Arrangement of Electrons.—In each of these structures there is 3-fold symmetry around the vertical axis passing through each atomic center. There are but two ways in which the 4 valence electrons per atom can be arranged in accord with this symmetry: 1 electron from each atom must be on the vertical axis through the nucleus (A, Fig. 1), the other 3 being in equivalent positions around this axis, either (1) on (or near) the lines joining A with the 3 nearest atomic nuclei (B, C, D) in the same layer, or (2) on (or near) the lines connecting A with the centers (E, F, G) of the 3 surrounding hexagons.

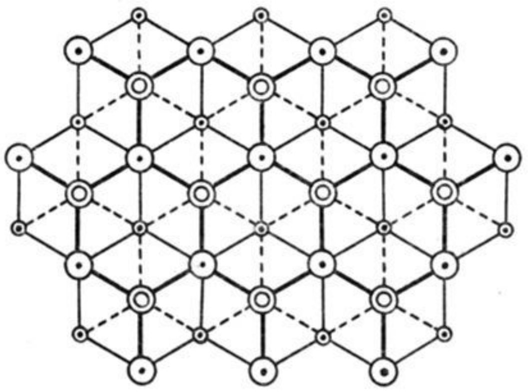

Fig. 2*a*.—Plan of the graphite structure. Debye and Scherrer : • Atomic centers in layer 1; ○ Atomic centers in layer 2; ⊙ Atomic centers in layer 3.

Hull: ◉ ⊙ Atomic centers in layer 1;

● ◎ Atomic centers in layer 2.

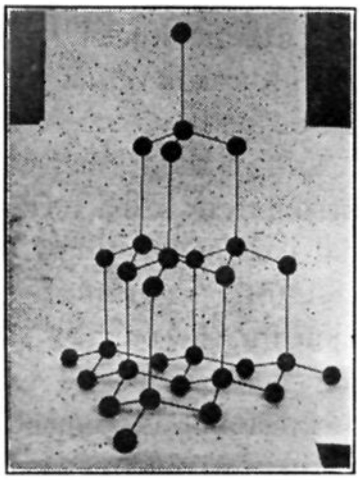

Fig. 2*b*.—Possible arrangement of atomic centers in graphite. The arrangement of the layers is according to Debye and Scherrer; the "puckering" in each layer is as determined by Hull.

Considering now the structure of Figs. 2*a* and 2*b*, the first alternative places 4 electron pairs in tetrahedral fashion around each atomic kernel, bonding it to the 4 neighboring atoms. This marshaling *of atoms and of electrons* is exactly the same as in diamond, and it can in no way account for the large distortions from the diamond structure. The second alternative results in a pair of electrons between nearest atoms in adjacent layers, and a *sextet* of electrons around the center of each hexagon within each layer. Representing each carbon atom by a tetrahedron (each corner being an electron), the arrangement in each layer is as illustrated in Fig. 4.

If we consider each *electron group* in such a structure as a scattering center for X-rays (scattering approximately in proportion to the number of electrons it contains), the distances between equivalent reflecting planes in the various directions are *exactly the same* as if all the scattering came from the atomic centers, the only differences in the spectra to be expected being small ones in the relative intensities of some of the lines. The available intensity data are so meager and unreliable that they cannot be used to check such differences.

The distortions from the diamond structure are easily accounted for by this electron arrangement. Each kernel is surrounded by 3 electron sextets and 1 electron pair, whereas in diamond there are 4 electron pairs around each kernel. Because of the much greater repulsion between electron sextets than between electron pairs, and the much greater attraction for atomic nuclei by sextets than by pairs, the distance between electron groups is much greater in graphite (2.47 Å. between the centers of electron sextets, according to Hull) than in diamond (1.26 Å. between pairs), and in the former each atomic nucleus is very close to the base of the surrounding valence tetrahedron. The distance between each nucleus and the pair connecting it to the next layer of atoms is nearly twice as great (1.46 Å.) in graphite as in diamond (0.77 Å.), because of the greater repulsion for the pair by the sextets at the base of the tetrahedron.

Since each pair is, therefore, but loosely held by the nuclei above and below it, the bonds connecting the layers are all very weak, thus accounting for the ready cleavage and gliding between layers, the great absorption of light (making the substance black), and the electrical conductivity of graphite.

In spite of the fact that the distance between each atomic nucleus and the center of each of the sextets around it is considerably greater than the distance from atomic center to electron pair in diamond, since the sextets in graphite are not on the atomic center lines (that is, since adjacent atoms are connected by double rather than single bonds), the distance *between atomic centers* in the same layer is even less in graphite (1.51 Å.) than in diamond (1.54 Å.).

If Hull's arrangement of atoms (Fig. 3) were correct, there would be the same two alternative arrangements of electrons within each layer, and *single* electrons on the vertical axes between layers, directly over or under each atomic kernel. Neither electron arrangement would account for the atomic arrangement above, a given layer being different from that below it, or for that above and below half of the layers being different from that above and below the other half. Also, the well-established tendency of valence electrons, in the outer shells of all but the most electropositive elements, to form groups of two or more,[5] makes such an arrangement of single electrons seem very improbable. For these reasons, Hull's interpretation of his X-ray data must be discarded, *in so far as the arrangement of layers over each other is concerned.*

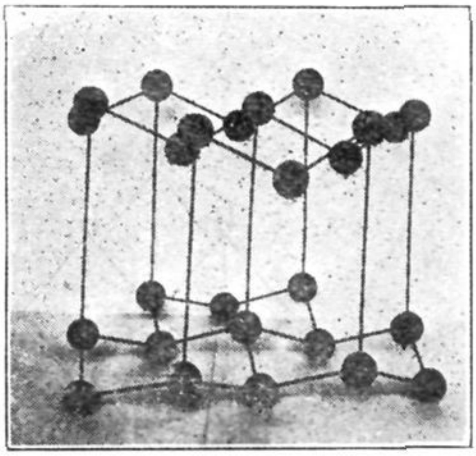

Fig. 3.—Arrangement of atomic centers in graphite, according to Hull.

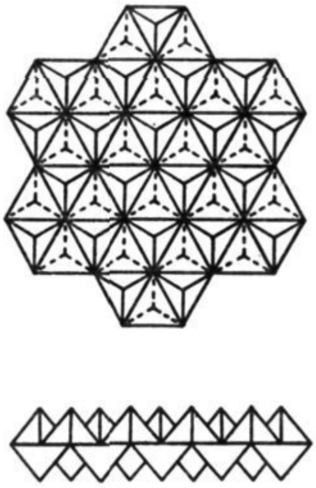

Fig. 4.—Arrangement of carbon tetrahedra in each layer in graphite.

Another Possible Structure.—There is another structure, very similar to those of Hull and of Debye and Scherrer, which, although it does not fully satisfy the experimental data, *considering the atoms as point-scattering centers,* may do so when electron positions are taken into account. This is the hexagonal arrangement represented in Figs. 4 and 5. It differs from the modified Debye-Scherrer structure (Figs. 2 and 4) only in the arrangement of the layers over each other, the two structures being related to each other as are the two forms of zinc sulfide, ZnS.

Considering the electron sextets as the major scattering centers, and the kernel electrons and the electron pairs between the layers as minor scattering centers, the interplanar distances to which X-ray spectrum lines should correspond are the same as for the structure given by Hull (on the basis of atomic center scattering). The relative intensities from the two structures should also be nearly the same.

The explanation already given for the distortions of graphite, based on the trigonal structure of Figs. 2 and 4, applies equally well to the hexagonal structure of Figs. 5 and 4. No attempt will be made here to decide between these two structures. (It is quite possible that both are correct.)

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[5] Lewis, This Journal, 38, 762 (1916).

For the present purpose it is unnecessary; the layers are the same in the two cases, and they are held together in the same manner.

Relation to the Structure of Benzene.—If we apply the Lewis theory of valence[5] to the *centroid* model[6] for benzene illustrated by Fig. 6, we obtain an electron sextet in the center of the structure, an electron pair joining each carbon to a hydrogen atom, and an electron pair at each of the hexagon corners. If units of this type are close-packed side by side, they form a layer such as that illustrated in Fig. 5, *in which the molecular boundaries are no longer distinguishable.*[7] Removing the hydrogen atoms and placing layer upon layer in such a way as to produce carbon-carbon bonds where carbon-hydrogen bonds had been, gives one or the other of the two possible graphite structures described above.[8]

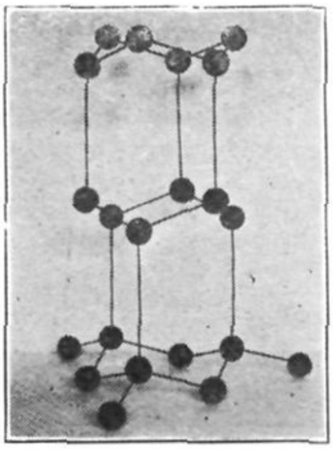

Fig. 5.—Another possible arrangement of atomic centers in graphite.

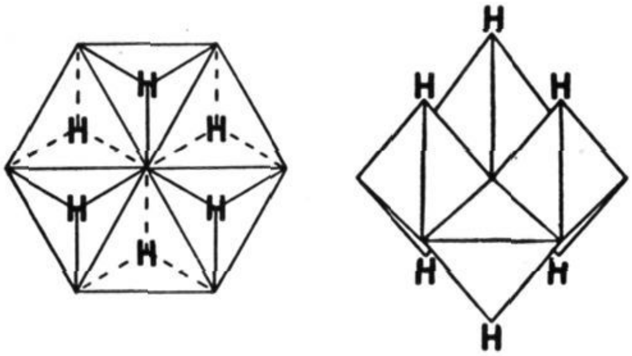

Fig. 6.—Körner's centroid model of benzene.

Dimensions.—From Hull's data the distance between electron sextets—the half-length of the benzene hexagon—is 2.47 Å.; the half-width of this hexagon is 2.14 Å.; and its area is 15.84 Å^2. The corresponding figures from Debye and Scherrer's data are 2.52 Å., 2.18 Å., and 16.47 Å^2., respectively. The probable error is given in each case as about 1%.

The Structures and Dimensions of Crystals of Aromatic Compounds

According to the writer's theory[6d] of the attraction between structures

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[6] (a) Körner, *Gazz. chim. ital.*, **4**, 444 (1874). (b) Marsh, *Phil. Mag.*, **26**, 426 (1888). (c) Vaubel, *J. prakt. Chem.*, [2] **44**, 137 (1891); **49**, 308 (1894); **50**, 58 (1894); "Lehrbuch der Theoretischen Chemie," Springer, Berlin, **1**, 468 (1903). (d) Huggins, *Thesis* for the Degree of Master of Science, Univ. of California, **1920**; THIS JOURNAL, **44**, 1607 (1922).

[7] This is important; only one other proposed benzene model (Baeyer's) can be close-packed in this manner, and layers composed of molecules of that kind could not possibly account for the reflections observed. Hence, if graphite is composed of benzene complexes, they *must* be of the type of Fig. 6.

[8] As is well known, benzene derivatives (graphitic and mellitic acids) are obtained by the oxidation of graphite.

containing valence electrons not on or near the center lines between atoms, molecules of benzene (or of many of its simple derivatives) should tend to associate, so as to form close-packed layers (Fig. 4), due to the *apparent* attractions between the electron pairs at the corners of the hexagons in different molecules. Since the forces tending to produce such a structure come into play most during the formation of crystals, we might expect crystals of these substances to be composed of layers of this kind. Provisionally assuming this to be the case, the dimensions of the centroid hexagon, in a number of such crystals, can be computed from the crystallographic data.

Quinol, $C_6H_4(OH)_2(1,4)$.—

Trigonal.[9] $a{:}c = 1 : 0.6680$.

$\rho = 1.328 - 1.332$ (mean $= 1.330$) g./cc.; $V^{10} = 136.54$ Å³.

Making the *preliminary* assumptions that the crystal is composed of close-packed hexagons, each of approximately the same area as one of the hexagons in graphite, and that the distance between layers is c, the volume of the unit cell, containing n molecules, must be roughly $nc \times 15.84$ Å². This is equal to nV; then, approximately,

$c \times 15.84$ Å² $= 136.54$ Å³, whence $c = 8.61$ Å., $a = 12.9$ Å. $= 6 \times 2.15$ Å.

Fig. 7 shows the only possible close-packed arrangement, possessing trigonal symmetry, of the molecules in each layer. The unit distance a computed above is equal to the shortest distance between equivalent points in each layer, thus checking the preliminary assumptions.

We can now proceed to determine the value of a more accurately.

$$3 \times \frac{a}{6} \times \frac{a \times 0.668\,a}{6 \sin 60^\circ} = V = 136.54 \text{ Å}^3$$

$a = 12.85$ Å. $= 6 \times 2.14$ Å. and $c = 0.668\,a = 8.59$ Å.

The half-width of the centroid hexagon ($a/6$) is 2.14 Å., *exactly the same as the corresponding distance in graphite* (as determined by Hull). This constitutes a remarkable verification of the assumptions upon which the preliminary calculations were based.

The precise manner in which the layers are situated with respect to each other is largely indeterminate by this method, and need not be considered here.

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[9] Crystals belonging to the trigonal system possess 3-fold symmetry about the vertical (c) axis. The ratio $a{:}c$ is that between the unit distance along either of the three equivalent a axes and that along the c axis.

The crystallographic data for this and the other compounds to be considered are from Groth's "Chemische Krystallographie," Wm. Engelmann, Leipzig, **4** (1917) and **5** (1919).

[10] The molecular volume, V, is computed from the relation $V = M/N\rho$, where M is the weight of a mol, N is Avogadro's constant (the number of molecules per mol), and ρ is the density.

Benzene, C_6H_6.—

Rhombic.[11] $a{:}b{:}c = 0.891 : 1 : 0.799$; ρ[12] = 1.015 g./cc.; V = 126.89 Å^3

Assuming, as before, that the crystal is composed of layers of close-packed hexagons, that the area of each hexagon is approximately equal to 15.84 Å^2, and that the distance between layers is c, we can calculate the preliminary values,

$$b = \frac{126.89\ \text{Å}^3}{0.779 \times 15.84\ \text{Å}^3} = 10.01\ \text{Å}. = 4 \times 2.50\ \text{Å}^3$$

$$a = 0.891\, b = 8.92\ \text{Å}. = 4 \times 2.23\ \text{Å}.$$

Since 2.50 Å. and 2.23 Å. correspond fairly closely to the distances 2.47–2.51 Å. and 2.14–2.17 Å. in graphite, we can assume a and b to be the distances indicated in Fig. 7, and proceed to calculate them directly from the axial ratios and the density.

$$b = \sqrt[3]{\frac{126.89\ \text{Å}^3}{\frac{0.891}{4} \times \frac{0.799}{4} \times 3}} = 9.83\ \text{Å}. = 4 \times 2.46\ \text{Å}.$$

Then $a = 0.891\, b = 8.76$ Å. $= 4 \times 2.19$ Å.; and $c = 0.799\, b = 7.86$ Å.

The elementary distances $a/4$ and $b/4$ compare favorably with the corresponding distances in graphite, but show that the benzene structure is considerably distorted (at least if the axial ratios are correct) due, no doubt, to the way in which the layers are superimposed on each other; a is twice and b is $^4/_3$ what we should expect if the hexagons in each layer were directly over those in the next layer underneath, without rotation. The reason for this must also be looked for in the arrangement of the layers relative to each other.[13]

Resorcinol, $C_6H_4(OH)_2$ (1, 3).—

Rhombic. $a{:}b{:}c = 0.9105 : 1 : 0.5404$.
ρ = 1.281 – 1.285 (Mean = 1.283) g. /cc.; V = 141.53 Å^3

Proceeding in the same way as for benzene, we can calculate for resorcinol

b = 16.63 Å. = 8 × 2.08 Å.; a = 15.14 Å. = 6 × 2.52 Å.; c = 8.99 Å.

The centroids are slightly elongated in the a direction and shortened in the b direction, but no more than might be expected from the fact that

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[11] Rhombic crystals possess 3 unequal axes at right angles to each other.

[12] Richards, Bartlett and Hodges, This Journal, **43**, 1538 (1921).

[13] The method of calculation gives the unit distances in each layer, assuming that the axial ratios are correctly given, and that c is the distance between adjacent layers. If c is n times this distance, then a and b are each n times the unit distances calculated for them. Since the dimensions calculated for the unit hexagon would be the same, whether c is the inter-layer distance or a multiple of it, for the present purpose we can assume it to be the former, even if that does lead us to such values for a and b as those computed above. In benzene, the value computed for b indicates that the true unit distances are probably 3 times those given.

The unusual multiples of the dimensions of the unit hexagon obtained for the unit distances in benzene and the fact that the agreement with the graphite dimensions is only fair may perhaps indicate that the crystallographic data are unreliable or that the assumption of close-packing is *in this case* wrong.

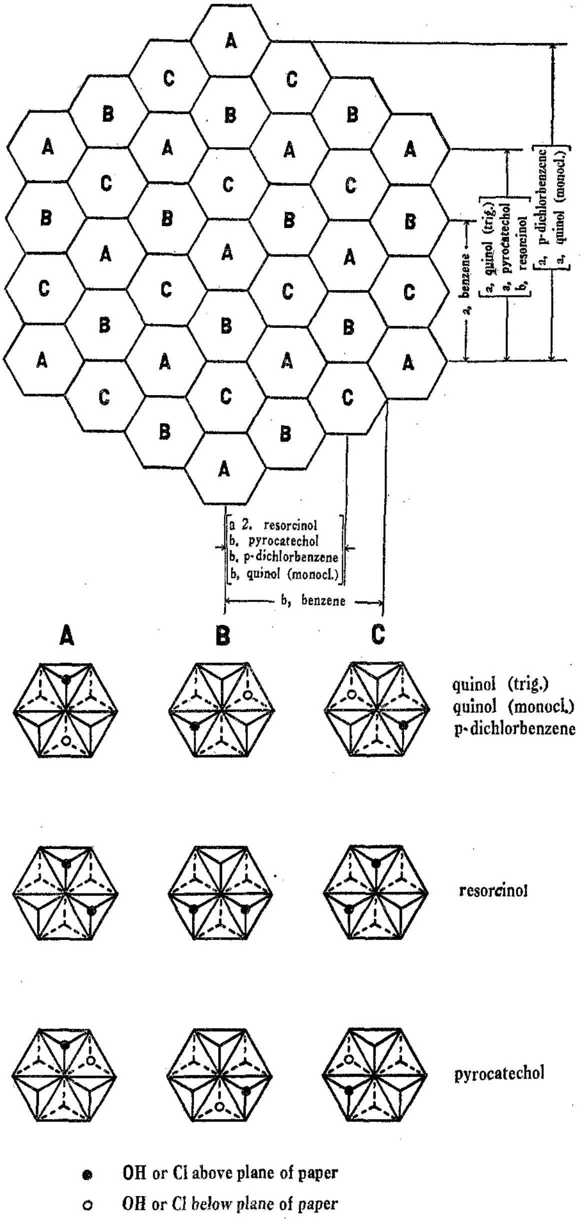

Fig. 7.—Arrangement of the atoms and molecules in crystals of various aromatic compounds, with the unit distances (or simple divisors of them).[13]

the crystal does not possess 3-fold symmetry around the vertical axis. The distances a and b are indicated in Fig. 7.

***p*-Chloro-aniline,** $C_6H_4NH_2(1)Cl(4)$.—

Rhombic. $a{:}b{:}c = 0.935:1:0.804$; $\rho = 1.427$ g./cc.; $V = 147.44$ Å^3.

In crystals of this substance (010) faces, but no (001) faces have been observed. This suggests that if the molecules are in close-packed layers, these layers are parallel to the (010) planes, rather than to the (001) planes. In corroboration of this idea, if we put $b' = c$ and $c' = b$, obtaining $a{:}\,b'{:}\,c' = 1.165{:}\,1{:}\,1.245$, and perform the calculations as for the previous compounds, we can compute

$b' = c = 7.42$ Å. $= 3 \times 2.47$ Å.; $a = 8.62$ Å. $= 4 \times 2.16$ Å.; $c' = b = 9.22$ Å.

Pyrocatechol, $C_6H_4(OH)_2(1, 2)$.—

Monoclinic.[14] $a{:}b{:}c = 1.6086:1:1.0229$; $\beta = 95°15'$.
$\rho = 1.367 - 1.375$ (mean $= 1.371$) g./cc.; $V = 132.45$ Å^3.

If we assume the centroids to be close-packed in the ab planes, the distance between layers, along a line normal to them, is

$c' = c \sin \beta = 1.0186\, b$.

We then have $a{:}\,b{:}\,c' = 1.6086{:}\,1{:}\,1.0186$ and, using the same method of calculating these distances as in the foregoing examples, we obtain

$b = 7.86$ Å. $= 3 \times 2.62$ Å.; $a = 12.64$ Å. $= 6 \times 2.11$ Å.; $c' = 8.00$ Å. $c = 8.04$ Å.

The most probable arrangement of the molecules in each layer is that pictured in Fig. 7.

***p*-Dichlorobenzene,** $C_6H_4Cl_2(1, 4)$.—

Monoclinic. $a{:}b{:}c = 2.5193:1:1.3920$; $\beta = 122°30'$; $a{:}b{:}c' = 2.5193:1:1.286$.
$\rho = 1.526$ g./cc.; $V = 158.69$ Å^3.

Performing the calculation as for the preceding compound, the unit distances are found to be

$b = 7.61$ Å. $= 3 \times 2.54$ Å.; $a = 19.18$ Å. $= 9 \times 2.13$ Å.; $c' = 9.79$ Å.; $c = 10.60$ Å.

The marshaling of the molecules in each layer is probably the same as in the trigonal form of quinol. If so, considering each layer separately, the unit distance would be 6 (instead of 9) times 2.13 Å. The discrepancy must be attributed, as before, to the way in which the layers are laid over each other.

Quinol, $C_6H_4(OH)_2(1, 4)$.—

Monoclinic. $a{:}b{:}c = 2.605:1:1.558$; $\beta = 107°$.

The density of this form of quinol is apparently not in the literature, and without it the unit distances cannot be directly computed. The axial ratio, however, is very similar to that of *p*-dichlorobenzene, and if we assume that the two substances possess the same type of structure, consider the axial ratio and angle as correctly determined, and take a as about 19.26 Å. $= 9 \times 2.14$ Å. (from graphite, *p*-dichlorobenzene, and the

---

[14] Monoclinic crystals have two axes, a and b, at right angles with each other, and a third, c, making a right angle with b, but some other angle, β, with a.

trigonal modification of quinol), then we can compute approximate values of b, c, and the density. We obtain in this way,

$$b = a/2.605 = 7.39\ \text{Å.} = 3 \times 2.46\ \text{Å.};\ c = 1.558\,b = 11.52\ \text{Å.};\ c' = c \sin 107° = 11.02\ \text{Å.}$$

$$V = abc'/9 = 174.3\ \text{Å}^3;\ \rho = M/VN = 1.04\ \text{g./cc.}$$

If the axial ratio and angle were accurately known, we might expect the true density to be very near the above value; but the crystallographic data are admittedly only approximate, due to the fact that the crystals measured were very thin (001) flakes. Some of these crystals have been prepared by the author and found to have a density of 1.18 g./cc. This may be taken to indicate that the true distances c and c' are shorter than those computed, which is what we should expect, for the inter-layer distance in the trigonal form of quinol is but 8.59 Å.

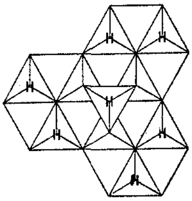

Fig. 8.—Triphenylmethane.

Triphenylmethane, $(C_6H_5)_3CH$, and Its Derivatives.—The triphenylmethane molecule is illustrated in Fig. 8. The 3 centroids lie in (or nearly in) the same plane, held together by the "residual affinity" at the corners of each hexagon. The methane hydrogen atom is directly over the center of the complex. These triphenyl units, like the simple hexagons, may readily form close-packed layers (Figs. 9 and 10). They

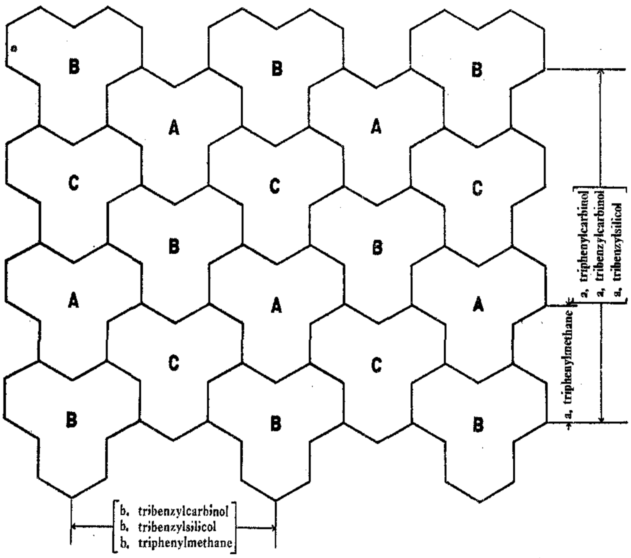

Fig. 9.—Arrangement of triphenyl units in close-packed layers, with unit distance[14] for various compounds.

may also form layers containing holes the size and shape of a single centroid (Figs. 11 and 12).[15]

Triphenyl carbinol, $(C_6H_5)_3COH$.—

Trigonal. $a:c = 1 : 0.6984$.
$\rho = 1.188$ g./cc.; $V = 361.3$ Å^3

A molecule of triphenyl carbinol does not possess 3-fold symmetry about a central axis normal to the plane of the 3 centroids, for, due to the tetrahedral shape of the oxygen atom, the hydroxyl hydrogen atom cannot lie on this axis. If these molecules are close-packed in a crystal layer so as to give trigonal symmetry, then (Fig. 9) they must be oriented in three different ways, differing in the position of this hydrogen relative to the molecular axis (compare quinol, Fig. 7). These three orientations are denoted in Fig. 9 by the letters A, B and C.

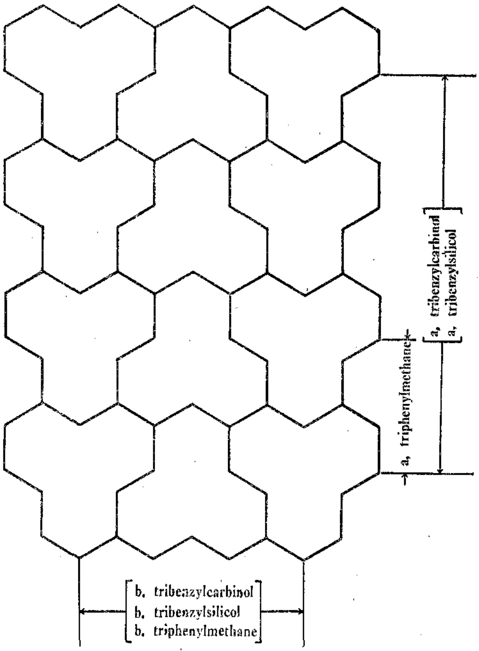

Fig. 10.—Another possible arrangement of close-packed triphenyl units.

Assuming close-packing and that c equals the inter-layer distance we can compute,

$a = 11.04$ Å. $= 4.5 \times 2.45$ Å.; $c = 7.71$ Å.

This value of a is just half what we should expect from the structure of Fig. 11; hence, the real unit distances are probably,

$a = 22.08$ Å. $= 9 \times 2.45$ Å.; and $c = 15.43$ Å.,

the distance between layers, however, remaining[16] 7.71 Å.

The triphenyl carbinol molecules might possibly be assembled in the manner depicted in Fig. 11. The unit distances calculated on this assumption are

$a = 8.42$ Å. $= 4 \times 2.11$ Å.; $c = 5.88$ Å.

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[15] Compare Barlow and Pope, *J. Chem. Soc.*, **89**, 1675 (1906). When triphenylmethane is crystallized from benzene, the crystals contain a molecule of benzene for each molecule of triphenylmethane, the former in all probability occupying the hexagonal spaces between the molecules of the latter, marshaled as in Fig. 11 or Fig. 12.

[16] If the hydroxyl groups in each layer are all on the same side of the plane of the centroids, then the layers must alternately have these groups above and below this plane in order to give the required symmetry. If this is the case, the distance between 2 adjacent planes will be alternately less and greater than 7.71 Å.

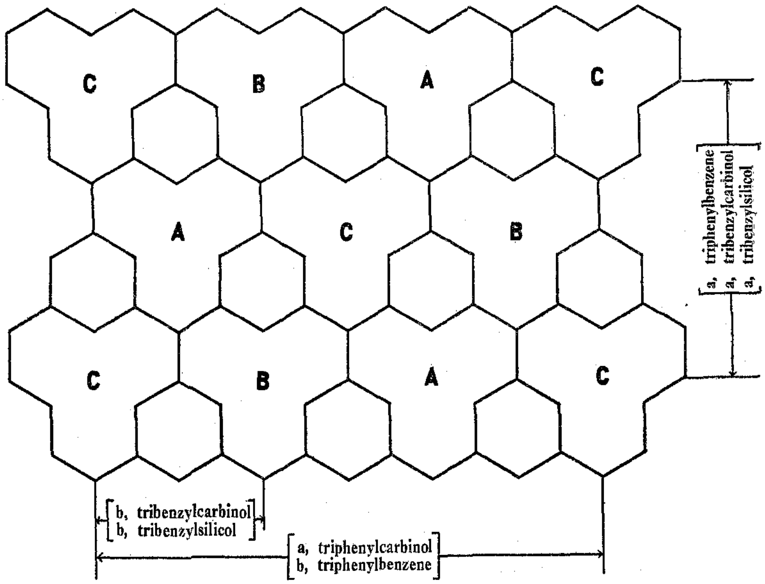

Fig. 11.—Arrangement of triphenyl units in semi-close-packed layers.

a corresponds to the shortest distance between molecular centers. Either the three orientations of the hydroxyl hydrogen atoms do not affect the crystallographic form, or the true unit distances are 3 times those given above.

Triphenylbenzene, $C_6H_3(C_6H_5)_3$.—

Rhombic. $a:b:c = 0.5662 : 1 : 0.7666$.

$\rho = 1.206$ g./cc.; $V = 418.9$ Å^3

The triphenylbenzene molecule (Fig. 13) according to the writer's theory, should also contain a triphenyl unit of approximately the same size and shape as that in triphenylmethane (as well as a single centroid, in another parallel

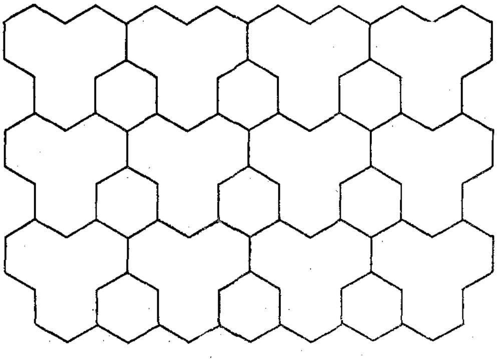

Fig. 12.—Another possible arrangement of triphenyl units in semi-close-packed layers.

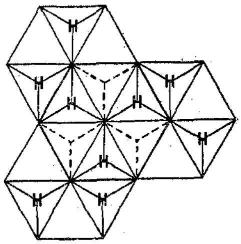

Fig. 13.—Triphenylbenzene.

plane, over the center of the triphenyl unit). Calculations similar to those for triphenyl carbinol show that these molecules form layers of the type of Fig. 11, and that c is 3 times the distance between layers. The unit distances are,

b = 25.90 Å. = 12 × 2.16 Å.; a = 14.66 Å. = 6 × 2.44 Å.; c = 19.85 Å. = 3 × 6.62 Å.

Tribenzyl carbinol, $(C_6H_5CH_2)_3COH$.—

Rhombic. $a{:}b{:}c$ = 1.7166 : 1 : 2.1574.
ρ = 1.187 g./cc.; V = 420.1 Å^3.

Molecules of tribenzyl carbinol also contain triphenyl complexes. If we assume close packing in each layer, and take c as 3 times the interlayer distance, we can compute,

b = 12.69 Å. = 6 × 2.11 Å.; a = 21.78 Å. = 9 × 2.42 Å.; c = 27.37 Å. = 3 × 9.12 Å.

Another alternative is to assume a structure of the type of Fig. 11. Then, taking c as twice the distance between layers, we find,

b = 8.46 Å. = 4 × 2.11 Å.; a = 14.52 Å. = 6 × 2.42 Å.; c = 18.25 Å. = 2 × 9.12 Å.

Either assumption gives reasonable values for the unit distances, although a per cent. or two lower than we might expect, due probably to inaccurate axial ratio or density determinations.

Tribenzyl silicol, $(C_6H_5CH_2)_3SiOH$.—

Rhombic. $a{:}b{:}c$ = 1.7214 : 1 : 2.1384.
ρ = 1.177 g./cc.; V = 446.5 Å^3.

Making the same assumptions as for the preceding compound, the unit distances may be calculated to be,

b = 12.97 Å. = 6 × 2.16 Å.; a = 22.33 Å. = 9 × 2.48 Å.; c = 27.74 Å. = 3 × 9.25 Å.

or,

b = 8.65 Å. = 4 × 2.16 Å.; a = 14.89 Å. = 6 × 2.48 Å.; c = 18.49 Å. = 2 × 9.25 Å.

Triphenylmethane, $(C_6H_5)_3CH$.—

Rhombic. $a{:}b{:}c$ = 0.5716 : 1 : 0.5867.

The writer has been unable to find the density of crystals of this substance in the literature. It is significant, however, that the ratio of a to b is nearly that of the unit distances (0.5774 : 1) in undistorted close-packed layers of the type represented by Fig. 9 or that of Fig. 10. Taking either of these marshalings as correct, the density has been calculated from the axial ratio, first on the assumption that a = 3 × 2.47 Å. = 7.41 Å., then assuming that b = 6 × 2.14 Å. = 12.84 Å. The values obtained are 1.103 g./cc. and 1.135 g./cc.

When these calculations were made, it was predicted that the true density would be between these values. Since then, a rough determination of this constant has been made, the value obtained being 1.106 g./cc., in full agreement with the prediction.

Using the experimental value to calculate the unit distances, we find,

b = 12.95 Å. = 6 × 2.16 Å.; a = 7.40 Å. = 3 × 2.47 Å.; c = 7.60 Å.

Comparative Distances.—More examples might be given, but those already discussed are sufficient to show conclusively that the elementary hexagon has practically the same dimensions in these aromatic compounds as it has in graphite; also that these hexagons tend to form close-packed layers, resembling those in the graphite structure.

For purposes of comparison, the computed half-lengths and half-widths of the centroid hexagons in the various crystals considered are given in Table I.

TABLE I

COMPARATIVE DIMENSIONS OF THE BENZENE HEXAGON COMPUTED FOR VARIOUS CRYSTALS

	Half-length (Å.)	Half-width (Å.)		Half-length (Å.)	Half-width (Å.)
Graphite (Hull).....	2.47	2.14	p-$C_6H_4Cl_2$.......	2.54	2.13
Graphite (D. and S.)	2.52	2.18	$(C_6H_5)_3COH$.....	2.45 (or 2.43)	2.13 (or 2.11)
p-$C_6H_4(OH)_2$, trigonal	2.47	2.14	$C_6H_3(C_6H_5)_3$.....	2.44	2.16
C_6H_6..............	2.46	2.19	$(C_6H_5CH_2)_3COH$.	2.42	2.11
m-$C_6H_4(OH)_2$.......	2.52	2.08	$(C_6H_5CH_2)_3SiOH$	2.48	2.16
p-$C_6H_4(Cl)NH_2$.....	2.47	2.16	$(C_6H_5)_3CH$......	2.47	2.16
o-$C_6H_4(OH)_2$........	2.62	2.11			

Limitations of the Methods of Calculation.—The methods of calculation used in this paper can be applied (without X-ray data) to but a limited class of compounds. Fairly accurate axial ratio, axial angle, and density data must be available; the molecules must form close-packed layers or be assembled in some other regular manner for which (in the preliminary calculations) the approximate area per molecule can be computed; and the distortions from the graphite dimensions must not be very great. For instance, in compounds in which there is attached to the centroid a group containing a double bond in such a position that it can conjugate with the ring (usually —A = B; in general, a *meta*-directing group), we should not expect close-packing, if the author's theory of the structure of such compounds is correct.[6d] In crystals of naphthalene, anthracene,[6d] and their derivatives, close-packing is also impossible.

Summary

1. The X-ray experimental data of Hull and of Debye and Scherrer indicate a structure for graphite composed of layers of close-packed benzene complexes of the type originally proposed by Körner. (See Fig. 6.)

2. Assuming similar close-packed layers in crystals of benzene and many of its derivatives, the dimensions of the benzene hexagon can be computed from the crystallographic data. This has been done for the compounds listed in Table I, the dimensions in each case being within a few per cent. of the corresponding distances in graphite.

3. Incidental to the above, the arrangements of molecules, atoms, and electrons in the crystals considered have been partially determined.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

LUMINESCENCE OF COMPOUNDS FORMED BY THE ACTION OF MAGNESIUM ON PARA-DIBROMOBENZENE AND RELATED COMPOUNDS

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The ethereal solution formed by the action of magnesium on *p*-dibromobenzene, when exposed to the action of air or oxygen, is strongly chemiluminescent. Since this reaction is more luminescent than the oxidation of pyrogallol, or the chloropicrin and phenylmagnesium iodide (Wedekind)[1] reaction, and can be maintained for some time, it was thought worthy of investigation. Furthermore, both light emission and light absorption promise to show us a relation between radiation and chemical energy. Heczko[2] has shown that ethereal Grignard solutions react with oxygen with light emission, and Moeller[3] shows later that this luminescence appears only with aromatic compounds.

Previous work on the action of magnesium on dihalogen aromatic compounds points to the fact that with dibromobenzene but one halogen reacts, while with di-iodo-benzene both halogens are active. Tschitschibabin,[4] who used the reaction in the preparation of *p*-bromobenzaldehyde, claims that only one halogen reacts. F. Bodroux[5] in his work on nuclear dihalogen aromatic compounds found only one halogen active. Gomberg and Cone[6] also obtained the monohalogen derivative. On the other hand, E. Votocek and J. Kohler[7] find that with *p*-di-iodobenzene both halogens react.

Experimental Part

The *p*-bromophenylmagnesium bromide was prepared by the usual method.

The best results were obtained when 2.4 g. of magnesium and 23.6 g. of *p*-dibromobenzene were mixed in 130 cc. of dry ether in a flask connected with a reflux condenser. If the materials are perfectly dry, and iodine is used as a catalyst, the reaction begins at once and progresses smoothly. At the conclusion the flask was heated and a slight

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[1] Wedekind, *Z. wiss. Phot.*, **5**, 29 (1907).

[2] Heczko, *Chem.-Ztg.*, **35**, 199 (1911).

[3] Moeller, *Arch. Pharm. Chem.*, **1914**.

[4] Tschitschibabin, *Ber.*, **37**, 186 (1904).

[5] Bodroux, *Compt. rend.*, **136**, 1138 (1903).

[6] Gomberg and Cone, *Chem. Centr.*, **1906**, II, 1612.

[7] Votocek and Kohler, *Ber.*, **47**, 1219 (1914).