

THE CRYSTAL STRUCTURES OF ORGANIC COMPOUNDS¹

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Received July 29, 1930

Methods for the analysis of crystal structures of inorganic compounds have been greatly extended since M. von Laue's prediction of x-ray diffraction by crystalline lattices. Within recent years generalizations based upon physical laws and upon empirical analyses of existing structural information, together with increase in knowledge concerning the factors affecting the intensities of x-ray reflections from crystals, have made possible determinations of the structure of very complex compounds having low crystallographic symmetries. The concept of inorganic compounds as composed of spatial arrays of approximately spherical atoms of "constant radii" in contact (1) has, in a somewhat modified form, proven of great utility in structure determinations (2, 3, 4).

Complete determinations of structure have been made for but few organic compounds. The results obtained have not markedly facilitated the analysis of other structures. The difficulties of analysis partially arise from the low crystallographic symmetries of most organic crystals. The factors determining the intensities of the x-radiation coherently scattered from atoms of low atomic number, such as oxygen, nitrogen, carbon, and hydrogen, are not as completely evaluated as for heavier atoms. Thus such atoms can not easily be allocated in the structures, and in the case of hydrogen atoms the data as to the intensity of reflection alone are insufficient to permit their allocation.

¹ To economize space no exposition of the notation employed for crystal structures is included in this review. Reference 6a cites a complete discussion of notation and technical terms.

Completely determined atomic arrangements for some organic compounds indicate that there are groups of atoms in such crystals that are repeated as groups throughout the crystals. The groups that are to be identified as the organic molecules are probably to be characterized by the approximate constancy of distances of closest approach between adjacent atoms within the groups. It should be possible to determine from the derived crystal structures alone the characteristic carbon to nitrogen, carbon to carbon, etc., distances in molecules of organic compounds in the solid state, and to check the constancy of the distances. The spatial distributions of the molecules and their distances of approach to other molecules have not yet been shown to be similar in different compounds. Since the intensities of the x-ray beams diffracted from the crystals are functions of both the intramolecular and the intermolecular configurations, this apparent lack of regularity increases most markedly the difficulties of the structure analyses.

Information obtained from the x-ray diffraction patterns of some organic crystals is described in this paper. Results of particular significance to structural organic chemistry are discussed under the specific compounds. An attempt is made to obtain from the structures discussed certain relationships which might be of assistance in structural analysis. No effort is made to give an exhaustive survey of all available x-ray diffraction data from organic compounds, since the greater part of these data merely serve to extend the crystallographic descriptions. Such information is summarized in standard references (5) and is currently abstracted in the *Zeitschrift fur Kristallographie*.

TYPES OF INFORMATION OBTAINED

The analysis of the x-ray diffraction data from a particular compound leads to a determination of the smallest parallelepiped which, when repeated, gives the macroscopic crystal. This is the "unit of structure." It must contain an integral number of molecules or formula weights of the substance.

The characteristic types of reflections observed to be absent, together, if necessary, with a crystallographic determination of

the crystal class, determine the symmetry elements of the unit of structure and thus lead to one of the 230 groups of operations giving crystalline symmetry. This is the space-group.

The observation that the number of molecules in the unit of structure is less than the number of asymmetrical points obtained by repeating a point according to the symmetry operations of the space-group requires the molecule to have symmetry. This, with certain exceptions noted later, gives the minimum possible symmetry of the molecule. The actual symmetry may be, and sometimes is, greater than this minimum. If the number of molecules in the unit of structure is greater than the number of asymmetrical points, then the molecular groups must be either crystallographically non-equivalent or associated in groups that are crystallographically (6) equivalent. The structures of the aromatic hydrocarbons which are discussed later illustrate these requirements.

It is sometimes possible to determine completely the position of each constituent atom without the use of assumptions concerning the probable arrangement. Such complete structure determinations have supplied information of fundamental importance to structural organic chemistry. The complexity of the problem, however, usually necessitates the reverse procedure of assuming structures which are chemically logical and ascertaining whether they can or cannot explain the observed intensities of reflections.

In the following partial review complete structure determinations are first considered. The structures, if they are sufficiently complete, are described by giving the atomic positions in terms of coördinates referred to specified axes (6a). Some results of determinations of the unit of structure, of the space-group and of molecular symmetry are discussed. Atomic positions are represented by small circles on the figures; these circles do not indicate the relative atomic sizes. The distances on the figures are given in Ångström units ($1 \text{ \AA} = 10^{-8} \text{ cms.}$).

STRUCTURE DETERMINATIONS

The crystal structures of halogen substituted compounds

The amplitudes of the waves coherently scattered by various kinds of atoms in a crystal are, in the first approximation, func-

tions of the atomic number and of $\sin \theta/\lambda$, where θ is the angle of reflection and λ the wave length of the x-radiation. It is usually assumed that at 0° the amplitude of the scattered wave is directly proportional to the atomic number. In a crystal containing atoms of high and low atomic number the intensities of reflection

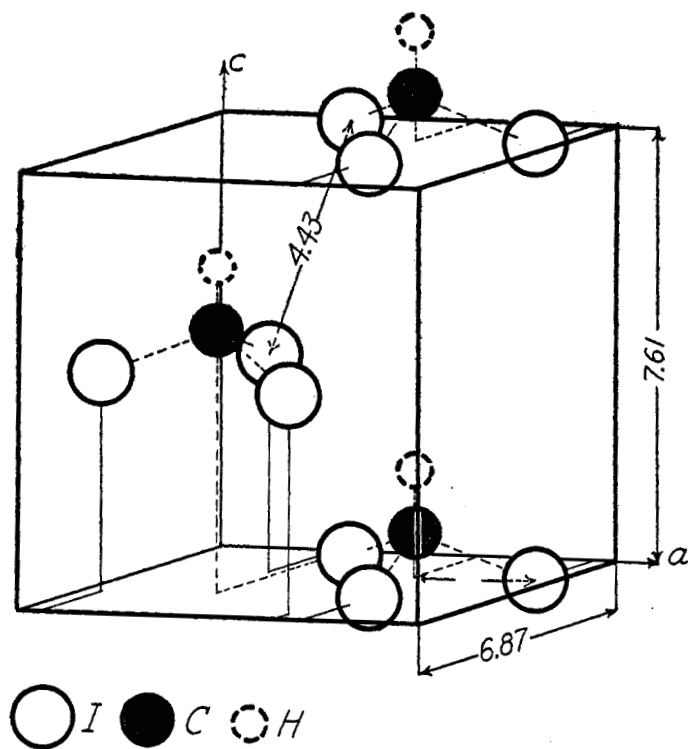


FIG. 1a. IODOFORM, CHI_3 . THE UNIT OF STRUCTURE

The indicated positions of the hydrogen atoms are hypothetical.

of x-radiation depend most markedly upon the distributions of atoms of high atomic number. In a crystal containing, for instance, carbon, hydrogen, and iodine, the effect of the carbon and hydrogen on the intensities of reflection often can not be detected. For this reason it is sometimes possible to determine quite accurately the positions of the heavier atoms in crystals

having complex structures. Advantage has been taken of this fact in the structure analyses of a number of aliphatic compounds discussed below.

Iodoform (7). The hexagonal unit of structure containing

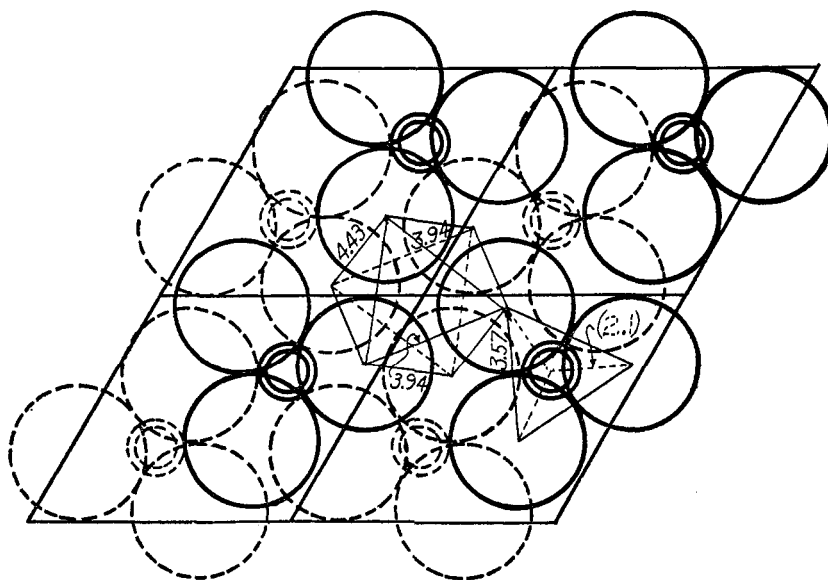


FIG. 1b. IODOFORM, CHI_3 . A PROJECTION ON THE BASAL PLANE (00.1)

The octahedral arrangements of atoms of separate molecules are shown on the projection. Iodine atoms below the plane of projection are shown as large dotted circles; the carbon and hydrogen atoms are shown as small dotted circles.

2CHI_3 has $c = 7.61 \text{ \AA}$. and $a = 6.87 \text{ \AA}$. The iodine atoms are at space-group C_3^6 (6a)

$$x, y, z; y - x, \bar{x}, z; \bar{y}, x - y, z$$

$$\bar{x}, \bar{y}, z + \frac{1}{2}; x - y, x, z + \frac{1}{2}, y, y - x, z + \frac{1}{2}$$

with $x = 0.346 - 0.362$, and $y = 0.038 - 0.056$. (Limits of certainty are given; z may be assumed to be zero.) The minimum molecular symmetry is probably a threefold axis. The unit of structure and a projection on (00.1) are shown in figures 1a and 1b.

The relative positions of the iodine atoms are defined by two

determined parameters. The interatomic distances are shown in figures 1 and 2. If the carbon atoms are at $\frac{1}{3}, \frac{2}{3}, u; \frac{2}{3}, \frac{1}{3}, u + \frac{1}{2}$ (u_c is undetermined), then the minimum I—I distance, about 3.57 Å., is that between atoms of the same molecule. In this case the iodine atoms of separate molecules are located at the corners of octahedra the edges of which are 3.94 Å. and 4.43 Å. in length (note figure 1).

A representation of a single molecule is shown in figure 2. In this figure the dotted portions are unknown. It is possible, but quite improbable, that the carbon atoms are at $00u; 00, u + \frac{1}{2}$ (space-group C_{6v}^2). In either this or the above case the C—I distance is > 1.97 Å., and is probably about 2.10 Å.

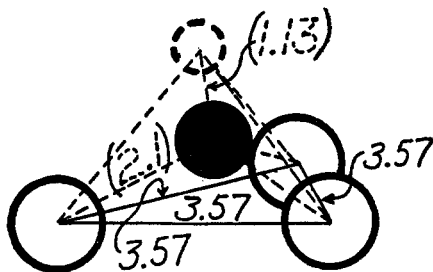


FIG. 2. IODOFORM, CHI_3 . MOLECULAR CONFIGURATION

The undetermined portions are dotted. See figure 1b for description.

1,2,3,4,5,6-Hexabromo- and hexachloro-cyclohexane (8). The cubic units of structure containing $4\text{C}_6\text{H}_6\text{X}_6$ have the dimensions $a = 10.49$ Å. ($\text{C}_6\text{H}_6\text{Br}_6$) and $a = 10.07$ Å. ($\text{C}_6\text{H}_6\text{Cl}_6$). The halogen atoms are in the general positions of the space-group T_h^6 . The peculiarities in the intensities of reflection from (111) in various orders made possible determinations of the three parameters defining the positions of the halogen atoms. The parameter values are: $x = 0.39$, $y = 0.22$, and $z = 0.085$ for both $\text{C}_6\text{H}_6\text{Br}_6$ and $\text{C}_6\text{H}_6\text{Cl}_6$.

The minimum molecular symmetry is a threefold axis and a center of symmetry. The molecular centers are at

$$(a) \quad 0, 0, 0; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}$$

or

(b) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; 0, 0, \frac{1}{2}$

These two possible molecular configurations are shown in figure 3. It is quite probable that the correct structure is as shown in figure 3a and that figure 3b represents the closest approach of halogen atoms of separate molecules (3.74 Å.). Here, as for CHI_3 (compare), the halogen atoms of separate molecules are approximately at the corners of an octahedron (figure 3b).

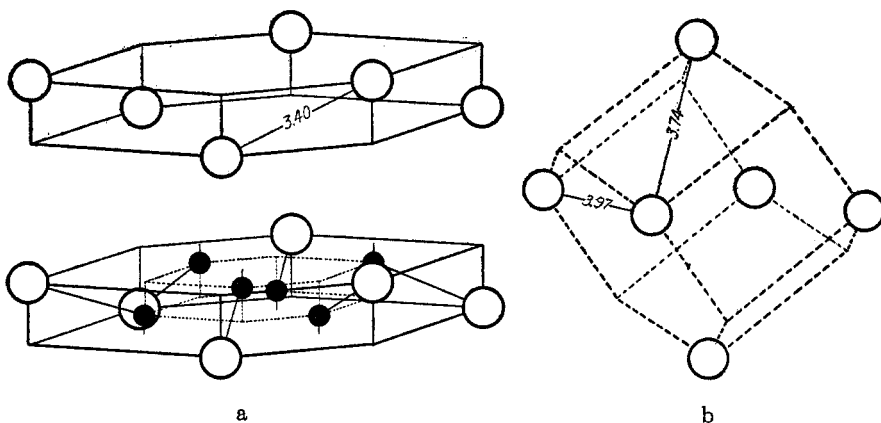


FIG. 3a. 1,2,3,4,5,6-HEXABROMOCYCLOHEXANE, $\text{C}_6\text{H}_6\text{Br}_6$. MOLECULAR CONFIGURATION

Possible positions of the carbon atoms (black circles) are indicated.

FIG. 3b. 1,2,3,4,5,6-HEXABROMOCYCLOHEXANE, $\text{C}_6\text{H}_6\text{Br}_6$. OCTAHEDRAL ARRANGEMENT OF ATOMS OF SEPARATE MOLECULES

Bromine atoms alone are shown.

If the carbon atoms are assumed to be situated as shown in figure 3a, the C—C distance being 1.54 Å. as in the diamond, with $x = -0.076$, $y = +0.099$, and $z = -0.065$ for the bromide, and $x = -0.079$, $y = +0.103$, and $z = -0.068$ for the chloride, then the C—Br distance is about 1.94 Å., and the C—Cl distance is about 1.81 Å. This assumed structure gives a tetrahedral distribution of the carbon valences, which might be expected from the aliphatic nature of the compound.

Some simple derivatives of ethane (9). The results obtained from x-ray examinations of a number of orthorhombic derivatives of ethane are partially shown in table 1.

The dimensions of the orthorhombic unit of structure containing $4C_2X_aY_{6-a}$ are given in table 1. The space-group is V_h^{16} and the positions of the halogen atoms are defined by ten parameters. A molecule possesses a plane of symmetry and it is probable that two of the halogen atoms are in this plane and four are outside it as a plane of symmetry. The probable distances (r) of the halogen atoms from this plane are given in the fifth column of table 1, and a halogen to halogen distance ($2r$) in the last column.

TABLE 1
A summary of the results obtained from some simple derivatives of ethane

COMPOUND	a IN Å.	b IN Å.	c IN Å.	r IN Å.	$2r$
C_2Cl_6	11.51	10.14	6.39	1.45 ± 0.04	2.90
C_2Br_6	12.07	10.70	6.72	1.58 ± 0.04	3.16
$C_2Cl_4Br_2$	11.73	10.37	6.50	1.55 ± 0.04	3.10
	11.61	10.35	6.31	1.55 ± 0.04	3.10
$C_2Br_4F_2$	11.84	10.75	6.56	1.58 ± 0.03	3.16
$C_2Cl_3Br_3$	11.77	10.44	6.54	1.52 ± 0.09	3.04
$CH_3CBr_2 \cdot CBr_2CH_3$	11.70	10.90	6.55	1.59 ± 0.05	3.18
	11.70	10.44	6.57	1.78 ± 0.01	3.56

The observed quartering of planes ($hk0$) (for C_2Cl_6 and C_2Br_6) for which h is odd and halving of planes ($hk0$) for which h is a multiple of four require the parameters of the halogen atoms in the a direction to be $\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$, or $\frac{7}{8}$. The observed presence of planes ($h0l$) for C_2Cl_6 and C_2Br_6 with h odd prohibits a molecule from having a second plane of symmetry, parallel to (100), and suggests instead that it has an approximate center of symmetry. If this is true, then the shortest Br—Br distance in C_2Br_6 between bromine atoms on different carbon atoms would probably be about 3.40 Å., in contrast with about 3.16 Å. on the same carbon atom. This second distance is somewhat less than the x - x separation in $C_6H_6Br_6$, but the distances, nevertheless, are closely similar. The halogen atoms of one molecule are at the corners of an octahedron (see figure 4).

The structure analyses were not carried further, but if one assumes that the carbon atoms are in the plane of symmetry, as seems highly probable, that their separation is about 1.54 Å., that the bromine or chlorine atoms in the plane of symmetry are a distance $2r$ from those outside that plane, and that the carbon atoms are equidistant from the halogen atoms attached to one carbon atom, then a molecule of the type shown in figure 4 is obtained. In such a molecule the halogen-carbon distances, not assumed, are for Br—C, 1.97 Å., for Cl—C, 1.81 Å., in agreement with the values found on the basis of certain assumptions

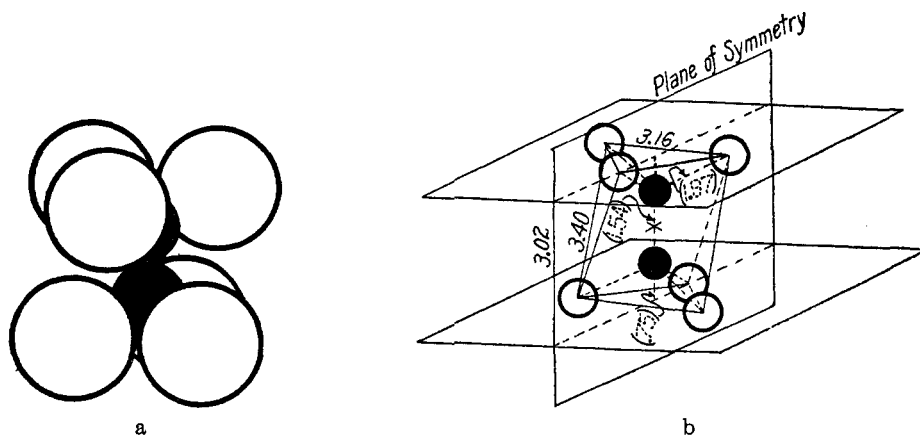


FIG. 4. HEXABROMOETHANE, C_2Br_6 . A POSSIBLE MOLECULAR CONFIGURATION

The pseudo center of symmetry is indicated by the cross mark. The carbon atoms are represented by black circles, the halogen atoms by open circles.

for $C_6H_6Br_6$ and $C_6H_6Cl_6$. The parameters in the c direction have not been determined, so it is impossible to allocate the molecules in the structure.

In the case of the last four compounds given in table 4 the plane of symmetry is present (requiring for instance the F atom of C_2Br_3F to be on the plane of symmetry) but the peculiarities of reflections from $(hk0)$ are absent, so that their structures, although closely similar to those of C_2Cl_6 and C_2Br_6 , can not be as thoroughly determined.

The two modifications of $C_2Cl_4Br_2$ have in the past been assumed to be $CCl_2Br \cdot CCl_2Br$, and $CCl_3 \cdot CClBr_2$. The intensity measurements for the two compounds, however, show none of the differences which would be expected if the first of these formulas is correct. The analysis of the results rather suggests that both crystalline modifications have the formula $CCl_3 \cdot CClBr_2$. It is difficult on this basis to see why crystallization from particular solvents should not result in changing one modification into the other.

Observations were also made on tetragonal modifications of $CH_3 \cdot CBr_2 \cdot CBr_2 \cdot CH_3$ and $C_2(CH_3)_4Br_2$ and on the orthorhombic $(CH_3)_3C \cdot C(CH_3)_2OH$, but the structures were more complex in these cases; the analyses were not as complete as for the orthorhombic crystals described above.

Other halogen compounds. Iodosuccinimide (10), *m*-iodobenzoic acid (11), carbon tetraiodide (12), carbon tetrabromide (12), hexachloro- and hexabromo-benzene (12), tetrachloronaphthalene (13, 14), and 1,2,3,4,5,8-hexachloronaphthalene-1,2,3,4-tetrahydride (14).

Observations have been made on the above compounds, but the positions of the halogen atoms have not been determined, although this could perhaps readily be done in some of the cases if sufficient experimental data were available. In particular the observations on Cl_4 and CBr_4 (12) may be insufficient, since similar results obtained from the analogous SnI_4 have been shown to be seriously in error (15).

The determined units of structure of hexabromobenzene and hexachlorobenzene are shown in table 5. It is to be noted that the length of the *b* axis (the symmetry axis) is 3.84 Å. for the chloro derivative and 4.04 Å. for the bromo derivative. These values are but slightly greater than the halogen to halogen distances of separate molecules previously noted in aliphatic compounds. It suggests that the length of the *b* axis is determined by the closest distance of approach between carbon and halogen atoms of separate units of structure.

Observations on vapors

Interference has been noted in x-radiation and in high velocity electron beams, scattered from vapors of organic compounds containing chlorine. The interference maxima are determined by the intramolecular relationships. Results obtained from CCl_4 (16, 17) indicate that the Cl—Cl distance within the molecule, assuming a regular tetrahedral configuration, is 3.3 Å. (16), or 3.14 Å. (17); the corresponding C—Cl distance is 2.02 Å. or 1.91 Å.

TABLE 2
Halogen to halogen distances in some organic compounds

DISTANCE	COMPOUND	SEPARATION			REMARKS
		On same carbon atom	On adjacent carbon atoms	On separate molecules	
I—I.....	CHI_3	3.57	—	3.94	
Br—Br.....	$\text{C}_6\text{H}_6\text{Br}_6$	—	3.40	3.74	
Br—Br.....	C_2Br_6	3.16	3.40	—	
Br—Br.....	C_6Br_6	—	—	4.04	Questionable
Cl—Cl.....	$\text{C}_6\text{H}_6\text{Cl}_6$	—	3.26	3.59	
Cl—Cl.....	C_2Cl_6	2.90	3.33	—	
Cl—Cl.....	C_6Cl_6	—	—	3.84	Questionable
Cl—Cl.....	$\text{C}_2\text{H}_2\text{Cl}_2$ <i>cis</i>	—	3.6	—	Gas
Cl—Cl.....	CCl_4	3.30	—	—	Gas
		3.15	—	—	
Cl—Cl.....	$\text{C}_2\text{H}_4\text{Cl}_2$ (1, 1)	3.40	—	—	Gas
Cl—Cl.....	$\text{C}_2\text{H}_4\text{Cl}_2$ (1, 2)	—	4.4	—	Gas
Cl—Cl.....	$\text{C}_2\text{H}_2\text{Cl}_2$ <i>trans</i>	—	4.1	—	Gas

These values agree within the limits of experimental error with those obtained from C_2Cl_6 and $\text{C}_6\text{H}_6\text{Cl}_6$.

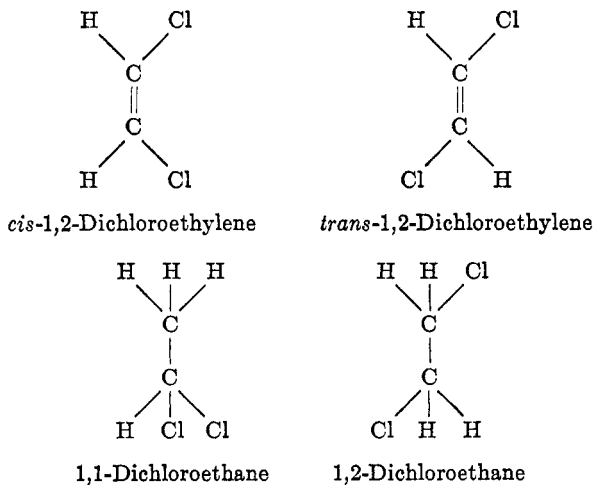
Observations of x-radiation scattered by *cis*- and *trans*-1,2-dichloroethylene and by 1,1- and 1,2-dichloroethane (18) indicate that in these compounds the Cl—Cl distances are:

$$a_{cis} = 3.6 \text{ \AA.} \quad a_{trans} = 4.1 \text{ \AA.}$$

$$a_{1,1} = 3.4 \text{ \AA.} \quad a_{1,2} = 4.4 \text{ \AA.}$$

These distances are compared in table 2 with those obtained from crystal structure determinations.

The values obtained for the Cl—Cl distances in 1,2-dichloroethane and *trans*-1,2-dichloroethylene are probably not to be compared with the values found for 1,2,3,4,5,6-hexabromocyclohexane and hexabromoethane, since these latter correspond to other than minimum distances of separations. The structural formulas are probably:



The particular formula of 1,2-dichloroethane is required by the rather large chlorine to chlorine distance in that compound (table 2).

The results obtained from the limited number of aliphatic halogen compounds examined indicate that the halogen-carbon distances are approximately constant in such substances. The values determined from various compounds are listed in table 6.

It is known from theories of organic chemistry that the halogen atoms of the compounds listed in table 2 are not united to one another by "primary" valence forces. The interatomic distances, since they are much greater than those required by probable atomic diameters, are in agreement with this concept. There is, however, a greater constancy in the halogen-halogen distances listed in table 2 than would perhaps be required by the constraints of characteristic carbon-halogen distances. The persistent regularity in the relative positions of the halogen atoms of

separate molecules also suggests that interaction of halogen atoms plays a prominent rôle in both the intermolecular and the intramolecular relationships.

Structure determinations for carbon and some carbon compounds

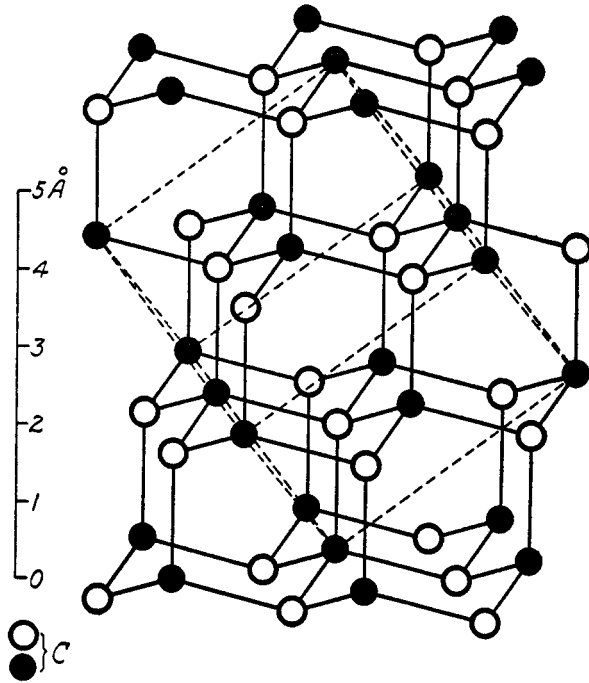
The high crystallographic symmetry of a few organic compounds has facilitated their complete structure determinations. In one case the analysis was markedly aided by selecting a compound which contains only one molecule in the unit of structure, thus avoiding the difficulty produced by the intermolecular relationships. Examinations of the members of homologous series, although complete structure determinations could not be made, have nevertheless yielded much information.

In the following discussion the possible positions of the hydrogen atoms will not be considered, save in the case of hexamethylenetetramine. It is probable that these atoms play some rôle in determining the intermolecular relationships. One can assume that the C—H distance is about 1.13 Å., and the N—H distance about 1.08 Å., corresponding to the values found from analysis of band spectra of CH and NH (19).

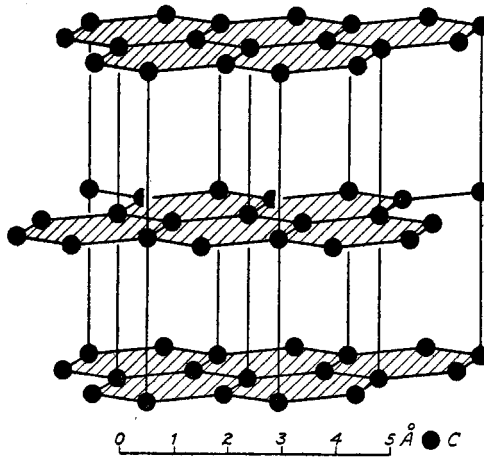
Diamond (20), graphite (21, 22). The crystal structures of the two crystalline modifications of carbon are shown in figure 5.

In the diamond, which has a cubic structure, each carbon atom is surrounded by four other carbon atoms placed at the corners of a regular tetrahedron. This supports the original van't Hoff hypothesis of the tetrahedral arrangement of the carbon valencies. This arrangement was early introduced as a prototype for the crystal structures of aliphatic compounds. The observed C—C distance in the diamond is 1.54 Å. This distance has been introduced as a basic assumption in some structure determinations.

In graphite, the hexagonal modification of carbon, the carbon atoms in one plane are associated as an interlocked group of hexagons. The closest distances of approach of carbon atoms in this plane are 1.42 Å., while carbon atoms in separate planes are at least 3.40 Å. apart. A flat hexagonal configuration is similar to the formula usually assigned to benzene. For this reason it



a



b

Fig. 5a. DIAMOND, C. 5b. GRAPHITE, C. ATOMIC ARRANGEMENTS IN THE TWO CRYSTALLINE MODIFICATIONS OF CARBON

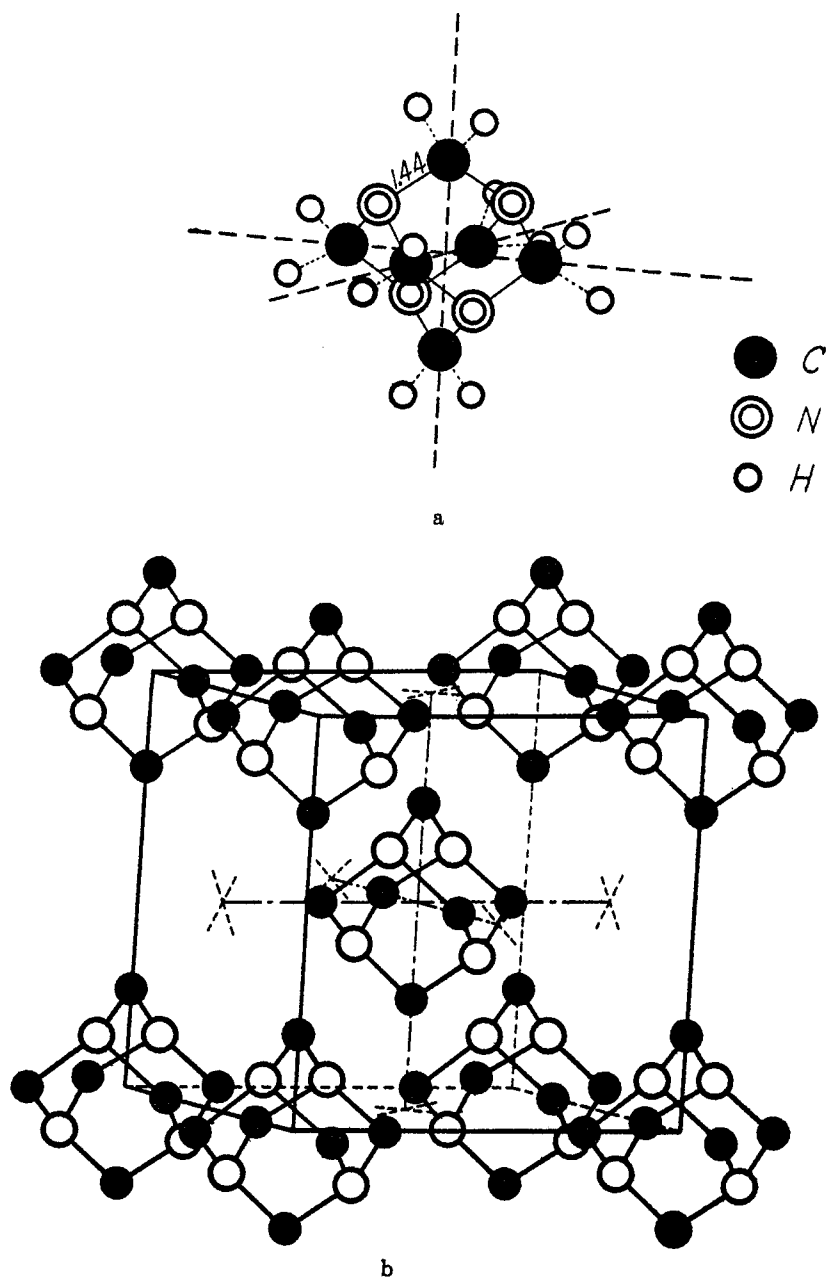


FIG. 6. HEXAMETHYLENETETRAMINE, $C_6H_{12}N_4$. THE UNIT OF STRUCTURE AND THE MOLECULAR CONFIGURATION
Possible positions of the hydrogen atoms are indicated.

was expected that the crystal structures of benzene derivatives might be more closely related to that of graphite than to that of diamond. Hexagonal groups of atoms are also present in the diamond structure, but the atoms of these groups are not coplanar. In the diamond each carbon atom is surrounded most closely by four other carbon atoms, rather than by three other carbon atoms as is the case for graphite. Similarities are to be noted between the structures of hexamethylbenzene and graphite.

Hexamethylenetetramine (23). The body-centered cubic unit of structure containing $2\text{C}_6\text{H}_{12}\text{N}_4$ has $a_0 = 7.02 \text{ \AA}$. The analysis was facilitated by assuming the existence of $\text{C}_6\text{H}_{12}\text{N}_4$ molecules. The determined atomic positions are:

C at $u00$; $0u0$; $00u$; $\bar{u}00$; $0\bar{u}0$; $00\bar{u}$

$\frac{1}{2} + u, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2} + u, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} + u; \frac{1}{2} - u, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2} - u, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} - u$

N at vvv ; $v\bar{v}\bar{v}$; $\bar{v}v\bar{v}$; $\bar{v}\bar{v}v$

$\frac{1}{2} + v, \frac{1}{2} + v, \frac{1}{2} + v; \frac{1}{2} + v, \frac{1}{2} - v, \frac{1}{2} - v; \frac{1}{2} - v, \frac{1}{2} + v, \frac{1}{2} - v; \frac{1}{2} - v, \frac{1}{2} - v, \frac{1}{2} + v$

with $u = .235$ and $v = 0.12$.

The unit of structure and the molecular configuration, with possible positions of the hydrogen atoms, are shown in figure 6. The minimum molecular symmetry is that of the point group T or T_d . Each carbon atom is surrounded by four atoms at least two of which, nitrogen atoms, are approximately at the vertices of a regular tetrahedron. Each nitrogen atom is equidistant from three carbon atoms, but is not in the plane of the carbon atoms. The minimum N—C distance is about 1.44 \AA . The minimum distance between the C atom of a (CH_2) group of one molecule and that of another is about 3.72 \AA .

Urea (24), *thiourea* (24, 25), *acetamide* (26). Both urea and hexamethylenetetramine are monoacidic bases and form addition compounds with salts and with molecular compounds. The crystal structures of these substances might be expected to give some indication of these heteropolar characteristics.

The tetragonal unit of structure contains $2\text{CO}(\text{NH}_2)_2$ (see figure 7a) and has $a = b = 5.73 \text{ \AA}$, $c = 4.77 \text{ \AA}$. The atomic positions are:

$$\text{O and C at } 0 \frac{1}{2} v; \frac{1}{2} 0 \bar{v}$$

$$\text{N at } u, \frac{1}{2} - u, v; \frac{1}{2} - u, \bar{u}, \bar{v}; \bar{u}, u + \frac{1}{2}, v; u + \frac{1}{2}, u, \bar{v}$$

with $u_{\text{N}} = .13 \pm .01$, $v_{\text{N}} = .20 \pm .02$, $v_{\text{C}} = .32 \pm .02$, and $v_{\text{O}} = .57 \pm .03$.

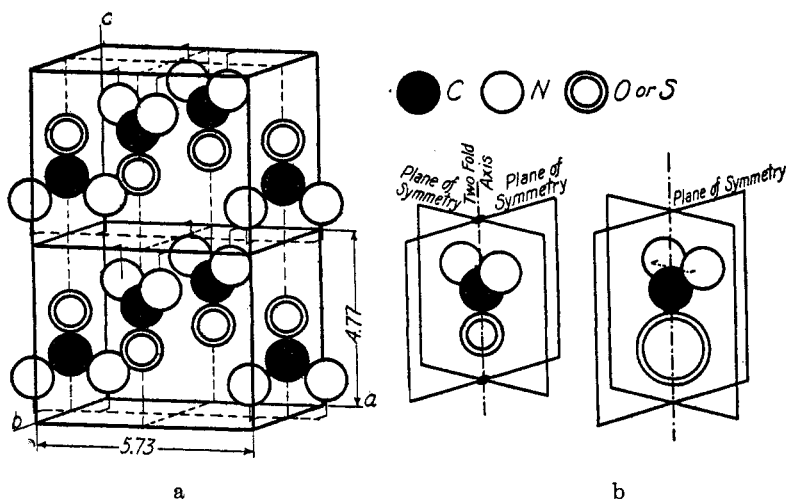
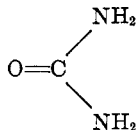


FIG. 7a. UREA, $\text{CO}(\text{NH}_2)_2$. THE ATOMIC ARRANGEMENT

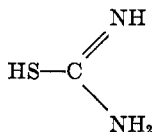
FIG. 7b. UREA, $\text{CO}(\text{NH}_2)_2$, AND THIOUREA, $\text{CS}(\text{NH}_2)_2$. THE MOLECULAR CONFIGURATIONS AND MINIMUM MOLECULAR SYMMETRIES

The urea molecule is required to have two planes of symmetry and a twofold axis of symmetry (figure 7b). The interatomic distances within a urea molecule are C—O, 1.05 – 1.42 (about 1.30); C—NH₂, 1.07 to 1.30 (about 1.20). The NH₂ groups of one molecule are most closely surrounded by the oxygen ends of other molecules (figure 7a), as might be expected from the heteropolar nature of the compound. The minimum distance between an O atom and an NH₂ group of separate molecules is about 3.15 Å.

In the crystalline state the formula must be a symmetrical one,



The seven parameters defining the atomic positions for the orthorhombic $\text{CS}(\text{NH}_2)_2$ have not been satisfactorily determined. Quantitative measurements of intensities of x-ray reflections would probably lead to a complete structure determination. The minimum molecular symmetry is a plane of symmetry (figure 7b), and it is possible that the molecule has the same symmetry as urea. It is probable that the C—S distance is about 1.81 Å. (25). (Compare C—Cl in $\text{C}_6\text{H}_6\text{Cl}_6$ and C_2Cl_6 .) In the crystalline state the formula must be the symmetrical one rather than



Acetamide, CH_3CONH_2 , has been studied, but a complete structure determination was not possible. The rhombohedral unit of structure having $\alpha = 90^\circ 17'$, and $a_0 = 8.05$ Å. contains $6\text{CH}_3\text{CONH}_2$. The molecule is asymmetrical (space-group C_{3v}^6). It is possible that three molecules are associated in $3\text{CH}_3\text{CONH}_2$ groups.

Some observations have been made on methylurea $\text{CO}(\text{NH}_2)(\text{NHCH}_3)$ and on symmetrical dimethylurea $\text{CO}(\text{NHCH}_3)_2$ (12). It is possible that each of the molecules of the latter compound has a plane of symmetry as the formula suggests, but this could be ascertained only from a re-examination of the compound.

Hexamethylbenzene (27). This is the only aromatic compound for which a satisfactory structure determination has been made. The dimensions of the triclinic unit of structure containing one centrosymmetrical molecule of $\text{C}_6(\text{CH}_3)_6$ are:

$$a = 9.010 \text{ \AA.} \quad b = 8.926 \text{ \AA.} \quad c = 5.344 \text{ \AA.}$$

with

$$\alpha = 44^\circ 27' \quad \beta = 116^\circ 43' \quad \gamma = 119^\circ 24'$$

The intensities of reflections were measured quantitatively. The peculiarities in the determined structure factors, arising from a pseudo hexagonal atomic arrangement in (001), allowed the complete determination of the structure even though the atomic positions are defined by eighteen parameters. The space-group is C_6^1 .

The atomic arrangement in (001) is shown in figure 8b. Groups of atoms are present. These groups are to be identified as the molecules of $C_6(CH_3)_6$. Their presence demonstrates the existence of the organic molecule as a separate entity in the crystalline state. A molecule not only has a center of symmetry but also possesses a pseudo sixfold axis and a pseudo plane of symmetry, that is, the plane in which all of the carbon atoms are located. Six of the carbon atoms of a particular molecule are arranged in a closed hexagonal grouping. The minimum C—C distances in such a group are $1.42 \pm 0.03 \text{ \AA}$., in agreement with one of the characteristic C—C distances of graphite. The six CH_3 groups of a molecule are arranged as shown in figure 8a. The distance between a carbon atom of the hexagon and its adjacent methyl group is $1.54 \pm 0.12 \text{ \AA}$., in agreement with the minimum C—C distance in the diamond. The coördinates of the atomic positions in the $a b$ plane, expressed as fractions of the axes of the unit of structure are:

	(a)	(b)		(a)	(b)
A	$(\pm 0.071 \pm 0.182)$		G	$(\pm 0.145 \pm 0.371)$	
D			K		
B	$(\mp 0.109 \pm 0.073)$		H	$(\mp 0.222 \pm 0.149)$	
E			L		
C	$(\mp 0.180 \mp 0.109)$		J	$(\mp 0.367 \mp 0.222)$	
F			M		

The closest distances of approach of carbon atoms of separate molecules is approximately $d_{(001)} = 3.694 \text{ \AA}$. The projection of two units of structure on (001) is shown in figure 8b. The closest distances of approach between CH_3 groups of separate molecules in (001) are about 4.1 \AA .

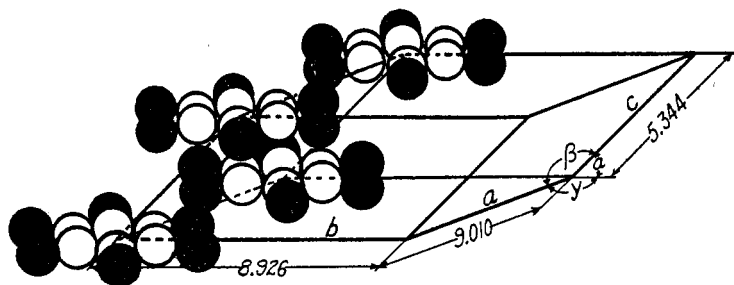


FIG. 8a. HEXAMETHYLBENZENE, $C_6(CH_3)_6$. A PARTIAL REPRESENTATION OF THE UNIT OF STRUCTURE

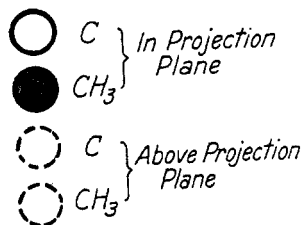
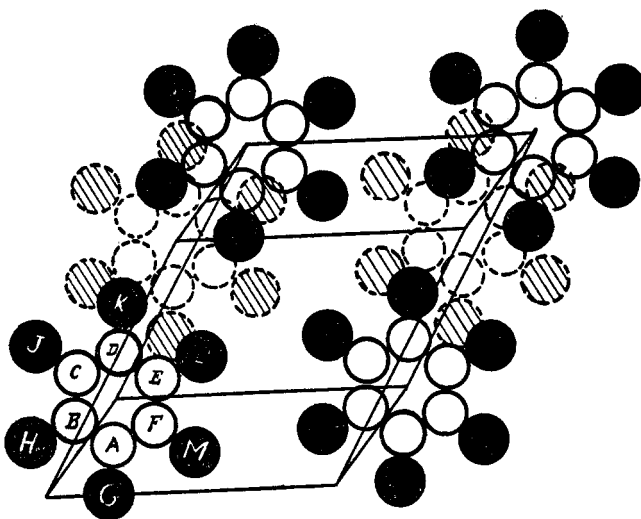


FIG. 8b. HEXAMETHYLBENZENE, $C_6(CH_3)_6$. A PROJECTION OF THE ATOMIC ARRANGEMENT ON (001)

The projection was made from below a.

Methane (28), ethane (29). Molecular rotation in the solid state (30). The crystal structures of methane and ethane have been determined from powder photographs at liquid nitrogen temperatures. Methane has been examined at liquid hydrogen temperatures. It has a cubic close-packed structure with $a_0 = 6.35 \text{ \AA}$. (figure 9b).

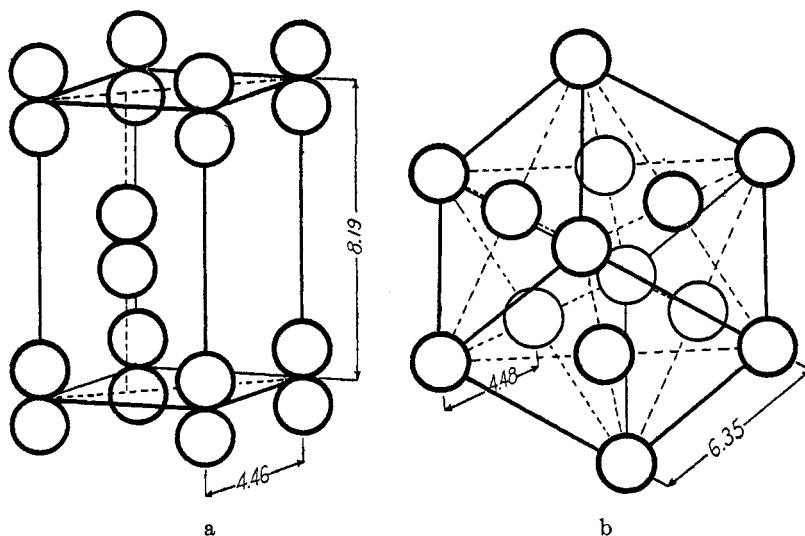


FIG. 9a. ETHANE, C_2H_6 . 9b. METHANE, CH_4 . UNITS OF STRUCTURE
Carbon atoms only are shown.

The hexagonal unit of structure containing $2C_2H_6$ (figure 9a) has $a = b = 4.46 \text{ \AA}$. and $c = 8.19 \text{ \AA}$. The positions of the carbon atoms are:

$$\frac{1}{3}, \frac{2}{3}, u; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}-u; \frac{2}{3}, \frac{1}{3}, u + \frac{1}{2}; \frac{2}{3}, \frac{1}{3}, \bar{u}$$

The value of u_C is probably .15 - .16, corresponding to a minimum C—C distance of $1.46 - 1.64 \text{ \AA}$. (1.55). The determined association of two atoms to form a molecule need not be assumed in the structure determinations.

In the case of methane it has been pointed out (30), from consideration of the specific heat data, that the molecules are

probably rotating above 20°K and that the structure, a closest packing of spheres, is partially determined by this rotation. Molecular rotation in the solid state is probably a determinative factor in the x-ray diffraction patterns of many crystals. In particular the rotation of the ammonium ion and the water molecule in compounds at ordinary temperatures probably accounts

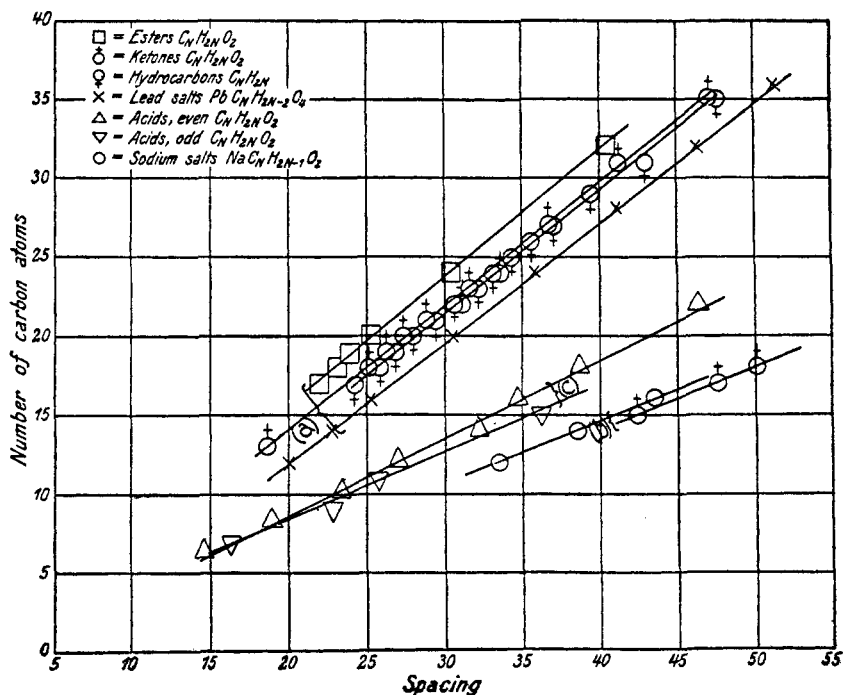


FIG. 10. A PARTIAL GRAPHICAL SUMMARY OF THE LONG SPACING DATA FOR SOME ALIPHATIC COMPOUNDS

for the fact that these molecules occupy positions in crystals with symmetry elements not compatible with those of the non-rotating molecule (30).

The structure of ethane may be considered as a hexagonal "close packing" of ellipsoids of revolution which are the rotating C_2H_6 groups. For this reason it is without significance to compare the intermolecular distances in ethane with those found for

hexamethylenetetramine and hexamethylbenzene. One distance of approach for ethane molecules, a of the hexagonal unit of structure, is 4.46 Å., that is, approximately equal to the distance 4.48 Å. between rotating CH_4 molecules in the methane structure. The closest distance between carbon atoms of separate ethane molecules is about 3.64 Å., in agreement with distances found for the two previously mentioned compounds.

Results obtained from long chain aliphatic compounds. Diffraction patterns from paraffin were noted as early as 1913 (31). Later observations (32) made by reflecting x-radiation from films of sodium oleate solidified on glass surfaces demonstrated the presence of reflections from some plane of great spacing. System-

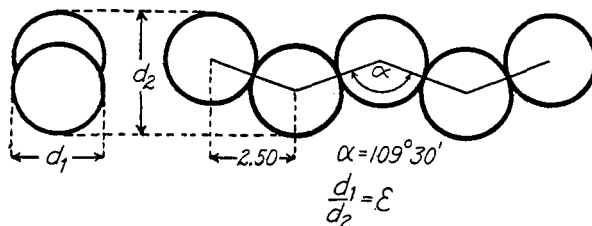


FIG. 11. A POSSIBLE CHARACTERISTIC ATOMIC ARRANGEMENT IN A SATURATED ALIPHATIC HYDROCARBON GROUP

Carbon atoms only are shown.

atic investigations have now been carried out on the x-ray diffraction characteristics of the various members of a number of homologous series.

The published data from long chain aliphatic compounds have usually been obtained from powder photographs and from reflection photographs made from thin films solidified on flat surfaces (glass). The photographs are characterized by the presence of a number of orders of reflection from a plane having a great spacing and by reflections from a few planes having spacings between 2.0 and 5.0 Å. A portion of the long spacing data as listed in the International Critical Tables (33) is summarized in figure 10. The data may be considered to fall into three groups having the following increases in spacing with the addition of

each methylene group: (a) about 1.30 Å.; (b) about 2.60 Å.; and (c) values intermediate between these two.

It was first suggested (34) that the long spacing measurements (a) and (b) were obtained from planes normal to the axes of the hydrocarbon chains, and that the change of this spacing with addition of methylene groups is a measure of the changes or twice the changes in the length of the chain. In case (c) the hydrocarbon chains are inclined to the planes of maximum spacings (35). The diffraction data from a number of compounds may be explained (36) by a coplanar "zig-zag" arrangement of the carbon atoms in a particular hydrocarbon group (figure 11). It is possible for the angle α_0 to be that of a regular tetrahedron.

Investigations have now been carried out upon (1) single crystals or flattened crystalline aggregates of several hydrocarbons (class (a)) and (2) single crystals of several fatty acids (class (c)). The results of these investigations have supported in part the conclusion of the earlier work.

(1) *Nonacosane (37) and other hydrocarbons.* Crystals of nonacosane, $C_{29}H_{60}$, are probably orthorhombic, as is shown by the approximate orthogonality of the crystallographic axes and more definitely by the absence of particular reflections. The dimensions of the unit of structure containing $4C_{29}H_{60}$ are given in table 3. The space-group is C_{2v}^0 , in which case the molecule does not have an element of symmetry, or V_h^{16} , in which case the molecule has a plane of symmetry perpendicular to the axes of the chains which are parallel to the c axis of the crystal. It is possible, but not probable, that the substance is monoclinic and the space-group is C_{2h}^5 . The molecules are at $x, y, \frac{1}{4}; \bar{x}, \bar{y}, \frac{3}{4}; x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \frac{1}{4}; \bar{x} + \frac{1}{2}, y + \frac{1}{2}, \frac{3}{4}$. If the space-group is V_h^{16} , the fifteenth carbon atom must be on the plane of symmetry. The molecule need have no other element of symmetry, but if the carbon atoms have a "zig-zag" arrangement in the chain, it is possible for them all to be in the same plane. This arrangement was assumed in the analysis of the structure, and results were obtained which explained satisfactorily the observed intensities of reflection.

A model of $C_{29}H_{60}$ is shown as figure 12. The following values were determined:

$$w = 1.62 - 1.23; \phi = 23^\circ - 30^\circ; S = 2.54;$$

$$\psi = 44^\circ - 52^\circ; D_2 = 3.6 - 3.9 \text{ \AA}; D_1 = 1.8 - 2.0 \text{ \AA}.$$

$$D_3 = \text{about } 4.00 \text{ \AA}; \bar{x} + x - \alpha_0 = \text{about } 1/7.5.$$

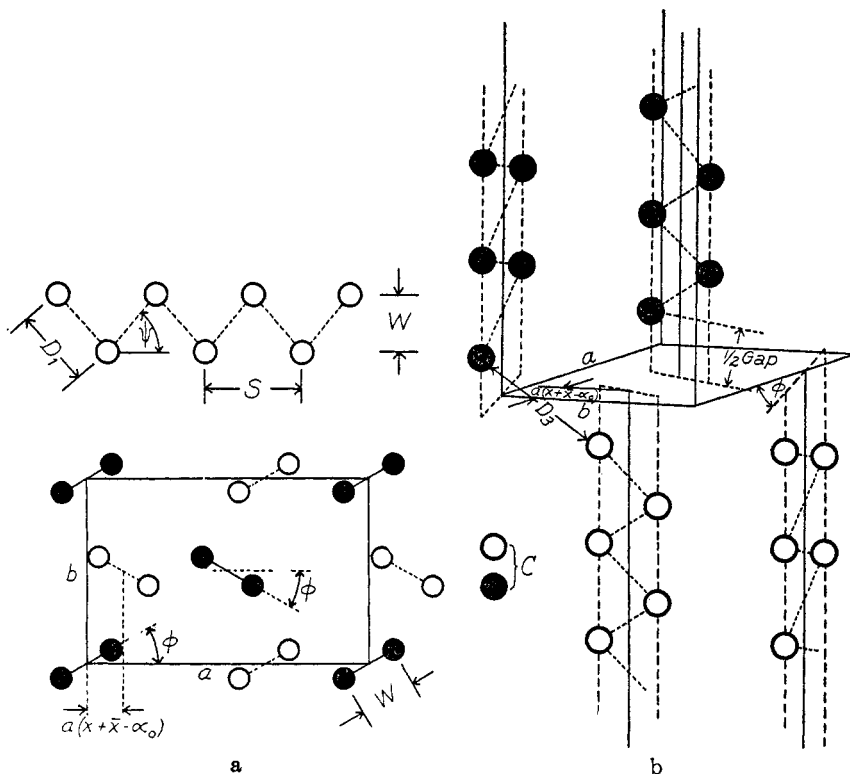


FIG. 12. NONACOSANE, $C_{29}H_{60}$. A PARTIAL REPRESENTATION OF THE STRUCTURE

The lettered designations are discussed in the text. Carbon atoms alone are shown.

It is to be noted that the values of D_2 and D_3 are approximately the same as those found for simple compounds. The value D_1 , of the minimum distance between scattering centers (assumed to be CH_2 groups) is much greater than the probable value found for simpler compounds (compare C_2H_6).

TABLE 3
Results of x-ray examinations of some fatty acids and aliphatic hydrocarbons

COMPOUND	FORMULA	a	b	c	β	a-b	$\frac{ab}{\sin \beta}$	$\frac{c}{\sin \beta}$	$\frac{a}{\sin \beta}$	ϵ
Lauric acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	9.76	4.98	36.9	48° 6'	48.6	36.527.6	7.32	0.681	
Stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	5.55	7.38	48.84	63° 16'	40.94	36.643.76	4.95	0.671	
Behenic acid	$\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$	9.55	4.69	59.10	53° 30'	44.76	36.647.51	7.67	0.612	
Stearolic acid	$\text{CH}_3(\text{CH}_2)_{17}\text{C}:\text{C}(\text{CH}_2)_7\text{COOH}$	9.55	4.69	49.18	53° 4'	44.76	35.839.28	7.63	0.614	
Bromostearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{CHBrCOOH}$	11.04	4.90	52.88	43° 15'	54.13	37.136.23	7.56	0.648	
Nonacosane	$\text{CH}_3(\text{CH}_2)_{27}\text{CH}_3$	7.45	4.97	77.2	90°	37.0	37.077.2	7.45	0.667	

TABLE 4
Results of x-ray measurements for some dicarboxylic acids

ACID	FORMULA	a	b	c	β	MOLECULES IN ELEMENTARY CELL	$ac \sin \beta$	DISTANCE BETWEEN END GROUPS
Adipic	$\text{C}_6\text{H}_{10}\text{O}_4$	10.27	5.16	10.02	137° 5'	2	36.18	3.70
Pimelic	$\text{C}_7\text{H}_{12}\text{O}_4$	9.93	4.82	22.12	130° 40'	4	36.26	3.47
Suberic	$\text{C}_8\text{H}_{14}\text{O}_4$	10.12	5.06	12.58	135° 0'	2	36.24	3.73
Azelaic	$\text{C}_9\text{H}_{16}\text{O}_4$	9.72	4.83	27.14	129° 30'	4	36.22	3.47
Sebacic	$\text{C}_{10}\text{H}_{18}\text{O}_4$	10.05	4.96	15.02	133° 50'	2	35.96	3.65
Brassylic	$\text{C}_{13}\text{H}_{24}\text{O}_4$	9.63	4.82	37.95	128° 20'	4	36.41	3.81
Hexadecanedicarboxylic	$\text{C}_{16}\text{H}_{30}\text{O}_4$	9.76	4.92	25.10	131° 10'	2	36.20	3.62
Oxalic	$\text{C}_2\text{H}_2\text{O}_4$	6.46	7.79	6.02	90°	4		
Succinic	$\text{C}_4\text{H}_6\text{O}_4$	5.07	8.92	5.52	91° 20'	2		

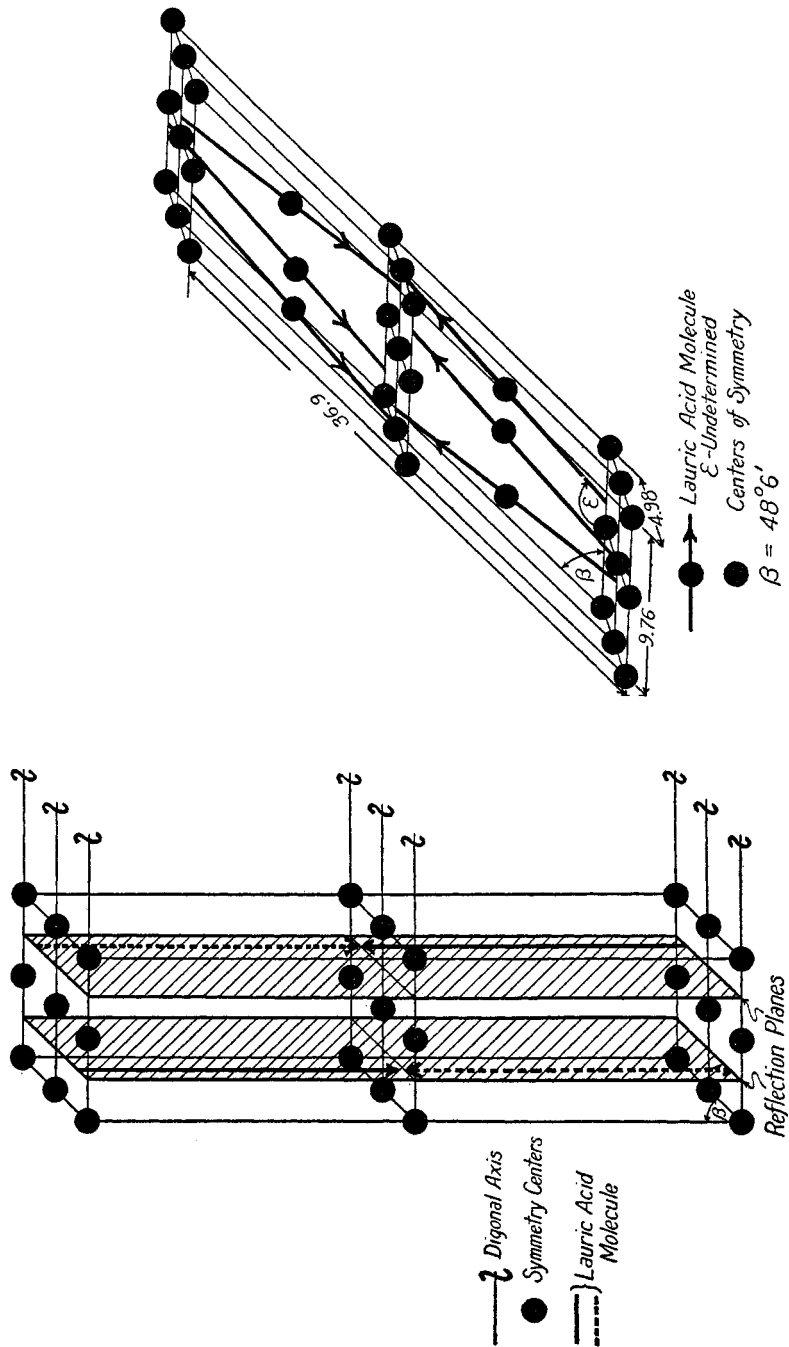


Fig. 13. LAURIC ACID, $C_{11}H_{23}COOH$. THE UNIT OF STRUCTURE SHOWING TWO POSSIBLE MOLECULAR ARRANGEMENTS

Photographs of $C_{29}H_{60}$ made at liquid air temperatures and near the melting point merely show slight alterations in the diffraction patterns as produced by expansion of the lattice. It is improbable that the molecules are rotating at room temperature. Detailed observations have also been made on compressed powders of $C_{35}H_{72}$ and $C_{70}H_{142}$ (?). The results were similar to those obtained from $C_{29}H_{60}$ (33).

A hydrocarbon containing an even number of carbon atoms can not have a plane of symmetry perpendicular to the axis of a "zig-zag" chain. For this reason it is probable that the space-group would be other than V_h^6 for such compounds, unless the unit of structure contained eight non-equivalent molecules.

(2) *Lauric acid* (39), *stearic acid* (35), *bromostearic acid* (35), *stearolic acid* (35), and *behenolic acid* (35). The results obtained from these compounds are summarized in table 3. The crystals are all monoclinic prismatic; the point-group is C_2^h . The monoclinic unit of structure for lauric acid, containing $4CH_3(CH_2)_{10}COOH$, is shown in figure 13. The meaning of the symbols a , b , c , and β used in table 3 are perhaps evident from this figure.

Lauric acid probably has an atomic arrangement derivable from space-group C_{2h}^1 or C_{2h}^2 . If the structure is to be derived from one of these space-groups the molecules probably can not be crystallographically identical since the formula does not permit a center of symmetry. Two possible structures are shown in figure 13. In either case the lauric acid molecule has a plane of symmetry perpendicular to the symmetry axis. Structures in which the molecules have centers of symmetry are precluded by the formula of the compound. A spiral structure of the chain is impossible, and if the molecule has a "zig-zag" configuration the carbon atoms must all lie in the plane of symmetry. The great length of the c axis suggests that the hydrocarbon chains are approximately parallel to that axis.

Stearic acid too has a structure isomorphous with point-group C_2^h , and it is assumed that the molecule has a plane of symmetry. For all the acids studied the value of $a b \sin \beta$, which is supposedly the cross-sectional area occupied by two molecules, is approximately constant, and is the same as for the hydrocarbon non-

acosane, $C_{29}H_{60}$. It has been suggested that ϵ , i.e. $\frac{a \sin \beta}{b}$ or $\frac{b}{a \sin \beta}$ depending upon whether $b > a \sin \beta$ or $b < a \sin \beta$, is a measure of d_1/d_2 in the hypothetical chain shown in figure 11. That this is probably not the case can be ascertained by an inspection of figure 12. It is to be noted, however, that in all cases save that of stearic acid, ϵ is expressed as $\frac{b}{a \sin \beta}$. The fact that the b axis of stearic acid is approximately equal to $a \sin \beta$ for lauric acid makes it very difficult to see exactly what structural relationships they have in common. It is possible that stearic acid only simulates monoclinic symmetry.

From the indicated variations of the angle β (table 3) it perhaps can be seen that no direct significance could be attached to the long spacing measurements ($c \sin \beta$) for the fatty acids listed in figure 10. If it is assumed that the axes of the hydrocarbon groups are approximately parallel to the c axis of the crystal, then the increase in the length of this axis might be used as a measure of the increase in chain length on addition of methylene groups. This change between lauric and stearic acids is 11.9 Å., corresponding to about 1.98 Å. for each methylene group. This value is markedly smaller than that of the compounds of type (a) shown in figure 10, for which the more complete examination of nonacosane suggests an increase of 2.5 Å. in the length of two hydrocarbon chains upon addition of a methylene group. It would seem that the molecules of the fatty acids do not have their chain axes accurately parallel to the c axes of the crystals.

Aliphatic dicarboxylic acids (40). The results of examination of a number of aliphatic dicarboxylic acids are shown in table 4. The crystals are all monoclinic and it is probable that the space-group is C_{2h}^5 . The acids with an even number of carbon atoms in the chain have but two molecules in the unit of structure. In such cases the space-group symmetry requires each molecule to have at least a center of symmetry; this is possible from the chemical formula, since the end groups are similar (see figure 14).

The acids with an odd number of carbon atoms in the chain

have four molecules in the unit of structure which are not required to have an element of symmetry. This might be expected since the formula will not admit of a center of symmetry. The values of $a c \sin \beta$ (table 4) are the same for these compounds as for the fatty acids and the hydrocarbons listed in table 3. This suggests that this constant area is a characteristic of two hydrocarbon chains and is unaffected by the presence of dissimilar end groups or by atoms such as bromine.

As is the case for monocarboxylic acids, no direct significance can be attached to the values of the maximum spacings ($c \sin \beta$),

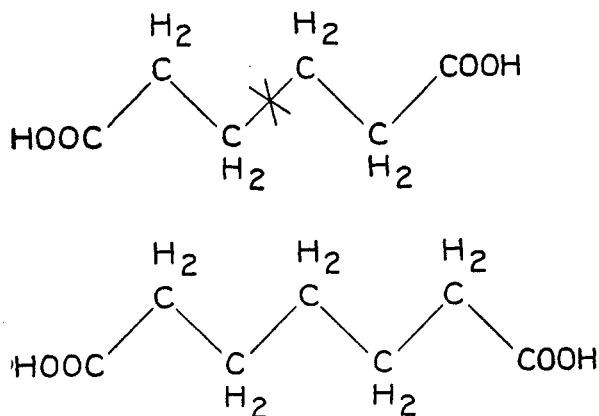


FIG. 14. DICARBOXYLIC ACIDS. STRUCTURAL FORMULAS

The possible symmetry center is indicated by the cross mark.

although the variations in β are quite small. The dicarboxylic acids, however, clearly illustrate the characteristics (a) and (b) of figure 10. The increase in the length of the c axis between adipic acid and hexadecanedicarboxylic acid (even numbers of carbon atoms) is 15.08 Å., corresponding to 1.25 Å. for each added methylene group (a). The change in the length of the c axis between pimelic acid and brassylic acid corresponds to an increase of 2.65 Å. for each CH₂ group. The axes of the hydrocarbon chains are probably closely parallel to the c axes of the crystals. The suggested separations of the end groups of different molecules are listed in table 4; these distances are approximately the same as those found for simple compounds.

Observations have also been made on a series of mono-*n*-alkylmalonic acids, di-*n*-alkylmalonic acids and acid amides (41). Single crystals were not used. Measurements have been made on single crystals of oxalic acid (42), and of succinic acid (43). These structures are not to be compared with those discussed above since their properties are more dependent upon the carboxyl groups.

Alkylammonium halides. Molecular rotation in the solid state. X-ray investigations have been carried out on single crystals of a number of primary (44, 45), tertiary (46), and quaternary (47, 48, 49) alkylammonium halides, tetramethylammonium perchlorate and permanganate (50), and some alkylammonium chlorostannates and platinates (51). These compounds have structural characteristics similar both to ionic inorganic compounds and to molecular organic compounds. A few typical structures are discussed below.

The results are best exemplified by primary *n*-amylammonium chloride, $C_5H_{11}NH_3Cl$ (30, 44, 52). This compound is tetragonal. A straightforward analysis of the x-ray data obtained at room temperatures leads to the conclusion that the unit of structure contains $2NH_3C_5H_{11}Cl$ and has $a = b = 5.01 \text{ \AA}$. and $c = 16.69 \text{ \AA}$. The Cl, N, and C atoms are at $0\frac{1}{2}u$, $\frac{1}{2}0\bar{u}$ with $u_{Cl} =$ about .095. The absence of reflections in odd orders from planes ($hk0$) with ($h + k$) odd and the intensities of reflections from other planes such as (200) require the carbon atoms of the C_5H_{11} group to scatter x-radiation as if they were arranged colinearly in each group. The determined atomic arrangement is shown in figure 15, in comparison with that of ammonium chloride.

It has been pointed out (30) that this result, that is quite incompatible with the results obtained from other long chain aliphatic compounds, might arise from rotation of the molecule about its long axis at room temperatures in the solid state. Photographs made at liquid air temperatures support this prediction and indicate that the true unit of structure contains $4NH_3C_5H_{11}Cl$ and that it has the approximate dimensions $a = b = 7.0 \text{ \AA}$., $c =$ about 16.6 \AA . A possible resulting atomic configuration is shown in figure 15 (it is assumed that the crystals are tetragonal

at liquid air temperatures). This has not yet been accurately determined. The C—C distance along the chain axis is probably about 1.25 Å., in agreement with the data from other long chain

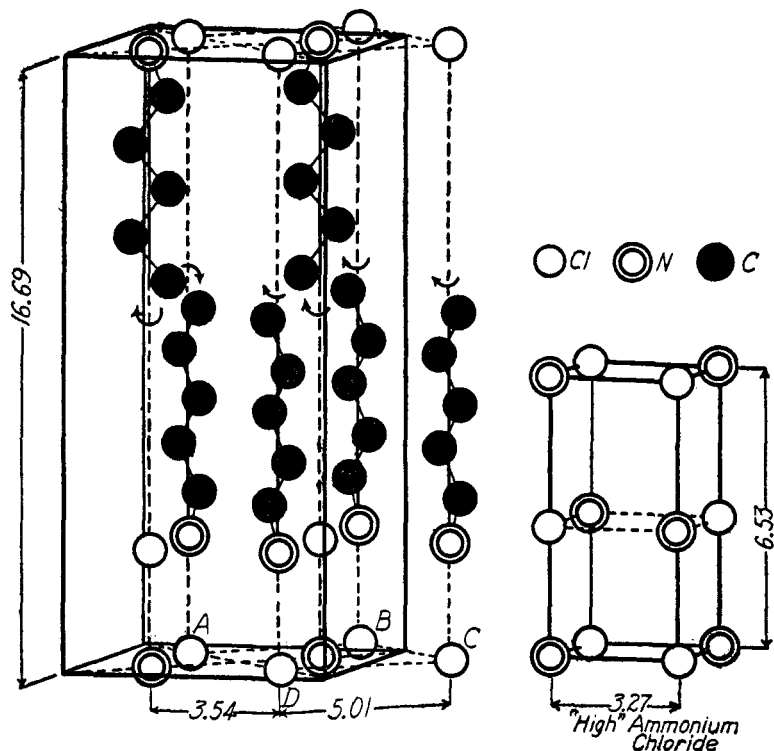


FIG. 15. PRIMARY *n*-AMYLAMMONIUM CHLORIDE, $\text{NH}_3\text{C}_8\text{H}_{11}\text{Cl}$. A REPRESENTATION OF THE TRUE UNIT OF STRUCTURE AND OF THE PSEUDO UNIT DUE TO MOLECULAR ROTATION, WHICH IS INDICATED BY ARROWS

The positions of the carbon atoms are in part hypothetical. A portion of the unit of structure of "high" ammonium chloride is shown for comparison.

compounds, and it is possible that the C—C separation is about 1.54 Å.

The ionic characteristics of the structure of primary amyllumonium chloride suggest that in the crystals at room temperatures the nitrogen atoms are on the axes of the hydrocarbon

chains. The value of $a b \sin \beta$ (for the smaller unit of structure) is approximately 25.0 Å., but it is hardly to be compared with the values listed in table 3 since it seems rather to be determined by salt-like properties of the compound, such as the separation of the RNH_3^+ ion and the Cl^- ion. This large area occupied by a *single* hydrocarbon chain (figure 15) probably reduces the crystal forces and the geometrical constraints sufficiently to allow molecular rotation at room temperatures. The minimum distance

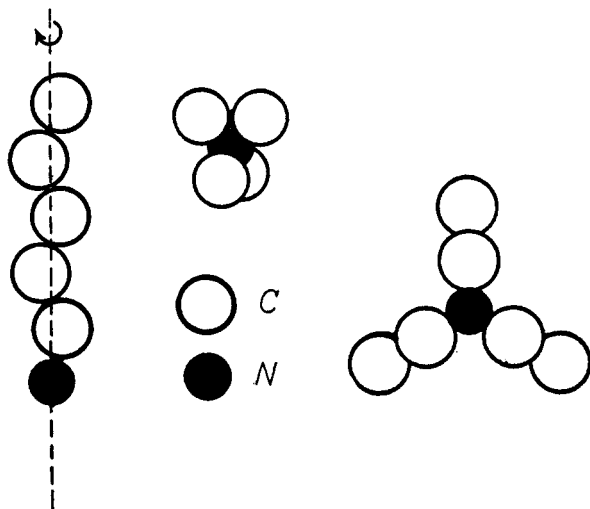


FIG. 16. $(\text{NH}_2\text{C}_5\text{H}_{11})^+$, $\text{N}(\text{CH}_3)_4^+$, AND $\text{NH}(\text{C}_2\text{H}_5)_3^+$. MOLECULAR CONFIGURATIONS

between the end groups of separate hydrocarbon molecules might well be approximately the same as that found for other organic molecules. The configuration of a single $(\text{NH}_2\text{C}_5\text{H}_{11})^+$ group is shown in figure 16.

The crystal structures of the primary *n*-butyl- to heptylammonium halides, and primary methylammonium bromide and iodide are similar to that of sodium chloride or "high" ammonium chloride, as may perhaps be seen by inspection of figure 15. The structures of primary methylammonium chloride and the primary propylammonium halides (figure 17) are more closely

related to that of caesium chloride or "low" ammonium chloride. Molecular rotation in the solid state probably modifies the structures of these compounds at room temperatures.

A representation of the unit of structure of $N(\text{CH}_3)_4\text{Cl}$ (47) is shown in figure 17, in comparison with that of ammonium chloride. The structures of the other tetramethylammonium com-

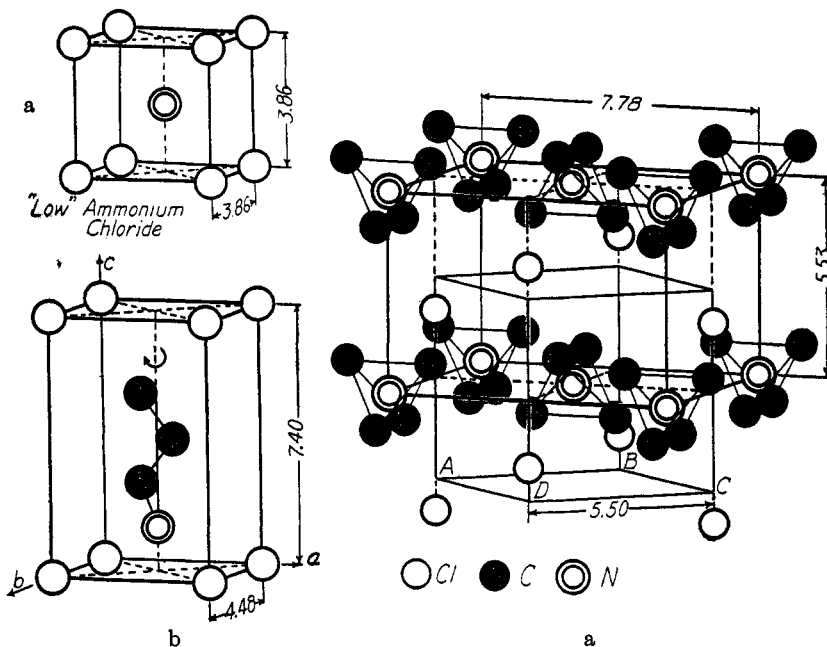


FIG. 17a. TETRAMETHYLAMMONIUM CHLORIDE, $N(\text{CH}_3)_4\text{Cl}$. THE UNIT OF STRUCTURE SHOWING THE PSEUDO SUB UNIT (ABCD AS BASE) WHICH IS TO BE COMPARED WITH THE UNIT OF STRUCTURE OF "LOW" AMMONIUM CHLORIDE

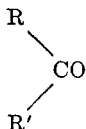
FIG. 17b. PRIMARY PROPYLAMMONIUM CHLORIDE, $\text{NH}_3\text{C}_3\text{H}_7\text{Cl}$. THE PSEUDO UNIT OF STRUCTURE WITH INDICATED MOLECULAR ROTATION

pounds are similar. In these compounds the nitrogen atom of each alkylammonium group is surrounded by four methyl groups at the corners of a tetragonal bispennoid (figure 17). The configuration of a $\text{NH}(\text{C}_2\text{H}_5)_3^+$ group as derived from the determined crystal structures of the triethyl ammonium halides (46) is shown in figure 16. It is possible that, in both these types of

compounds, the alkyl groups are rotating in the crystalline state at room temperatures, but it is improbable that the $\text{N}(\text{CH}_3)_4^+$ and $\text{NH}(\text{C}_2\text{H}_5)_3^+$ groups as a whole are rotating.

The group configurations shown in figure 16 are probably to be found in such compounds as substituted ammonium alums and in the alkylammonium halogen stannates and platinates (51).

Further discussion of results obtained from some long chain compounds. "Long spacing" measurements for hydrocarbons and related compounds have permitted certain structural deductions even though complete structure determinations could not be made. In the first place the hydrocarbon chain is very long in one direction and is not in part folded back on itself. Ketones, such as RCOCH_3 , show an increase of about 2.5 Å. in the "long spacing" for the addition of each (CH_2) group (53). This suggests (note the structure of lauric acid) that these groups are sufficiently polar to cause an end-to-end orientation of two molecules. A ketone, RCOR' , must have an extended structure rather than a folded one, such as



It has been shown that there are probably two or more modifications of the fatty acids (55) and of the saturated aliphatic hydrocarbons (56).

It has been suggested (54) that the well-known oscillations in properties between compounds with even and with odd numbers of carbon atoms arise in part from the "zig-zag" nature of the grouping. The alterations of the chemical relationships in dicarboxylic acids (57) are probably to be accounted for by their derived structures (40).

Observations made on polymerized formaldehyde products (58, 59) show that the condensation products are greatly elongated in one direction. A number of diacetate derivatives of polymerized formaldehyde

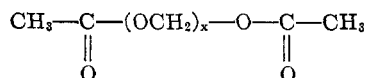
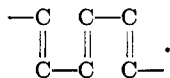


TABLE 5
Unit of structure and space-group determinations for some organic compounds

COMPOUND	SYMMETRY	a	b	c	β	SPACE GROUP	MOLECULES PER UNIT CELL	MINIMUM MOLECULAR SYMMETRY	REFERENCES
Naphthalene.....	Monoclinic	8.34	5.98	8.68	122° 44'	C_{2h}^5	2	Center of symmetry	(61, 62, 63)
Anthracene.....	Monoclinic	8.58	6.02	11.18	125° 0'	C_{2h}^5	2	Center of symmetry	(61, 62, 63)
Diphenyl.....	Monoclinic	8.22	5.69	9.50	94° 46'	C_{2h}^5	2	Center of symmetry	(64, 69)
Phenanthrene.....	Monoclinic	8.60	6.11	19.24	98° 15'	C_{2h}^5	4	None	(64)
Fluorene.....	Monoclinic	8.48	5.73	19.24	101° 53'	C_{2h}^5	4	None	(64)
Dimesityl.....	Monoclinic	8.21	8.58	22.25	96° 30'	C_{2h}^5	4	None	(69)
Dibenzyl.....	Monoclinic	12.82	6.18	7.74	115° 54'	C_{2h}^5	2	Center of symmetry	(64)
Stilbene.....	Monoclinic	12.42	5.73	16.0	114° (approx.)	C_{2h}^5	4	None	(64)
Indigo.....	Monoclinic	11.00	5.8	10.09	107° 30'	C_{2h}^5	2	Center of symmetry	(68)
<i>d</i> -Glucose.....	Orthorhombic	10.40	14.89	4.99	90°	V^4	4	None	(65)
α -Methyl glucoside...	Orthorhombic	11.29	14.72	5.29	90°	V^7	4	None	(66)
<i>d</i> -Fructose.....	Orthorhombic	8.06	10.06	9.12	90°	V^4	4	None	(65)
α -Methyl mannoside.	Orthorhombic	9.44	10.06	9.33	90°	V^7	4	None	(66)
<i>d</i> -Cellulose.....	Monoclinic	5.00	13.2	11.1	90°	C_2^3	2	None	(65)

<i>o</i> -Dinitrobenzene.	Monoclinic	7.95	13.0	7.45	112°	7'	C_{2v}^5	4	None	(67)
<i>m</i> -Dinitrobenzene.	Orthorhombic	13.3	14.2	3.82	90°		V_h^{16}	4	Probably plane of symmetry; center of symmetry	(67)
<i>p</i> -Dinitrobenzene.	Monoclinic	11.3	5.55	5.8	92°	18'	C_{2v}^5	2	Center of symmetry	(67)
Hexachlorobenzene.	Monoclinic	8.06	3.84	16.6	116°	50'		2		(12)
Hexabromobenzene.	Monoclinic	8.44	4.04	17.3	116°	30'		2		(12)

with 8-19 CH_2O groups show an increase in the long spacing from 23.7 Å. to 43.7 Å., corresponding to about 1.9 Å. for each CH_2O group. Preliminary observations on a number of "polyenes," $\text{C}_6\text{H}_5-\text{C}=\text{C}-\text{C}=\text{C}\cdots\text{C}_6\text{H}_5$ (60), indicate that the long spacing increases about 1.5 Å. for each added $-\text{C}=\text{C}-$ group; this suggests that the arrangement might be



It is probable in these cases that the increase in the "long spacing" is not a true measure of the change in the length of the chain upon addition of groups (note the fatty acids).

UNIT OF STRUCTURE, SPACE-GROUP, AND MOLECULAR SYMMETRY DETERMINATIONS

The complexity of the structures of most organic compounds and the lack of guiding principles to aid in their elucidation has prevented a more thorough analysis than a unit of structure and space-group determination in some cases. Efforts have been made to detect structural similarities from the dimensions of the units of structures of related compounds. Some instances in which such a method has met with an element of success are described below.

Aromatic hydrocarbons

The results obtained from a number of aromatic hydrocarbons are listed in table 5. In each case the space-group is C_{2h}^5 . The units of structure contain four asymmetric molecules or two molecules that must at least have a center of symmetry. Thus naphthalene, anthracene, diphenyl and dibenzyl have at least a center of symmetry. Stilbene and dimesityl with symmetrical formulas do not necessarily have an element of symmetry. The values of a , of $a \sin \beta$, and of b , and therefore of $ab \sin \beta$, are similar for naphthalene, anthracene, diphenyl, phenanthrene and fluorene.

It has been suggested (63) that the change in the length of the c axis, 2.50 Å., between naphthalene and anthracene is a measure

of the width of the benzene ring. It is said that a calculated periodicity of scattering matter along the c axis supports this suggestion. An effort has been made to determine these structures (61). Simplifying assumptions were made to reduce the fifteen parameters for anthracene to four. The structure determined, in which the benzene ring had characteristics similar to aliphatic compounds, was said to be compatible with the experimental data. Later work, however, indicates that the correct structure is one in which all of the atoms of a particular

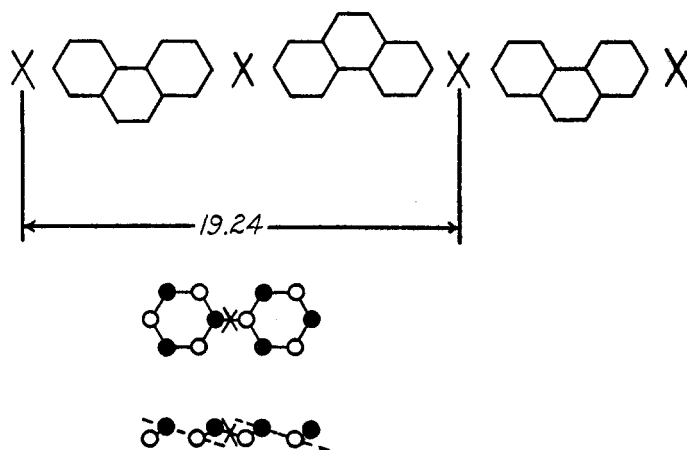


FIG. 18. STRUCTURAL FORMULAS FOR PHENANTHRENE AND FOR DIPHENYL
Centers of symmetry are indicated by cross marks.

molecule are in one plane (61a). This is in agreement with the results obtained from the structure determination of hexamethylbenzene (27), which is a more complete structure determination.

A close similarity is to be observed in the values of c or of $c \sin \beta$ for fluorene, phenanthrene, and diphenyl; the values of $c \sin \beta$ are $2 \times 9.42 \text{ \AA.}$, $2 \times 9.52 \text{ \AA.}$, and 9.45 \AA. , respectively. The suggestion has been made (64) that the phenanthrene molecules are arranged along the c axis as shown in figure 18. The similarities between these compounds and naphthalene and anthracene suggest that the molecules are oriented relative to the crystallographic axes, approximately as shown in figure 19. The actual

dimensions of the unit of structure are not relative measures of the molecular dimensions.

The dimensions of the units of structure for stilbene and dibenzyl are similar in the length of the b axis to those of the compounds mentioned above. In all of the above cases the formulas are probably extended rather than folded back in part.

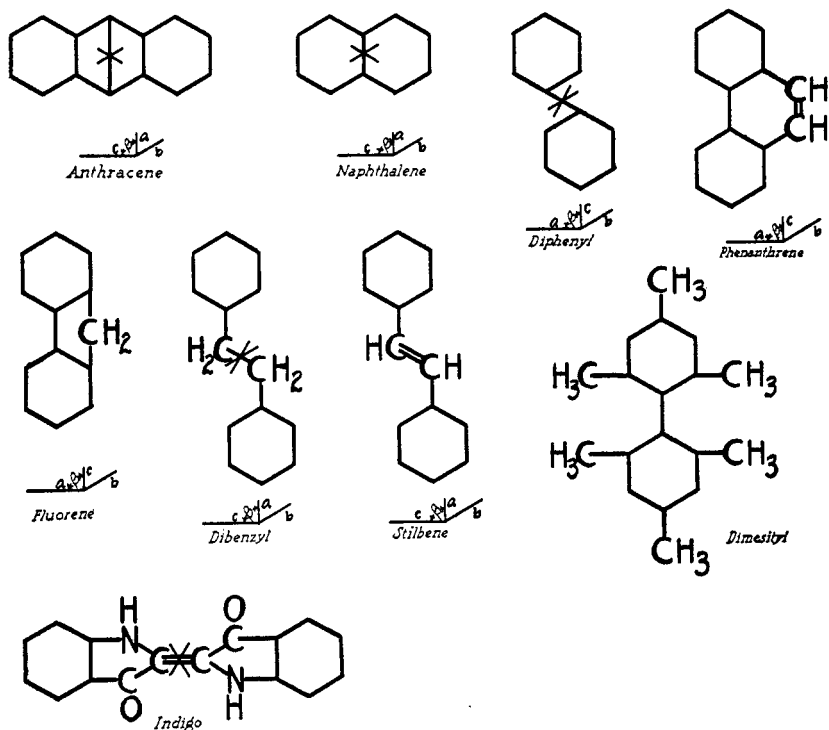


FIG. 19. STRUCTURAL FORMULAS OF A NUMBER OF AROMATIC HYDROCARBONS

Centers of symmetry are indicated by cross marks. Possible positions of the axes relative to the molecules are shown schematically.

Sugars and sugar-like compounds

The units of structure of *d*-glucose, *d*-fructose, *d*-cellobiose (65) α -methylglucoside (m.p. 110°C .), and α -methylmannoside (66) are listed in table 5. In each case the molecule, as might be expected from its chemical formula, does not necessarily have an

element of symmetry. Close similarities are to be noted in the dimensions of the units of structure of *d*-glucose and α -methylglucoside, and of *d*-fructose and α -methylmannoside. The volumes of the units of structure of α -methylglucoside and α -methylmannoside are the same within experimental error; the densities are the same, although the dimensions of the units of structure are markedly different.

Dinitrobenzenes (67)

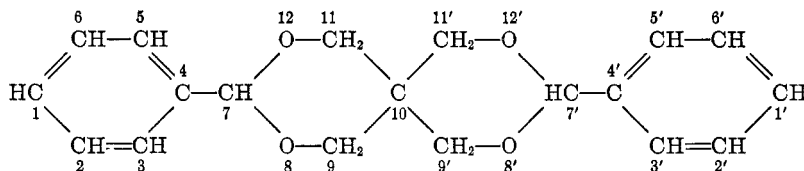
Unit of structure and space-group determinations have been carried out for *o*-, *m*-, and *p*-dinitrobenzenes (table 5). *p*-Dinitrobenzene has at least a center of symmetry, as might be expected from its formula. *m*-Dinitrobenzene has either a center of symmetry or a plane of symmetry; the former can hardly be the case. An inspection of the published data (67) does not show clearly whether the plane of symmetry is perpendicular to the benzene ring as suggested, or whether the benzene ring and the nitrogen atoms, as well as perhaps the oxygen atoms, are in the plane of symmetry. In either case the length of the *c* axis, 3.82 Å., is a measure of the closest distance of approach between two molecules of separate units of structure. This distance is approximately the same as the closest distances of approach between atoms of separate molecules of other organic compounds (table 7).

Compounds CR₄

The minimum molecular symmetry has been determined for some tetrasubstituted products of methane. Pentaerythritol $C(CH_2OH)_4$ (70), pentaerythritol tetraacetate $C(CH_2OCOCH_3)_4$ (71) and the tetramethyl ester of methanetetracarboxylic acid $C(COOCH_3)_4$ (72) probably have molecular symmetry corresponding to that of the point-group S_4 . The substituted groups are arranged tetrahedrally around the central carbon atom. In each of the above cases the tetragonal unit of structure contains $2CR_4$, and the space-group is S_4^2 , C_{4h}^4 , and C_{4h}^3 respectively. The results are in agreement with the accepted tetrahedral distribution of the valences of carbon in aliphatic compounds.

Observations on dibenzalpenterythritol (73) indicate that

the molecule must have three twofold axes which are perpendicular one to the other, corresponding to the symmetry of the point group V . The hexagonal unit of structure contains $3C_{19}H_{20}O_4$;



and has $a = b = 6.03 \text{ \AA}$, $c = 36.7 \text{ \AA}$. The space-group is D_6^4 . The molecule has a twofold axis along which the atoms designated as 1, 4, 7, 10, 7', 4' and 1' must be placed. The constituents of the benzene ring (1, 2, 6, 4; 4, 3, 5, 1; 4', 3', 5', 1'; 1', 2', 6', 4') must in each set be in a plane, as must also be the atoms 4, 7, 8, 12; 4', 7', 8', 12'. It is possible for all of the atoms of one molecule to be in a plane. These results might in part arise from molecular rotation in the solid state, but the symmetry requirements of the molecule do not suggest such an explanation.

Crystals of pentaerythritol tetraformate (74) have been examined. The orthorhombic unit of structure containing eight molecules has $a = 19.80 \text{ \AA}$, $b = 9.90 \text{ \AA}$, $c = 11.70 \text{ \AA}$. The molecule does not necessarily have an element of symmetry.

Cellulose and other fibrous materials

A fiber x-ray diagram is obtained from an aggregate of crystals or crystallites of a particular material which have some common parallel crystallographic direction. Such a diagram was first noted for hemp fibers in 1913 (75). Investigations have now been carried out on a number of fibrous organic materials—cellulose, hair, muscle, nerves, etc. The characteristics of the fiber diagrams give some indications of the physical properties of the materials.

Attempts have been made to determine the structure of the cellulose residue $(C_6H_{10}O_5)_n$ from ramie fiber diffraction data (76, 77). The spacings of the observed interference pattern can best be explained by a monoclinic unit of structure containing $4C_6H_{10}O_5$, having $a = 8.3 \text{ \AA}$, $b = 10.3 \text{ \AA}$ (fiber axis), $c = 7.9 \text{ \AA}$,

and $\beta =$ about 84° . This small number of $C_6H_{10}O_5$ groups in the unit of structure is hardly in conflict with the known high molecular weight of cellulose, since it is probable that only a periodicity along the fiber axis is determined from the diffraction data. The postulated atomic arrangements in the glucose residue of ramie (76, 77) are hardly to be emphasized, since even the structure of crystalline glucose is yet unknown.

TABLE 6
Interatomic distances in some organic compounds

DISTANCE	COMPOUND	VALUE IN Å.
C—I.....	CHI ₃	>1.94 (2.10)
C—Br.....	C ₆ H ₆ Br ₆	1.94
	C ₂ Br ₆	1.97
C—Cl.....	C ₆ H ₆ Cl ₆	1.81
	C ₂ Cl ₆	1.81
	CCl ₄	1.91
C—N.....	C ₆ H ₁₂ N ₄	1.44
C—O.....	CO(NH ₂) ₂	1.25 ±0.17
C—S.....	CS(NH ₂) ₂	1.81 (?)
C—C.....	C ₂ H ₆	1.55 ±0.09
	C ₆ (CH ₃) ₆	1.54 ±0.12
	Long chain compounds	1.54
	Diamond	1.54
C—C.....	Graphite	1.44
	C ₆ (CH ₃) ₆	1.42 ±0.03
C—H.....	CH (band spectra)	1.13
N—H.....	NH (band spectra)	1.08

GENERAL DISCUSSION

It was pointed out in the introduction that complete crystal structure determinations of some organic compounds indicate the presence of groups of atoms in such compounds. These groups, which are the chemical molecules, are characterized by certain minimum distances of approach between separate atoms within the groups, which are markedly smaller than the shortest distances between the atoms of different groups. The interatomic distances within the molecules, as determined from a few compounds that have been discussed, are listed in table 6. The

values are quite constant but, on account of the wide limitations of parameter values, minor variations could not necessarily be detected. It is expected that these values are approximately the ones to be found in other organic compounds.

The distances between atoms of separate molecules are not as constant as are those between atoms of the same molecule. Some regularity, however, is to be noted in the values for a number of halogen compounds (see table 2). Results obtained from a few compounds which contain only carbon, hydrogen, nitrogen, and oxygen are given in table 7. The values are quite similar, even though the possible effects produced by the hydrogen atoms in the different compounds might be expected to cause variations.

TABLE 7

Minimum distances of approach between carbon atoms of adjacent organic molecules

COMPOUND	DISTANCE IN Å.
C_2H_6	3.64
$C_6(CH_3)_6$	3.69
$C_6H_{12}N_4$	3.72
<i>m</i> - $C_6H_4(NO_2)_2$	3.82
$C_{25}H_{60}$	3.6-3.9
$C_6H_{10}O_4$ - $C_{18}H_{34}O_2$	3.5-3.8
Graphite	3.35

That these values should be greater than those listed in table 6 is perhaps to be expected from the molecular nature of organic compounds, which implies differences between the intermolecular and intramolecular forces. These differences are exemplified by such physical properties as low melting points, high compressibility coefficients, etc., of molecular compounds as compared with ionic ones.

In some cases the heteropolar characteristics of the compound result in certain regularities in the arrangement of molecules within the structures. This is to be noted in urea and in some of the halogen compounds which have been studied. It is perhaps also true of nitro derivatives of benzene. Such compounds usually have melting points which are comparatively higher than those of other organic substances.

The determined atomic arrangements in aliphatic compounds are in agreement with the concept of a tetrahedral distribution of the carbon valencies. For reasons necessitated by the structure analyses the compounds examined have usually been quite symmetrical ones. In these cases a carbon atom could have a regular tetrahedral distribution of its valencies, but such an arrangement is not necessarily general. One might expect that if several dissimilar atoms are connected to the same carbon atom, the departure from a regular figure might be quite marked. This concept, however, is not supported by any results yet obtained.

In graphite and hexamethylbenzene the three directions in which a carbon atom is surrounded most closely by other atoms are all in the same plane. It is possible that this arrangement is a characteristic one for aromatic compounds. The tetrahedral distribution of carbon valencies is probably to be found only in aliphatic compounds.

The determined minimum molecular symmetries of organic compounds are usually in agreement with expectations based on the structural formulas. In the case of indigo, however, the presence of a center of symmetry was not necessarily expected. The symmetry of dibenzalpenterythritol could be compatible both with the requirement of "plane" benzene rings and with the tetrahedral configuration of the aliphatic carbon atoms. It is to be emphasized that the symmetry determined from the x-ray diffraction data is the minimum one, except in a few special cases.

Attempts have been made to determine the atomic configurations of special isomers, such as maleic and fumaric acids and of optically active compounds such as *d*- and *l*-tartaric acids. These attempts have not been very successful. The diffraction characteristics of optical isomers of a compound are necessarily the same since reflection of x-radiation adds an effective center of symmetry. Optically active compounds always crystallize in forms belonging to one of the eleven crystal classes which possess no planes of symmetry.

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