

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

X-RAY INVESTIGATIONS OF OPTICALLY ACTIVE COMPOUNDS.

II. DIPHENYL AND SOME OF ITS ACTIVE AND INACTIVE DERIVATIVES^{1,2}

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The problem to which this x-ray diffraction analysis is being applied as a mode of attack is that of the stereoisomerism of derivatives of diphenyl. It is known that the substitution of certain groups in the 2,2',6,6'-positions of diphenyl gives compounds which may be resolved into stereoisomers. Many of these compounds have been prepared by Dr. Roger Adams³ and his students for the purpose of determining which groups give rise to this effect. It is thought that the presence of sufficiently large groups prevents a free rotation of the two rings and hence two active forms of such a compound exist. The crystallographic examination was undertaken in order to find, in the crystal at least, the positions, symmetry, and approximate shape of the molecules of the derivatives of diphenyl, and to see whether there is any differentiation apparent in the crystalline structure between those compounds which resolve into active isomers and those which do not.

Experimental

1. General Methods Employed

(a) **Preparation of Sample.**—Well-formed crystals of the substance under investigation were prepared by the slow evaporation of a barely saturated solution protected from dust. A single crystal, preferably one millimeter in its longest dimension, was selected for mounting. This was examined under the microscope for vibration axes and mounted either by eye or under the microscope on a glass fiber which was then attached to a goniometer head.

(b) **A Rotation Photograph.**—Rotation and oscillation photographs were used in the greater part of this work. The single crystal, mounted so that an important crystallographic direction was parallel to the axis of rotation, was rotated in a pin-hole defined beam of copper radiation from a Siegbahn-Hadding or Shearer gas-type tube. Inasmuch as the general radiation is inappreciable in intensity and the $K\alpha$ can easily be distinguished from the $K\beta$, unfiltered radiation was employed in practically all of the work. A circular camera of 5-cm. radius surrounded the crystal as a center. Exposures varied from two to eight hours depending on the focus of the beam and the size and absorption of the crystal.

When the crystal was lined up with the crystallographic axis coinciding with the

¹ For the first paper in this series see Clark and Yohe, *THIS JOURNAL*, 51, 2791 (1929).

² Part of a thesis submitted by Lucy W. Pickett to the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

³ Hyde and Adams, *THIS JOURNAL*, 50, 2499 (1928); Moyer and Adams, *ibid.*, 51, 630 (1929); Stanley and Adams, *Rec. trav. chim.*, [4] 48, 1035 (1929); *THIS JOURNAL*, 52, 1200 (1930).

axis of rotation, the photograph consisted of spots arranged in straight rows. If the two axes made an angle with each other, this was evidenced by the fact that the central line of spots was split into two lines crossing each other at an angle which is twice the angle between the axis of the crystal and the axis of rotation. Thus a correction could be made in the goniometer setting and the correct lining up of the axis obtained by somewhat of a trial and error process. The rows of spots in the photograph are termed layer lines, the one containing the undeviated beam being the 0 line and the others numbering 1, 2, 3, etc., from that line.

The unit length along the axis of rotation may be calculated directly from the photograph through the use of the relation $I \sin \Phi = n \lambda$ where λ is the wave length of the radiation used (1.54 for Cu-K α), n is the number of the layer line, I is the desired unit, and Φ may be measured as the angle whose tangent is the distance from the 0 layer line to layer line n , divided by the distance from crystal to film.

Rotation pictures can then be taken about the other two axes, and their position measured from the settings on the goniometer head. From measurements of the layer lines of each of these, the dimensions of the unit cell are directly obtained.

The number of molecules in the unit cell may be calculated from these data together with the experimentally measured density of the crystal by means of the following formula

$$a \times b \times c \times \sin \beta = \frac{\text{mol. wt.} \times n}{\text{Avogadro's number}} \times d$$

a , b and c are lengths of the unit cell expressed in cm., d is density and n is number of molecules in the unit cell.

The assignment of indices to the spots on the films is the next step and is attended with somewhat more difficulty. In a rotation photograph about the c axis, for instance, reflections from all the planes with index $hk0$ are present in the zero layer line, while planes of the $hk1$ series reflect in the first layer line, $hk2$ planes in the second layer line, etc. The spacings corresponding to the spots on the zero line can be calculated by means of the usual Bragg formula $n\lambda = 2d \sin \theta$. Furthermore, spots with the same h and k indices lie on lines which are curved but nearly vertical in general. The exact position of these lines has been worked out. In spite of these very helpful principles, the complexity of the photographs makes a certain identification of the spots difficult and two devices were employed in this work to make the identification less arduous.

One was the construction of a table which gave for each distance on the film under the conditions used the corresponding interplanar spacing. Thus, once the table was constructed, a large number of individual calculations was avoided.

The second was the use of oscillation photographs to analyze and simplify the diagram. Instead of rotating the crystal through 360° , it was oscillated 15° at a time, and a series of overlapping oscillation pictures

were taken. As there were fewer spots on each of these, each spot could be identified with more certainty, especially as one could calculate from the position of the crystal whether the plane which was suspected could have been in position within that 15° oscillation to give a reflection.

(c) **A Laue Photograph.**—To aid in determining the symmetry in certain cases Laue photographs were taken. Unfiltered molybdenum radiation was employed for this purpose, and the crystal was mounted in a pin-hole beam so that the beam was parallel to a crystallographic axis. If the alignment was perfect, a symmetrical design of spots was obtained, to which indices could be ascribed after a gnomonic projection.

(d) **Assignment of Space Group.**—Astbury and Yardley⁴ have compiled tables in which the missing reflections characteristic of each of the 230 space groups are listed. After the spots have been identified by the method described in the previous section, the classes which are consistently absent are noted and the space group found from reference to the tables. Often several space groups have the same missing reflections, in which case the number of molecules in the unit cell, the external symmetry, and other information about the crystal may help to clear the ambiguity. Further information must be obtained by individual methods varying with the substance used.

2. Data for Crystals

(a) **Diphenyl.**—The commercial product was purified by recrystallization four times from 95% alcohol followed by a slow recrystallization from absolute alcohol. Diphenyl crystallizes in thin flat plates with the 001 planes as the extended face and shows preferred cleavage along the a and b axes. The crystal unit was found to be monoclinic with the dimensions $a = 8.11$, $b = 5.67$, $c = 9.57$, $\beta = 94.5^\circ$. After this work was completed, an analysis by Hengstenberg and Mark⁵ was found in which the following dimensions were obtained: $a = 8.22$, $b = 5.69$, $c = 9.50$, $\beta = 94.8^\circ$. The two sets of data show very fair agreement. An analysis of the spacings showed that the reflections from all of the planes $h0l$, where h is odd, were absent as well as those from the $0k0$ planes where k is odd. This indicates that the structure is of monoclinic prismatic type and belongs to the space group C_{2h}^5 , which is based on the simple monoclinic lattice. From the fact that the density of diphenyl is 1.165, the number of molecules in the unit cell must be 2. The space group C_{2h}^5 requires 4 asymmetric molecules in the unit cell or two molecules each of which contains a center of symmetry and therefore diphenyl in the crystalline state must possess centro-symmetry.

There are four possible equivalent positions for two molecules which may be expressed analytically as follows

⁴ Astbury and Yardley, *Phil. Trans. Roy. Soc. (London)*, **A224**, 221 (1926).

⁵ Hengstenberg and Mark, *Z. Krist.*, **70**, 285 (1929).

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|--|--|
| (a) $1/4 \ 1/4 \ 0; \ 3/4 \ 3/4 \ 0$ | (c) $1/4 \ 3/4 \ 0; \ 3/4 \ 1/4 \ 0$ |
| (b) $1/4 \ 1/4 \ 1/2; \ 3/4 \ 3/4 \ 1/2$ | (d) $1/4 \ 3/4 \ 1/2; \ 3/4 \ 1/4 \ 1/2$ |

(b) **Dimesityl**.—Dimesityl crystallizes from an alcohol-water mixture in colorless rectangular plates or in needles. The product used was obtained prepared in this Laboratory from Dr. Stanley. Its density, determined by immersing a crystal in an aqueous salt solution of the same density, is 1.020.

Rotation and oscillation pictures indicated the following dimensions: $a = 8.21$, $b = 8.58$, $c = 22.25$, $\beta = 96.30^\circ$. There are, therefore, four molecules in the unit cell.

A table showing the relative intensities of the reflections noted is found in Table I. A scrutiny of this table reveals the fact that the planes $h0l$ where l is odd as well as the plane 010 , show no reflection. The only space group that fits these facts is C_{2h}^6 based on the simple monoclinic lattice Γ_m . Either two molecules with a center of symmetry or four asymmetric molecules may be placed in one unit cell in this space group. Hence the dimesityl molecule must be asymmetric.

The equivalent positions in this space group may be expressed by the coordinates xyz ; $x, y + 1/2, \bar{z}$; $x + 1/2, \bar{y}, z$; $1/2 - x, 1/2 - y, \bar{z}$.

(c) **3,3'-Diaminodimesityl**.—This compound has been resolved into two active forms by Adams and Moyer. Samples of each of these were loaned for crystal analysis. The compound formed fine crystals and proved very difficult to obtain in crystals large enough to work with. After repeated trials lasting over several months, one crystal of the l -form was obtained, and soon after a very tiny crystal of the d -form. The crystals formed in six-sided, colorless, slightly yellow plates from an alcohol-water mixture containing about 80% alcohol.

A very complete series of oscillation photographs of the former was taken. Powder photographs of the d - and l -forms showed the same spacings, and the few oscillation photographs of the d -form which were taken were exactly like those of the l -form in a similar position. Thus it was concluded that the d - and l -forms were identical as regards x-ray reflection, a fact which has been noted before where stereoisomers were concerned.

The dimensions of the unit cell were calculated as $a = 8.26$, $b = 8.58$, $c = 22.62$. The three axes were obtained at right angles to each other on the goniometer. The number of molecules in the unit cell is four.

The photographs obtained were so nearly similar to those of dimesityl that they might easily have been mistaken for each other. A detailed comparison of the intensity of the individual spots is presented in Table I. It may be seen from the table that those reflections are missing for the planes $h0l$ where l is odd, while 010 is either missing or extremely weak. Although the angle β cannot be distinguished with absolute certainty from 90° , the similarity to dimesityl indicates that the space groups are probably the same, C_{2h}^6 , and that β is within $30'$ of 90° .

TABLE I
COMPARISON OF INTENSITIES OF REFLECTIONS FROM DIMESITYL AND *l*-3,3'-DIAMINO-DIMESITYL

Planes	Dimesityl	Diamino-dimesityl	Planes	Dimesityl	Diamino-dimesityl
001	0	0	101	0	0
002	7	5	102	5	6
003	0	0	103	0	0
004	7	7	104	4	7
005	0	0	105	0	0
006	6	7	106	4	6
007	0	0	107	0	0
008	5	5	201	0	0
010	0	1	202	4	5
020	5	6	203	0	0
011	1	1	110	1	2
012	6	7	210	5	6
013	5	5	220	7	6
014	4	4	310	0	1
015	4	2	410	0	0
016	5	5	211	4	5
017	4	4	212	5	6
021	0	1	213	4	5
022	4	4	214	2	1
023	4	1	215	2	4
100	7	7	311	2	4
200	6	5	312	2	4
300	1	1	313	2	3

0 absent; 1 very weak; 2 weak; 3 medium weak; 4 medium; 5 medium strong; 6 strong; 7 very strong.

(d) **Hexachlorodiphenyl.**—The photographing of hexachlorodiphenyl involved a difficulty not encountered in any of the foregoing work in that the compound because of its many chlorine atoms is highly absorptive to the copper radiation. On this account very small crystals were used and longer exposures were necessary.

Hexachlorodiphenyl was prepared by Mr. Julius White in this Laboratory. It crystallizes from alcohol in colorless six-sided tablets. Optical measurement disclosed a monoclinic habit of the crystal with $\beta = 88^\circ$. Three photographs at right angles showing clearly defined layer lines were obtained and the dimensions of the unit cell calculated as follows: $a = 15.80$, $b = 8.54$, $c = 10.74$. A closer examination of the diagrams about the c axis showed that very faint lines of spots lay between those taken as the layer lines and hence that the above c dimension should be doubled. Thus the true dimensions of the unit cell are $a = 15.80$, $b = 8.54$, $c = 21.48$.

The following spots were identified as present: 002, 004, 022, 024, 026, 020, 013, 015, 200, 400, 210, 310, 410, 320, 420, 520, 202, 204, 120, 210, 310, 110, 220, 330, 111, 112, 113, etc., while 001, 003, 010, 012, 014, 100, 300,

102, 103, 104, 105 were absent. This may be summarized by stating that interferences for those planes are absent which have indices $0kl$ where $k + l$ is odd, and $h0l$ if h is odd.

The density as measured by the flotation method in a sulfuric acid and water mixture was 1.655. The number of molecules in a unit cell calculated from this figure is 7.98 or 8.

The only space groups in the orthorhombic or monoclinic systems which have the above mentioned spacings absent are C_{2v}^9 and Q_h^{16} (also written V_h^{16}). The first allows for only four asymmetric molecules in the unit cell and hence would necessitate the assumption of polymerization. The second allows eight asymmetric molecules and hence is the more probable.

The space group Q_h^{16} has eight equivalent positions as follows: xyz ; $x + 1/2, 1/2 - y, \bar{z}$; $\bar{x}, y + 1/2, 1/2 - z$; $1/2 - x, \bar{y}, z + 1/2$; $1/2 - x, 1/2 - y, \bar{z}$; $\bar{x}yz$; $x + 1/2, \bar{y}, z + 1/2$; $x, y + 1/2, 1/2 - z$.

After an optical examination indicated a monoclinic form while the x-ray data very clearly indicated an orthorhombic space group, all of the diffraction films were carefully reexamined. It is absolutely impossible to fit these data to any monoclinic space group, so the conclusion is that the crystal was not sufficiently perfect to enable unambiguous microscopic examination or else that the crystal actually has an outer pseudo-monoclinic form. There can be absolutely no question concerning the clear-cut x-ray data.

(e) **Diphenic Acid.**—Diphenic acid crystallizes readily from an acetic acid and water mixture in colorless six-sided tablets. Its density as determined by flotation in a sulfuric acid and water mixture is 1.40. It exhibits parallel extinction between two crossed nicol prisms.

An optical examination by Dr. E. T. Wherry of the U. S. Department of Agriculture of diphenic acid crystals disclosed the following facts. Making the shortest dimension axis a and the longest axis c and then making the prism (120) and the side-dome (011) gives

$$\text{Axis } c = \tan \rho \text{ of } (011); \rho \text{ observed } 49^\circ; c/b = 1.15$$

$$\text{Axis } a = \cot \phi \text{ of } (120); \phi \text{ observed } 59^\circ; a/b = 1.20$$

Rotation photographs of three axes at right angles to each other were taken in the usual manner. The dimensions of the unit cell were calculated as $a = 13.80$, $b = 11.90$, $c = 14.12$ with eight as the number of molecules in the unit cell with $b = 1$, $c/b = 1.15$ and $a/b = 1.19$, in excellent agreement with optical data. A series of oscillation pictures indicated that the following planes gave reflections: 002, 003, 004, 006, 106, 107, 108, 109, 116, 117, 118, 126, 127, 012, 014, 021, 022, 023, 024, 200, 110, 310, 211, 221, 020, 012, 032, 022. Inspection shows that the following set of planes are definitely present; hkl where $h + k + l$ is odd, $0kl$ where $k + l$ is odd, $h0l$ where $h + l$ is odd, $hk0$ where h or k is odd, $0kl$ where k or l is odd, $h0l$ where h or l is odd. None of the planes $hk0$ for which $h + k$ is

odd are present. The following planes are definitely absent: 210, 410, 010, 030, 100, 300, 011, 013, 031, 033. The first six of these are characterized by the classification, $hk0$ where $h + k$ is odd. The last four are probably missing for some other reason than that of space groups. Only those planes have been listed which could be identified without ambiguity, though further inspection strengthened the conclusion that only those planes were consistently absent which had the indices $hk0$ where $h + k$ is odd.

The only space group which necessitates this particular spacing is the orthorhombic group Q_h^{13} (V_h^{13}) based on the simple orthorhombic lattice. This group contains eight unsymmetric molecules in the unit cell. Hence the diphenic acid molecule possesses no symmetry in the crystalline state, a result to be anticipated from the formula. The eight equivalent positions in this space group may be expressed analytically: x, y, z ; $x + 1/2, 1/2 - y, \bar{z}$; $1/2 - x, y + 1/2, \bar{z}$; \bar{x}, \bar{y}, z ; $1/2 - x, 1/2 - y, \bar{z}$; \bar{x}, y, z ; x, \bar{y}, z ; $x + 1/2, y + 1/2, \bar{z}$.

(f) *o*-Tolidine.—The tolidine used was prepared in this Laboratory as the crude product and purified in the following manner: 10 g. was suspended in hot water and hydrochloric acid added to form the soluble hydrochloride. This was boiled with norite for twenty minutes, filtered hot, allowed to cool somewhat and neutralized with sodium hydroxide. The product was recrystallized from 80% alcohol. It crystallized nicely in rectangular tablets slightly brown in color.

An examination under the polarizing microscope showed that the crystals exhibit parallel extinction. An optical examination by Dr. Wherry proved the crystals to be orthorhombic. According to the classification of Wherry and Adams,⁶ the material is endo-rhombic, but often ecto-monoclinic. With the longest dimension of the crystal oriented as axis a , and the shortest dimension c , the front-dome (101) and the side-dome (102), the measurements gave

$$\text{Axis } c = 1/2 \tan \rho \text{ of } (012); \rho \text{ observed } 57^\circ 30'; c/b = 3.14$$

$$\text{Axis } a = c/\tan \rho \text{ of } (101); \rho \text{ observed } 75^\circ; a/b = 0.84$$

Examinations by Laue, rotation and oscillating crystal methods revealed the unit cell as orthorhombic with the dimensions $a = 6.50$, $b = 7.48$, $c = 23.62$ Å.; with $b = 1$, $c/b = 3.15$ and $a/b = 0.86$, in excellent agreement with the optical data. The density was determined as 1.215 and from this the number of molecules in the unit cell was found to be four.

The $00l$ planes where l is odd, and the $h00$ planes where h is odd are definitely absent, while the $0k0$ planes where k is odd are either absent or extremely weak. No other class of reflections is absent. Hence the space group is either the orthorhombic group Q^3 or Q^4 (V^3 or V^4). There is the possibility that the crystal might be monoclinic with an angle of $90^\circ \pm 0.5^\circ$

⁶ Wherry and Adams, *J. Washington Acad. Sci.*, 9, 153 (1919).

and hence belong to the space group C_{2h}^2 . In any case the molecule is asymmetric since there are four molecules in the unit cell.

The following table summarizes the results obtained for the crystal structures of the compounds.

	System	Unit cell dimensions			n	Space group	Symmetry of molecule
		a	b	c			
Diphenyl	Mono.	8.11	5.67	9.57	$94^\circ 30'$	C_{2h}^5	Center of symmetry
Dimesityl	Mono.	8.21	8.58	22.25	$96^\circ 30'$	C_{2h}^5	None
3,3'-Diaminodimesityl	Mono.	8.26	8.58	22.62	$90^\circ \approx 30'$	C_{2h}^5	None
Hexachlorodiphenyl	Orth.	15.80	8.54	21.48	90°	C_h^{16}	None
<i>o</i> -Tolidine	Orth.	6.50	7.48	23.62		C_h^4	None
Diphenic acid	Orth.	13.80	11.90	14.12		C_h^{18}	None

Discussion of Results

The table just preceding summarizes the information which may be deduced directly from the x-ray data. Without accurate measurements of intensities and interpretations based thereon, statements concerning the disposition or size of molecules within the crystal unit cells and the exact relation of the parts of the molecule to each other must be partly in the nature of speculations. In the following discussion all available data have been called on to construct what appears to be rational conclusions concerning those questions of great theoretical chemical interest. These are to be considered as suggestions rather than as certain facts, pending exact assignment of coördinates for all the atoms within the unit cell.

The first conclusion to be drawn is that the two benzene rings in the diphenyl molecule are in prolongation of each other rather than doubled over on each other. This picture is one that is accepted by most organic chemists today and this serves as interesting confirmation. The evidence for this is that the molecule possesses a center of symmetry, a condition that could only be true for the prolonged molecule.

Secondly, the rings probably are not flat. In that case the molecule would be expected to have at least one plane of symmetry, and such is not present. Furthermore, assuming the molecules to be exactly in the bc plane, the intensities of successive order of the $h00$ planes would fall off regularly and such is not the case. Thus it is probable that the carbon atoms are in staggered or puckered rings, a conclusion which was reached by Hengstenberg and Mark. The 9.57 dimension may represent the length of the molecule, while the halvings of the 8.11 dimension show that two molecules share this length. Thus a single molecule might be considered to occupy a space approximately $4 \times 5.7 \times 9.5$. It is probable that 5.7 is the width of the molecule, *i. e.*, the length in the meta direction of a benzene ring, and that the molecule is at a slight angle to the c axis in the ac plane, so that the actual thickness is less than 4.1 and the length greater than 9.5.

It is of interest to compare the unit cell dimensions for para benzene derivatives obtained by Dr. Caspari with the data for diphenyl derivatives. He recorded the following measurements.

	<i>a</i>	<i>b</i>	<i>c</i>	π
Quinol	13.24	5.20	8.11	4
<i>p</i> -Aminophenol	13.06	5.32	8.25	4
<i>p</i> -Phenylenediamine	12.46 \times 2	5.93	8.29	8

The dimension of 5+ corresponding to the width of the ring checks with that obtained for diphenyl. The dimension 8-8.5 is also common to the diphenyl derivatives. Caspari suggests that it may correspond to the length of the molecule, while the hypothesis in this work is that it represents the thickness of two molecules and the longest dimension represents the length of two molecules. The halving of the 8.3 dimension in phenylenediamine as well as the space group involved suggests that the latter interpretation may be correct, although the evidence is not conclusive.

Hengstenberg and Mark obtained the following comparison for diphenyl, phenanthrene and fluorene.

	<i>a</i>	<i>b</i>	<i>c</i> sin β
Diphenyl	8.22	5.69	9.45
Fluorene	8.48	5.73	2 \times 9.42
Phenanthrene	8.60	6.11	2 \times 9.52

If the *b* axis represents the width, the *c* axis the length and the *a* axis the width of two molecules, the dimensions are very consistent with those obtained in the present work.

In the case of dimesityl and also of hexachlorodiphenyl, the molecule possesses no symmetry. This is of significance because the structural formulas of these two substances indicate the same symmetry that diphenyl itself possesses. The fact that such symmetry is missing leads to the conclusion that the two rings are either bent or turned at an angle to each other in these compounds. The other compounds exhibit asymmetry, as is to be expected from their formulas.

The spacings observed in the diagrams of dimesityl indicate that two molecules share the *c* axis and also the *b* axis, and that the molecule may extend with its length along the *c* axis, with a tilt of unknown amount. Thus the approximate volume occupied by one molecule might be 8.2 \times 4.3 \times 11.1. The difference between 11.12 and 9.57 represents the difference between the space occupied by two methyl and two hydrogen groups together with the change in space caused by a distortion of the molecule as a whole or a change in tilt. Inasmuch as one-half of the difference, 0.8, is too small to account for the replacement of hydrogen by methyl alone, there must be a tilt or a compression of the molecule as a whole. The thickness of the molecule is slightly greater than that of diphenyl, while the

width is increased by 2.55, a change which might be expected from the substitution of two hydrogens by two methyl groups.

The dimensions and intensities of reflection of 3,3-diaminodimesityl, both as the levo and dextro form, show that the structure is nearly identical with that of dimesityl, except for a very slight increase in the width of the molecule and in the length. This confirmed the expectation that the insertion of amino groups between the 2- and 4-substituted methyl groups would cause little change in the structure of the molecule as a whole. The similarity is interesting in view of the fact that although dimesityl cannot be resolved because the benzene rings are symmetrical, both compounds offer the same resistance to free rotation about the diphenyl linkage.

While hexachlorodiphenyl at first glance appears different from the others, its similarity becomes apparent when the a unit length is halved. Since all three of the spacings are halved, the domain of each molecule is approximately $7.9 \times 4.3 \times 10.74$. This is exactly equal in thickness and shorter in both length and width than dimesityl. If it is assumed for the moment that the difference in width, $8.21 - 15.80/2 = 0.31$, represents the difference in space occupied by two methyl groups and two chlorine atoms, while the difference in length, $22.25 - 21.48 = 0.77$, accounts for the substitution of four methyl by four chlorine, the average difference between one methyl group and one chlorine atom would be 0.17.

The *o*-tolidine and the diphenic acid are not strictly comparable to the other compounds and were analyzed as incidental to the main problem. The dimensions of the *o*-tolidine indicate that it is similar in general structure to the other compounds. The unit c axis, 23.62, probably represents the length of two molecules, while 6.50 is reasonably the width of a molecule. The fact that the molecule would be longer than dimesityl and less thick than diphenyl indicates that this picture may not be correct in detail. However, this investigation was not pursued further, inasmuch as the compound bore little relation to the problem under investigation.

It is evident from the dimensions and also from the space group that diphenic acid crystallizes in a very different arrangement from that of the other compounds. The fact that carboxyl groups exert forces upon each other which result in a doubling of molecules has already been noted in the case of aliphatic long-chain compounds. It is probable that the presence of these polar groups distorts the diphenyl molecule into a very different orientation. It is certain from the dimensions that the molecule cannot lie elongated along any of the axes and it is reasonable to suppose that the two rings are bent or turned at an angle to each other. The fact that this acid forms an anhydride readily would indicate that the two carboxyl groups are in close proximity. The solution of this problem, though interesting in itself, would shed no light on the question of stereoisomerism and therefore was not studied further.

The following premises have emerged from the above discussion as a basis for the complete picture of the positions of the molecules of diphenyl derivatives. The diphenyl molecule is symmetrical about a center; dimesityl and hexachlorodiphenyl have no symmetry. The molecules in all cases lie with their length parallel or at a slight tilt to the *c* axis. The rings of carbon atoms are in each case probably staggered and have a thickness which is constantly 4.3 for the derivatives and 4.1 for diphenyl itself. The width across the ring is 5.6 for diphenyl, 7.9 for hexachlorodiphenyl and 8.1 for dimesityl and its diamino derivative. The respective lengths of these compounds are 9.5, 10.75, 11.1 and 11.3.

Discounting the staggering for the moment, there are the possibilities that the two rings may lie in the same plane, in planes at small angles to each other, or at right angles. The space considerations do not favor the first. The facts that the molecules are asymmetric and that they occupy the spaces given in the preceding paragraph lead to the conclusion that the two rings are in planes turned from each other at an angle of not greater than 45° in the 2,2',6,6'-derivatives of diphenyl, while the rings in diphenyl itself are coplanar.

Summary

1. Unique solutions of the crystal structure for diphenyl and five of its derivatives have been determined by rotating and oscillating crystal methods.
2. The possible size, shape and position of the molecules of these compounds are discussed.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

SYNTHESIS OF QUINOLINE COMPOUNDS. VI. PREPARATION OF CERTAIN ACYLAMINO DERIVATIVES OF 8-HYDROXYQUINOLINE

BY KONOMU MATSUMURA AND CHUSABURO SONE

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The acyl derivatives of aminohydroxyquinoline described in this paper were prepared in connection with a study of the bactericidal action of quinoline compounds.

Experimental

The aminohydroxyquinoline (1 mole) and acetic anhydride (1.1 moles) were allowed to react in ether solution for three days at room temperature in the presence of finely ground sodium acetate, with occasional stirring. The ether was then evaporated and sufficient water was added to dissolve the sodium acetate. The product was filtered, washed and finally recrystallized. The yields were very good.