

## CRYSTAL STRUCTURES OF SOME DERIVATIVES OF DIPHENYL

By GEORGE L. CLARK AND LUCY W. PICKETT

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS

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A two-fold interest attaches itself to x-ray studies of structure of diphenyl derivatives in that they offer a mode of attack on the problem of the shape and symmetry of the benzene ring, and also on that of the stereoisomerism of 2,2'-6,6' substituted diphenyls now being intensively investigated by Roger Adams and associates. An x-ray study of a series of derivatives of diphenyl is being carried out with these interests, and unique solutions have been reached for diphenyl, dimesityl and *o*-tolidine.

The analysis in each case has been carried out with the use of single crystals of one or two millimeters for the longest dimension. Although sharper diffraction spots are obtained from smaller crystals, the difficulties of mounting and the length of time of exposure increase greatly, so that this size was found to give the most satisfactory results. Laue photographs were taken using the unfiltered radiation from a molybdenum target tube; for the rotation and oscillation patterns the characteristic K radiation of copper was employed. No filter was used inasmuch as the  $\alpha$ -radiation could be easily distinguished from the  $\beta$  by the great difference in intensity, and served as a check on calculations. The crystallographic system was determined in each case with the x-ray goniometer as described by Clark and Yohe,<sup>1</sup> with further verification from Laue patterns and optical examinations. The dimensions of the unit cell were obtained from rotation photographs about each of the three axes of the crystal, while identification of the reflections corresponding to each set of planes could be made with certainty from sets of oscillating photographs, each covering a range of 15°. This is perhaps the first time that these oscillation patterns have been used to such good advantage. Typical photographs of each type are reproduced in this note.

*Diphenyl*.—Although an analysis of diphenyl was recently published by Mark,<sup>2</sup> the following results, obtained independently, are presented in confirmation of his conclusions. The crystal unit was found to be monoclinic with the dimensions  $a = 8.11$ ,  $b = 5.67$ ,  $c = 9.57$  and  $\beta = 94.5^\circ$ . From the facts that 010 is halved and also  $h0l$  where  $h$  is odd, the crystal is assigned to the monoclinic prismatic class with the space group  $C_{2h}^5$  based on the simple monoclinic lattice.<sup>3</sup> Inasmuch as there are two molecules in the unit cell, conditions of symmetry demand that the molecule should have a center of symmetry only and hence a staggered ring is probable. These results are identical with those of Mark except for slight differences in the length of the axes.

*Dimesityl*.—Dimesityl crystallizes from an alcohol water mixture in thin rectangular plates or in needles. Rotation and oscillation photographs taken about each of the three axes indicate that the unit cell is monoclinic prismatic with  $\beta = 96^\circ 30'$ ;  $a = 8.21$ ,  $b = 8.58$ ,  $c = 22.25$ . The space group, based on the simple monoclinic lattice,  $\Gamma_m$ , is  $C_{2h}^5$ , and the unit cell contains four asymmetric molecules. The following data are presented in support of these conclusions:

Rotation about  $a$  axis

$n$	Distance of line from equator	$a$
1	0.95 cm.	8.238
2	2.03	8.180
3	3.40	8.211
		Ave. 8.21

Rotation about  $b$  axis

		$b$
1	0.915	8.545
1	0.815	8.638
2	1.915	8.604
2	1.72	8.538
		Ave. 8.58

Rotation about  $c$  axis

		$c$
1	0.345	22.20
2	0.70	22.20
2	0.63	22.26
3	1.06	22.34
		Ave. 22.25

The density of dimesityl, determined by immersing a crystal in an aqueous salt solution of the same density, is 1.020. Thence

$$\sin 83'30' \times 10^{-24} \times 8.21 \times 8.58 \times 22.25 = \frac{238.176 \times n}{6.06 \times 10^{23} \times 1.02}$$

$n = 4.034$  or 4 molecules in the unit cell.

Oscillation photographs about the 001 axis show that the 100 spacing is present in all orders, but that the 010 is halved. Photographs about the 010 axis show that the 001 spacing is halved, while a photograph about 001 shows that 101, 201, 103, 203, etc., are missing. All other reflections seem to be present. Thus it is obvious that the planes  $h0l$  where  $l$  is odd are halved and 010 is halved. The only space group which meets this condition is  $C_{2h}^5$ . Since there are four molecules in the unit cell, the molecule must be asymmetric.

It is of interest that the space group is the same as that of diphenyl. In the latter case, however, there are but two molecules in the unit cell

and each molecule has a center of symmetry. The introduction of the three methyl groups in each ring, though in seemingly symmetrical positions evidently destroys the symmetry of the molecule.

The equivalent points in the space group  $C_{2h}^5$  are represented in figure 1 which is a diagram of the unit cell. The positions marked 1 at the eight corners of the cell are equivalent; those marked 2 are separated from the former by a rotation of  $180^\circ$  and a translation of  $1/2$ ; those marked 3, at

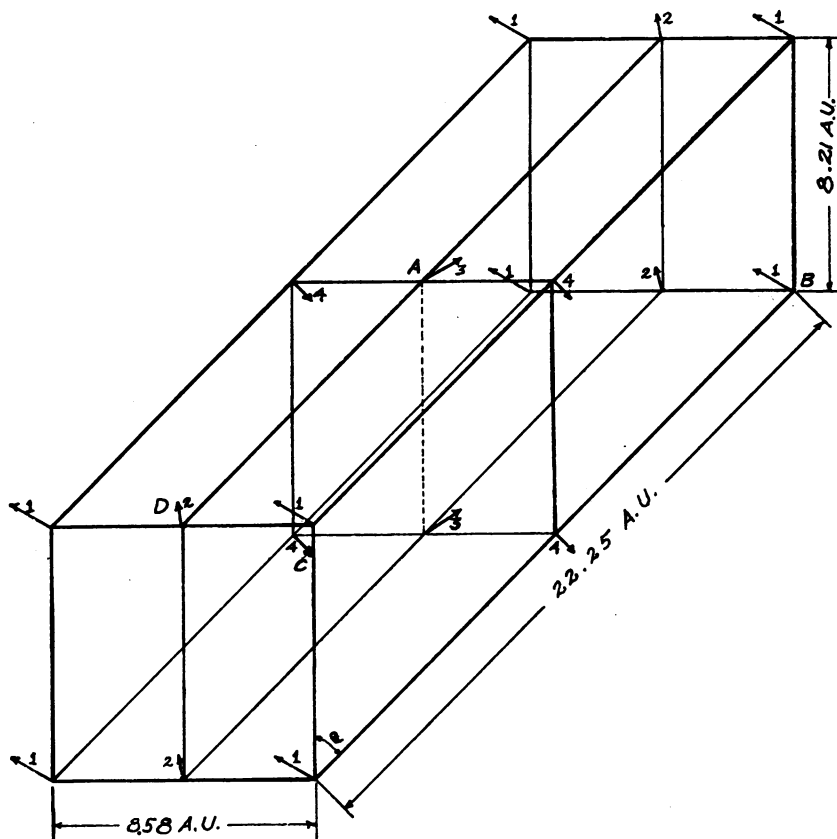


FIGURE 1

top and bottom have a center of symmetry with the elements at 1 and are related to those at 2 by reflection in a glide plane; those at 4 have a center of symmetry with the ones at 2, and are enantiomorphous to those at 1. The coordinates of these points may be expressed:  $x, y, z$ ;  $\bar{x}, \bar{y}, z + 1/2$ ;  $x + 1/2, y, \bar{z}$ ;  $1/2 - x, \bar{y}, 1/2 - z$ .

The exact position of the molecules is not known from the present data. It is probable that in the case of diphenyl, the two molecules occupy positions with their axes parallel to  $AB$  and  $CD$ , respectively, in which case

the length of the axis would be about 9.8. For dimesityl, however, the long axis of the molecule could hardly be in this direction, since two molecules would have to have a combined length of 14.46.

*3,3'-Diamino-dimesityl*.—Upon the theory that certain substituent groups on the two phenyl groups are sufficiently large in their spacial spheres of influence so that free rotation around the diphenyl linkage would be prevented by interference at 2 and 2', and 6 and 6' positions dimesityl with interfering CH<sub>3</sub> groups should come under this classification. Two optical isomers of course could not be expected on account of the

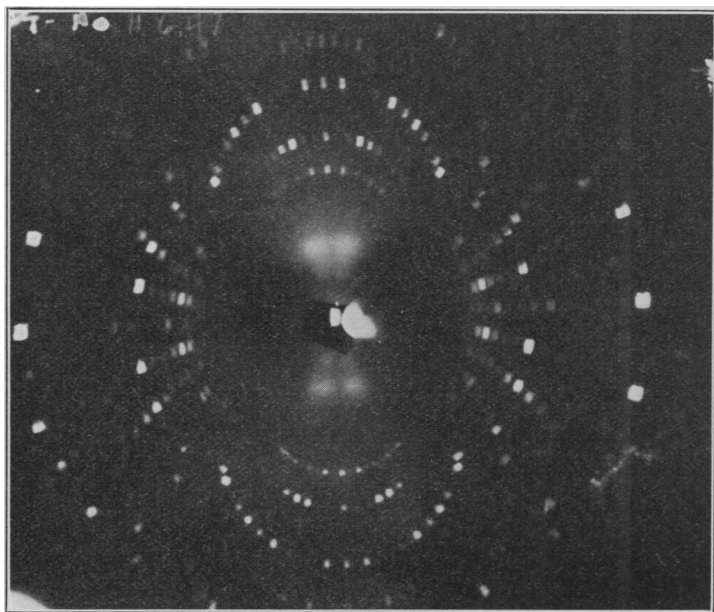


FIGURE 2

symmetrical placing of groups all alike (six methyl groups). By introducing an additional single substituent group on each phenyl, thus unsymmetrically loading the molecule, the interference of 2,2'-6,6' methyl groups should be manifest in the resolution of optical isomers.<sup>5</sup> Such a compound is 3-3' diamino-dimesityl which may be resolved into *d* and *l* forms. X-ray patterns prove that these *d* and *l* forms are identical, and that the crystalline structure is similar to that of dimesityl. A detailed analysis will be presented later.

*o-Tolidine*.—Ortho-tolidine, or 4,4' diamino- 3,3' dimethyldiphenyl crystallizes from 95% alcohol in rectangular plates slightly brownish in color. Examination of single crystals by Laue, rotation and oscillation

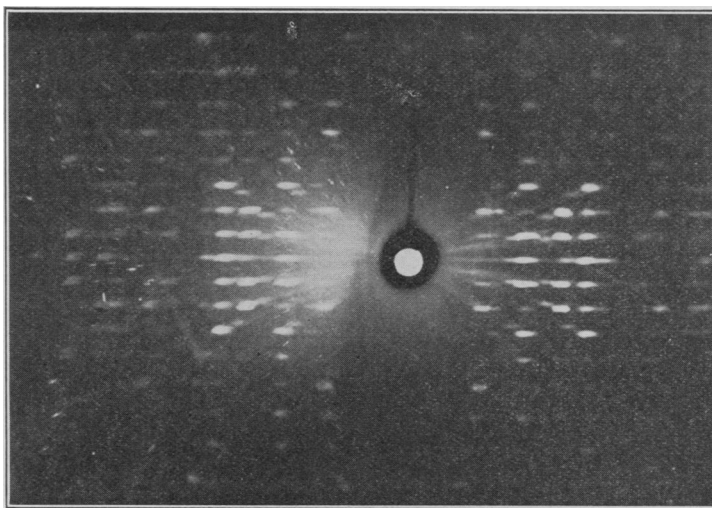


FIGURE 3

photographs showed that the unit cell is orthorhombic, contains four molecules, and has the dimensions  $a = 6.50$ ,  $b = 7.48$  and  $c = 23.62$  A.U.

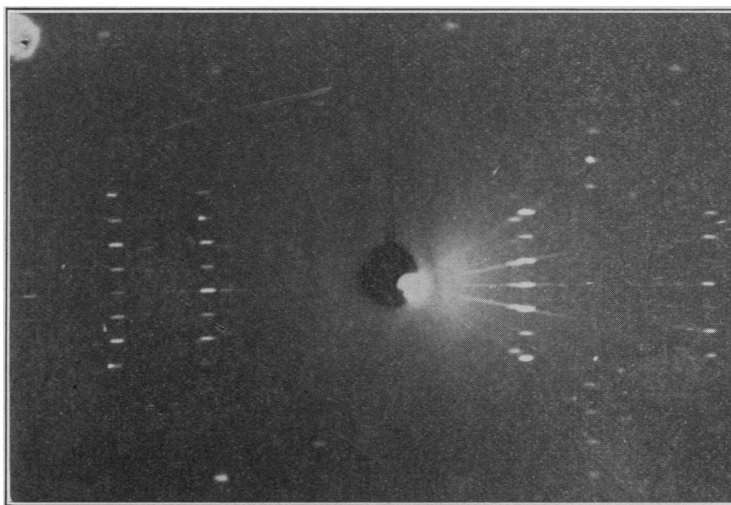


FIGURE 4

Figure 2 represents a Laue photograph of *o*-tolidine with the beam of x-rays parallel to the  $a$  axis; the planes with indices from 1,6,0 to 1,0,20 are to be identified on this photograph. A typical rotation diagram is illustrated in figure 3 where the  $c$  axis is the axis of rotation and its length

may be calculated from the distance between the layer lines on which the spots lie. Figure 4 is one of a series of oscillation photographs covering a range of  $25^\circ$  to  $40^\circ$  taken about the  $c$  axis of tolidine. This method proved the most valuable in the identification of reflections, inasmuch as in this way the most complicated rotation diagram could be analyzed into a number of simpler diagrams on which spots could be identified with certainty because the position of the crystal was known and spots are not likely to be superimposed. Thus in figure 4, the vertical line of spots at the right of the central beam refer to the planes 110, 111, 112, 113, etc. Those at the left near the central beam are 210, 211, 212, 213, 214, interferences, etc., and the line of spots further removed corresponds to 310, 311, 312, 313, 314, etc., planes.

The dimensions of the unit cell were obtained from the following measurements of rotation photographs.

Rotation about  $a$  axis

$n$	Distance of line from 0 line	$a$
1	1.215 cm.	6.52
2	2.695	6.49
2	2.70	6.47
2	2.35	6.53
		Ave. 6.50

Rotation about  $b$  axis

		$b$
1	1.05	7.48
2	2.24	7.51
2	2.26	7.45
2	2.00	7.48
		Ave. 7.48

Rotation about  $c$  axis

		$c$
1	0.325	23.68
2	0.65	23.86
3	1.00	23.50
4	1.36	23.59
5	1.725	23.56
6	2.125	23.57
		Ave. 23.62

The density of the crystal was experimentally determined as 1.215. From these values the number of molecules in the unit cell may be calculated:

$$6.50 \times 7.48 \times 23.62 \times 10^{-24} = \frac{212.2 \times n}{6.06 \times 10^{-23} \times 1.215}$$

$$n = 3.985, \text{ or } 4.$$

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 so weak that they are only detectable on an overexposed photograph. No other group is consistently absent. Hence the space group is probably  $Q^4$ , also symbolized as  $V^4$ ; if the  $0k0$  planes are present and weakened by some other cause than that of space group considerations, the group  $Q^3$  in the alternative. Both groups are based on a simple orthorhombic lattice,  $\Gamma_0$ , and require four unsymmetrical molecules in the unit cell.

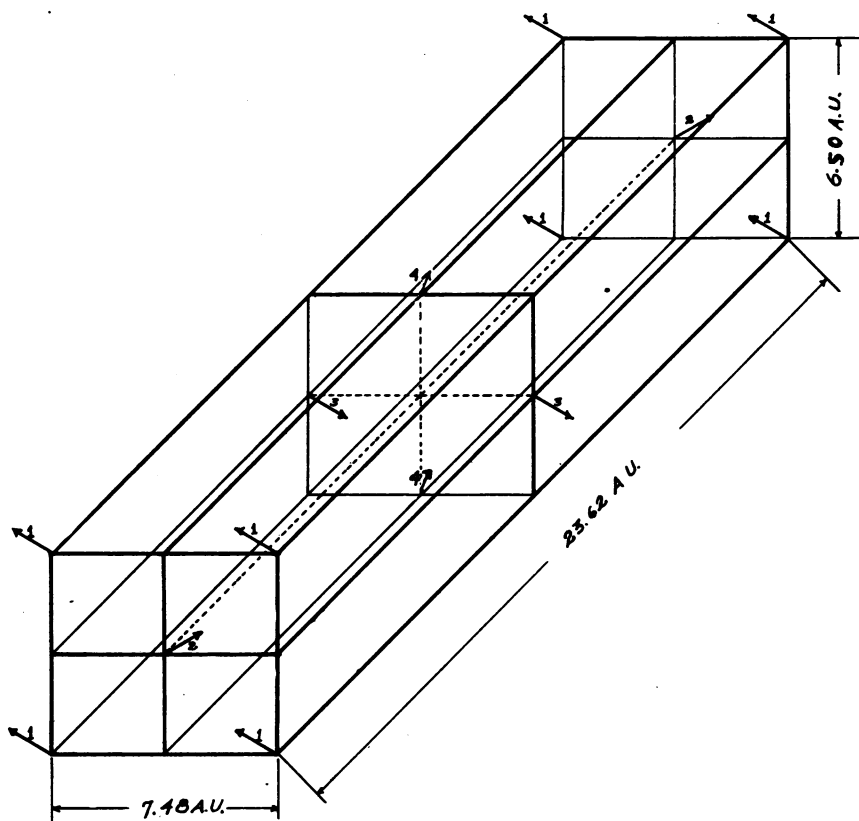


FIGURE 5

The four equivalent positions for the space group  $V^4$  may be designated by the coordinates  $xyz$ ;  $x + \frac{1}{2}, \frac{1}{2} - y, \bar{z}$ ;  $x, y + \frac{1}{2}, \frac{1}{2} - z$ ;  $\frac{1}{2} - x, \bar{y}, z + \frac{1}{2}$ .

Figure 5 represents the unit cell with equivalent points at the corners and three other sets at the centers of opposite faces. Those at 1 and 3, and at 2 and 4 are related by dyad screw axes parallel to the edge with

spacing 23.62; those at 1 and 2, and at 3 and 4 have dyad screw axes parallel to the edge with spacing 6.50.

*Diphenic Acid.*—The analysis of this compound is not complete. The results obtained show that the crystal is orthorhombic with the dimensions  $a = 14.12$ ,  $b = 11.90$ ,  $c = 13.75$ , and that there are eight molecules in the unit cell. This indicates an arrangement quite different from the other compounds studied as the unit cell is approximately half as long in one dimension and twice as wide in the other two. It is possible that this is caused by the attraction and consequent doubling of COOH groups such as is found in the case of aliphatic compounds.

Other compounds now being investigated are: difluoro-diphenic acid, hexachloro-diphenyl, octamethyl diphenyl, diphenyl benzene. Thanks are due Professor Roger Adams for suggesting this research and for providing the necessary materials.

<sup>1</sup> *J. Am. Chem. Soc.*, **51**, 2796 (1929).

<sup>2</sup> *Zeit. Krist.*, **70**, 285 (1929).

<sup>3</sup> Astbury and Yardley, *Phil. Trans. Roy. Soc. London*, **224A**, 221 (1924).

<sup>4</sup> Wyckoff, *Analytical Expression of the Results of the Theory of Space Group*, Carnegie Institute, Washington, p. 51.

<sup>5</sup> See papers by Roger Adams and associates on diphenyl derivatives in *J. Am. Chem. Soc.*

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## THE TEMPERATURE COEFFICIENT OF THE PHOTOCHEMICAL FORMATION OF HYDROGEN CHLORIDE

BY OLIVER R. WULF

BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.

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In the theory of the temperature coefficient of photochemical reaction developed by Tolman<sup>1</sup> the probability that a molecule will react, once it has acquired by absorption the energy necessary for reaction, is taken to be not markedly dependent on the temperature. In the case of unimolecular reactions it is important to notice that one then has simply the theory of the temperature coefficient of light absorption. Kistiakowsky<sup>2</sup> has discussed this in his recent book. It is especially important to remember that this remaining temperature coefficient of light absorption can appear experimentally to its full extent only in those cases of small fractional reduction of the intensity of the incident beam. The temperature coefficient of light absorption for molecules is a quantity regarding which the theory and the data of band spectra should be able to give complete information. It will be noted that in Tolman's theory extended