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## X-Ray and Electron Diffraction of Iodine and the Diiodobenzenes

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(Received May 9, 1933)

The crystal structures of 1,3 and 1,4 diiodobenzene were determined from the x-ray diffraction patterns of single crystals. The separations of the iodine atoms in the molecules were found to be 6.85 and 5.92 Å, respectively. These values are in agreement with results obtained by analysis of the electron diffraction patterns given by the vapors of these compounds. The most satisfactory explanation of the electron diffraction results for 1,2 diiodobenzene requires the I—C valence directions to be bent by about 10° from symmetrical positions in the plane of the

benzene ring. In this molecule the I—I distance was found to be 4.00 Å, which is approximately the same as the minimum intermolecular iodine distances in crystals of the other isomeric diiodobenzenes. Electron diffraction was obtained from vapors of carbon tetrachloride and iodine. The separation of the iodine atoms in the latter molecule was found to be 2.64 Å; a value in agreement with band spectra data and with previous crystal structure analysis.

COHERENT scattering of electrons and x-rays are utilized in the present work for determining the atomic configurations of iodine and the three isomeric diiodobenzenes. Analyses of x-ray diffraction patterns of crystalline 1,3 and 1,4 diiodobenzene readily led to the allocation of the iodine atoms in the units of structure and to knowledge of the molecular orientations. Diffraction of electrons from vapors of these compounds and from 1,2 diiodobenzene and iodine permitted determinations of iodine to iodine distances within the molecules.<sup>1</sup>

### ELECTRON DIFFRACTION

#### Theory

The angular distribution of electrons elastically scattered from a molecular vapor can be ex-

plained by use of the Debye interference formula<sup>2</sup> developed for coherent scattering of x-rays from polyatomic molecules together with the theory of Mott<sup>3</sup> and Bethe<sup>4</sup> for elastic scattering of electrons by monatomic gases. The formulas of Mott and Bethe have been found to agree approximately with results of experiments<sup>5</sup> provided that the electron velocities are sufficient so that the effect of atomic polarizations and electron interchanges will be unimportant. These theories are contained in the following formula<sup>6</sup> for  $I(\theta)$ , a quantity that is directly proportional to the number of electrons scattered elastically, at an angle  $\theta$ , per unit solid angle per unit intensity of the primary beam.

$$I(\theta) = \sum_{i=1}^n \sum_{j=1}^m \psi_i \psi_j (\sin x_{ij} / x_{ij}) \quad (1)$$

<sup>1</sup> *Preparation of compounds.* We are indebted to Mr. E. F. Jansen of this laboratory for the preparation of 1,2 diiodobenzene. 1,2 Iodonitrobenzene was made by the diazotization of 1,2 nitroaniline followed by treatment with KI (Busch and Walbring, *J. prakt. Chem.* (2) **71**, 374 (1905)). The reduction of this compound to 1,2 iodoaniline was effected by treatment with SnCl<sub>2</sub> in acetic acid solution. (Thiele, *Ann. d. Chemie* **305**, 114 (1899)). Diazotized 1,2 iodoaniline reacts explosively with KI to form 1,2 diiodobenzene (m. p. 26°). 1,3 diiodobenzene was prepared by the tetra-azotization of *m*-phenylenediamine followed by treatment with KI (cold). It was separated by steam distillation, extracted with ether, dried, and distilled (m. p. 39°). 1,4 diiodobenzene was purchased from the Eastman Company.

<sup>2</sup> P. Debye, *Ann. d. Physik* **46**, 809 (1915).

<sup>3</sup> N. F. Mott, *Proc. Camb. Soc.* **25**, 304 (1929); *Proc. Roy. Soc.* **A127**, 658 (1930).

<sup>4</sup> H. Bethe, *Ann. d. Physik* **87**, 55 (1928); *ibid.* **5**, 325 (1930).

<sup>5</sup> For the extent of experimental confirmation of the theory of Mott and Bethe see: N. F. Mott, reference 3; H. Mark and R. Wierl, *Zeits. f. Physik* **60**, 741 (1930); F. L. Arnot, *Proc. Roy. Soc.* **A133**, 615 (1931); A. L. Hughes and J. R. McMillen, *Phys. Rev.* **39**, 585 (1932); John T. Tate and R. Ronald Palmer, *Phys. Rev.* **40**, 731 (1932); A. L. Hughes, J. H. McMillen and G. M. Webb, *Phys. Rev.* **41**, 154 (1932); A. L. Hughes, *Phys. Rev.* **42**, 147 (1932).

<sup>6</sup> See R. Wierl, *Ann. d. Physik* **8**, 521 (1931).

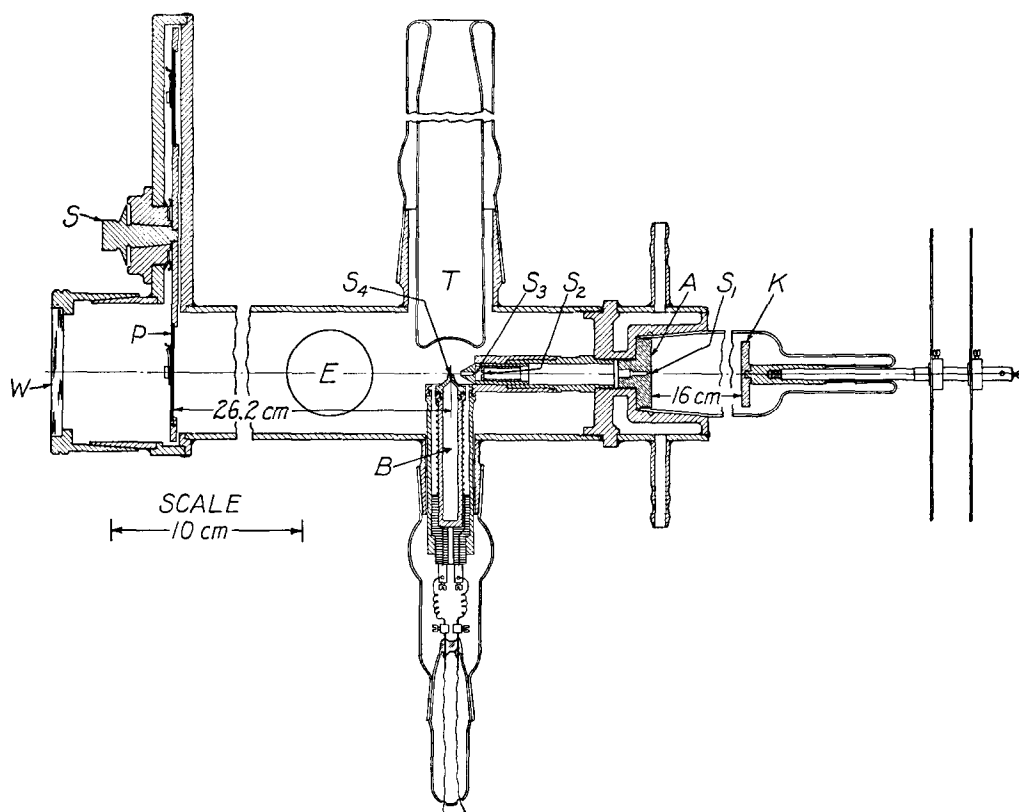


FIG. 1. Diagram of the apparatus.

where

$$x_{ij} = 4\pi l_{ij} [(\sin \theta/2)/\lambda] \quad (2)$$

$$\psi_{ij} = (Z_i - F_i) / [(\sin \theta/2)/\lambda]^2. \quad (3)$$

In these expressions  $l_{ij}$  is the distance between the  $i$ th and the  $j$ th atom,  $\lambda$  is the de Broglie wave-length of the electrons, and  $Z_i$  and  $F_i$  are the atomic number and atomic scattering factor of the  $i$ th atom, respectively.

### Experimental arrangement

The apparatus used, a modification of that described by Wierl,<sup>6</sup> is diagrammatically shown in Fig. 1. Electrons originating from the cold cathode  $K$  of a gas discharge tube were limited to a fine beam by a tube  $S_1$  0.2 mm in diameter and 2 mm long and by two holes  $S_2$  and  $S_3$  each 0.1 mm in diameter. The electrons, after penetrating the molecular beam formed by the vapor coming from the nozzle  $S_4$ , were finally recorded on the photographic plate  $P$ . Vapors issuing from the nozzle, which was about 0.3 mm in diameter and 5 mm long, were condensed on the liquid air

trap  $T$ . The pressure in the boiler  $B$  was usually about 10 mm Hg, while a pressure of less than  $10^{-3}$  mm Hg was maintained in the diffraction chamber. This was obtained by rapid pumping at  $E$  with a three-stage Gaede steel pump supported by a Cenco megavac pump.

Eastman lantern slide plates were used for recording the diffraction patterns. They were mounted at  $P$  in sectors of a disk that could be rotated by means of the cone  $S$  so that five consecutive exposures could be taken. The diffraction pattern appearing on a fluorescent screen placed in one of the sectors could be observed through the clear glass window  $W$ .

This discharge tube was operated with constant d.c. potential supplied by a filter circuit similar to that described by Hull.<sup>7</sup> The primary excitation of the high voltage transformer was supplied by a 60-cycle a.c. generator driven by a synchronous motor. Two Meirowsky condensers connected in parallel, having a total capacity of

<sup>7</sup> A. W. Hull, Gen. Elec. Rev. 19, 173 (1916).

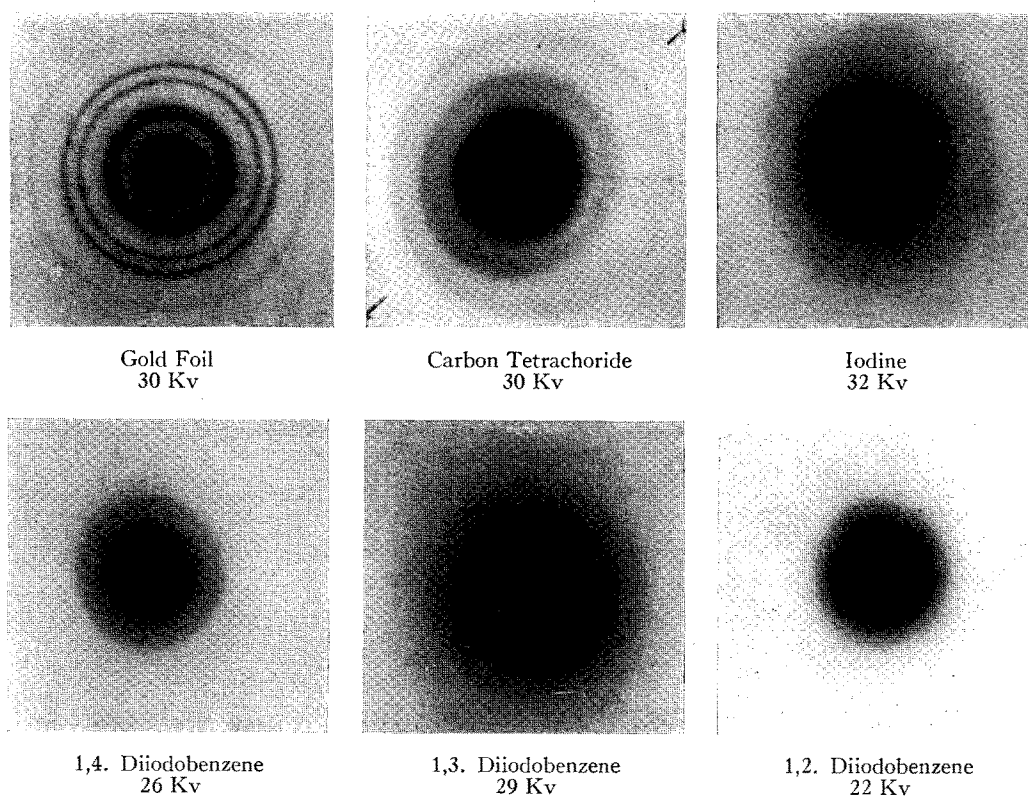


FIG. 2. Electron diffraction photographs, exposure times 3 seconds to 2 minutes.

0.2 microfarad, were used for maintaining a constant voltage together with an inductance of about 2000 henries. The potential across the discharge tube, 40 kv maximum, was measured by a static voltmeter according to the design developed by W. W. Nicholas.<sup>8</sup> The voltmeter was calibrated by the use of electron diffraction patterns obtained from a thin gold foil. These results were compared with voltage measurements made by means of Taylor high voltage resistances.<sup>9</sup> After including a small relativity correction, it was found that the two methods of determining the de Broglie wave-lengths of the electrons were in agreement to within about one percent.

### Experimental results

*Carbon tetrachloride.* The densitometer record of an electron diffraction photograph, reproduced

<sup>8</sup> W. W. Nicholas, Bur. Standards J. Research **8**, 111 (1932).

<sup>9</sup> We are indebted to Dr. L. S. Taylor of the United States Bureau of Standards, for the loan of the resistances used.

in Fig. 2, given by carbon tetrachloride vapor is shown in Fig. 3. A true interference maximum is obtained that is in better agreement with the theoretical intensity curve<sup>10</sup> than has been reported heretofore for the case of electron diffraction. In this particular instance the compound was placed in a glass container connected through a stopcock to the jet shown at  $S_4$ , Fig. 1.

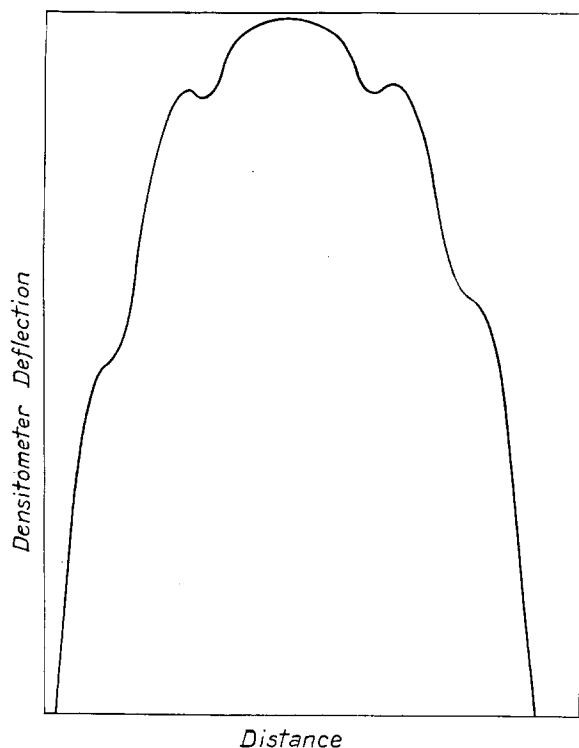
Values of  $(1/\lambda) \sin \theta/2$  for the first three maxima as measured by various observers are listed in Table I. The values obtained by Wierl, Hengstenberg and Brú<sup>11</sup> and by the writers are in

TABLE I. Comparison of electron diffraction values of  $(\sin \theta/2)/\lambda$  for carbon tetrachloride.

Maximum	Wierl	Brockway & Pauling	Hengstenberg & Brú	Present work
1	0.197	0.212; 0.220	Agreement with Wierl to within $\frac{1}{2}\%$	$0.197 \pm 0.003$
2	.364	.376; .385		$.364 \pm .003$
3	.543	.558; .569		$.548 \pm .005$

<sup>10</sup> For theoretical intensity curve for  $\text{CCl}_4$  see R. Wierl, reference 6.

<sup>11</sup> J. Hengstenberg and L. Brú, Anales Soc. Espana. Fis y Quim. **30**, 341 (1932).

FIG. 3. Densitometer record for electron diffraction of  $\text{CCl}_4$ .

good agreement. The Cl—Cl distance for the tetrahedral molecule calculated from these data is 2.98Å. The results of Brockway and Pauling<sup>12</sup> differ appreciably from those obtained by other observers. Our values for the first two maxima are averages obtained from eight photographs at various voltages, exposure times and molecular beam concentrations. The third maximum was measured on only two plates.

*Iodine.* The theoretical scattering curve for iodine is obtained from Eq. (1) which reduces to

$$I(\theta) = 2\psi_I\psi_I(1 + \sin x/x) \quad (4)$$

where  $\psi_I = (Z_I - F_I)/((\sin \theta/2)/\lambda)^2$ . Fig. 4 shows  $I(\theta)$  plotted as a function of  $x$  and of  $(1/\lambda) \sin \theta/2$ . The I—I distance was assumed to be 2.66Å as found from band spectra data<sup>13</sup> and in this instance as well as in the case of subsequent molecules the values of  $F_i$  used were obtained from Pauling's and Sherman's<sup>14</sup> calculations for electron distributions corresponding to Schrödinger eigenfunctions for hydrogen-like atoms.

<sup>12</sup> L. A. Brockway and Linus Pauling, Proc. Nat. Acad. Sci. 19, 68 (1933).

The apparent diffraction rings do not correspond to true maxima but rather to points of inflection (note Fig. 4). Their diameters depend upon  $\psi_I$  which is a function of the atomic separation, the quantity to be measured. Fortunately small changes in  $l_{ij}$  do not greatly affect the maxima or inflection points expressed as a function of  $x_{ij}$ . This justifies the use of approximate values of  $l$  in computing the intensity curve.

The experimental results are given in Table II.

TABLE II. Electron diffraction results for iodine.

Plate No.	Wave-length in Å	$(\sin \theta/2)/\lambda$	
		1st Maximum	2nd Maximum
1	0.0638	0.223	0.403
2	.0648	.224	.402
3	.0667	.236	.415
4	.0667	.222	.402
5	.0667	.222	.402
6	.0667	.222	.408
7	.0695	.226	
8	.0695	.226	
9	.0748	.239	
Average values		$0.226 \pm 0.002$	$0.405 \pm 0.002$
I—I = $2.64 \pm 0.15\text{Å}$ ; $2.65 \pm 0.10\text{Å}$			

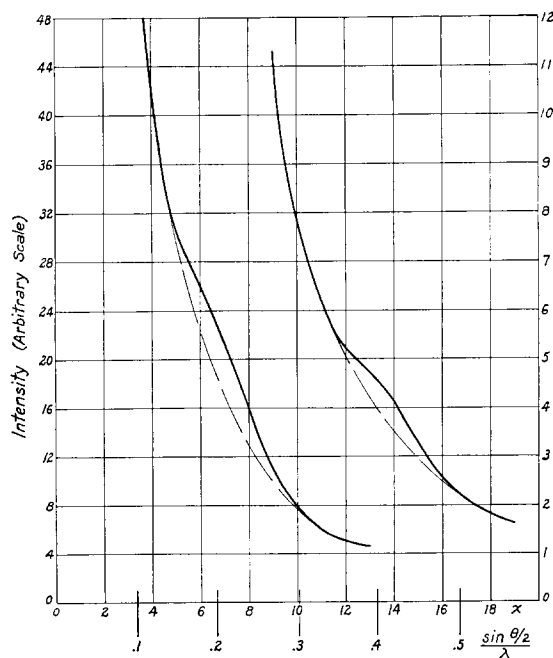


FIG. 4. Theoretical electron diffraction curve for iodine.

<sup>13</sup> R. T. Birge, Int. Crit. Tab. 5, 409 (1929).

<sup>14</sup> L. Pauling and J. Sherman, Zeits. f. Kristallographie 81, 1 (1932).

The average values obtained for  $(1/\lambda) \sin \theta/2$  are 0.226 and 0.405 for the first and second diffraction rings, respectively. The theoretical values of  $x$  corresponding to these rings are 7.5 and 13.5 as seen from Fig. 4. From Eq. (2) we obtain 2.64Å and 2.65Å as the I—I distance.

**1,4 diiodobenzene.** The chief interest in the analyses of the diiodobenzenes lies in the determination of the I—I distances. The iodine atoms produce the majority of the scattering, and consequently afford a method for measuring the I—I separations. However, the scattering from the other atoms cannot be neglected for although the scattering produced by them is small it is also a very irregular function of  $(\theta)$  and when superimposed upon the iodine-iodine scattering may give maxima or minima of importance.

In general the procedure adopted has been to calculate a complete scattering curve for a molecular model based upon prior information. The positions of the maxima or prominences are then compared and in case of poor agreement the calculations are repeated for a somewhat different model. This procedure is followed until good agreement is obtained. The solution, although not unique, is sufficient and in the case of the

diiodobenzenes undoubtedly gives the separation of the iodine atoms and confirms the geometry of the molecules.

The assumed structure of 1,4 diiodobenzene is shown in Fig. 5. The C—C distance of 1.42Å is the value obtained from x-ray measurements on hexamethyl benzene<sup>15</sup> and from electron diffraction data of benzene vapor.<sup>6</sup> The value of 1.12Å for the C—H distance was obtained from band spectra data on CH<sup>16</sup> while the I—C separation, 2.10Å, was obtained as an extrapolation of the Cl—C and Br—C distances in a number of organic compounds.<sup>17</sup>

On applying Eq. (1) we can evaluate  $I(\theta)$  for 1,4 diiodobenzene as follows

$$I(\theta) = I_{II} + I_{IC} + I_{CC} + I_{IH} + I_{HC} + I_{HH} \quad (5)$$

where  $I_{nm}$  is the intensity of coherent scattering between atoms of type  $n$  and  $m$ . The  $\psi_i \psi_j$  factors are important in determining the relative magnitudes of the various terms in Eq. (5). The terms  $I_{HC}$  and  $I_{HH}$  can be shown to be negligibly small while the contribution of  $I_{IH}$  is small and in most instances can be omitted although it should be included for an accurate analysis. If the distances assumed above are used Eq. (5) reduces to

$$I_{II} = 2\psi_I \psi_I (1 + \sin 4.95x_{cc}/4.95x_{cc}), \quad (6)$$

$$I_{IC} = 4\psi_C \psi_I \left[ \frac{\sin 1.48x_{cc}}{1.48x_{cc}} + 2 \frac{\sin 2.14x_{cc}}{2.14x_{cc}} + 2 \frac{\sin 3.1x_{cc}}{3.1x_{cc}} + \frac{\sin 3.48x_{cc}}{3.48x_{cc}} \right], \quad (7)$$

$$I_{CC} = 6\psi_C \psi_C [1 + 2 \sin x_{cc}/x_{cc} + \sin 2x_{cc}/2x_{cc} + 2 \sin 3^{\frac{1}{2}}x_{cc}/3^{\frac{1}{2}}x_{cc}], \quad (8)$$

$$I_{IH} = 8\psi_I \psi_H [\sin 2.2x_{cc}/2.2x_{cc} + \sin 3.70x_{cc}/3.70x_{cc}], \quad (9)$$

where

$$x_{cc} = 4\pi l_{cc}(\sin \theta/2)/\lambda = x_{II}/4.95, \quad (10)$$

$l_{cc}$  = C—C distance = 1.42Å.

The complete intensity curve is shown in Fig. 5. In order to determine the dependence of the position of the diffraction rings on the I—C distance similar curves were calculated for values of  $l_{IC}$  = 1.90Å and 2.30Å.

The experimental results are summarized in Table III. Values of  $x_{cc}$  listed in this table are indicated in Fig. 5 by the arrows  $a$ ,  $b$  and  $c$  for comparison with the calculated maxima which are indicated by smaller arrows. A photometer

record of a typical plate, No. 15, is shown in Fig. 6. It is to be noted that this record gives a curve of approximately the type required by theory. The second maxima, ( $b$ ), was used for the analysis since it could be measured with the greatest accuracy. Its mean position is between

<sup>15</sup> K. Lonsdale, Proc. Roy. Soc. (London) **A123**, 494 (1929).

<sup>16</sup> R. S. Mulliken, Rev. Mod. Phys. **4**, 83 (1932).

<sup>17</sup> S. B. Hendricks, Chem. Rev. **7**, 431 (1930).

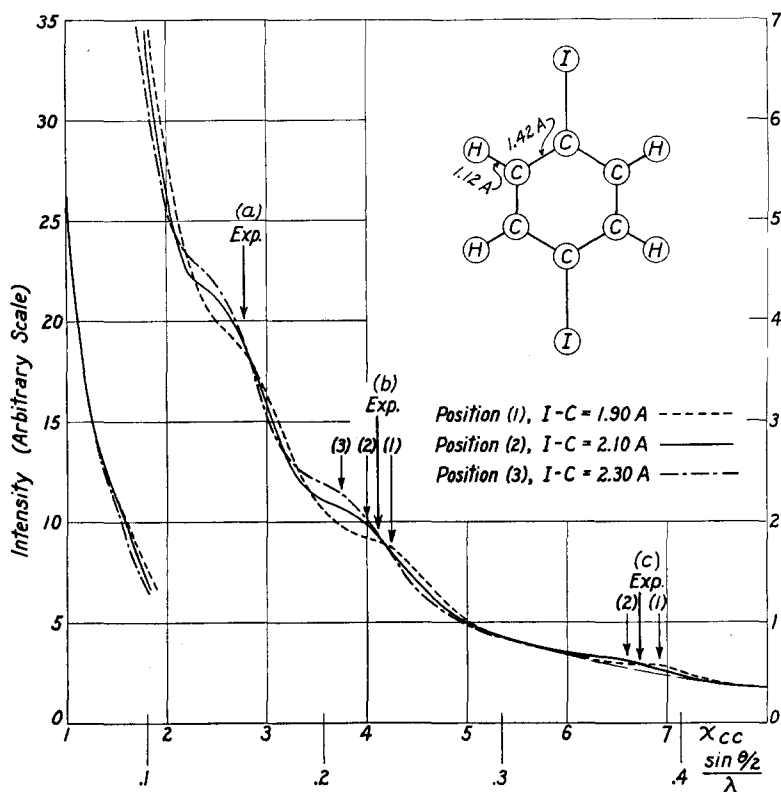


FIG. 5. Theoretical electron diffraction curves for 1,4 diiodobenzene. The arrows (a), (b) and (c) show the average positions of the observed diffraction rings in relation to the prominences on the theoretical curve. Similar comparisons are made in Figs. 7, 9 and 10.

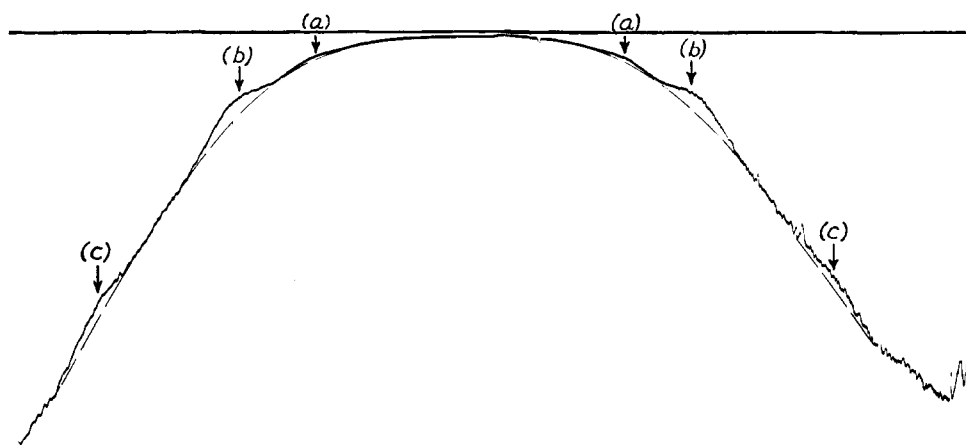


FIG. 6. Densitometer record for 1,4 diiodobenzene.

TABLE III. *Electron diffraction results for 1,4 diiodobenzene.*

Plate No.	Wave-length in Å	$(\sin \theta/2)/\lambda$		
		(a) 1st Maximum	(b) 2nd Maximum	(c) 3rd Maximum
1	0.0626	0.161	0.226	0.370
2	.0641	.161	.235	.376
3	.0648	.162	.236	.382
4	.065	.151	.226	
5	.0653	.156	.236	.380
6	.0672	.157	.230	.378
7	.069	.156	.230	
8	.074	.152	.226	present
9	.074	.154	.222	
10	.075	.146	.226	
11	.0778	.157	.223	
12	.0879	.158	.239	.380
13	.0883	.162	.239	.380
14	.0903	.164	.232	.377
15	.0960	.151	.223	present
Average values		0.156	0.230	0.378
$x_{cc}$		2.78	4.10	6.75
I-I = 6.85 ± 0.10 Å; I-C = 2.00 Å				

the corresponding points on the curves calculated for I-C distances of 1.90 Å and 2.10 Å. Interpolation shows that the most probable I-C distance is 2.00 Å which gives an I-I separation of 6.85 ± 0.10 Å.

Several photographs in which the rings *a*, *b* and

TABLE IV. *Electron diffraction results for 1,3 diiodobenzene.*

Plate No.	Wave-length in Å	$(\sin \theta/2)/\lambda$		
		(a) 1st Maximum	(b) 2nd Maximum	(c) 3rd Maximum
1	0.0620	0.185	0.268	0.352
2	.0623	.185		.351
3	.0662	.187		.359
4	.0664	.188	.276	.361
5	.0665			.359
6	.0666			.356
7	.0667			.360
8	.0715	.187		.360
9	.0717	.189		.358
10	.0720			.358
11	.0720			.358
Average values		0.186	0.272	0.357
$x_{cc}$		3.32	4.85	6.37
I-I = 5.97 ± 0.10 Å; I-C = 2.00 Å				

*c* were very intense showed faint halos at  $(1/\lambda) \sin \theta/2$  equal to about 0.3 and 0.45. The theoretical curve does not have corresponding points of inflection. Such a slight discrepancy is not unexpected in view of the approximations used in the theory.

*1,3 diiodobenzene.* Formulas for computing the scattering from this molecule are of the same form as for 1,4 diiodobenzene. Numerical quantities are changed, however, and the  $I_{IH}$  term becomes

$$I_{IH} = 4\psi_I\psi_H \left[ \frac{2 \sin 2.2x_{cc}}{2.2x_{cc}} + \frac{\sin 4.26x_{cc}}{4.26x_{cc}} + \frac{\sin 3.7x_{cc}}{3.7x_{cc}} \right]. \quad (11)$$

A complete intensity curve was calculated for an I-C distance of 1.90 Å and a partial curve for 2.10 Å in the region including the third and most pronounced maxima as shown in Fig. 7. A densitometer record with prominences (*b*) and (*c*) quite apparent may be seen in Fig. 8. (*c*) is the prominent ring noticeable in Fig. 2. It was used for determining the positions of the iodine atoms.

The experimental results are summarized in Table IV. The mean values obtained for  $x_{cc}$  are indicated in Fig. 7. The position of the third maxima lies between the maxima on the curves calculated for I-C distances of 1.90 Å and 2.10 Å. Interpolation gives 2.03 Å as the best value for

this distance, the corresponding I-I distance being 5.97 ± 0.10 Å.

*1,2 diiodobenzene.* Experimental results obtained from this compound are shown in Table V. A typical densitometer record is reproduced in Fig. 11. The most prominent ring appears at  $x_{cc} = 2.73$  with two other rings apparent at  $x_{cc} = 4.65$  and  $x_{cc} = 6.55$  on the photographs.

Values of  $I(\theta)$  were calculated by the above methods for a model in which the I-C distances were assumed to be 2.10 Å and the I-C directions symmetrically placed with respect to the benzene ring, thus making the I-I separation 3.52 Å. The arrows (*a*), (*b*), and (*c*) on Fig. 9 show the location of the experimentally observed rings;



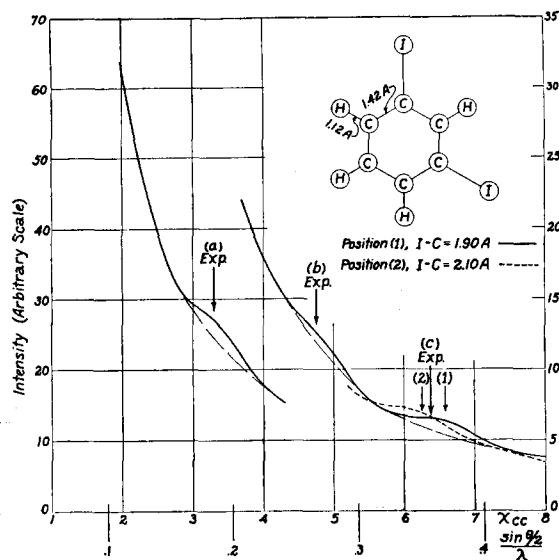


FIG. 7. Theoretical electron diffraction curves for 1,3 diiodobenzene.

these are to be compared with the calculated prominences. Although the first diffraction ring is in good agreement with the experiment, the theoretical curve does not account for the observed rings (b) and (c).

A theoretical scattering curve was calculated for this molecule in which the I-C distance was increased to 2.60A thus making the I-I separation 4.00A. The second and third maxima predicted by this curve were again out of agreement with the positions of the observed diffraction rings, whereas the position of the first maxima corresponded approximately with the

TABLE V. Electron diffraction results for 1,2 diiodobenzene.

Plate No.	Wave-length in A	$(\sin \theta/2)/\lambda$		
		1st Maximum	2nd Maximum	3rd Maximum
1	0.0639	0.157	0.261	
2	.0642	.148	.252	
3	.0648	.149	.265	
4	.0648	.154	.265	
5	.0648	.151	.279	0.368
6	.0648	.151		
7	.0649	.150	.264	
8	.0650	.151	.249	
9	.065	.151		
10	.0797	.156	.258	
11	.0797	.156	.252	
12	.0805	.154	.261	.366
13	.0805	.154	.261	.368
14	.0810	.153		
Average values		0.153	0.261	0.367
$x_{cc}$		2.73	4.65	6.55
I-I = $4.00 \pm 0.10$ A; I-C = $2.00 \pm 0.10$ A				

first experimental ring observed. The lack of agreement between the results and the theory for these two cases justifies the elimination of these models as possible representations of the structure of 1,2 diiodobenzene.

Calculations made for a third model in which the I-C distance was assumed to be 2.00A and the I-I distance to be 4.00A are illustrated in Fig. 10. This corresponds to a change in the I-C direction of about  $10^\circ$  from the former case and leaves a resultant unsymmetrical molecule. The curve shows three regions of inflection points agreeing approximately with the experimentally observed rings. The agreement is, however, not as good as obtained in the compounds previously

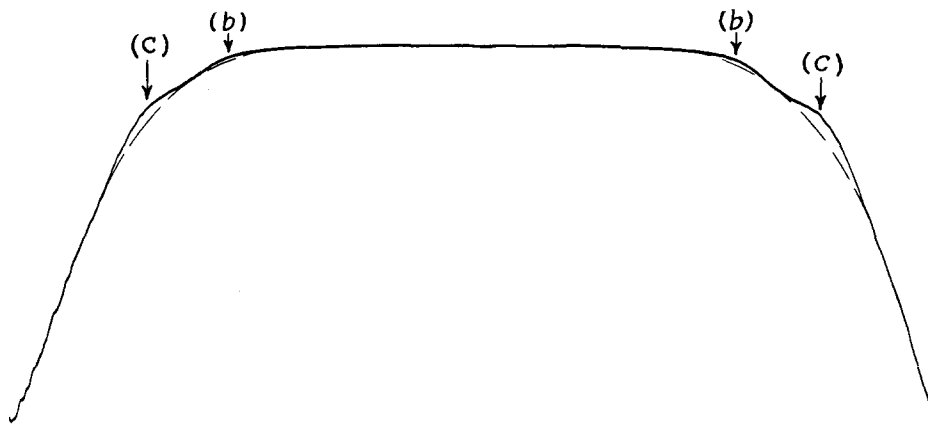


FIG. 8. Densitometer record for 1,3 diiodobenzene.

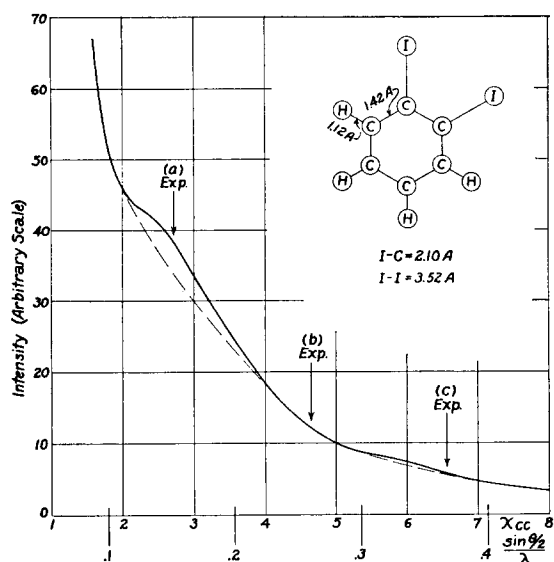


FIG. 9. Theoretical electron diffraction curve for 1,2 diiodobenzene with  $I-C = 2.10 \text{ \AA}$  and  $I-I = 3.52 \text{ \AA}$ .

discussed. The theoretical position of the first maxima is somewhat closer to the origin than is the observed ring. We conclude, however, that the atomic arrangement approximates that shown in Fig. 10.

#### X-RAY DIFFRACTION

Analysis of x-ray diffraction patterns from crystalline 1,4 and 1,3 diiodobenzene led to

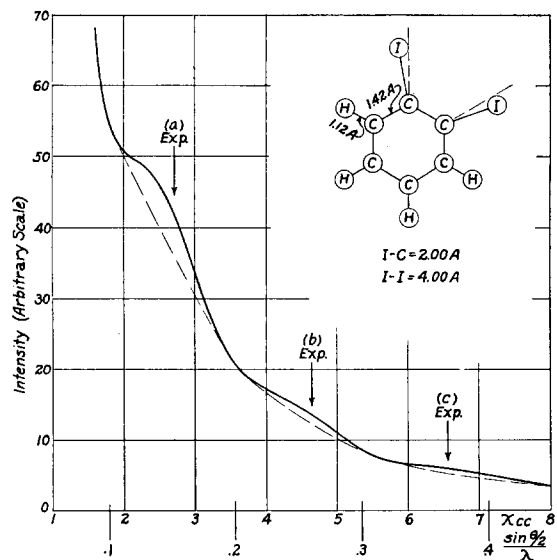


FIG. 10. Theoretical electron diffraction curve for 1,2 diiodobenzene with  $I-C = 2.00 \text{ \AA}$  and the valence direction bent by approximately  $10^\circ$  to give  $I-I = 4.00 \text{ \AA}$ .

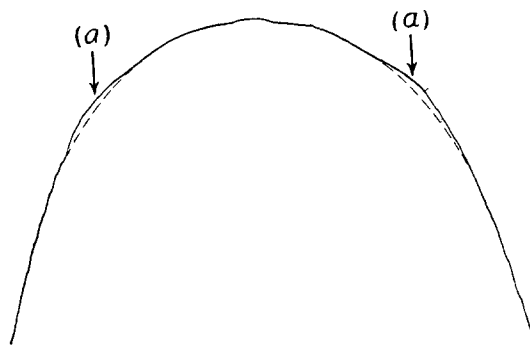


FIG. 11. Densitometer record for 1,2 diiodobenzene.

independent determinations of the molecular structures. The intensity of x-radiation coherently scattered at a particular angle by a free atom is a function of  $F^2$  rather than of  $(Z-F)^2$  as for electron diffraction. The probability for scattering by an iodine atom relative to a carbon atom, for values of  $(1/\lambda) \sin \theta/2$  greater than 0.2, is considerably enhanced for x-rays, as compared with electrons; thus, for example, with  $(1/\lambda) \sin \theta/2$  equal to 0.3 the ratios are:  $(Z-F)^2_{\text{I}} / (Z-F)^2_{\text{C}} = 26$  and  $F^2_{\text{I}} / F^2_{\text{C}} = 207$ . In the case of x-ray diffraction from a crystalline diiodobenzene the absolute intensities of the interference maxima will consequently be determined by the arrangement of the iodine atoms. The carbon atoms also can be expected to contribute partially out of phase to all reflections and thus further decrease their contributions to the amplitudes of the scattered waves. For these reasons the scattering from the carbon atoms has been neglected in the crystal structure determinations.

The relative intensities of "reflection" were qualitatively determined by visual comparison. Reflections from a number of planes were either absent or very weak in intensity. These data were first considered in the limitation of the parameters. The final restriction was obtained by comparing the values of  $S/64 F^2_{\text{I}}$  for various planes where  $S = (F_{\text{I}} S')^2$ ,  $S'$  being the structure amplitude.

On inspecting Tables VII-IX it should be borne in mind that the maximum value of  $S/64 F^2_{\text{I}}$  is 1.0 and that  $F_{\text{I}}$  is a function of  $\theta$ , i.e., a variable from plane to plane that decreases with increase in  $\theta$ . The parameters were determined by considering the various intensities of reflection in

the orders given. The usual graphical methods of presenting these essential data would be too detailed for inclusion here.

### Experimental methods

Crystals of 1,4 diiodobenzene were grown by cooling saturated solutions in absolute alcohol; those of the 1,2 compound, by crystallization at constant temperature from supersaturated solutions. Crystals of 1,3 diiodobenzene were prepared by sublimation. The densities, where unknown, were determined by suspension in Rohrbach's solution in glycerine.

Weissenberg, rotating crystal, and oscillating crystal photographs were made with Cu *K* and Mo *K* $\alpha$  radiations. It was necessary, on account of the thinness of the crystals, to use Laue photographs from 1,3 diiodobenzene. These were produced with radiation from a tube with a tungsten anticathode operated at 26,000 *V* peak (minimum  $n\lambda = 0.48\text{\AA}$ ).

One lattice dimension, usually that of the prominently developed face, was measured accurately against  $\beta$   $\text{Al}_2\text{O}_3$  as a reference ( $d_{0001} = 22.480\text{\AA}$ ). Cu *K* radiation was used in order to reduce the transmission of the crystals and thus to enhance the accuracy of the measurements. The other two dimensions were checked approximately from layer line separations and then calculated from the axial ratios. The crystallographic properties as listed by P. Groth<sup>18</sup> are summarized in Table VI.

TABLE VI. Crystallographic properties of the diiodobenzenes.

Substance	m.p.	Crystal system and axial ratio (Groth)	Density obs.	calc.	Cleavage
1,2 diiodobenzene	27.0	Mon. Pris. = $93^\circ 56'$ $a:b:c = 1.0489:1:1.5466$	2.73 <sub>10</sub>	2.72	11 to (010)
1,3 diiodobenzene	40.4	Rhom. Bipyramidal $a:b:c = 1.1399:1:2.7704$	2.80	2.88	11 to (100)
1,4 diiodobenzene	129.4	Rhom. Bipyramidal $a:b:c = 0.4342:1:0.3653$	2.79	2.79	none

#### 1,4 diiodobenzene. $\text{C}_6\text{H}_4\text{I}_2$

Orthorhombic	$4\text{C}_6\text{H}_4\text{I}_2$ in unit
bipyramidal	of structure
Lattice dimensions	Types of absences
$a = 17.00_4$	(0 $kl$ ), $k$ odd
$b = 7.38_1$	( $h0l$ ), $l$ odd
$c = 6.21_0$	( $hk0$ ), $h$ odd
Space Group	$P m m m$ , $P m c m$ , $P m a b$ , $P c a b$

<sup>18</sup> P. Groth, *Chemische Kristallographie*, Vol. IV, Leipzig (1917).

Over twenty-five planes of each type given above in positions to reflect were observed to be absent. The observed intensities of reflection were satisfactorily accounted for by an atomic arrangement derived from space group  $P c a b - V_k^{15}$ . Each molecule must have at least a center of symmetry.

*Atomic arrangement and parameter determinations.* The possible atomic positions are:<sup>19</sup>

$$xyz; x + \frac{1}{2}, \frac{1}{2} - y, \bar{z}; \bar{x}, y + \frac{1}{2}, \frac{1}{2} - z; \frac{1}{2} - x, \bar{y}, z + \frac{1}{2} \\ \bar{x}\bar{y}\bar{z}; \frac{1}{2} - x, y + \frac{1}{2}, z; x, \frac{1}{2} - y, \frac{1}{2} + z; x + \frac{1}{2}, y, \frac{1}{2} - z. \quad (a)$$

The molecular centers are at (b) or (c).

$$000; \frac{1}{2} \frac{1}{2} 0; 0 \frac{1}{2} \frac{1}{2}; \frac{1}{2} 0 \frac{1}{2}, \quad (b)$$

$$\frac{1}{2} \frac{1}{2} \frac{1}{2}, 00 \frac{1}{2}; \frac{1}{2} 00; 0 \frac{1}{2} 0. \quad (c)$$

The three separable parameters defining the positions of the iodine atoms are determined below.

(1) The observed intensities of (*h*00), note (16.0.0)*a.*, (11.0.2)*m.w.* (702)*m.* and (902)*a.* requires

$$x = 0.172 \pm 0.002.$$

(2) The observation that (*h*20) and (*h*00) have approximately the same intensities of reflection and that both (022) and (002) are v.s. requires  $\cos 2\pi(2y)$  to have near its maximum value. The orders of intensities of (*h*00), (*h*10), (*h*20), (*h*30) requires  $\sin 2\pi(y)$  and  $\sin 2\pi(3y)$  to have near their maximum values but with  $\sin 2\pi(3y)$  somewhat the greater. Finally (043) > (023), (060) and (080) absent with (040) *m.w.*, (250) *m.s.*, and (450)*m.* requires

$$y = 0.40 \pm 0.01.$$

(3) The observations (024) > (023); (041) > (042); (043) > (042), (004)*m.s.*, (006)*w.*, the observed intensities of (*h*00) and (*h*02), and (023) *m.w.*, (025)*v.w.*, (043)*m.*, (045)*w.* requires

$$z = 0.22 \pm 0.01.$$

An inspection of Table VII will perhaps serve to show the concordance between observed intensities and calculated structure factors.

The positions of the iodine atoms in the

<sup>19</sup> See P. Niggli, *Geometrische Kristallographie des Diskontinuums*, p. 201, Leipzig (1919).

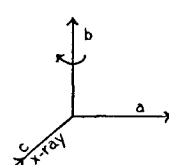
structure are shown in Fig. 12. There are as many possible positions for the molecules as there are symmetry centers in the crystals. Only one of these positions can be considered as probable however if the crystals are holohedral, namely

A—I as shown. The indicated positions of the carbon atoms are ones giving an intermolecular separation of ca 3.70Å. The cleavages and optical properties of the crystals are satisfactorily accounted for.

TABLE VII. Intensities of reflections, estimated, and structure factors, calculated for iodine atoms alone, for some planes of 1,4 diiodobenzene.

Mo K radiation, 30°–45° oscillation of the crystal.

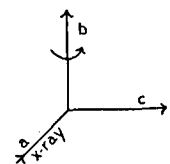
(1) (hk0) with  $h$  odd required to be absent



Equatorial zone			1st layer line			2nd layer line			3rd layer line		
Plane	Int.	$S/64F^2_I$	Plane	Int.	$S/64F^2_I$	Plane	Int.	$S/64F^2_I$	Plane	Int.	$S/64F^2_I$
(200)	m.	0.22			0.04						
(400)	m.	.14	(410)	w.	.06				(430)	m.w.	0.45
(600)	v.s.	.96	(610)	a.	.00	(620)	m.s.	0.73	(630)	a.	.02
(800)	s.	.51	(810)	w.	.03	(820)	m.s.	.39	(830)	m.w.	.24
(10.0.0)	v.w.	.04	(10.1.0)	w.	.06	(10.2.0)	v.w.	.03	(10.3.0)	m.w.	.45
(12.0.0)	m.s.	.85	(12.1.0)	a.	.02	(12.2.0)	m.	.65	(12.3.0)	a.	.07
(14.0.0)	m.w.	.69	(14.1.0)	a.	.06	(14.2.0)	w.	.52			
(16.0.0)	a.	.00	(16.1.0)	a.	.06	(16.2.0)	a.	.00			
(18.0.0)	m.w.-w.	.69	(18.1.0)	a.	.06	(18.2.0)	w.	.52			
(20.0.0)	m.	.85	(20.1.0)	a.	.01	(20.2.0)	m.w.				
(22.0.0)	a.	.04									

(1) Also from Weissenberg photographs, Cu K radiation.

(2) (0kl) with  $k$  odd } required to be absent  
(h0l) with  $l$  odd }

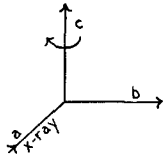


Equatorial zone				2nd layer line				4th layer line		
Plane	Int.	$S/64F^2_I$		Plane	Int.	$S/64F^2_I$		Plane	Int.	$S/64F^2_I$
		$Z=0.20$	$Z=0.22$			$Z=0.20$	$Z=0.22$			$Z=0.22$
				(021)	S.	0.23	0.25	(041)	m.s.	0.70
(002)	v.s.	0.65	0.87	(022)	v.s.	.50	.67	(042)	m.w.	.25
(202)	m.w.	.19	.25							
				(023)	m.w.	.09	.17	(043)	m.	.50
(004)	m.s.	.10	.54	(024)	m-m.s.	.08	.41	(044)	w.	.16
				(025)	v.w.	.00	.09	(045)	w.	.25
(006)	m.	.10	.17	(026)	m.w.	.08	.15	(046)	a.	.05

Reflections were present from a number of planes in the 1, 3, and 5 layer lines ((212), (232), (113) etc.), they are not included since trustworthy intensity observations could not be made for them.

TABLE VII.—(Continued.)

(3)  $\left. \begin{array}{l} (hk0) \text{ with } h \text{ odd} \\ (0kl) \text{ with } k \text{ odd} \end{array} \right\} \text{required to be absent}$



Equatorial zone			1st layer line			2nd layer line			3rd layer line			4th layer line		
Plane	Int.	$S/16F^2_I$	Plane	Int.	$S/16F^2_I$	Plane	Int.	$S/16F^2_I$	Plane	Int.	$S/16F^2_I$	Plane	Int.	$S/16F^2_I$
(020)	v.s.	0.79	(021)	v.s.	0.25	(022)	v.s.	0.67	(023)	m.	0.17	(024)	m.s.	0.41
(220)	w.	.16				(222)	v.w.	.13						
(230)	m.s.	.32	(231)	m.s.	.37	(232)	w.	.30	(233)	w.	.43	(234)	v.w.	.18
(430)	m.s.	.45	(431)	m.s.	.52	(432)	w.	.36						
(040)	m.w.	.29	(041)	m.s.	.70	(042)	w.	.25	(043)	m.	.50	(044)	a.	.16
(240)	v.w.	.07	(241)	w.	.18	(242)	v.w.	.06						
(250)	m.s.	.62	(251)	v.w.	.06									
(450)	m.	.87	(451)	v.w.	.10									
(060)	a.	.00	(061)	m.w.	.95									

*1,3 diiodobenzene*

Rhombic pyramidal  $4C_6H_4I_2$  in the unit  
lattice dimensions of structure

$a = 17.20\text{\AA}$  (measured) Types of absences  
 $b = 7.08$   $(hkl)$  with  $(h+k)$  odd  
 $c = 6.21$   $(h0l)$  in odd orders.

*Crystal symmetry.* 1,3 diiodobenzene is listed by Groth as crystallizing in the bipyramidal division of the rhombic system. The x-ray results, however, require the crystals to be pyramidal. Dr. A. Hettich of the *Mineralogische-Geologisches Institut der Technischen Hochschule*, München, kindly tested the piezoelectric properties of a sublimed sample of the substance, using the method of Giebe and Scheibe.<sup>20</sup> A positive effect was found somewhat less in intensity than that given by sucrose.

*Space group and atomic arrangement.* Possible space groups are:

Orthorhombic holohedral  $C m m m$  and  $C m c m$   
hemihedral  $C m m$ ,  $C m c$   
 $A m m$ ,  $A m a$   
Monoclinic holohedral  $C 2/c$ ,  $C 2/m$

The absence of odd order reflections from  $(00l)$  requires the iodine atoms to have a translation of  $\tau c/2$  and the intensities of the various reflections require their positions to be fixed by parameters

in both the  $a$  and  $b$  directions. For these reasons the iodine atoms cannot be in the 8 equivalent positions of  $C m m m$ , the general positions of  $C m m$ ,  $A m m$  or  $A m a$  or in 8 equivalent positions other than

$$uv\frac{1}{4}; \bar{u}\bar{v}\frac{1}{4}; u + \frac{1}{2}, v + \frac{1}{2}, \frac{1}{4}; \frac{1}{2} - u, v + \frac{1}{2}, \frac{1}{4}\bar{u}\bar{v}\frac{3}{4};$$

$$u\bar{v}\frac{3}{4}; \frac{1}{2} - u, \frac{1}{2} - v, \frac{3}{4}; u + \frac{1}{2}, \frac{1}{2} - v, \frac{3}{4} \quad (a)$$

of  $C m c m$ . The general positions of  $C m c$  contain (a) above as a special and only case if one type of atom alone is considered in the lattice. Arrangement (a) also results from the general positions of  $C 2/c$ , and  $C 2/m$  for special parameter values. The intensities of the various reflections do not permit of combinations of iodine atoms in four equivalent positions.

If the compound is truly orthorhombic the minimum molecular symmetry is that of the point group  $C_s - m$  (space group  $C m c$ ), a plane of symmetry. It seems improbable, since logical positions are not afforded for the carbon atoms, that the structure could be derived from space group  $C m c m$ . Possible positions for the carbon atoms in  $C m c$  are

$$4(a)ouv; o, \bar{u}, v + \frac{1}{2}; \frac{1}{2}, \frac{1}{2} + u, v; \frac{1}{2}, \frac{1}{2}, -u, v + \frac{1}{2}$$

and the general positions.

*Parameter determinations.* There are two parameters for the iodine atoms to be determined. The intensities of  $(h00)$  in various orders,

<sup>20</sup> E. Giebe and A. Scheibe, *Zeits. f. Physik* **33**, 760 (1925).

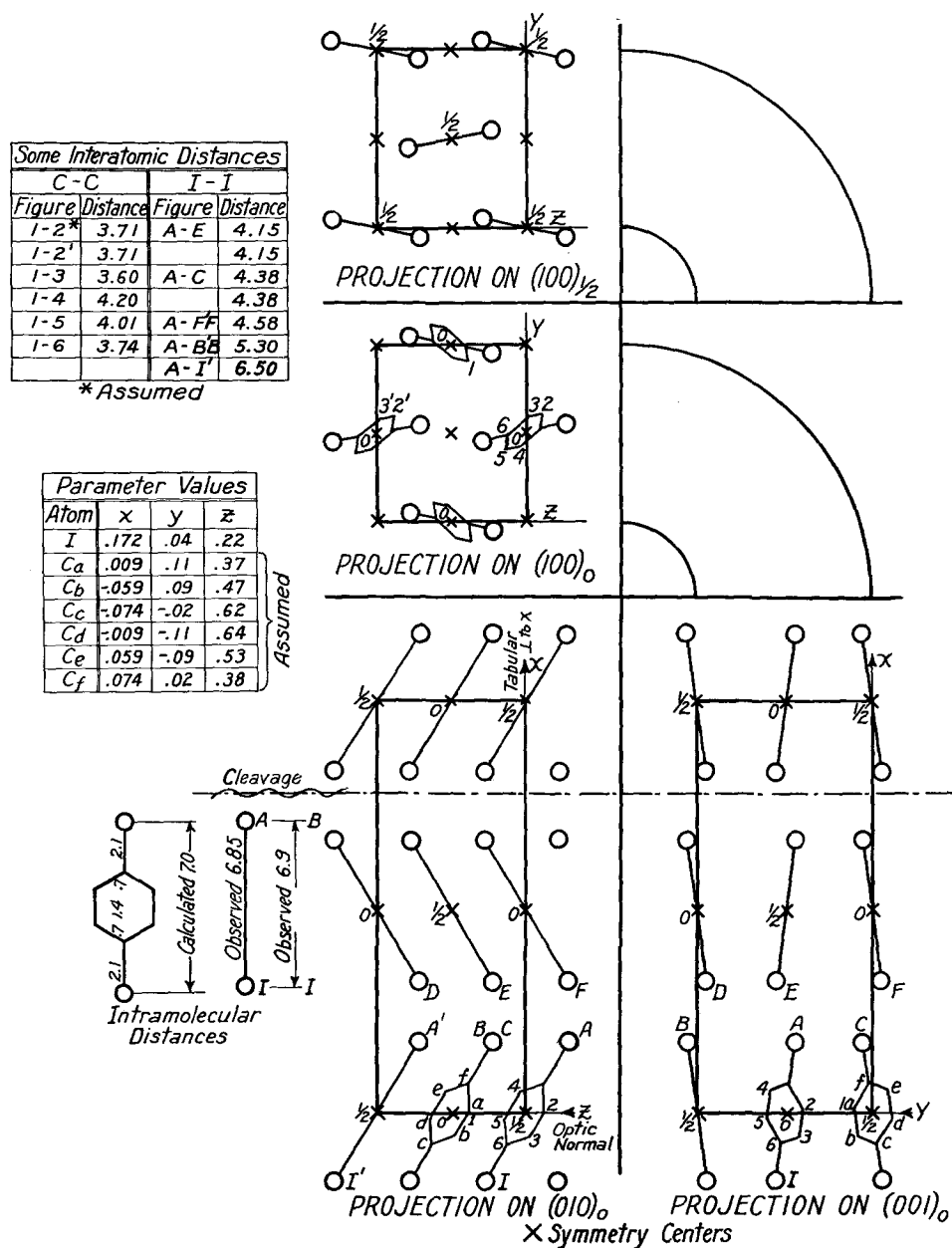
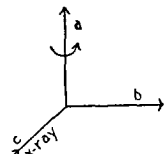


FIG. 12. The crystal structure of 1,4 diiodobenzene.

TABLE VIII. Oscillating crystal photographic data from 1,3 diiodobenzene.

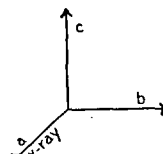
Mo K radiation, 45° oscillation.

(1)



(hk0) with (h+k) odd absent

(2)



(0kl) with k odd required to be absent. (Note below)

Equatorial zone			1st layer line		2nd layer line		3rd layer line			2nd layer line	
Plane	Int.	$S/64F_I^2$	Plane	Int.	$S/64F_I^2$	Plane	Int.	$S/64F_I^2$	Plane	Int.	$S/64F_I^2$
(200)	m.w.	0.31									
(400)	w.	.14	(310)	w.	0.10	(420)	v.w.	0.09			
(600)	v.s.	.96	(510)	v.w.	.04	(620)	s.	.61	(602)	v.s.	0.96
(800)	s.	.50	(710)	a.	.01	(820)	m.	.32	(802)	m.s.	.50
(10.0.0)	a.	.04	(910)	w.	.09	(10.2.0)	a.	.03	(930)	m.	.58
(12.0.0)	s.	.85	(11.1.0)	v.w.	.07	(12.2.0)	m.	.55	(11.3.0)	m.w.	.40
(14.0.0)	m.s.	.72	(13.1.0)	a.	.00	(14.2.0)	m.w.	.46	(13.3.0)	a.	.01
(16.0.0)	a.	.00	(15.1.0)	v.w.	.08	(16.2.0)	a.	.00	(15.3.0)	m.w.	.49
(18.0.0)	m.	.69	(17.1.0)	v.w.	.08	(18.2.0)	w.	.44	(17.3.0)	m.w.	.51
(20.0.0)	m.	.87	(19.1.0)	a.	.00	(20.2.0)	w.	.56	(19.3.0)	a.	.00
(22.0.0)	a.	.04	(21.1.0)	a.	.05	(22.2.0)	a.	.03	(20.0.2)	m.w.	.87
(24.0.0)	a.	.50									
(26.0.0)	w.	1.00									

The intensities in the equatorial zone are given under (1). Some reflections other than (0kl) Int. *a* were present in the 1st and 3rd layer lines. These are not listed since they could not be identified with certainty.

particularly the absence of the 10th, 16th, and 22nd orders requires  $u = 0.172 \pm 0.002$  or  $0.078 \pm 0.002$ . The absence of (13.1.0) with the presence of (9.1.0), (11.1.0), (15.1.0) etc. requires,

TABLE IX. Laue photographic data from 1,2 diiodobenzene.  
W. anticathode 26,000 v. peak. X-ray beam  
at about 7° to normal to (100).

Plane	$d_{hkl}$	$n$	Est. Int.	$S/64F_I^2$
(223)	1.75	0.52	3	0.11
		.66	6	
		.72	6	
		.90	8	
(241)	1.67	.76	7	0.28
(314)	1.47	.67	5	0.10
(350)	1.37	.68	>10	1.00
(351)	1.34	.78	0.5	0.00
(334)	1.27	.74	7	0.65
(352)	1.25	.69	9	1.00
(443)	1.28	.62	1	0.12
(534)	1.22	.74	3	0.27
(315)	1.20	.62	5	0.91
(515)	1.15	.68	3	0.37
(461)	1.12	.70	1	0.12
(625)	1.08	.73	3	0.35
(863)	0.92	.72	0.5	0.48
(023)*	3.57	.54	5	0.35
(041)	3.40	.52	6	0.90

\* A second photograph at a greater angle to the normal to (100).

$$u = 0.172 \pm 0.002.$$

The observed low intensities of (hk0) with  $k=1$ , the approximate equality in the intensities of (11.3.0) and (14.2.0), the very high intensity of (350) and low intensity of (351) require,

$$v = 0.20 \pm 0.01.$$

The value cannot be exactly 0.20 since (351) is present.

Structure factors are of the type—

$$l \text{ even } A/8F_I = \cos 2\pi n(hu) \cos 2\pi n(kv)$$

$$l \text{ odd } B/8F_I = \cos 2\pi n(hu) \sin 2\pi n(kv).$$

The concordance between observed intensities of reflection and calculated structure factors is shown in Tables VIII and IX.

*Optical properties.* 1,3 diiodobenzene has been described as optically negative with the interference figure of the obtuse bisectrix visible through (100)<sub>sp.G.</sub>, the plane of the optic axis being (001)<sub>sp.G.</sub>. The indices of refraction determined by the immersion method under the microscope are  $\alpha = 1.611$  ( $n_D$ ),  $\beta > 1.78$ ,  $\gamma > 1.80$ . The high birefringence is determined by the orientation of the benzene rings, which thus

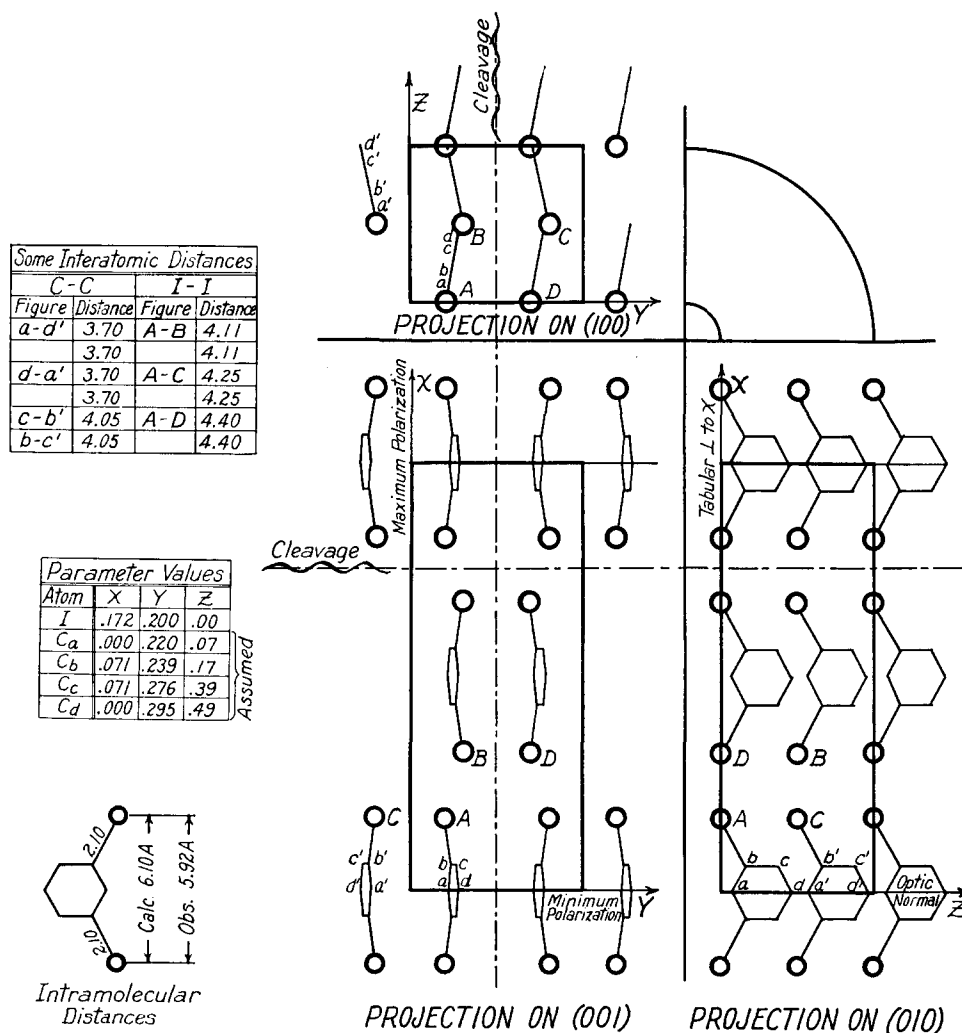


FIG. 13. The crystal structure of 1,3 diiodobenzene.

must be approximately but not exactly parallel to  $(010)_{\text{sp.G.}}$ .

The structure as determined is shown in Fig. 13. The perfect cleavages parallel to  $(010)$  and  $(100)$  are readily explained. The indicated positions of the carbon atoms are ones giving an intermolecular distance of about 3.70 Å.

#### 1,2 diiodobenzene

Monoclinic prismatic

Lattice dimensions

$$a = 8.29 \text{ Å}$$

$$b = 12.23 \text{ (} d_{(010)} = 12.20 \text{ Å)} \quad 4\text{C}_6\text{H}_4\text{I}_2 \text{ in unit of structure}$$

$$c = 7.91$$

$$\gamma = 93^\circ 56' \text{ (Goldschmidt)} \quad \gamma = 93.8^\circ \text{ (Weissenberg photographs).}$$

A satisfactory structure determination was not made for 1,2 diiodobenzene. The lattice is apparently the simple monoclinic one, the space group probably  $P2_1/m$  or  $P2/m$ . In any case the positions of the iodine atoms are determined by six parameters. The intensities of the first ten orders of interference from  $(010)$  apparently are: 1, a.; 2, a.; 3, a.; 4, v.s.; 5, w.; 6, m.; 7, a.; 8, m.s.; 9, a.; 10, m. If iodine atoms are at  $y_1$ ,  $-y_1$ ,  $y_2$ , and  $-y_2$  the values of  $y$  must be about

$$y_1 = 0.13, \quad y_2 = 0.37 \text{ or } -0.37,$$

$$y_1 = 0.37, \quad y_2 = 0.13 \text{ or } -0.13.$$

The crystals are optically positive which indicates that the planes of the benzene rings are not approximately parallel.



## DISCUSSION

The separation of the iodine atoms in the various compounds studied are listed in Table X. Molecular iodine affords the most extensive test of the methods used in the analysis of electron diffraction data. The I—I distance determined by us is in good agreement with both the band spectra and x-ray diffraction results.

TABLE X. Summary of iodine to iodine distances (A).

Molecule	Electron diffraction	X-ray crystal structure	Band spectra
Iodine	2.64A	2.70A*	2.66A
1,4 Diiodobenzene	6.85	6.85	
1,3 Diiodobenzene	5.97	5.92	
1,2 Diiodobenzene	4.00		

\* P. M. Harris, E. Mack, Jr., and F. C. Blake, J. A. C. S. **50**, 1583 (1928).

Electron and x-ray diffraction data obtained from 1,3 and 1,4 diiodobenzenes indicate that the atomic arrangements within these molecules are invariant with vaporization of the solid. The I—C distances for the diiodobenzenes are 2.00A in all cases and the assumed C—H, and C—C distances are verified since they are consistent with the results obtained. These results are in harmony with the concept of approximately constant homopolar distances of particular types in such compounds.

In 1,4 and 1,3 diiodobenzene the line joining the center of an iodine atom to the adjacent carbon atom, which might be referred to as the valence direction, is symmetrically disposed in the plane of the benzene ring. In 1,2 diiodobenzene, however, this direction is distorted by about 10° from the symmetrical position. The I—I distance in this molecule is 4.00A, which is far greater than the value 3.52A required by the symmetrical arrangement and slightly less than 4.10A, the minimum intermolecular separation of the iodine atoms in the other crystalline diiodobenzenes.

It was not possible to determine whether the deformations of the valence directions in 1,2 diiodobenzene are in or out of the plane of the benzene ring. The absence of optical and of

geometrical isomerism in simple derivatives of such a compound, however, have usually been taken as evidence for a coplanar atomic arrangement. Some support is also given to this point of view by the structure of hexamethylbenzene.<sup>15</sup>

*This irregularity in ortho substitution is perhaps the first clear physical evidence for the phenomenon of "steric hindrance."* In general the reactivity of a group on a benzene ring is markedly affected by the presence of groups ortho to it. This has perhaps been most clearly shown by the work of V. Meyer<sup>21</sup> and his students on the esterification of carboxylic acids. In 1,2 diiodobenzene it is impossible to meet the requirements imposed by the I—I separation, that is the steric effect, without modification of the molecule in a manner that would probably affect its reactivity.

From consideration of heats of combustion for a number of benzene derivatives Stuart<sup>22</sup> concluded that the C—CH<sub>3</sub> valence directions are not distorted in 1,2 xylene. He calculated that an energy greater than 2000 cal./mole would be required for a 10° distortion of that direction. This value probably will serve to indicate there is a considerable increase in the potential energy of 1,2 diiodobenzene as compared with the 1,3 and 1,4 derivatives.

In principle, crystal structure analysis offers an almost unique method for determining the atomic arrangement within complex molecules. Unfortunately, it is limited in application by the necessary simultaneous determination of the molecular orientations. There is considerable hope that regularities will be found in the intermolecular distances of approach in solids of a particular type. Careful study of Figs. 12 and 13 will perhaps make apparent the regularities in the packing of iodine atoms of separate molecules. Six iodine atoms are so arranged that their separations are between 4.11 and 4.6A. This minimum distance of approach is approximately the same as that found in other iodine substituted compounds.<sup>17,23,24</sup> Although the assumption of a minimum intermolecular C—C distance was

<sup>21</sup> V. Meyer, *Berichte* **27**, 510, 1580 (1894); **28**, 1255, 2774, 3197 (1895).

<sup>22</sup> H. A. Stuart, *Phys. Rev.* **38**, 1372 (1931).

<sup>23</sup> H. P. Klug, *J. Am. Chem. Soc.* **55**, 1430 (1933).

<sup>24</sup> E. Halmöy and O. Hassel, *Zeits. f. physik. Chemie* **B16**, 234 (1932).

used in the analysis of the crystal structures, the structure of 1,3 diiodobenzene really serves independently to verify it.

The methods that we have used are perhaps capable of extension to the study of a larger

number of compounds containing two or more heavy atoms. In particular, observations on substances such as 2,6 diiodobenzoic acid would probably lead to important information bearing on steric hindrance.