A Study of the Molecular Structure of Diiodoethane Iodine Bond Resonance and the Molecular Structure of Diiodoethylene. Molecular Packing in Their Crystal Lattices

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tetrahedral positions the intensity calculations would be but little different from those given in this paper, although it would probably mean a small increase in the parameter value. The intensity data, however, do not warrant this calculation.

Evidence for three coordinated silver atoms has been found by Dr. Harker of this laboratory in a preliminary investigation of proustite and

pyrargyrite where he also finds silver in a flattened pyramidal arrangement with a silver radius of approximately 1.45A. The silver radii from this investigation are: tetrahedral -1.53A, three coordinated -1.46A. The radius of the nonbonded silver is 1.77A.

Thanks are due to Professor Linus Pauling and to Dr. J. H. Sturdivant for valuable assistance with this work.

A Study of the Molecular Structure of Diiodoethane

Iodine Bond Resonance and the Molecular Structure of Diiodoethylene. Molecular Packing in Their Crystal Lattices

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Using data from an x-ray study of the crystal structure of *sym*-diiodoethane and *sym*-diiodoethylene (*trans* form) the positions of the iodine atoms in the crystal cells were located. Iodine bond resonance is discussed and a factor of 0.92 of the length of the longer bond proposed for evaluating the interatomic distance for any resonating bond. On the basis of the concepts of tetrahedral carbon bonds, bond resonance, Pauling's normal convalent bond radii, etc., reasonable molecular models for the above substances were predicted. Comparison of these with the x-ray data showed the iodine-iodine distances to be in excellent agreement with certain iodine-iodine distances within the crystal cells, thus locating the molecules within the cells. These models together with Mack's concept of the atomic domain radius of atoms in crystals permitted a consideration of the packing of the molecules in the crystal lattice, thus locating the atomic coordinates of the carbon and hydrogen atoms in the cell. The domain radii found were; iodine $=1.97$A, and hydrogen$=1.23$A. The resulting molecular packing is seen to explain and be in excellent agreement with observed physical properties of the two crystals.

INTRODUCTION

AT present our most important methods for investigating molecular structure are based on comparison of experimental data with the results to be expected from a model which we have visualized from our best theoretical and experimental knowledge.

The results of x-ray diffraction studies on crystals give important data for consideration of the structure of the crystal molecule, especially in the case of organic substances. It is often possible to determine important interatomic distances in the molecule from these studies, thus permitting a study of the structure of the molecule, constancy of bond radii, bond angles, bond resonance, etc., by comparison with reasonable molecular models.

In a recent x-ray study[1] of the crystal structures of *sym*-diiodoethane and *sym*-diiodoethylene it was found possible to locate the iodine atoms in the unit cells with considerable accuracy. Using data from this investigation we have made a study of the molecular structures and molecular packing in the crystals of these compounds.

CRYSTAL STRUCTURE DATA

s-diiodoethane was found to possess a two-molecule monoclinic cell with the following dimensions:

$$a_0' = 4.768\text{A}, \qquad b_0' = 12.897\text{A},$$
$$c_0' = 4.784\text{A}, \qquad \beta' = 105° \ 5'.$$

Its space group is C_{2h}^5. The four-molecule pseudo-

[1] The detailed results of this study are reported in Zeits. f. Krist. **90**, 495 (1935).
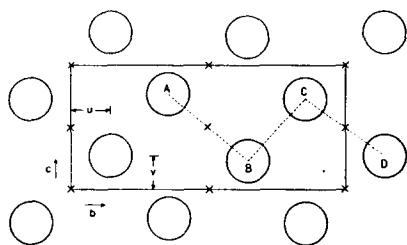
FIG. 1. Section through the cell of diiodoethane in the $(100)_0$ plane showing the location of the iodine atoms in the symmetry plane. The crosses indicate the positions of the symmetry centers. The circles do not indicate the size of the iodine atoms.

orthorhombic unit with

$$a_0 = 7.582A, \qquad b_0 = 12.897A,$$
$$c_0 = 5.810A, \qquad \beta = 90° \ 12',$$

is of remarkable interest. In fact the x-ray data from this unit were not observed to show any deviations from perfect orthorhombic symmetry. Treating the crystal as orthorhombic it possesses the space group V_h^{18}, and the eight iodine atoms in the cell are located at the points

$$0uv; \quad \tfrac{1}{2}, \tfrac{1}{2}-u, v; \quad \tfrac{1}{2}, u, v+\tfrac{1}{2}; \quad 0, \tfrac{1}{2}-u, v+\tfrac{1}{2};$$
$$0\bar{u}\bar{v}; \quad \tfrac{1}{2}, u+\tfrac{1}{2}, \bar{v}; \quad \tfrac{1}{2}, \bar{u}, \tfrac{1}{2}-v; \quad 0, u+\tfrac{1}{2}, \tfrac{1}{2}-v;$$

with $u = 0.145 \pm 0.005$ and $v = 0.27 \pm 0.01$. Each of the four molecules of this unit must then possess a minimum molecular symmetry of a twofold axis with a plane perpendicular to it. This symmetry plane is parallel to the (100) plane. The molecules will, therefore, have a center of symmetry, and they will be located in the cell on the symmetry planes with their centers at the symmetry centers of the space group.

In Fig. 1 is shown a section of the cell at $(100)_0$. The distances $AB = 4.88A$, $BC = 3.97A$, and $CD = 4.60A$ are the closest distances of approach of two iodine atoms in the symmetry plane. Either AB or CD, and not BC, represents the iodine-iodine distance within the molecule, since the midpoint of BC is not a symmetry center.

The x-ray study showed s-diiodoethylene (*trans* form) to be isomorphous with s-diiodo-ethane, and to have the following dimensions for its two-molecule monoclinic cell:

$$a_0' = 4.58 \pm A, \qquad b_0' = 13.310A,$$
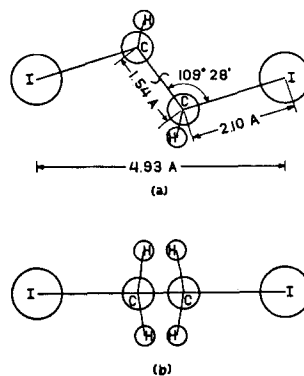$$c_0' = 4.58 \pm A, \qquad \beta' = 105° \ 20' \pm.$$

FIG. 2. (a) Projection of the molecule of diiodoethane on the symmetry plane (100). The $C-H$ distance, seen only in projection, is 1.06A. The location of the twofold axis and symmetry center is shown at the center of the $C-C$ bond. The circles do not indicate the relative sizes of the atoms. (b) Projection showing the distribution of the hydrogen atoms on either side of the symmetry plane.

The four-molecule pseudo-orthorhombic cell, whose diffraction effects likewise show no deviations from orthorhombic symmetry, has the dimensions:

$$a_0 = 7.280A, \ b_0 = 13.310A, \ c_0 = 5.553A, \ \beta = 90° \pm.$$

The space groups, of course, are the same as for the corresponding cells of diiodoethane. The eight iodine atoms of the orthorhombic cell have the same coordinates and the same identical values of u and v as in diiodoethane. The molecular symmetry of diiodoethylene is, therefore, the same as that of diiodoethane, and the section of its cell at $(100)_0$ is very similar to Fig. 1 except for slight differences in the dimensions. These lead to $AB = 4.89A$, $BC = 3.94A$, and $CD = 4.63A$. As above, the iodine-iodine distance in the molecule must be AB or CD. The remaining considerations of this paper are based on the orthorhombic units described above.

STRUCTURE OF A MOLECULE OF s-DIIODOETHANE

The diiodoethane molecules must possess a plane of symmetry with a twofold axis perpendicular to it. The assumption of normal covalent single bonds throughout the molecule, and of tetrahedral bond angles would seem justifiable. The only reasonable configuration satisfying the above considerations is that shown in Fig. 2.

The interatomic distances are those of Pauling's normal covalent bond radii.[2] The iodine-iodine distance is calculated to be 4.93A. This is in excellent agreement with the distance $AB = 4.88A$ in the crystal cell, which is to be considered the distance between two iodine atoms of a molecule in the crystal. The possibility that the distance CD in the crystal cell represents the iodine-iodine distance in the individual molecule is not likely in consideration of the poor agreement with our model. To reduce the iodine-iodine distance in our molecular model to $CD = 4.60A$ would require considerable change in the bond radii or bond angles, both of which are well established by theory and experiment. For instance it would require reduction of the tetrahedral bond angle to approximately 95°.

Further discussion of the structure of this molecule will be reserved until the discussion of molecular packing.

## IODINE BOND RESONANCE AND THE STRUCTURE OF MOLECULES OF s-DIIODOETHYLENE

To construct a satisfactory molecular model for diiodoethylene we must consider one of the peculiar valence properties of iodine together with the phenomenon of bond resonance. A number of compounds are known in which certain electronegative elements possess more than four electron-pairs in their valence shell.[3] Iodine is such an element since it apparently has five electron-pairs in its valence shell in certain of its compounds. In fact a satisfactory explanation of the $(ClICl)^-$ ion, the I_3^- ion and of ICl_3 necessitates such an assumption.

Pauling[2] has pointed out that the phenomenon of resonance is to be expected when two or more reasonable Lewis structures can be written for a molecule. This resonance leads to interatomic distances within the molecule nearly as small as the smallest of those for the individual structures. With a few exceptions the values of the interatomic distances for these resonating bonds have never been observed to be as small as the value for the smaller normal bond. The empirically determined factor of 0.92 of the value of the larger bond (Table I) seems to fit the observed

data quite well. In considering models of molecules in which resonance occurs it would seem more satisfactory to use the value based on this factor rather than any other values of bond radii.

With iodine's ability to hold five electron-pairs bond resonance is expected to occur where possible. The work of Hendricks and associates[4] on p-diiodobenzene clearly demonstrates this bond resonance although they do not point it out. They determined the iodine-iodine distance in the p-diiodobenzene molecule to be $6.85 \pm 0.10A$ from electron diffraction in the gaseous state, and 6.85A from x-ray diffraction in the crystals. From these results they pointed out that the carbon-iodine distance was 2.00A instead of 2.10A expected from Pauling's normal covalent bond radii for single bonds.

The following Lewis structures can be written for p-diiodobenzene:
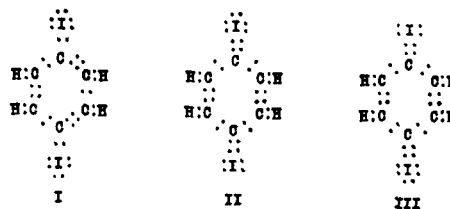
Now the theoretical iodine-iodine distance to be expected for each of these structures can be calculated for comparison with Hendricks' experimental value. The distance across the *para* positions of the resonating hexagonal benzene ring is quite accurately known from the value, 1.42A, the carbon-carbon distance in benzene and other aromatic structures (Table I). This distance is 2.84A, and will be the same for all of the above structures. The iodine-iodine distance for structure I with two carbon-iodine single bonds is calculated to be 7.04A by using Pauling's bond radii. Structures II and III, which are identical except for the five electron-pairs being on different iodine atoms, will have an iodine-iodine distance of 6.62A as a result of the carbon-iodine double bonds. Comparison of these with Hendricks' value points unquestionably to bond resonance. Considering the carbon-iodine

[2] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).
[3] See M. L. Huggins, Chem. Rev. **10**, 427 (1932).

[4] S. B. Hendricks, L. R. Maxwell, V. L. Mosley and M. E. Jefferson, J. Chem. Phys. **1**, 549 (1933).

TABLE I. *Values of resonating bonds.*

BOND	BOND VALUE FROM PAULING'S RADII		0.92 OF 1ST BOND	EXP. VALUE OBS.	COMPOUND	NATURE OF OBS.	REFERENCES
	1ST BOND	2ND BOND					
$C : C \rightleftharpoons C :: C$	1.54A	1.38A	1.418A	1.42A	Graphite	C. S.*	Bernal, Proc. Roy. Soc. **A106**, 749 (1924)
				1.42 ±0.03	$C_6(CH_3)_6$	C. S.	Lonsdale, Proc. Roy. Soc. **A123**, 494 (1929)
				1.412	Naphthalene	C. S.	Robertson, Proc. Roy. Soc. **A142**, 674 (1933)
				1.41	Anthracene	C. S.	Robertson, Proc. Roy. Soc. **A140**, 79 (1933)
				1.42	Terphenyl	C. S.	Pickett, Proc. Roy. Soc. **A142**, 333 (1933)
				1.41	Chrysene	C. S.	Iball, Proc. Roy. Soc. **A146**, 140 (1934)
				1.41	Durene	C. S.	Robertson, Proc. Roy. Soc. **A142**, 659 (1933)
				1.43 ±0.03	Diacetylene	E. D.	Brockway, Proc. Nat. Acad. Sci. **19**, 868 (1933)
				1.43 ±0.03	Cyanogen	E. D.	Brockway, Proc. Nat. Acad. Sci. **19**, 868 (1933)
				1.390 ±0.005	Benzene	E. D.	Pauling and Brockway, J. Chem. Phys. **2**, 867 (1934)
$B : N \rightleftharpoons B :: N$	1.59	1.43	1.463	1.47 ±0.07	$B_3N_3H_6$	E. D.	Stock and Wierl, Zeits. anal. Chemie **203**, 228 (1931)
				1.45	Boron Nitride	C. S.	Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932)
$N : O \rightleftharpoons N :: O$	1.36	1.22	1.251	1.26	NO_2^- ion	C. S.	Wyckoff, *The Structure of Crystals*, 2nd Ed., p. 272
$C : O \rightleftharpoons C :: O$	1.43	1.28	1.316	1.26	CO_3^- ion	C. S.	Wyckoff. *The Structure of Crystals*, 2nd Ed., p. 272
				1.25 ±0.05	$(COOH)_2 \cdot 2H_2O$	C. S.	Zachariasen, Zeits. f. Krist. **89**, 442 (1934)
				1.29	$Be_4O(C_2H_3O_2)_6$	C. S.	Pauling and Sherman, Proc. Nat. Acad. Sci. **20**, 340 (1934)
				1.25	Urea	C. S.	Wyckoff and Corey, Zeits. f. Krist. **89**, 462 (1934)
				1.29 ±0.02	$(HCOOH)_2$	E. D.	Pauling and Brockway, Proc. Nat. Acad. Sci. **20**, 336 (1934)
$C :: O \rightleftharpoons C ::: O$	1.28	1.13	1.178	1.15	CO	?	Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932)
				1.15	CO_2	R. S.	Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932)
				1.13	CO_2	C. S.	Wyckoff, *Structure of Crystals*, 2nd Ed. Supplement, p. 30
				1.15 ±0.05	NCO^- ion	C. S.	Hendricks and Pauling, J. Am. Chem. Soc. **47**, 2904 (1925)
$N :: N \rightleftharpoons N ::: N$	1.26	1.10	1.160	1.15 ±0.05	N_3^- ion	C. S.	Hendricks and Pauling, J. Am. Chem. Soc. **47**, 2904 (1925)
$C : N \rightleftharpoons C :: N$	1.47	1.32	1.353	1.37	Urea	C. S.	Wyckoff and Corey, Zeits. f. Krist. **89**, 462 (1934)
				1.35	Thiourea	C. S.	Wyckoff and Corey, Zeits. f. Krist. **81**, 386 (1932)
$C : S \rightleftharpoons C :: S$	1.81	1.63	1.665	1.64	Thiourea	C. S.	Wyckoff and Corey, Zeits. f. Krist. **81**, 386 (1932)
$N :: C \rightleftharpoons N ::: C$	1.32	1.16	1.214	1.15 ±0.05	NCO^- ion	C. S.	Hendricks and Pauling, J. Am. Chem. Soc. **47**, 2904 (1925)
				1.16 ±0.02	Cyanogen	E. D.	Brockway, Proc. Nat. Acad. Sci. **19**, 868 (1933)
$C : I \rightleftharpoons C :: I$	2.10	1.89	1.931	1.96	*trans*-$C_2H_2I_2$	C. S.	Klug, this paper
				2.00	*p*-$C_6H_4I_2$	C. S. and E. D.	Hendricks and Associates, J. Chem. Phys. **1**, 549 (1933)

* C. S. = Crystal Structure, E. D = Electron Diffraction, and R. S. = Raman Spectra.

bond as a resonating bond its value is 0.92 of the single bond value, and the iodine-iodine distance in the molecule becomes 6.70A. This is slightly less than Hendricks' value which is a bit larger than would be expected from these considerations. It has been suggested that the double bonds are somewhat less important in this case than the single bonds, thus requiring a slightly larger factor, 0.93 or 0.94. The factor 0.93 leads to the value 6.76A, which is within the limits of error of Hendricks' data.

Iodine bond resonance is to be expected in the molecule of diiodoethylene, the following Lewis structures being reasonable ones:
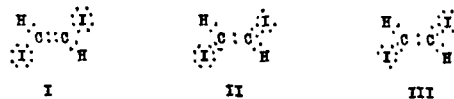
By using Pauling's bond radii and assuming a tetrahedral angle between the carbon-hydrogen and carbon-iodine bonds, the iodine-iodine distance in the molecule is readily calculated for the above structures with normal bonds, and for a molecule with resonating bonds. The iodine-iodine distance for structure I is found to be 5.13A, while that for structures II and III is 4.83A. The value for a resonating molecule (factor 0.92) is 4.84A.

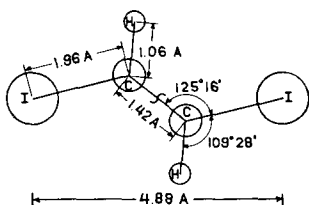Since diiodoethylene and diiodoethane are

FIG. 3. Projection of the molecule of diiodoethylene on the symmetry plane (100). All atoms of the molecule lie in a plane.

isomorphous the distance $AB = 4.89A$ in the diiodoethylene cell will be expected to represent the iodine-iodine distance within the molecule of diiodoethylene. The value 4.84A for a resonating diiodoethylene molecule is in quite satisfactory agreement with this. The iodine bond resonance is, thus, very strikingly shown. In fact it might be said that the isomorphism of diiodoethylene with diiodoethane is a result of this bond resonance, since it reduces the iodine-iodine distance within the diiodoethylene molecule to almost exactly that in diiodoethane. The approximate equivalence of this value for the two molecules is a requirement for the isomorphism of the two substances.

Calculating the value of a resonating carbon-iodine bond from the x-ray data ($AB = 4.89A$) we have 1.96A as given in Table I. The corresponding factor is 0.93. Fig. 3 is a diagram of the molecule of diiodoethylene in accordance with the above considerations and the molecular symmetry demanded by the x-ray data. Further discussion of its structure is reserved until the discussion of molecular packing.

MOLECULAR PACKING AND THE CRYSTAL-CHEMICAL PROPERTIES

The x-ray data cannot locate the positions of the hydrogen atoms in the molecules and crystal cells of compounds, and in the case of the substances being discussed, even the carbon atoms are not susceptible to location from the x-ray intensities because of the much greater scattering power of the iodine atoms.

Mack[5] has shown that these light atoms can be located in the molecule and in the crystal cell,

and a satisfactory stereochemical picture of the crystal lattice explaining many of the observed properties of the crystal obtained, by a study of the spatial packing of molecular models. In the molecular model each atom possesses, in addition to its known values of bond radii and bond angles, an atomic domain which represents its extension in space. This domain is essentially spherical, and for a given kind of atom has a reasonably constant radius from crystal to crystal as long as the conditions remain the same; i.e., same type of binding, no molecular rotation, etc. The domains of separate atoms do not interpenetrate each other except when those atoms are attached to the same atom, as for example, the hydrogens of a methyl group. Atoms on separate molecules will be expected not to interpenetrate each other's domain. Finally, of course, the size and shape of the unit cell as determined by x-ray diffraction are accurately accounted for. The number of positions, satisfying the above conditions, which a given atom can occupy in the molecule or crystal cell is narrowed down in most cases to a single position.

A study of the molecular packing in crystals of these two compounds is of considerable interest. For diiodoethane the molecular model of Fig. 2 has been used, thereby increasing the distance AB (Fig. 1) in the cell to 4.93A. Keeping the angle between AB and the b axis as observed, then $u = 0.146$ and $v = 0.273$, values well within the limits of the x-ray data. BC then becomes 3.947A and $CD = 4.61A$. Fig. 4 (a) shows the packing in the $(100)_0$ plane. The contacts in this plane are across the iodine atoms (represented by large circles). An iodine atom B just kisses an iodine atom C in a neighboring molecule when its domain radius is 1.974A, a value in excellent agreement with the results from other organic compounds containing iodine.[6] The carbon atoms (not shown in Fig. 4) lie in the plane of the iodine atoms, and have the choice of two positions. Indicating the bonds in the molecule by the light lines shown in Fig. 4 (a), position No. 1 is at the intersections P_1. Position No. 2 is at P_2 indicated by the dotted lines on the molecule in the lower left-hand corner. The hydrogen atoms

[5] E. Mack, Jr., J. Am. Chem. Soc. 54, 2141 (1932).

[6] See S. B. Hendricks. Chem. Rev. 7, 431 (1930); M. L. Huggins and B. A. Noble, Am. Mineral. 16, 519 (1931); and H. P. Klug, J. Am. Chem. Soc. 55, 1430 (1933).
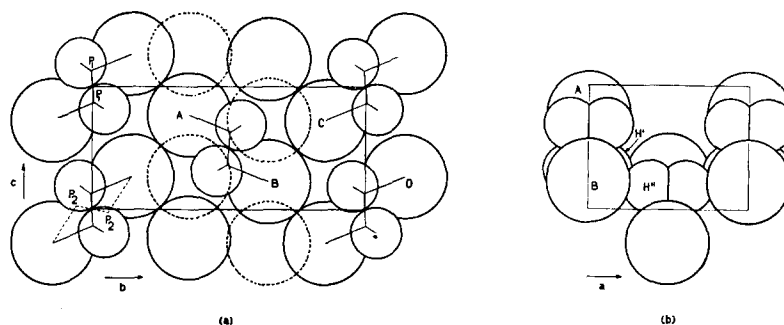
FIG. 4. (a) Section through the cell of diiodoethane in the $(100)_0$ plane showing the packing of the molecules. The large dotted circles locate in projection the iodine atoms of two molecules in the plane $(100)_{a/2}$. (b) Section through the cell in the plane $(010)_{b/2}$.

(small circles in Fig. 4) attached to the carbons by tetrahedral bonds do not lie in the plane of the iodine atoms but at equal distances on each side of it as shown in Figs. 2 (b) and 4 (b). The hydrogen atoms make no contacts with atoms of other molecules in the same plane, but a hydrogen atom H' just makes contact with the hydrogen atom H'' on a molecule in the $(100)_{a/2}$ plane when its domain radius is 1.23A (Fig. 4 (b)). It is possible that at the same time H'' makes contact with iodine atom B, the required hydrogen atom domain radius being 1.246A. A hydrogen domain radius of 1.23A is slightly smaller than 1.29A found by Mack for hexamethylene tetramine. It is, however, in perfect agreement with 1.23A the domain radius just permitting contacts between hydrogen atoms on adjacent carbon atoms of a long chain aliphatic hydrocarbon molecule in the crystal. This considers the carbon atoms of the chain to lie in a plane,[7] the bond angles to be tetrahedral, and Pauling's bond radii throughout. The condition for contacts between hydrogen atoms of adjacent molecules is not essentially different from this case.

Position No. 1 is seen to be the correct position for the carbon chain since position No. 2 would result in hydrogen atoms and iodine atoms approaching each other along the a direction so closely as to reduce the hydrogen domain radius to 1.146A. A hydrogen domain radius as small as this is not to be expected except where we have

[7] See A. Müller, Proc. Roy. Soc. A120, 437 (1928).

molecular rotation. A calculation shows, however, that complete rotation of the C_2H_4 group about an axis through the two iodine atoms of the molecule would reduce the hydrogen domain radius to approximately 0.95A. This is smaller than Mack[5] observed in crystalline methane in which the occurrence of molecular rotation is well established. The possibility of molecular rotation in diiodoethane seems very unlikely, and position No. 2 is not a possible one. Two attempts, however, were made to locate transitions, indicative of molecular rotation, on its warming curve between liquid air and room temperatures. These somewhat crude preliminary studies by a differential thermocouple method failed to give any evidence of such a transition. The possibility of a slight oscillatory motion about this axis has not been ruled out, but cannot profitably be discussed here.

From the above considerations the carbon atoms are located in another set of the same equivalent positions as the iodine atoms with the calculated values of the parameters as follows: $u_C = -0.0036$ and $v_C = 0.132$. The sixteen hydrogen atoms are in Wyckoff's[8] set of sixteen most generally equivalent positions. Interchanging his b and c axes to agree with my choice of axes, and moving the origin to the same symmetry center as in the case of the iodine atoms, these positions are as follows:

[8] R. W. G. Wyckoff, *The Analytical Expression of the Results of the Theory of Space-Groups* (Carnegie Institution Publication No. 318, Washington, 1922), p. 65.

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

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

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

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

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

$\quad x, y+\frac{1}{2}, \frac{1}{2}-z; \qquad x, \frac{1}{2}-y, z+\frac{1}{2}.$

The calculated values of the parameters are as follows: $x=0.114$, $y=-0.044$, and $z=0.188$.

By using the molecular model of Fig. 3, the molecular packing in the case of diiodoethylene in the $(100)_0$ plane is very similar to that for diiodoethane with contacts across iodine atoms and also between a hydrogen of one molecule and an iodine of an adjacent molecule along the c axis. The one hydrogen atom on each carbon atom lies in the plane of the carbon and iodine atoms. No molecular rotation is possible because of the double bonds resulting from the bond resonance. There are, therefore, no contacts between atoms in the a direction. The sheets of atoms perpendicular to the a direction are held together by extremely weak binding forces as in graphite perpendicular to the rings. The iodine atom domain radius is 1.97A and that of the hydrogen is 1.21A in quite satisfactory agreement with the values for diiodoethane. The carbon and hydrogen atoms occupy other sets of the same equivalent positions as the iodine atoms with the calculated values of the parameters as follows: $u_C=0.0533$, $v_C=-0.0079$, $u_H=0.095$, and $v_H=-0.17$.

The molecular packing and atom contacts as just discussed are in excellent accord with the cleavage properties, hardness, and melting points of the crystals. Diiodoethane[9] is reported to show perfect cleavage along (100) and (010). On Fig. 4 (a) it is very evident that excellent cleavage parallel to (010) is to be expected at the points $b/4$ and $3b/4$. The cleavage parallel to (100) is equally evident from Fig. 4 (b). From the molecular packing the same cleavage would be expected for diiodoethylene as for diiodoethane. That none has been reported is probably due to the extreme softness and plasticity of diiodoethylene. Jaeger[9] reports that the crystals are "incredibly plastic and bend corkscrew-like at the least touch." This extreme softness and plasticity is readily explained by the very weak binding forces along the a direction. The sheets of molecules in the (100) plane, held together by somewhat stronger forces, are tough but can slip over each other with extreme ease, hence corkscrew-like deformation occurs so readily. The melting points of both crystals are low, but, as would be expected, diiodoethylene with much weaker binding forces along the a direction melts at the lower temperature, 73°C, while the melting point of diiodoethane is 82°C. Thermal motions of the molecules would be expected to overcome the crystalline forces at a lower temperature in the case of the former.

No optical properties of the crystals are available in the literature, and their softness and extreme solubility in the usual refractive index liquids makes the determination of such properties very difficult. A brief optical study of diiodoethane was made with the following results: Acute bisectrix is a, obtuse bisectrix is b, optic normal c of the orthorhombic unit. Minimum refractive index is for light vibrating parallel to the a axis and is approximately 1.65. This is α, and B_{x_a} is X, thus the crystal is negative. Wooster[10] has attempted to correlate the structures of inorganic crystals with their optical properties. He pointed out that layer type lattices are negative with B_{x_a} perpendicular to the layers. The same undoubtedly holds for organic crystals,[11] and the structure of diiodoethane is seen to be in accord with its optical properties. It was not found possible to obtain optical data on diiodoethylene, however, it is predicted that they will be in keeping with its structure.

[9] F. M. Jaeger, Zeits. f. Krist. 45, 546 (1908), or P. Groth, *Chemische Krystallographie* (Engelmann, Leipzig, 1910), Vol. III, p. 35.

[10] W. A. Wooster, Zeits. f. Krist. 80, 495 (1931).
[11] See B. Orelkin and K. Lonsdale, Proc. Roy. Soc. A144, 630 (1934). Also iodoform with strong negative birefringence has essentially a layer type lattice. See reference 6.