

Effect of Pressure on the Lattice Parameters of Iodine, Stannic Iodide, and *p*-Di-iodobenzene*

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The effect of pressure to over 200 kbars has been measured on the lattice parameters of iodine, stannic iodide, and of *p*-di-iodobenzene. All three have a large component of van der Waals binding and each exhibits a compressibility which decreases with increasing pressure. On the basis of the estimated change in distances in the crystal, the approach to the metallic state in and perpendicular to the *ac* plane in iodine is explained. The approach to the metallic state and possible bond deformation in SnI_4 is discussed. Possible molecular realignments in *p*-di-iodobenzene are proposed. The results on molecular crystals are contrasted with the behavior of TlI previously published.

THE effect of pressure to over 200 kbars has been measured on the lattice parameters of iodine, stannic iodide, and of *p*-di-iodobenzene. The iodine was from Mallinckrodt (resublimed), the SnI_4 from Fisher Chemical (purified reagent), and the *p*-di-iodobenzene from Eastman Organic Chemicals and was resublimed. The high-pressure x-ray techniques have been described elsewhere,¹ except that the iodine was handled using platinum and Teflon instead of the usual steel guides and tools. The compounds are discussed individually below.

I. IODINE

Molecular iodine crystallizes in a base-centered-orthorhombic structure with the I_2 molecules lying in the *ac* plane. The crystal structure is shown in Fig. 1. The intramolecular bond length is 2.71 Å. The four shortest intermolecular iodine-iodine distances are labeled α , β , δ , and ϵ in order of increasing length; their lengths are 3.56, 4.04, 4.35, and 4.49 Å, respectively.

Pauling² assigns a van der Waals radius of 2.15 Å to the iodine atom. The intermolecular distance α is considerably less than twice the van der Waals radius (4.30 Å), suggesting weak covalent bonds between adjacent molecules within each layer.³ Yamasaki⁴ has shown that the crystal structure would be cubic if covalent intermolecular binding were totally absent. The energy of sublimation of crystalline iodine is 43% of the energy of dissociation of the molecules at 0°K indicating the strength of the intermolecular bonds.

The bonds could be formed by perfect pairing of *spd* hybrids giving localized bonds, but the electrical resistivity ($\rho_{11}=2 \times 10^{11} \Omega \cdot \text{cm}$, $\rho_1=6 \times 10^7 \Omega \cdot \text{cm}$) and bond angle (nearly 90°) suggest that the bonding functions are delocalized combinations of pure atomic

p functions. Recent Mössbauer studies⁵ substantiate the use of *p* functions. Bersohn⁶ describes the bonding within each layer by means of a two-dimensional band theory, i.e., by molecular orbitals which extend over the entire layer. The analogy to graphite is clear. In contrast to graphite, however, two atomic *p* functions are used for each atom and these lie in the layer rather than being normal to it.

As in graphite the bonding between layers is very weak. The interatomic distances δ and ϵ exceed the van der Waals diameter. Rosenberg⁷ has calculated

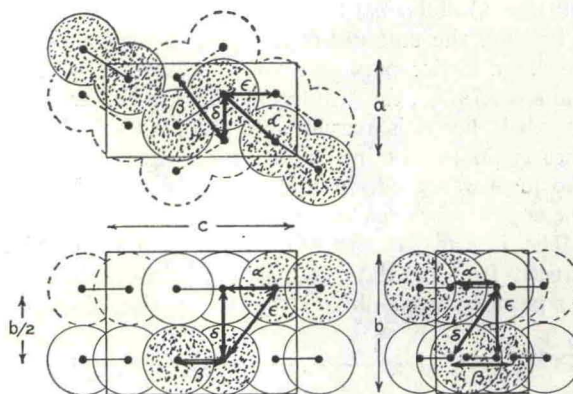


FIG. 1. The crystal structure of iodine.

the energy of sublimation of iodine by employing a Lennard-Jones 6-12 potential between iodine atoms not covalently bound. Thus $E(\text{sublimation}) = -E[\text{covalent (Hückel)}] - E_{6-12} - E_{\text{vib}} = 17.0 \text{ kcal/mole}$. The experimental value is 15.7 kcal/mole. The good agreement indicates that the covalent intermolecular bonding occurs only between nearest neighbors, all other interactions being satisfactorily accounted for by van der Waals forces.

From the lattice parameters *a*, *b*, and *c*, it is possible

* This work was supported in part by the U.S. Atomic Energy Commission.

¹ E. A. Perez-Albuerné, K. F. Forsgren, and H. G. Drickamer, *Rev. Sci. Instr.* **35**, 29 (1964).

² L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, N.Y., 1960), 3rd ed.

³ C. H. Townes and B. P. Dailey, *J. Chem. Phys.* **20**, 35 (1952).

⁴ K. Yamasaki, *J. Phys. Soc. Japan* **17**, 1262 (1962).

⁵ M. Pasternak, A. Simopoulos, and Y. Hazony, *Phys. Rev.* **140**, A1892 (1965).

⁶ R. Bersohn, *J. Chem. Phys.* **36**, 3445 (1962).

⁷ J. L. Rosenberg, *J. Chem. Phys.* **40**, 1707 (1964).

TABLE I. V/V_0 , b/b_0 , $b/2$, α , β , δ , and ϵ vs pressure for iodine [assuming $d(a/a_0) = d(c/c_0)$].^a

P (kbars)	V/V_0	b/b_0	$b/2$ (Å)	α (Å)	β (Å)	δ (Å)	ϵ (Å)
0	1.000	1.000	3.64	3.56	4.04	4.35	4.49
25	0.881	0.924	3.36	3.43	3.94	4.11	4.20
50	0.819	0.896	3.26	3.34	3.88	3.99	4.05
75	0.781	0.876	3.19	3.27	3.83	3.91	3.95
100	0.749	0.860	3.13	3.21	3.78	3.87	3.87
125	0.721	0.846	3.08	3.16	3.75	3.78	3.80
150	0.697	0.832	3.03	3.12	3.72	3.73	3.74
175	0.679	0.820	2.98	3.08	3.70	3.69	3.68
200	0.664	0.809	2.94	3.04	3.68	3.65	3.63
225	(0.651)	(0.798)	(2.90)	(3.01)	(3.66)	(3.62)	(3.58)
250	(0.641)	(0.787)	(2.86)	(2.98)	(3.64)	(3.59)	(3.54)

^a Marker used: NaF.

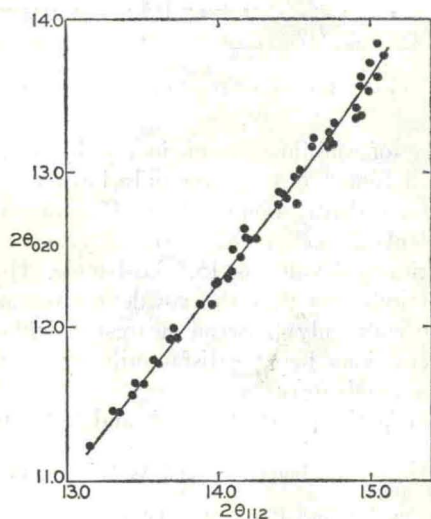
to evaluate the intermolecular iodine-iodine distances α , β , δ , and ϵ from the relations

$$\begin{aligned}\alpha &= [(a/2)^2 + (c/2 - 2vc_0)^2]^{1/2}, \\ \beta &= [(a - 2ua_0)^2 + (2vc_0)^2]^{1/2}, \\ \delta &= [(a/2)^2 + (b/2)^2]^{1/2}, \\ \epsilon &= [(b/2)^2 + (c/2 - vc_0)^2]^{1/2}.\end{aligned}\quad (1)$$

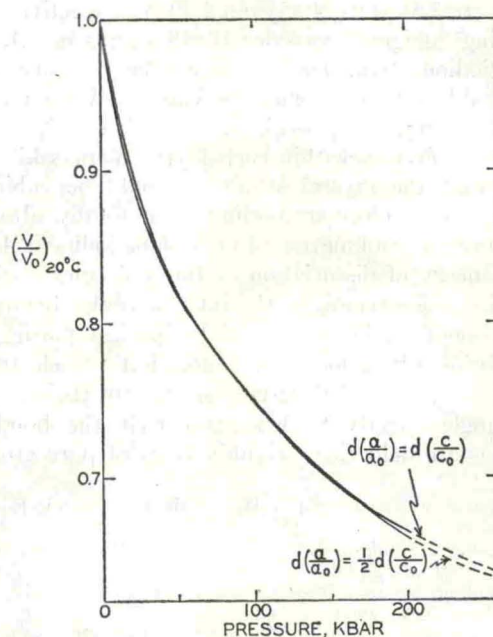
The coordinates $v(c_0)$ and $u(a_0)$ locate the centers of the iodine atoms with respect to the corners of the unit cell. As long as the molecules do not lengthen or rotate $v(c_0)$ and $u(a_0)$ remain constant.

Because the unit cell of iodine is orthorhombic and has large lattice parameters ($a_0 = 4.79$ Å, $b_0 = 7.27$ Å, and $c_0 = 9.79$ Å), the diffraction lines are numerous and crowded. For this reason only the (020) and (112) lines could be obtained clearly. The quality of these two lines was good. In Fig. 2 the shift of the (020) line is plotted versus the shift of the (112).

The interplanar distances which can be obtained directly from the data are $b/2$, d_{112} , and d_{102} . These do not permit an unambiguous determination of a and c .

FIG. 2. $2\theta_{020}$ vs $2\theta_{112}$ for iodine.

In Table I are listed smoothed values of V/V_0 , $b/2$, α , β , δ , and ϵ calculated on the assumption that $d(a/a_0) = d(c/c_0)$. In Figs. 3-5 are plotted these values as well as those calculated for the case $d(a/a_0) = \frac{1}{2}d(c/c_0)$. In no case is the spread significant in so far as our discussion is concerned. These, of course do not represent ultimate limits, but at 200 kbars calculations were made for the rather extreme assumptions: (1) a is totally incompressible and (2) c is totally incompressible. The effects on V/V_0 , β , δ , and ϵ were negligible within the limits of our discussion. For constant a , $\alpha = 2.99$ Å at 200 kbars; for constant c , $\alpha = 3.2$ Å, compared with the 3.04 Å of Table I. Even the value of 3.2 Å would not radically modify our conclusions. In these extreme cases, at 200 kbars $a/a_0 = 0.838$ for constant c and $c/c_0 = 0.829$ for constant a , while $b/b_0 = 0.805$, compared with the $c/c_0 = a/a_0 = 0.905$ from Table I. This reflects the significant component of covalent binding in the ac plane.

FIG. 3. V/V_0 vs pressure—iodine.

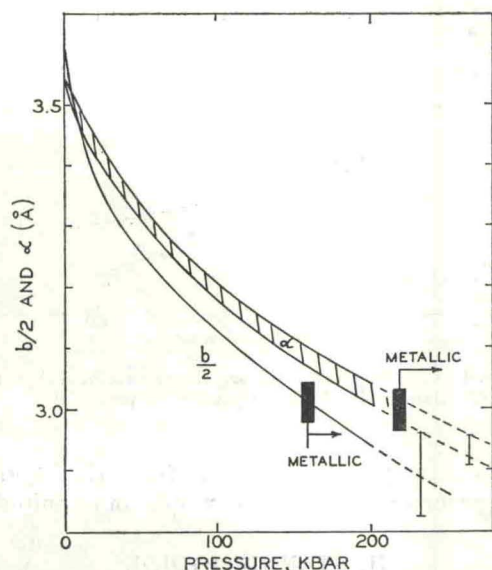


FIG. 4. Interlayer distance $b/2$ and intermolecular distance α vs pressure—iodine.

From Fig. 3 one sees the strong effect of pressure on the compressibility which is typical of crystals with a large component of molecular binding.

In Fig. 4, $b/2$ and α are plotted versus pressure. At 220 kbars the value of α is about 3.0 Å; $b/2 = 3.0$ Å at 160 kbars. The two vertical lines terminating on the α curves represent the effect on α of a 5% extension of the intramolecular bond. The upper curve and short vertical line correspond to the case $d(a/a_0) = d(c/c_0)$.

In Fig. 5 the values of β , δ , and ϵ calculated on the two bases are plotted versus pressure; all remain greater than 3.5 Å in the pressure range investigated.

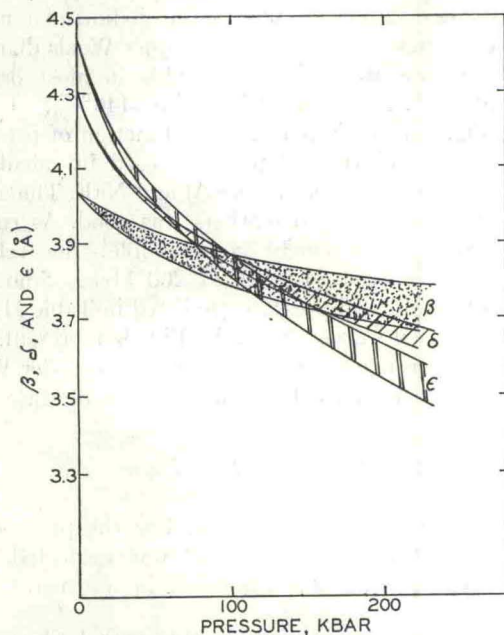


FIG. 5. Intermolecular distances β , δ , and ϵ vs pressure—iodine.

The optical absorption edge and electrical resistance of iodine has been studied rather extensively in a series of papers from this laboratory.⁸⁻¹² Iodine is an insulator at 1 atm with a resistivity perpendicular to the ac plane (in the b direction) about 10^4 greater than in the ac plane as mentioned above. The resistance decreases with increasing pressure by orders of magnitude. There is a distinct change in slope of the resistance-pressure curve measured in the b direction near 160 kbars. At this point the activation energy for conduction goes to zero and the resistance becomes "metallic," i.e., the resistance increases substantially linearly with increasing temperature. In the ac plane the change of slope occurs near 220 kbars and is again accompanied by a change from "semiconducting" to "metallic" behavior. Thus, between 160 and 220 kbars iodine is a semiconductor in one direction and a metal in the other, much like graphite at atmospheric pressure and one atmosphere. As in graphite,^{13,14} with the application of further pressure the conduction becomes metallic in either direction.

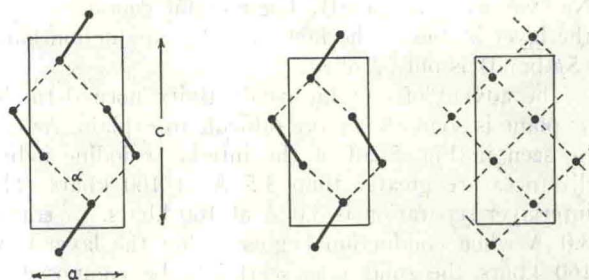


FIG. 6. The ac plane of iodine (iodine atoms not to scale): (a) 1 atm; (b) 220 kbar, lattice of molecules; (c) 220 kbar, lattice of atoms.

The advent of metallic conduction in the ac plane can be explained in at least two ways. It is possible that the molecules retain their identity and conduction is a result of band overlap. It is also possible that the molecules dissociate, resulting in an unfilled conduction band and normal metallic conduction. The two explanations are examined more fully below.

In Figs. 6(a) and 6(b) a comparison is made between the ac layer at one atmosphere and at 220 kbars as visualized in the first explanation. At pressures above 220 kbars the intermolecular and intramolecular bonds are of about the same length (and, consequently, of a

⁸ H. L. Suchan, S. Wiederhorn, and H. G. Drickamer, J. Chem. Phys. **31**, 355 (1959).

⁹ A. S. Balchan and H. G. Drickamer, J. Chem. Phys. **34**, 1948 (1961).

¹⁰ B. M. Riggleman and H. G. Drickamer, J. Chem. Phys. **37**, 446 (1962).

¹¹ B. M. Riggleman and H. G. Drickamer, J. Chem. Phys. **38**, 2721 (1963).

¹² H. G. Drickamer, Solid State Phys. **17**, 1 (1965). (This reference contains a review of both optical and electrical studies.)

¹³ R. B. Aust and H. G. Drickamer, Science **140**, 817 (1963).

¹⁴ R. B. Aust, W. H. Bentley, and H. G. Drickamer, J. Chem. Phys. **41**, 1856 (1964).

similar strength). The intramolecular bond may or may not have lengthened. The intermolecular and intramolecular bonds can be distinguished because of the different orientations of the bonding functions. The exchange between nearest neighbors not on the same molecule is large, resulting in wide bands. At some point in the Brillouin zone the valence and conduction bands either touch (as in graphite) or overlap. The result is metallic conductivity within the layers.

In the second explanation it is assumed that the iodine molecules dissociate at pressures above 220 kbars. The dissociation can be thought of as taking place in two steps. First, the intramolecular bond lengthens as the intermolecular exchange increases. (A 5% increase in the length of the intramolecular bond makes it equal to a at 220 kbars.) Second, the molecules rotate slightly so that the iodine atoms lie on a square lattice. The layer of atoms is contrasted with the layer of molecules in Figs. 6(b) and 6(c). The dissociation process is analogous to that experienced by alkali metal vapors when solidifying, e.g., $Na_2(\text{vapor}) \rightarrow Na(\text{metal})$. The metallic conductivity in the layer is due to the fact that the conduction band ($5p$ band) is only $\frac{5}{6}$ filled.

The advent of metallic conductivity normal to the ac plane is somewhat more difficult to explain. As can be seen in Fig. 5 all of the interlayer iodine-iodine distances are greater than 3.5 Å at 160 kbars. The interlayer separation is 3.0 Å at 160 kbars. (a equals 3.0 Å when conduction begins within the layer.) At 160 kbars the solid must certainly be composed of molecules. The metallic conductivity is probably best explained by an extension of Bershon's band calculation to three dimensions. In this case the atomic functions which become delocalized must be p_z functions, directed normal to the layers. The p_z functions of one layer could interact with the p_z , p_x , and p_y functions of the adjacent layers. In the absence of a detailed band calculation the relative importance of the terms is unknown. Although the exchange between atomic functions in different layers is initially small it apparently increases rapidly with decreasing b/b_0 . The

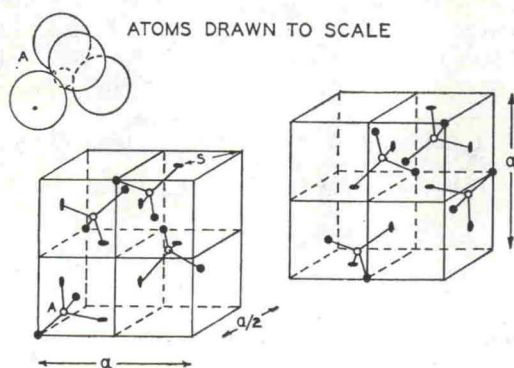


FIG. 7. The crystal structure of SnI_4 .

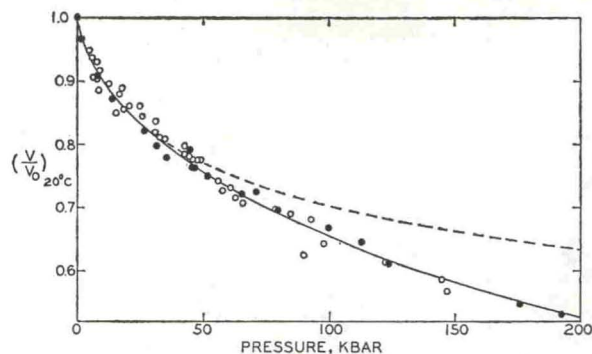


FIG. 8. V/V_0 vs pressure— SnI_4 . ●, Al marker; ○, NaF marker; ---, calculated using Lennard-Jones 6-12 potential.

behavior here parallels graphite where the interlayer exchange increases by at least an order of magnitude.

II. STANNIC IODIDE

SnI_4 crystallizes in a cubic lattice having eight molecules per unit cell. The crystal structure is shown in Fig. 7. Also in Fig. 7, one molecule is shown with its atoms drawn in their correct proportional sizes. The structure can best be visualized as deviating slightly from an idealized structure of iodine atoms on a face-centered cubic lattice with $\frac{1}{8}$ of the interstices filled with tin atoms. The actual structure deviates from the idealized structure by small extensions of the Sn-I bonds. The result is that the intramolecular iodine-iodine distance is 4.41 Å while the smallest intermolecular iodine-iodine distance S is 4.30 Å, twice the van der Waals radius of the iodine atom. The lattice parameter a is 12.26 Å.

The bonding in SnI_4 is apparently purely molecular: the smallest intermolecular iodine-iodine distance S is in exact agreement with the van der Waals diameter of the iodine atom; SnI_4 is soluble in most organic solvents and has a low melting point (146°C).

In Fig. 8 V/V_0 is plotted as a function of pressure. The (222) and (622) lines were used in calculating V/V_0 . The markers used were Al and NaF. The agreement between the two markers was good. As can be seen, SnI_4 is extremely compressible: the relative volume is reduced to 0.528 at 200 kbars. Smoothed values of V/V_0 and pressure are listed in Table II.

The dashed curve shown in Fig. 8 represents the results of a rough calculation assuming van der Waals forces between molecules. The equation of state used was¹⁵

$$dW_L/dV = -P + (T\alpha/\beta), \quad (2)$$

where W_L is the lattice energy. For the purposes of this calculation the term $T\alpha/\beta$ was neglected. The lattice energy W_L was expressed in a general form

¹⁵ E. A. Perez-Albuerné and H. G. Drickamer, J. Chem. Phys. **43**, 1381 (1965).

TABLE II. High-pressure data for stannic iodide.^a

V/V_0	$S_2(\text{\AA})$	$S_1(\text{\AA})$	$P(\text{kbars})$
1.000	4.30	4.30	0
0.950	4.24	4.16	3.5
0.900	4.16	4.02	10
0.850	4.07	3.86	20
0.800	3.98	3.68	35
0.750	3.90	3.51	53
0.700	3.82	3.35	75
0.650	3.72	3.17	102
0.625	3.68	3.06	118
0.600	3.62	2.96	136
0.575	3.57	2.84	156
0.550	3.51	2.72	177
0.525	3.45	2.58	203

^a $a_0=12.26 \text{ \AA}$; markers used: Al and NaF.

assuming a Lennard-Jones 6-12 potential

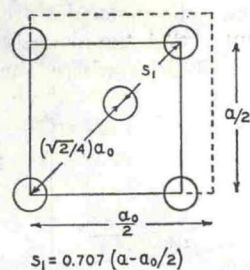
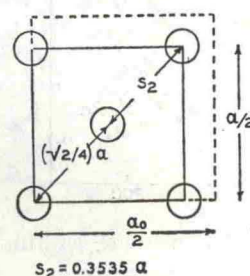
$$W_L = (A/R^{12}) - (B/R^6), \quad (3)$$

where R is the nearest-neighbor distance. The change in volume was assumed to be proportional to R^3 so that

$$-P = \frac{A'}{(V/V_0)^5} - \frac{B'}{(V/V_0)^3}. \quad (4)$$

A' and B' were evaluated from the volume at 0 and 10 kbars. As can be seen from the figure the calculated curve agrees with the data to about 30 kbars. At 200 kbars the difference between the two curves is large. Compression of the Sn-I bond could account for the difference.

Each iodine atom is surrounded by twelve nearest iodine neighbors: three of them intramolecular neighbors, nine of them intermolecular neighbors. When the lattice is compressed the intramolecular and inter-

FIG. 9. I-I distances S_1 and S_2 in SnI_4 (iodine atoms not to scale).TABLE III. High-pressure data for *p*-di-iodobenzene.^{a-c}

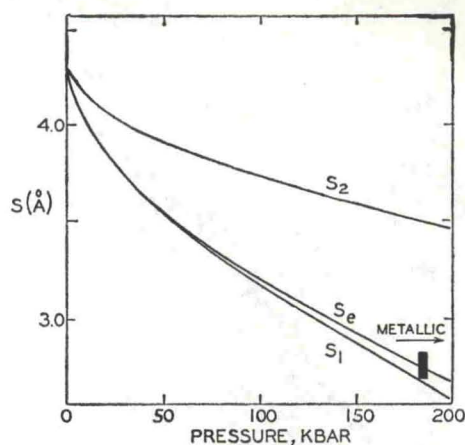
V/V_0	a/a_0	b/b_0	c/c_0	$P(\text{kbars})$
1.000	1.000	1.000	1.000	0
0.9381	0.9788	0.9764	0.9816	8
0.8831	0.9594	0.9538	0.9651	18
0.8330	0.9406	0.9329	0.9493	31
0.7870	0.9224	0.9137	0.9338	50
0.7464	0.9053	0.8967	0.9195	74
0.7103	0.8882	0.8824	0.9063	108
0.6780	0.8724	0.8694	0.8939	152
0.6490	0.8571	0.8574	0.8832	211
0.6244	0.8418	0.8488	0.8739	(272)
0.6139	0.8347	0.8455	0.8699	(296)

^a $a_0=17.00 \text{ \AA}$; $b_0=7.38 \text{ \AA}$; $c_0=6.21 \text{ \AA}$.^b Markers used: Al and NaF.^c Initial I-I distances: $A-E=4.15 \text{ \AA}$; $A-C=4.38 \text{ \AA}$.

molecular iodine-iodine distances decrease by different amounts. In Fig. 9 the two limiting cases are presented. In the top figure, the Sn-I bonds are assumed to be rigid so that the intramolecular iodine-iodine distances remain constant. The result is that the intermolecular iodine-iodine distances marked S_1 decreases rapidly. In the bottom figure, the opposite extreme is presented, i.e., the Sn-I bonds are assumed to be so weak that the intramolecular and intermolecular iodine-iodine distances decrease by the same amount. The iodine-iodine distances in this case are labeled S_2 .

The decrease of S_1 and S_2 with pressure is plotted in Fig. 10. The curve labeled S_e was calculated using the force constants for the Sn-I bond in SnI_4 obtained by Stammreich, Forneris, and Tavares.¹⁶ It is seen that the compression of the Sn-I bond is small, but it would account for the difference between the two curves of Fig. 8.

The heavy bar at 185 kbars indicates the point at which the resistance of SnI_4 becomes metallic as determined by Riggelman and Drickamer.¹⁰ At pressures above 185 kbars the temperature coefficient of re-

FIG. 10. S_1 , S_2 , and S_e vs pressure— SnI_4 .¹⁶ H. Stammreich, R. Forneris, and Y. Tavares, J. Chem. Phys. 25, 1278 (1956).

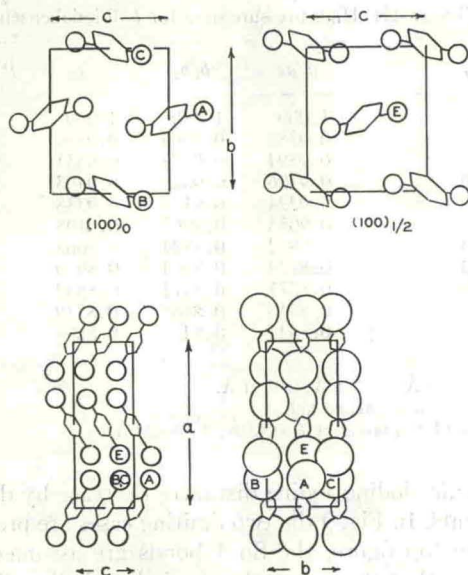


FIG. 11. Crystal structure of p - $C_6H_4I_2$ (bc plane drawn in expanded scale and iodine atoms drawn to scale in ab view only).

sistivity is positive. The intermolecular iodine-iodine distance S_e is about 2.8 Å at 185 kbars. This value is not too different from the value of 3.0 Å required for metallic conduction in iodine, and, in any case, distortion of the bond angle which has been ignored until now, could increase S_e , thus making the agreement closer. The mechanism for metallic conduction in SnI_4 is probably similar to that of iodine. At pressures above 185 kbars the exchange between iodine atoms on adjacent molecules is sufficiently great to cause an overlap of the valence and conduction bands at some point in the Brillouin zone.

III. p -DI-IODOBENZENE

p - $C_6H_4I_2$ crystallizes in an orthorhombic structure having four molecules per unit cell. The crystal structure is shown in Fig. 11. The molecular centers are at

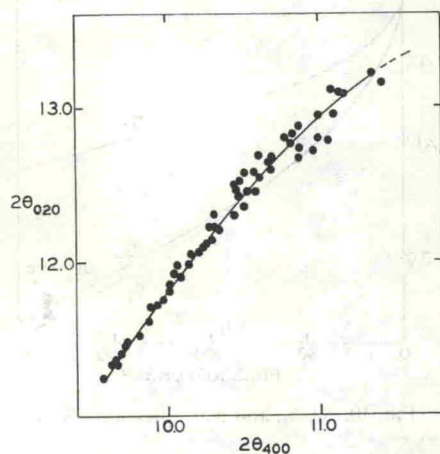


FIG. 12. $2\theta_{020}$ vs $2\theta_{400}$ — p - $C_6H_4I_2$.

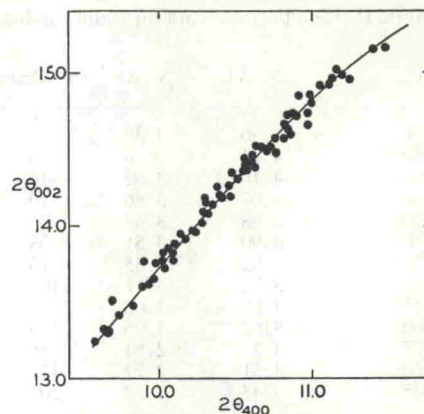


FIG. 13. $2\theta_{002}$ vs $2\theta_{400}$ — p - $C_6H_4I_2$.

$(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$, and $(\frac{1}{2}, 0, \frac{1}{2})$. The two bc planes shown in Fig. 11 are drawn in an expanded scale. The shortest iodine-iodine distances are $A-E$ (4.15 Å) and $A-C$ (4.38 Å). The atmospheric values of the lattice parameters are listed in Table III.

The (400), (020), and (002) diffraction lines of p - $C_6H_4I_2$ could be obtained clearly. In Fig. 12 the shift of the (020) line is plotted versus the shift of the (400) line. Figure 13 is a similar plot for the (002) and (400) lines. The smoothed curves of Figs. 12 and 13 were used to calculate a/a_0 , b/b_0 , and c/c_0 as functions of pressure as tabulated in Table III. Figure 14 shows a/a_0 , b/b_0 , c/c_0 , and V/V_0 plotted versus pressure. At low pressures the c axis is the least compressible, and the b axis most compressible. At the highest pressures the a axis becomes slightly less compressible than b .

The relative compressibility of the three axes can be understood from the crystal structure. The initial rapid compression of the b axis probably corresponds to aligning the axes of the molecules as viewed normal to the b axis. This results in equalizing the two iodine-iodine distances AB and AC . Once the molecules are aligned, the b -axis compressibility is not significantly different from the c -axis compressibility (where the

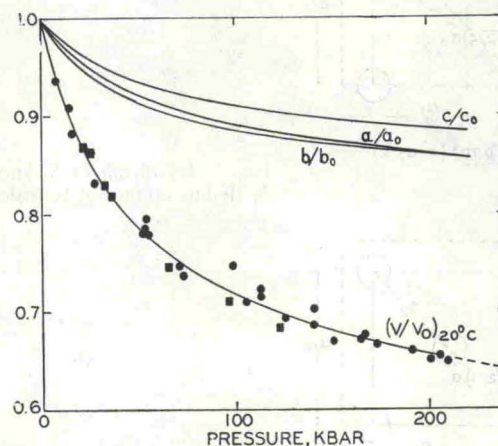


FIG. 14. a/a_0 , b/b_0 , c/c_0 , and V/V_0 vs pressure— p - $C_6H_4I_2$. ●, NaF marker; ■, Al marker.

molecular axes are aligned to begin with). One might suspect that rotation of the molecules contributes to the a -axis compressibility. This is not the case, as such a rotation would lengthen the c axis.

The iodine-iodine distances AE and AC remain greater than 3.6 Å even at the highest pressures. A high-pressure electrical resistance run was made on p -C₆H₄I₂ and the resistance remained above 10⁸ Ω (the limit of the electrical resistance apparatus), supporting the hypothesis that the iodine-iodine distance must approach 3.0 Å before the exchange is great enough to result in band overlap.

An interesting contrast is offered by the ionic crystal thallous iodide. Samara and Drickamer¹⁷ have measured the electrical resistance of TII as a function of pressure. At pressures above 160 kbars the resistance is metallic, having a positive temperature coefficient. Perez-Albuérne and Drickamer¹⁸ have measured the volume of TII as a function of pressure. At 160 kbars the nearest iodide-iodide separation is 3.73 Å. Metallic conduction occurs when the filled valence band (I-5 p) overlaps the empty conduction band (Tl-6 p).

¹⁷ G. A. Samara and H. G. Drickamer, J. Chem. Phys. **37**, 408 (1962).