

The Crystal and Molecular Structure of Phosphorus Thioiodide

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The crystal structure of phosphorus thioiodide has been determined by means of electron-density projections on to the (100) and (010) planes. The crystals are triclinic, space group $P\bar{1}$ with cell constants

$$a = 7.31 \text{ \AA}, \quad b = 7.35 \text{ \AA}, \quad c = 19.61 \text{ \AA}; \\ \alpha = 94^\circ 24', \quad \beta = 90^\circ 10', \quad \gamma = 90^\circ 55'.$$

There are four molecules, of composition $P_4S_3I_2$, in the unit cell, two crystallographically independent molecules forming the asymmetric unit. The approximate iodine coordinates were found as a result of direct determination of the signs of a number of ($0kl$) and ($h0l$) structure factors by the application of Harker Kasper inequalities and of sign relationships.

The $P_4S_3I_2$ molecule consists of two five-membered rings of three phosphorus and two sulphur atoms, joined by a common P-S-P angle, the iodine atoms being bonded to phosphorus atoms of different rings. The molecule has twofold rotation symmetry. Iodine coordinates and phosphorus (and sulphur) coordinates have been determined with standard deviations of 0.01 Å and 0.03 Å respectively, and observed bond lengths and angles are compared with those in the phosphorus sulphides and iodides.

1. Introduction

The existence of three phosphorus thioiodides, of composition $P_4S_3I_2$, PSI and P_2SI_4 respectively, together with several methods for their preparation were reported by Ouvrard (1892, 1894). An attempt to confirm these reports and to determine the interrelationships of the compounds was made recently in this department by Topsom & Wilkins (1956). They found that PSI and P_2SI_4 could not be prepared by the methods given and consider that their existence is open to serious doubt. It appears therefore that $P_4S_3I_2$, which is readily prepared, is probably the only thioiodide formed by phosphorus. An ebullioscopic molecular weight determination in carbon disulphide showed that this compound is monomeric.

A knowledge of the molecular configuration of $P_4S_3I_2$ was considered to be of interest, particularly with a view to comparisons with the known configurations of the phosphorus sulphides P_4S_{10} and P_4S_7 (Vos & Wiebenga, 1955), P_4S_5 (van Houten & Wiebenga, 1957), P_4S_3 (Leung, Waser *et al.*, 1957). The molecular configurations reported show that the arrangement of phosphorus and sulphur atoms in these molecules is remarkably flexible and difficult to predict. More than one chemically reasonable molecular configuration could be postulated for $P_4S_3I_2$ but there was no experimental evidence for distinguishing them prior to this investigation. The crystal structure, leading

to the molecular structure was found directly by X-ray crystallographic analysis.

2. Experimental

Phosphorus thioiodide was prepared by mixing white phosphorus, sulphur and iodine as their solutions in carbon disulphide (Topsom & Wilkins, 1956) and purified by recrystallization from this solvent at -78°C ., crystals of a size suitable for X-ray examination being obtained by controlled evaporation at room temperature. Invariably the crystals were found to be twinned on (001) but a few of them could be cleaved to give untwinned fragments. During recording of the diffraction data the crystals, which decompose fairly readily in moist air, were sealed in Lindemann glass capillaries.

Crystallographic data

Phosphorus thioiodide, $P_4S_3I_2$, m.p. 118°C . with decomposition. The crystals are triclinic with

$$a = 7.31 \pm 0.01, \quad b = 7.35 \pm 0.01, \quad c = 19.61 \pm 0.03 \text{ \AA}, \\ \alpha = 94^\circ 24', \quad \beta = 90^\circ 10', \quad \gamma = 90^\circ 55'; \quad \text{all} \pm 10'. \\ (\text{Cu } K\alpha, \lambda = 1.542 \text{ \AA}).$$

Density observed by flotation, $3.0 \pm 0.1 \text{ g.cm.}^{-3}$; calculated for four molecules per unit cell, 3.04 g.cm.^{-3} . The linear absorption coefficient for Cu $K\alpha$ radiation is 625 cm.^{-1} ; for Mo $K\alpha$ radiation 77 cm.^{-1} . The application of a statistical test (Howells, Phillips & Rogers, 1950) to the ($h0l$) intensities indicated the presence of a centre of symmetry. The probable space

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group was therefore $P\bar{1}$ with two $P_4S_3I_2$ molecules constituting the asymmetric unit, and this was confirmed by the structure analysis.

Relative intensities of $(h0l)$ and $(0kl)$ reflections were obtained for both Cu $K\alpha$ and Mo $K\alpha$ radiation by use of standard Weissenberg techniques and visual comparison of spots with intensity scales. $(1kl)$ intensities were derived from Mo $K\alpha$ radiation only. In the final refinement of atomic coordinates, the more accurate Mo $K\alpha$ data were used, obtained from crystals measuring approximately 0.2 mm. in each axial direction. These data comprised 258 $(h0l)$ reflections (68% of the possible to a limiting $\sin \theta/\lambda$ value of 0.65) and 184 $(0kl)$ reflections (60% of the possible to a limiting $\sin \theta/\lambda$ value of 0.58). No absorption corrections were made.

3. The approximate iodine positions

The essential problem in this structure analysis was the determination of the positions of the four crystallographically independent iodine atoms, for it was calculated by the method of Sim (1957) that 82–84% of all structure factors would have the same sign as their total iodine atom contributions (as compared with 84% found when refinement ceased). Iodine coordinates could not be determined from the Patterson projections $P(v, w)$ and $P(u, w)$ which were evaluated. Neither of these projections could be interpreted uniquely, partly because of the extent of the overlap of I–P and I–S type vectors.

The presence of several outstandingly strong $(0kl)$ reflections suggested the use of Harker Kasper inequalities (e.g. Harker & Kasper, 1948; Kasper, Lucht & Harker, 1950) to determine directly the signs of structure factors. As four of the unitary structure factors $U(0kl)$ were greater than 0.6, many sign relationships could be deduced. The signs of 59 structure factors were established in terms of three variables (which were the unknown signs of three large structure factors), while use of the sign relationship $s(\mathbf{H}) = s(\mathbf{H}') \cdot s(\mathbf{H} + \mathbf{H}')$, which is probably true for combinations involving only large structure factors, (Cochran, 1952; Cochran & Woolfson, 1955) established as probable a further 61 signs in terms of the same three variables although 9 of these probable signs were later shown to be wrong. By similar methods the signs of 25 $(h0l)$ structure factors were proved and a further four established as highly probable, this time in terms of only two variables.

The $(h0l)$ Fourier syntheses for the four sign combinations of the two variables were computed, including in the summation only the 29 terms whose signs were established. The correct partial electron-density projection on (010) was readily identified by consideration only of possible iodine peaks. The approximate iodine coordinates so obtained were used to determine more signs, including those of a number of $(00l)$ reflections, and with aid of these latter

signs, the correct combination of the variables for the $(0kl)$ structure factors was found. A Fourier synthesis with known $(0kl)$ terms was then computed and from the resulting partial electron-density projection on (100) the iodine peaks were readily identified.

4. Refinement of atomic coordinates

Refinement of the structure proceeded using Fourier and difference Fourier techniques, for both (100) and (010) projections. Initially signs of structure factors were regarded as determined only by large contributions of the iodine atoms. Most of the 14 phosphorus and sulphur atoms were located using the Cu $K\alpha$ data and all were clearly defined following extension of the refinement with Mo $K\alpha$ data.

In the (100) projection there were strong indications from difference maps that the iodine atoms were vibrating anisotropically, all four in the asymmetric

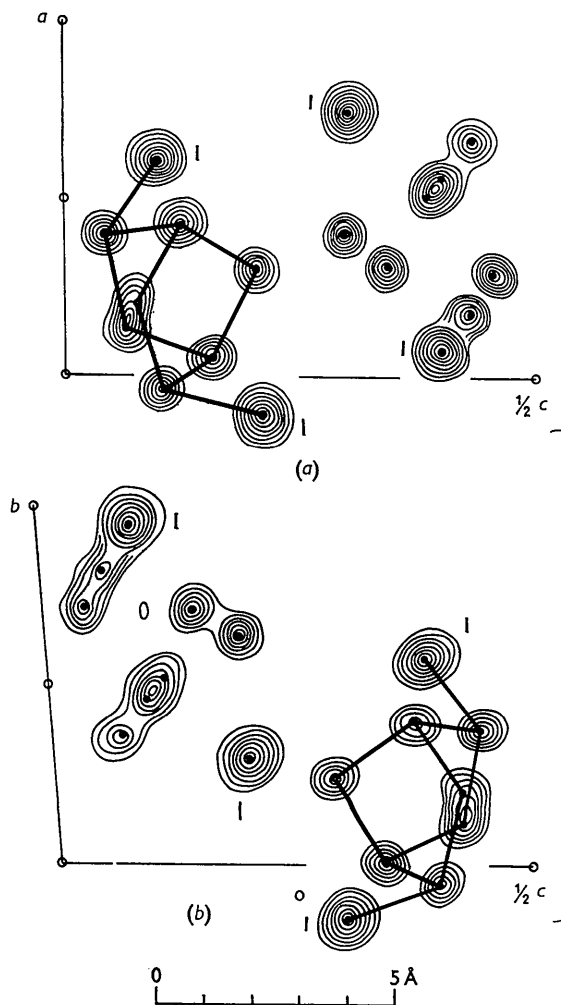


Fig. 1. Electron-density projections of the asymmetric unit (a) on (010) , (b) on (100) . Contours at an interval of 4 $e \cdot \text{\AA}^{-2}$ for P and S, 12 $e \cdot \text{\AA}^{-2}$ for I atoms, starting at 8 $e \cdot \text{\AA}^{-2}$. Final atomic positions indicated by black dots.

Table 1. Observed and calculated structure factors

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c							
0,0,0	857	857	2,0,0	16	16	3,0,6	71	64	5,0,16	37	36	7,0,15	40	38	0,1,0	11*	1-	0,2,7	20	20	0,4,4	29*	37	0,6,8	94	93-	
1,0,0	7*	5	4,0,0	16	16	6,0,12	197	258	8,0,20	17	17	9,0,18	15	15	1,1,0	67	59	1,2,0	8	252	263	1,3,0	30*	21-	1,4,0	9	30*
2,0,0	36	34-	6,0,0	16	16	9,0,18	141	60	11,0,22	18	18	12,0,24	18	18	2,1,0	17	19	2,2,0	9	118	107	2,3,0	51	55-	2,4,0	10	31*
3,0,0	9*	5	8,0,0	16	16	12,0,24	111	35	14,0,28	20	20	15,0,30	15	15	3,1,0	133	128	3,2,0	10	115	112	3,3,0	32*	25-	3,4,0	11	32
4,0,0	156	172-	10,0,0	16	16	15,0,30	111	58	17,0,34	17	17	18,0,36	16	16	4,1,0	165	172	4,2,0	11	39	33-	4,3,0	39	45-	4,4,0	12	32*
5,0,0	11*	1-	12,0,0	16	16	18,0,36	103	103	20,0,40	18	18	21,0,42	15	15	5,1,0	203	230	5,2,0	12	106	107	5,3,0	34*	11	5,4,0	13	33*
6,0,0	156	166-	14,0,0	16	16	21,0,42	140	51-	23,0,46	15	15	24,0,48	14	14	6,1,0	37	37	6,2,0	13	25*	21-	6,3,0	15	18	6,4,0	14	18
7,0,0	17	10-	16,0,0	16	16	24,0,48	135	53	26,0,50	14	14	27,0,51	13	13	7,1,0	6	18*	7,2,0	14	194	181-	7,3,0	14	146	7,4,0	15	115-
8,0,0	135	135-	18,0,0	16	16	27,0,54	115	125-	29,0,54	12	12	30,0,60	10	10	8,1,0	57	65	8,2,0	15	26*	17	8,3,0	133	130-	8,4,0	15	115-
9,0,0	27	23	20,0,0	16	16	30,0,60	115	125-	32,0,64	10	10	33,0,66	9	9	9,1,0	36	50	9,2,0	10	27	50-	9,3,0	14	45	9,4,0	14	42-
10,0,0	227	252	22,0,0	16	16	33,0,66	115	125-	35,0,66	9	9	36,0,72	8	8	10,1,0	35	59	10,2,0	17	29*	11	10,3,0	17	29*	10,4,0	15	22*
11,0,0	33	30-	24,0,0	16	16	36,0,72	115	125-	38,0,72	8	8	40,0,80	7	7	11,1,0	34	55	11,2,0	18	30*	25	11,3,0	18	30*	11,4,0	16	27*
12,0,0	94	87-	26,0,0	16	16	39,0,78	115	125-	41,0,78	7	7	44,0,88	6	6	12,1,0	33	55	12,2,0	19	31*	25	12,3,0	19	31*	12,4,0	17	28*
13,0,0	28	32	28,0,0	16	16	42,0,84	115	125-	44,0,84	6	6	48,0,96	5	5	13,1,0	32	55	13,2,0	20	32*	24	13,3,0	20	32*	13,4,0	18	27*
14,0,0	19*	1-	30,0,0	16	16	45,0,90	115	125-	47,0,90	5	5	52,0,108	4	4	14,1,0	31	55	14,2,0	21	34*	24	14,3,0	21	34*	14,4,0	19	26*
15,0,0	19	18	32,0,0	16	16	48,0,96	115	125-	50,0,96	4	4	56,0,112	3	3	15,1,0	30	55	15,2,0	22	36*	23	15,3,0	22	36*	15,4,0	20	25*
16,0,0	78	78	34,0,0	16	16	51,0,102	115	125-	53,0,102	3	3	60,0,120	2	2	16,1,0	29	55	16,2,0	23	38*	22	16,3,0	23	38*	16,4,0	20	24*
17,0,0	21*	13-	36,0,0	16	16	54,0,108	115	125-	56,0,108	2	2	63,0,126	1	1	17,1,0	28	55	17,2,0	24	40*	21	17,3,0	24	40*	17,4,0	20	23*
18,0,0	21*	20-	38,0,0	16	16	57,0,114	115	125-	59,0,114	1	1	66,0,132	0	0	18,1,0	27	55	18,2,0	25	42*	20	18,3,0	25	42*	18,4,0	20	22*
19,0,0	22*	1-	40,0,0	16	16	60,0,120	115	125-	62,0,120	0	0	69,0,138	0	0	19,1,0	26	55	19,2,0	26	44*	19	19,3,0	26	44*	19,4,0	20	21*
20,0,0	15	8-	42,0,0	16	16	63,0,126	115	125-	65,0,126	0	0	72,0,144	0	0	20,1,0	25	55	20,2,0	27	46*	18	20,3,0	27	46*	20,4,0	20	20*
21,0,0	24*	16-	44,0,0	16	16	66,0,132	115	125-	68,0,132	0	0	75,0,150	0	0	21,1,0	24	55	21,2,0	28	48*	17	21,3,0	28	48*	21,4,0	20	19*
22,0,0	63	64-	46,0,0	16	16	69,0,138	115	125-	71,0,138	0	0	78,0,156	0	0	22,1,0	23	55	22,2,0	29	50*	16	22,3,0	29	50*	22,4,0	20	18*
23,0,0	29	30	48,0,0	16	16	72,0,144	115	125-	74,0,144	0	0	81,0,162	0	0	23,1,0	22	55	23,2,0	30	52*	15	23,3,0	30	52*	23,4,0	20	17*
24,0,0	29	27*	50,0,0	16	16	75,0,150	115	125-	77,0,150	0	0	84,0,170	0	0	24,1,0	21	55	24,2,0	31	54*	14	24,3,0	31	54*	24,4,0	20	16*
25,0,0	27*	13	52,0,0	16	16	78,0,156	115	125-	80,0,156	0	0	87,0,174	0	0	25,1,0	20	55	25,2,0	32	56*	13	25,3,0	32	56*	25,4,0	20	15*
26,0,0	25	23	54,0,0	16	16	81,0,162	115	125-	83,0,162	0	0	90,0,180	0	0	26,1,0	19	55	26,2,0	33	58*	12	26,3,0	33	58*	26,4,0	20	14*
27,0,0	25	24	56,0,0	16	16	84,0,168	115	125-	86,0,168	0	0	93,0,186	0	0	27,1,0	18	55	27,2,0	34	60*	11	27,3,0	34	60*	27,4,0	20	13*
28,0,0	25	23	58,0,0	16	16	87,0,174	115	125-	89,0,174	0	0	96,0,192	0	0	28,1,0	17	55	28,2,0	35	62*	10	28,3,0	35	62*	28,4,0	20	12*
29,0,0	25	23	60,0,0	16	16	90,0,180	115	125-	92,0,180	0	0	99,0,200	0	0	29,1,0	16	55	29,2,0	36	64*	9	29,3,0	36	64*	29,4,0	20	11*
30,0,0	25	23	62,0,0	16	16	93,0,186	115	125-	95,0,186	0	0	102,0,204	0	0	30,1,0	15	55	30,2,0	37	66*	8	30,3,0	37	66*	30,4,0	20	10*
31,0,0	25	23	64,0,0	16	16	96,0,192	115	125-	98,0,192	0	0	105,0,208	0	0	31,1,0	14	55	31,2,0	38	68*	7	31,3,0	38	68*	31,4,0	20	9*
32,0,0	25	23	66,0,0	16	16	99,0,198	115	125-	101,0,198	0	0	108,0,212	0	0	32,1,0	13	55	32,2,0	39	70*	6	32,3,0	39	70*	32,4,0	20	8*
33,0,0	25	23	68,0,0	16	16	102,0,204	115	125-	104,0,204	0	0	111,0,216	0	0	33,1,0	12	55	33,2,0	40	72*	5	33,3,0	40	72*	33,4,0	20	7*
34,0,0	25	23	70,0,0	16	16	105,0,210	115	125-	107,0,210	0	0	114,0,220	0	0	34,1,0	11	55	34,2,0	41	74*	4	34,3,0	41	74*	34,4,0	20	6*
35,0,0	25	23	72,0,0	16	16	108,0,216	115	125-	110,0,216	0	0	117,0,222	0	0	35,1,0	10	55	35,2,0	42	76*	3	35,3,0	42	76*	35,4,0	20	5*
36,0,0	25	23	74,0,0	16	16	111,0,222	115	125-	113,0,222	0	0	120,0,228	0	0	36,1,0	9	55	36,2,0	43	78*	2	36,3,0	43	78*	36,4,0	20	4*
37,0,0	25	23	76,0,0	16	16	114,0,228	115	125-	116,0,228	0	0	123,0,234	0	0	37,1,0	8	55	37,2,0	44	80*	1	37,3,0	44	80*	37,4,0	20	3*
38,0,0	25	23	78,0,0	16	16	117,0,234	115	125-	119,0,234	0	0	126,0,240	0	0	38,1,0	7	55	38,2,0	45	82*	0	38,3,0	45	82*	38,4,0	20	2*
39,0,0	25	23	80,0,0	16	16	120,0,240	115	125-	122,0,240	0	0	129,0,246	0	0	39,1,0	6	55	39,2,0	46	84*	0	39,3,0	46	84*	39,4,0	20	1*
40,0,0	25	23	82,0,0	16	16	123,0,246	115	125-	125,0,246	0	0	132,0,252	0	0	40,1,0	5	55	40,2,0	47	86*	0	40,3,0	47	86*	40,4,0	20	0*
41,0,0	25	23	84,0,0	16	16	126,0,252	115	125-	128,0,252	0	0	135,0,258	0	0	41,1,0	4	55	41,2,0	48	88*	0	41,3,0	48	88*	41,4,0	20	0*
42,0,0	25	23	86,0,0	16	16	129,0,258	115	125-	131,0,258	0	0	138,0,264	0	0	42,1,0	3	55	42,2,0	49	90*	0	42,3,0	49	90*	42,4,0	20	0*
43,0,0	25	23	88,0,0	16	16	132,0,264	115	125-	134,0,264	0	0	141,0,270	0	0	43,1,0	2	55	43,2,0	50	92*	0	43,3,0	50	92*	43,4,0	20	0*
44,0,0	25	23	90,0,0	16	16	135,0,270	115	125-	137,0,270	0	0	144,0,276</															

Table 2. *Atomic coordinates*

Molecule (1)	<i>x</i>	<i>y</i>	<i>z</i>	<i>X'</i>	<i>Y'</i>	<i>Z'</i>
I ₁	0.607	0.950	0.0973	4.326 Å	6.952 Å	1.375 Å
I ₂	-0.106	0.287	0.2075	-0.809	2.101	3.908
P ₁	0.398	0.718	0.043	2.83	5.25	0.44
P ₂	0.423	0.519	0.123	3.03	3.80	2.12
P ₃	0.049	0.716	0.157	0.27	5.24	2.68
P ₄	-0.037	0.457	0.102 ₍₅₎	-0.32	3.34	1.75
S ₁	0.130	0.825	0.065 ₍₅₎	0.85	6.04	0.82
S ₂	0.204	0.354	0.075	1.45	2.59	1.27
S ₃	0.297	0.646	0.202 ₍₅₎	2.10	4.73	3.61
Molecule (2)						
I ₃	0.750	-0.154	0.2993	5.501 Å	-1.127 Å	5.956 Å
I ₄	0.071	0.579	0.4005	0.451	4.237	7.529
P ₅	0.287	0.378	0.454	2.05	2.77	8.69
P ₆	0.505	0.387	0.383	3.65	2.83	7.29
P ₇	0.307	0.012	0.342	2.24	0.09	6.70
P ₈	0.560	-0.059	0.399	4.10	-0.43	7.86
S ₄	0.397	0.241	0.297	2.87	1.76	5.69
S ₅	0.181	0.116	0.431	1.31	0.85	8.39
S ₆	0.665	0.199	0.431 ₍₅₎	4.84	1.46	8.53

theless, for these reflections R was 0.18 and there were no major discrepancies between F_o and F_c . In Table 2 the final atomic coordinates x, y, z are fractions of the unit-cell edges. Also listed are coordinates in Ångström units, X', Y', Z' referred to the orthogonal axes a, b', c where b' is normal to the ac plane, the angle $\beta(90^\circ 10')$ being assumed 90° .

5. Accuracy

The two independent values of z found for each atom were used to estimate errors in atomic coordinates. The standard deviation in a coordinate of an iodine atom was estimated to be not greater than 0.01 Å and that of a phosphorus or sulphur atom not greater than 0.03 Å. A calculation by the statistical method of Cruickshank (1949) gave values which were approximately half these estimates and clearly too low, because of the large number of unobserved reflections.

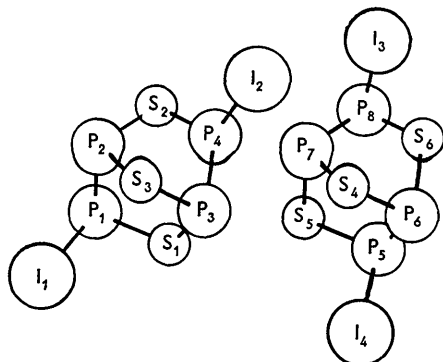


Fig. 2. The molecular configuration of $P_4S_3I_2$, showing the two enantiomorphous molecules of the asymmetric unit. Relative orientations arbitrarily chosen.

Assuming the larger estimated values, standard deviations in bond lengths are, 0.032 Å for I-P bonds and 0.042 Å for P-P and P-S bonds. Standard deviations of bond angles calculated by the method of Cruickshank & Robertson (1953) are 1.1° for I-P-P and I-P-S angles and 1.7° for P-S-P, S-P-S and P-P-S angles.

6. Description and discussion of structure

The molecular configuration of phosphorus thioiodide is shown in Fig. 2 and the bond lengths and angles

Table 3. *Bond lengths and angles in $P_4S_3I_2$*

Molecule 1		Molecule 2	
I ₁ -P ₁	2.45 Å	I ₃ -P ₈	2.46 Å
I ₂ -P ₄	2.53	I ₄ -P ₉	2.47
P ₁ -P ₂	2.23	P ₅ -P ₆	2.12
P ₃ -P ₄	2.19	P ₇ -P ₈	2.25
P ₁ -S ₁	2.16	P ₅ -S ₅	2.08
P ₄ -S ₂	1.99	P ₈ -S ₆	2.14
P ₃ -S ₁	2.10	P ₆ -S ₆	2.20
P ₂ -S ₂	2.16	P ₇ -S ₅	2.07
P ₂ -S ₃	1.99	P ₆ -S ₄	2.08
P ₃ -S ₃	2.11	P ₇ -S ₄	2.06
I ₁ -P ₁ -S ₁	103°	I ₄ -P ₈ -S ₅	104°
I ₂ -P ₄ -S ₂	101	I ₃ -P ₉ -S ₆	107
I ₁ -P ₁ -P ₂	96	I ₄ -P ₈ -P ₇	99
I ₂ -P ₄ -P ₃	98	I ₃ -P ₉ -P ₇	98
P ₁ -S ₁ -P ₃	106	P ₆ -S ₄ -P ₇	99
P ₂ -S ₂ -P ₄	110	P ₅ -S ₅ -P ₇	107
P ₂ -S ₃ -P ₃	101	P ₆ -S ₆ -P ₈	101
S ₁ -P ₃ -S ₃	106	S ₄ -P ₇ -S ₅	108
S ₂ -P ₂ -S ₃	102	S ₄ -P ₇ -S ₆	104
P ₁ -P ₂ -S ₂	90	P ₅ -P ₆ -S ₆	91
P ₄ -P ₃ -S ₁	92	P ₈ -P ₇ -S ₅	92
P ₂ -P ₁ -S ₁	101	P ₆ -P ₅ -S ₅	102
P ₃ -P ₄ -S ₂	101	P ₇ -P ₈ -S ₆	104
P ₁ -P ₂ -S ₃	102	P ₈ -P ₇ -S ₄	101
P ₄ -P ₃ -S ₃	102	P ₅ -P ₆ -S ₄	102

Table 4. Average bond lengths (with estimated standard deviations) and angles in some phosphorus compounds

	P-I (Å)		P-P (Å)		P-S (Å)		S-P-S	P-S-P	P-P-S	Reference
$P_4S_3I_2$	2.48	S.D. 0.032	2.20	S.D. 0.04	2.10	S.D. 0.04	105°	104°	102°, 91°	a
P_2I_4	2.48	0.028	2.21	0.06						b
PI_3^\dagger	2.52									c
	2.46									d
P_4S_{10}					2.085	0.01	109.5°	109.5°		e
P_4S_7			2.35	0.01	2.08	0.01	110°, 103°	103°*	102°	e, f
P_4S_5			2.21	0.025	2.08-2.19	0.025	105°*	103°*	104°, 87°	g
P_4S_3			2.235	0.005	2.090	0.005	100°	103°	103°	h
P_4^\dagger			2.21	0.02						i
Black phosphorus			2.18					Average P-P-P = 102°		j

* One bond angle observed significantly different from the value indicated. † Electron diffraction.

(a) This analysis; (b) Leung & Waser (1956); (c) Gregg *et al.* (1937); (d) Hassel & Sandbo (1938); (e) Vos & Wiebenga (1955); (f) Vos & Wiebenga (1956); (g) Van Houten & Wiebenga (1957); (h) Leung, Waser *et al.* (1957); (i) Maxwell *et al.* (1935); (j) Hultgren *et al.* (1935).

of the two independent molecules are given in Table 3. In Table 4 a comparison is made between the results of this investigation and of the structure determinations of the phosphorus sulphides and iodides and elementary phosphorus.

In the $P_4S_3I_2$ molecule, the phosphorus and sulphur atoms are arranged in two 5-membered rings having a common P-S-P angle. The iodines are bonded to phosphorus atoms in different rings in the *cis* configuration with respect to the P_4S_3 skeleton. There are three types of bond namely, P-I, P-P and P-S single bonds, averaging 2.48, 2.20, 2.09 Å respectively. There are six different sets of bond angles namely, I-P-P (average value 98°), I-P-S (104°), P-S-P (104°), S-P-S (105°) and two sets of P-P-S angles (91°, 102°), no observed length or angle differing significantly from these average values. The individual molecules show no significant deviations from twofold rotational symmetry and as this is the only molecular symmetry, the crystal structure is composed of pairs of optical isomers related through the centres of symmetry of the space group. The two 5-membered rings are folded about the plane of their common angle ($\angle P_2S_3P_3$, $\angle P_6S_4P_7$) and a measure of this folding is given by the four angles of the type $\angle P_1P_2S_2$ whose average value is 91°. These angles are significantly smaller than the P-P-P angle in black phosphorus (average 102°) and significantly smaller than the other P-P-S angles in the $P_4S_3I_2$ molecule (102°) and any such angle observed in the phosphorus sulphides (except for the value of 88° observed in the unique 4-membered ring in P_4S_5). These small angles are difficult to explain, especially as they give rise to the close non-bonded approaches of the type P_1-S_2 of 3.1 Å, 0.6 Å lower than the sum of van der Waals radii (Pauling, 1940).

The arrangement of the molecules in the crystal is shown in Fig. 3. The closest approach of iodine atoms is that of 3.90 Å between atoms of the type I_2 and I_3 , as compared with 3.54 Å the closest non-bonded

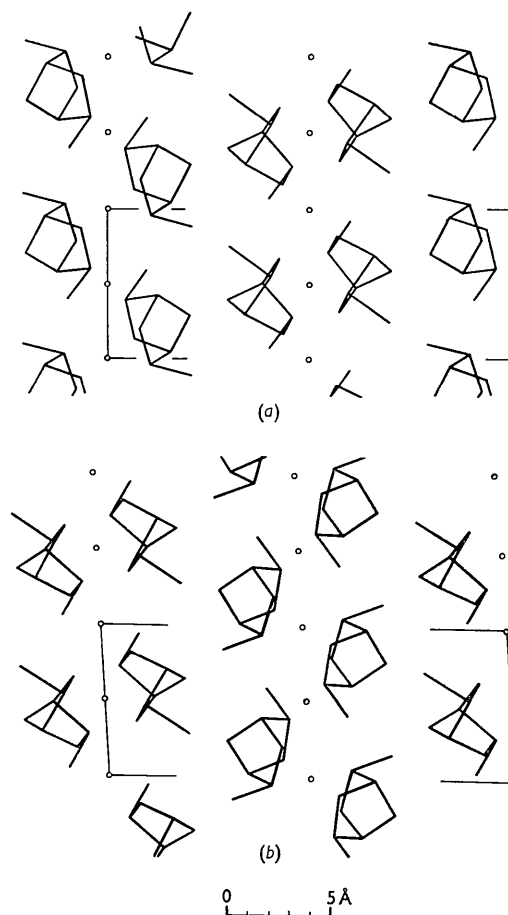


Fig. 3. Views of the arrangement of molecules (a) along the *b* axis, (b) along the *a* axis.

approach in crystalline iodine (Harris, Mack & Blake, 1928). Other intermolecular distances in $P_4S_3I_2$ are not less than 3.7 Å.

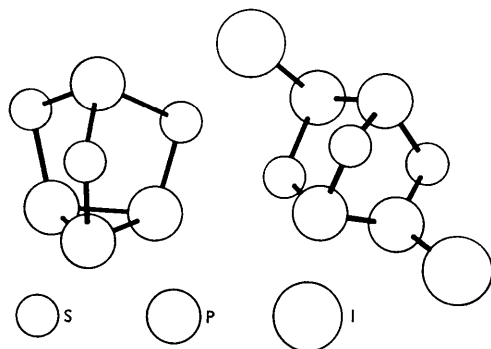


Fig. 4. The molecular configurations of P_4S_3 and $P_4S_3I_2$.

A comparison of the molecular configurations of $P_4S_3I_2$ and P_4S_3 (Fig. 4) provides further convincing evidence for the high mobility of P-P and P-S bonds. Although $P_4S_3I_2$ may be prepared from P_4S_3 by reaction with iodine in carbon disulphide, a reaction which proceeds readily, a rearrangement of the atoms of the P_4S_3 skeleton takes place during the process. As well as a P-P bond being broken, the positions of a phosphorus and a sulphur atom in one of the 5-membered rings are reversed.

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