Tableau 5. *Distances interatomiques les plus courtes*

L'indice ′ indique la transformation ($x, \frac{1}{2}-y, z-\frac{1}{2}$)
L'indice ″ indique la transformation ($2-x, \bar{y}, \bar{z}$)
L'indice ‴ indique la transformation ($1-x, \frac{1}{2}+y, \frac{1}{2}-z$)

C(3, I) ···· C(6, I+a)	3,68 Å
C(5, I) ···· C(14, II)	3,69
C(6, I) ···· C(14, II)	3,80
C(7, I) ···· C(12, II)	3,78
C(12, II)··· C(9, II+a)	3,72
C(14, II)··· C(9, II+a)	3,78
C(2, I) ···· C(8, II′)	3,79
C(2, I) ···· C(9, II′)	3,71
O(1, I) ···· C(8, II′+a)	3,41
O(1, I) ···· C(9, II′+a)	3,50
C(3, I) ···· C(7, I″)	3,64
C(4, I) ···· C(4, I″)	3,63
C(4, I) ···· C(7, I″)	3,68
C(14, II)··· O(2, II‴)	3,34
C(1, I) ···· O(2, II‴)	3,71
O(1, I) ···· C(8, II‴)	3,37
O(1, I) ···· C(13, II‴)	3,42
O(1, I) ···· O(2, II‴)	2,70
O(1, I) ···· O(2, II′+a)	2,66

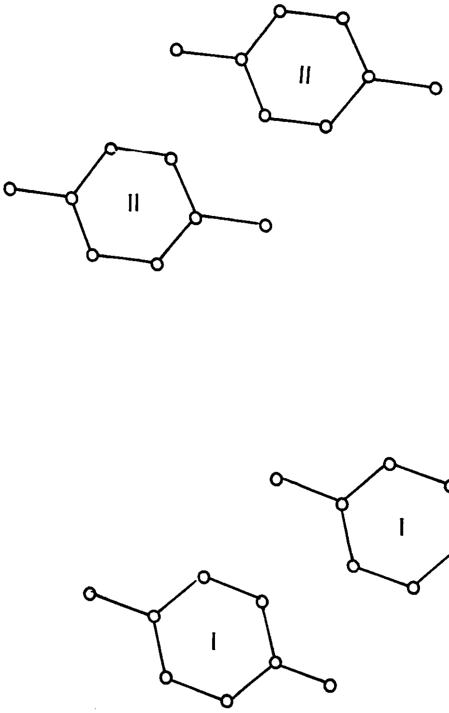

Fig. 7. Projection de deux molécules translatées de **a**, perpendiculairement à leur plan (molécules I et II).

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The Crystal and Molecular Structure of Tetraphosphorus Triselenodiiodide

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Crystals of $P_4Se_3I_2$ are orthorhombic, space group *Pnma*, with $a=9{\cdot}78$, $b=16{\cdot}32$, $c=6{\cdot}80$ Å, $D=3{\cdot}76$, and $D_x=3{\cdot}76$ for $Z=4$. The molecules possess a crystallographic plane of symmetry and a basket structure different from that of $P_4S_3I_2$. The P–I and P–P bond lengths are 2·47 and 2·22 Å respectively; the mean P–Se bond length is 2·24 Å.

Introduction

The phosphorus sulphides undergo complex reactions with bromine and iodine, and the structures of the products indicate that considerable skeletal rearrangements occur even under mild conditions (Topsom & Wilkins, 1956; Andrews, Ferguson & Wilkins, 1963; Einstein, Penfold & Tapsell, 1965). The only reported investigation of the phosphorus selenohalides is by Mai (1927), who prepared a compound of empirical formula $P_4Se_3I_2$ by the action of iodine on P_4Se_3 in carbon disulphide solution. In order to confirm this observation, and in view of the unique 'basket' structure of $P_4S_3I_2$ (Wright & Penfold, 1959), the crystal structure of $P_4Se_3I_2$ has been determined.

Experimental

Tetraphosphorus triselenodiiodide was prepared according to the method of Mai, by mixing carbon disulphide solutions of P_4Se_3 and iodine, and leaving the solution for three days at 0°C. A deep red precipitate was formed in low yield, and was well washed with warm carbon disulphide. Some decomposition was found to occur, the products being soluble in carbon disulphide. The infrared spectrum was obtained from a Nujol mull of the compound between CsBr plates, and showed the following rather weak absorption bands: 385(*m*), 345(*w*), 318(*s*), 302(*m*) cm^{-1} (*w*=weak, *m*=medium, *s*=strong). The mass spectrum showed a very weak molecular ion, but the complex base peak centred on $m/e=488$ was in good agreement with the multiplet predicted for $P_4Se_3I^+$ using the natural abundance isotopic distribution for selenium ($P_4S_3I_2$ similarly shows a very strong $P_4S_3I^+$ peak, but only a weak molecular ion). All the intensity data were collected using a single crystal sealed in a 0·5 mm Lindemann glass tube. This crystal was a lamina of approximate dimensions $0{\cdot}2\times 0{\cdot}2\times 0{\cdot}006$ mm, with principal faces of the form {010}.

Crystal data

$P_4Se_3I_2$, orthorhombic, $a=9{\cdot}783$ (9), $b=16{\cdot}320$ (22), $c=6{\cdot}800$ (6) Å, $U=1086$ Å^3. Density found by pycnometry under *o*-dichlorobenzene, 3·76; calculated for four molecules per unit cell, 3·76 g.cm^{-3}. $\mu_a=645{\cdot}7$ cm^{-1}. Systematic absences were $k+l=2n+1$ for $0kl$, and $h=2n+1$ for $hk0$, giving the centrosymmetric *Pnma* or the non-centrosymmetric $Pn2_1a$ as possible space groups; *Pnma* was confirmed by successful refinement of the structure. Intensities were estimated visually in the usual way from equi-inclination Weissenberg photographs (layers $0kl$ to $8kl$) taken with the crystal mounted about the [100] axis. Anti-equi-inclination zero-layer photographs ($\mu=9{\cdot}0°$) were recorded with the crystal mounted about [010], since $\mu=0$ would have led to the incident beam lying in the plane of the lamina, with virtually total absorption. Lorentz, polarization and absorption corrections were applied, the latter being calculated exactly for an infinite flat and a given value of $\mu_a t$. Eight reflexions were rejected because it was calculated that the incident or reflected beams lay very close to the plane of the lamina, resulting in very strong absorption and relatively large errors arising from edge effects. At this stage the $h0l$ data were incorporated in the rest of the data, placing all the reflexions on an approximately self-consistent scale using the linear least-squares method of Rae & Blake (1966).

The absorption coefficient was refined by the method of Sheldrick & Sheldrick (1970): a data reduction and least-squares refinement (as in the final refinement but with isotropic temperature factors for the selenium atoms) were performed for each of seven values of $\mu_a t$ ranging from 0·1 to 0·7. A plot of the resulting generalized index $R=\sqrt{(\sum w(|F_o|-|F_c|)^2/\sum wF_o^2)}$ against $\mu_a t$ consisted of a smooth curve with a minimum at $\mu_a t=0{\cdot}38$, corresponding to a crystal thickness of 0·0060 mm. This value of $\mu_a t$ was used in a final calculation of the absorption corrections.

Unit-cell dimensions were obtained by a least-squares fit to all 22 lines of a powder photograph taken with a Guinier focusing camera and silicon internal calibrant ($d=5{\cdot}4306$ Å). Each line found to correspond to a reflexion of high intensity on the single-crystal photographs. The estimated standard deviations in the unit-cell dimensions were multiplied by a factor of two to allow for possible systematic errors.

Table 1. *Observed and calculated structure factors*

Since the interlayer scale factors were refined, it is necessary to multiply these values (which are on an absolute scale) by 0·0154, 0·0160, 0·0181, 0·0208, 0·0195, 0·0198, 0·0224, 0·0316 and 0·0157 for $0kl$, . . ., $8kl$ respectively for use in the weighting scheme. The strong reflexion 002 was omitted from the final least-squares refinements owing to extinction.

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
2	0	0	87	67
4	0	0	391	340
6	0	0	121	142
8	0	0	105	106
-4	2	0	107	124
0	2	0	57	45
-6	3	0	31	52
-4	3	0	17	114
-2	3	0	503	357
-6	4	0	110	122
-4	4	0	70	72
-2	4	0	292	253
0	4	0	115	111
-6	5	0	72	57
-4	5	0	138	131
-2	5	0	33	48
-6	6	0	29	33
-2	6	0	132	149
0	6	0	69	42
-6	7	0	48	45
-4	7	0	151	144
-2	7	0	260	250
-6	8	0	27	35
-2	8	0	26	25
0	8	0	165	152
-6	9	0	128	114
-4	9	0	33	35
-2	9	0	297	280
-6	10	0	102	71
-4	10	0	164	136
0	10	0	499	402
-4	11	0	44	52
-4	12	0	115	97
0	12	0	121	115
-2	13	0	88	65
-4	14	0	62	57
-2	14	0	113	93
0	14	0	60	56
-4	15	0	35	42
0	16	0	74	56
0	18	0	67	85
0	-17	1	75	60
-2	-16	1	30	38
-4	-15	1	70	88
0	-15	1	85	88
-2	-14	1	164	169
-4	-13	1	70	79
-2	-13	1	32	29
0	-13	1	58	59
-4	-12	1	70	75
-2	-12	1	102	89
-4	-11	1	54	49
0	-11	1	80	85
-4	-10	1	73	77
-3	-10	1	48	53
-2	-10	1	65	58
-1	-10	1	49	47
-6	-9	1	135	127
-4	-9	1	50	45
-2	-9	1	31	32
-1	-9	1	64	67
0	-9	1	84	73
-6	-8	1	19	39
-3	-8	1	71	72
-2	-8	1	157	147
-6	-7	1	25	38
-4	-7	1	87	92
-2	-6	1	107	86
-1	-6	1	89	79
-6	-5	1	45	56
-5	-5	1	112	112
-4	-5	1	418	364
-2	-5	1	36	42
-1	-5	1	117	113
0	-5	1	483	475
-8	-4	1	23	27
-7	-4	1	25	30
-6	-4	1	136	160
-5	-4	1	86	83
-2	-4	1	450	345
-1	-4	1	99	67
-7	-3	1	27	31
-6	-3	1	69	64
-5	-3	1	68	63
-4	-3	1	25	23
-2	-3	1	99	98
-1	-3	1	70	66
0	-3	1	124	125
-8	-2	1	41	47
-7	-2	1	20	20
-6	-2	1	68	78
-5	-2	1	31	40
-4	-2	1	111	112
-3	-2	1	145	145
-2	-2	1	341	297
-1	-2	1	42	44
-8	-1	1	16	29
-7	-1	1	66	82
-6	-1	1	117	135
-5	-1	1	48	57
-3	-1	1	30	25
-1	-1	1	135	126
0	-1	1	45	41
-8	0	1	117	122
-7	0	1	21	27
-6	0	1	22	23
-4	0	1	172	166
-3	0	1	128	126
-2	0	1	139	139
-1	0	1	[illegible]	84
-4	-16	2	36	51
-4	-15	2	24	30
0	-14	2	56	72
-4	-12	2	112	[illegible]
0	-12	2	143	[illegible]
-4	-10	2	171	159
-2	-10	2	51	61
-1	-10	2	70	72
0	-10	2	157	164
-6	-8	2	160	126
-6	-7	2	49	59
-5	-7	2	22	33
-4	-7	2	30	48
-3	-7	2	63	63
-2	-7	2	126	122
-1	-7	2	57	50
-5	-6	2	17	30
-4	-6	2	146	137
-2	-6	2	25	21
-1	-6	2	38	33
0	-6	2	80	79
-8	-5	2	134	139
-5	-5	2	26	38
-4	-5	2	170	169
-3	-5	2	75	77
-2	-5	2	144	153
-1	-5	2	25	16
-8	-4	2	52	45
-6	-4	2	59	57
-5	-4	2	62	70
-4	-4	2	95	92
-2	-4	2	19	19
-1	-4	2	90	92
0	-4	2	36	28
-8	-3	2	29	32
-7	-3	2	14	20
-6	-3	2	79	80
-5	-3	2	42	51
-3	-3	2	52	59
-2	-3	2	138	152
-1	-3	2	61	55
-8	-2	2	30	28
-6	-2	2	136	164
-5	-2	2	9	11
-4	-2	2	135	144
-2	-2	2	57	56
-1	-2	2	16	10
0	-2	2	244	262
-7	-1	2	16	31
-6	-1	2	89	117
-4	-1	2	65	63
-3	-1	2	41	36
-2	-1	2	304	307
-1	-1	2	63	62
-8	0	2	110	105
-7	0	2	42	50
-6	0	2	80	83
-5	0	2	75	80
-4	0	2	328	319
-3	0	2	44	39
-2	0	2	105	90
-1	0	2	159	172
0	-15	3	89	89
-2	-14	3	117	138
-2	-13	3	43	49
0	-13	3	56	51
-2	-12	3	47	54
0	-11	3	123	123
-2	-9	3	53	50
0	-9	3	86	61
-2	-8	3	103	97
-6	-7	3	37	46
-5	-7	3	49	55
-4	-7	3	106	100
-2	-7	3	77	79
-1	-7	3	82	85
0	-7	3	211	215
-3	-6	3	25	37
-2	-6	3	111	112
-1	-6	3	60	64
-8	-5	3	78	89
-6	-5	3	21	26
-5	-5	3	27	39
-4	-5	3	195	189
-3	-5	3	52	52
-2	-5	3	82	82
-1	-5	3	59	64
0	-5	3	317	334
-7	-4	3	75	64
-6	-4	3	101	85
-5	-4	3	14	27
-3	-4	3	89	100
-2	-4	3	281	299
-1	-4	3	105	113
-7	-3	3	54	48
-6	-3	3	91	81
-5	-3	3	53	56
-4	-3	3	34	37
-2	-3	3	118	127
-1	-3	3	89	94
0	-3	3	117	123
-6	-2	3	79	71
-2	-2	3	136	154
-1	-2	3	19	20
-7	-1	3	28	36
-6	-1	3	15	14
-2	-1	3	28	27
-1	-1	3	33	30
0	-1	3	203	206
-8	0	3	105	92
-7	0	3	61	43
-6	0	3	29	24
-4	0	3	195	198
-3	0	3	181	192
-2	0	3	89	100
-1	0	3	68	69
0	-12	4	85	78
0	-10	4	188	181
-3	-9	4	127	125
-2	-9	4	141	148
0	-8	4	62	62
-6	-7	4	37	45
-4	-7	4	54	59
-2	-7	4	118	122
-5	-6	4	42	43
-4	-6	4	52	52
-2	-6	4	45	48
0	-6	4	43	39
-5	-5	4	71	68
-4	-5	4	58	62
-3	-5	4	89	83
-1	-5	4	118	127
-6	-4	4	81	69
-4	-4	4	23	23
-2	-4	4	83	81
-1	-4	4	26	28
-6	-3	4	78	60
-4	-3	4	31	34
-2	-3	4	157	179
-1	-3	4	24	23
-7	-2	4	87	75
-6	-2	4	27	31
-5	-2	4	84	73
-4	-2	4	68	69
-1	-2	4	89	101
0	-2	4	46	52
-7	-1	4	14	20
-6	-1	4	79	59
-4	-1	4	50	52
-3	-1	4	150	145
-2	-1	4	103	111
-1	-1	4	26	28
-8	0	4	71	63
-7	0	4	75	54
-5	0	4	77	74
-4	0	4	174	199
-3	0	4	33	26
-2	0	4	45	32
-1	0	4	77	80
0	0	4	345	387
-2	-8	5	91	102
-4	-7	5	26	37
-1	-7	5	49	44
0	-7	5	91	82
-4	-6	5	24	32
-5	-5	5	91	85
-4	-5	5	202	182
-3	-5	5	46	45
-2	-5	5	45	43
-1	-5	5	90	102
0	-5	5	144	167
-6	-4	5	104	82
-4	-4	5	41	46
-3	-4	5	52	49
-2	-4	5	91	89
-1	-4	5	47	50
-4	-3	5	31	26
-1	-3	5	35	32
-6	-2	5	66	53
-4	-2	5	53	61
-3	-2	5	77	76
-2	-2	5	134	149
-1	-2	5	44	51
-6	-1	5	132	104
-5	-1	5	50	41
-4	-1	5	30	47
-1	-1	5	34	31
-6	0	5	25	25
-3	0	5	79	79
-2	0	5	60	50
-1	0	5	55	43
-3	-7	6	69	68
-2	-7	6	46	48
-1	-7	6	49	53
-4	-6	6	46	42
0	-6	6	52	58
-4	-5	6	44	39
-3	-5	6	57	52
-2	-5	6	34	30
-5	-4	6	50	58
-4	-4	6	42	37
-2	-4	6	47	40
-1	-4	6	71	71
0	-4	6	53	60
-3	-3	6	68	64
-2	-3	6	86	82
-4	-2	6	71	53
-2	-1	6	71	74
-5	0	6	104	82
-4	0	6	84	75
-3	0	6	40	35
-1	0	6	165	138
0	-7	7	62	61
-2	-6	7	36	39
-2	-5	7	47	45
-1	-5	7	58	56
0	-5	7	65	63
-3	-4	7	46	49
-2	-4	7	76	83
-2	-3	7	32	34
0	-3	7	56	31
-3	-2	7	52	54
-2	-2	7	31	27
0	-1	7	95	106
-4	0	7	68	54
-3	0	7	34	24
-1	0	7	54	49

Structure solution and refinement

In the space group *Pnma* the asymmetric unit consists of half of one $P_4Se_3I_2$ molecule; at least one atom (Se) must lie in the mirror plane. A three-dimensional Patterson synthesis was interpreted to give the iodine coordinates; the other atoms were located by difference Fourier synthesis. The structure was refined by full-matrix least-squares with anisotropic temperature factors for the iodine and selenium atoms and isotropic temperature factors for the phosphorus atoms. Since it was also found necessary to refine the inter-layer scale factors, anisotropic temperature factors could not be refined for all atoms. The complex neutral-atom scattering factors of Cromer (1965) and Cromer & Waber (1965) were employed for all atoms. The weighting scheme adopted on the basis of an analysis of variance was $w=1/(0\cdot95-|F_o|+0\cdot35F_o^2)$; the mean value of $w(|F_o|-|F_c|)^2$ was almost independent of the magnitudes of F_o and sin θ. The refinement converged giving a weighted index $R=\sum w^{1/2}(|F_o|-|F_c|)/\sum w^{1/2}|F_o|$ of 0·109 and a corresponding unweighted R index of 0·112 for 337 unique non-zero reflexions. The 43 parameters refined consisted of 15 positional parameters, 16 anisotropic temperature factor components (for the iodine and selenium atoms), isotropic temperature factors for the three phosphorus atoms, 8 inter-layer scale factors and one overall scale factor. A final difference electron density synthesis showed no unexpected features; the strongest maxima were 0·2 times the intensity of the weakest P atom.

Observed and calculated structure factors are shown in Table 1 and the results from the final full-matrix least-squares cycle are given in Tables 2 and 3. These results together with the full covariance-matrix and the standard deviations in the unit-cell dimensions were used to calculate the bond lengths, angles, and standard deviations shown in Table 4 and Fig. 1, and also the non-bonded distances given in Tableo 5. Ncorrections for libration have been applied. The [010] projection of the structure is shown in Fig. 2.

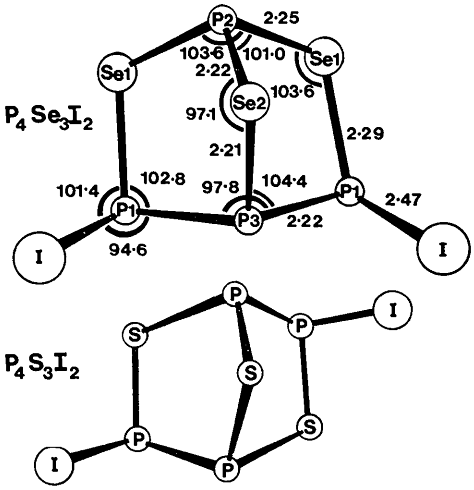

Fig. 1. The molecular dimensions of $P_4Se_3I_2$; comparison with the structure of $P_4S_3I_2$.

Discussion

The $P_4Se_3I_2$ molecules are approximately hexagonal close-packed, with layers parallel to the mirror planes at $y/b=0\cdot25$ and 0·75, consistent with the crystal habit of laminae with principal faces of the form {010}. The shortest intra-layer intermolecular contact is 3·46 Å, between Se(2) and P(3), both atoms lying on the mirror

Table 2. *Atom coordinates and isotropic vibrational amplitudes* (Å^2 × 1000) *with estimated standard deviations*

	x/a	y/b	z/c	$\bar{U}$
(P1)	0·4835 (23)	0·1476 (12)	0·4449 (25)	33 (6)
(P2)	0·2499 (44)	0·2500	0·7648 (53)	58 (9)
(P3)	0·3691 (38)	0·2500	0·3076 (36)	35 (7)

Table 3. *Atom coordinates and anisotropic vibrational amplitudes* (Å^2 × 1000) *with estimated standard deviations*

The anisotropic temperature factor takes the form:

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)\right].$$

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I	0·3526 (8)	0·0392 (3)	0·2745 (11)	93 (12)	50 (3)	54 (4)	−2 (4)	−19 (4)	−9 (5)
Se(1)	0·3920 (10)	0·1416 (5)	0·7549 (12)	58 (13)	54 (4)	32 (4)	10 (6)	−7 (4)	−11 (6)
Se(2)	0·1694 (15)	0·2500	0·4598 (17)	24 (14)	121 (14)	35 (6)	0	−8 (7)	0

Table 4. *Interatomic distances and bond angles with estimated standard deviations in parantheses*

Distances			
I——P(1)	2·47 (2) Å	P(1)—Se(1)	2·29 (2) Å
Se(1)-P(2)	2·25 (3)	P(2)—Se(2)	2·22 (4)
Se(2)-P(3)	2·21 (4)	P(3)—P(1)	2·22 (3)
Angles			
P(3)—P(1)—Se(1)	102·8 (1·1)°	Se(2)-P(3)—P(1)	104·4 (1·0)°
I——P(1)—Se(1)	101·4 (0·8)	P(1)—Se(1)-P(2)	103·6 (1·1)
Se(1)-P(2)—Se(2)	101·0 (1·2)	P(2)—Se(2)-P(3)	97·1 (1·5)
P(3)—P(1)—I	94·6 (1·0)	P(1)—P(3)—P(1)	97·8 (1·5)
Se(1)-P(2)—Se(1)	103·6 (1·3)		

Table 5. *Shortest non-bonded distances*

P(2)–P(3)	3·32 Å	intramolecular, through one angle
P(1)–P(1)	3·34	
Se(1)-Se(2)	3·45	
I——P(3)	3·45	
Se(2)-P(3)	3·46	intermolecular, within a layer
P(1)–Se(2)	3·50	intramolecular, through one angle
Se(1)-P(3)	3·53	
Se(1)-Se(1)	3·54	
P(1)–P(2)	3·57	
P(1)–P(2)	3·67	intermolecular, within a layer
I——Se(1)	3·69	intramolecular, through one angle
P(1)–Se(2)	3·70	intermolecular, within a layer
Se(1)-Se(2)	3·78	
I——Se(1)	3·80	intermolecular, between layers
I——Se(1)	3·87	

plane. The shortest inter-layer intermolecular distance is 3·80 Å, between I and Se(1). Both P_4S_3 (Leung, Waser, van Houten, Vos & Wiebenga, 1957) and P_4Se_3 (Keulen & Vos, 1959) have been reported in the space group *Pmnb*: if the axes are rotated into the conventional *Pnma* orientation, then both these molecules, like $P_4Se_3I_2$, are approximately hexagonal close-packed with layers perpendicular to {010} and the mirror planes bisecting the molecules. Thus the [010] projections of all three structures are remarkably similar. In $P_4Se_3I_2$, however, the iodine atoms project outwards from the layers, resulting in the value of 16·32 Å for *b*, compared with 9·66 Å in P_4S_3 and 9·74 Å in P_4Se_3.

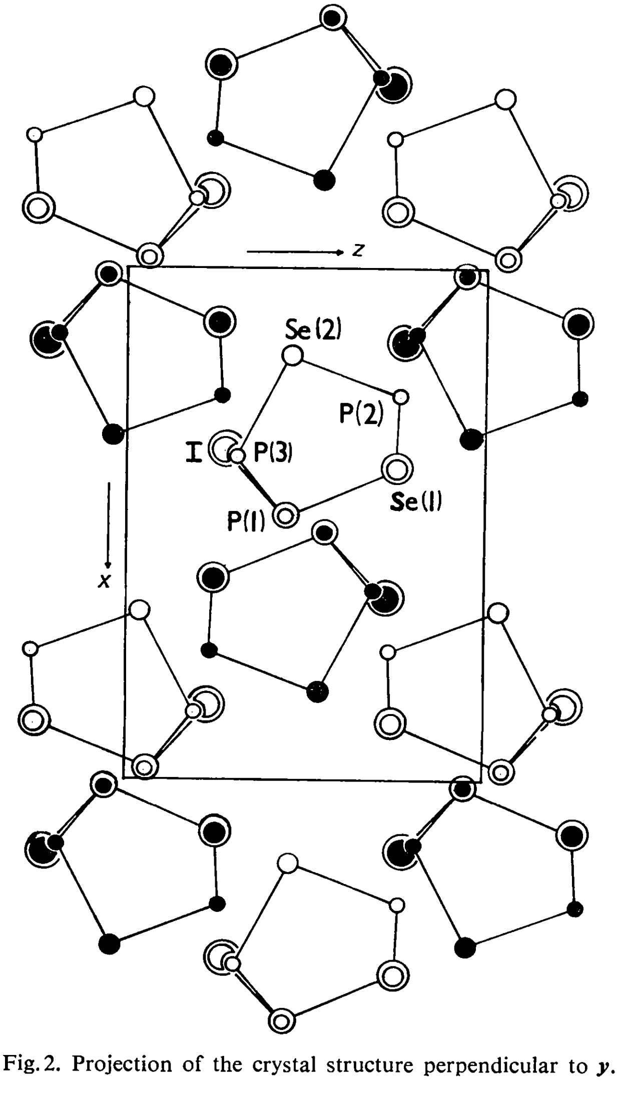

Fig. 2. Projection of the crystal structure perpendicular to *y*.

The structures of $P_4Se_3I_2$ and $P_4S_3I_2$ are compared in Fig. 1. The basket skeletons of the two molecules differ in that the two five-membered rings are related by a twofold axis in $P_4S_3I_2$ and by a mirror plane in $P_4Se_3I_2$. Whereas the formation of $P_4Se_3I_2$ from P_4Se_3 and I_2 involves merely the rupture of the P–P bond by the iodine molecule, in the corresponding sulphide reaction this step is presumably followed by a skeletal rearrangement. Except for a P–P–I angle of 95°, all the angles in $P_4Se_3I_2$ lie in the range 97–104°. It is rather curious that $P_4S_3I_2$ adopts a structure with the unusually small mean P–P–S angle of 'fold' of 91°. The values obtained for the P–P and P–I bond lengths are close to those in $P_4S_3I_2$ (2·20 and 2·48 Å respectively) and P_2I_4 (2·21 and 2·48 Å respectively; Leung & Waser, 1956). The mean P–Se bond length of 2·24 Å is the same as the mean value found by Keulen & Vos (1959) in P_4Se_3. The reasonable final values obtained for the *R* index and the thermal parameters indicate that the refinement of the absorption parameter has been successful. The thermal motion of the iodine atom is greatest along a line almost perpendicular to the P–I bond, consistent with less resistance to P–I deformation than stretching.

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