Table II

Composition of Niobium Oxyfluorides

Oxidation–reduction agent	% Nb	% F	% O[a]	Composition	a_0	ρ_{obsd}
9-1 P, red	61.3	28.2	10.5	$NbO_{0.99}F_{2.25}$	3.889	
9-2 As	59.7	26.4	13.8	$NbO_{1.34}F_{2.16}$	3.889	
9-7 P, red	63.7	20.6	15.7	$NbO_{1.43}F_{1.58}$	3.915	3.98
9-10 P, red	63.7	18.1	18.2	$NbO_{1.65}F_{1.39}$	3.906	
9-20 P, red	62.3	18.4	19.3	$NbO_{1.80}F_{1.44}$	3.908	4.01
9-27 Si	65.2	15.0	19.8	$NbO_{1.76}F_{1.12}$		4.10
8-73 Si	61.5	23.0	15.5	$NbO_{1.46}F_{1.83}$	3.917	

[a] Nb and F determined chemically, oxygen by difference.

arsenic, and antimony led to formation of a series of oxyfluorides, the oxygen being derived from the walls of the container. Mass spectroscopic analysis identified SiF_4 as one of the products. After a reaction time varying from 2 to 10 days, reduction was complete as evidenced by the absence of unreacted NbF_5 upon cooling the quartz tube. Heavy deposits of large crystals, dark gray to black, 0.1 to 1 mm., had built up along the entire length of the tube. These crystals were perfect cubes, many of them twinned. X-Ray diffraction studies showed these materials to have the ReO_3 type structure identical with that of NbF_3.[5] Chemical analysis of these materials showed the presence of only niobium, fluorine, and oxygen. Apparently oxygen can substitute for fluorine in the crystal to give a wide range of composition from NbO_xF_y to NbO_2F. Schäfer, *et al.*,[6] also reported the existence of a $Nb(O,F)_3$ phase with a ReO_3 structure and believe that NbF_3 completely free of oxygen is apparently not stable. We have observed that in the niobium oxyfluorides the sum of the number of anions per cation varies significantly from 3 in some cases. Tentatively, we interpret these results as indicating the presence of metal-deficient structures. A summary of the composition, density, and cell constant of these materials appears in Table II. The oxyfluoride materials are refractory and very resistant to attack by acids. No noticeable dissolution of the oxyfluoride occurred upon boiling a sample in a solution of concentrated H_2SO_4, HNO_3, and H_2O_2 for a 24-hr. period. The materials can be dissolved in molten alkali hydroxides.

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The Crystal and Molecular Structure of Diphosphorus Hexathiodibromide

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Crystal structure analysis of diphosphorus hexathiodibromide has established that the molecules contain a new type of six-membered ring of composition P_2S_4 in which there are two S–S linkages. The tetrahedral environment of each phosphorus is completed by a bromine atom and a double-bonded sulfur atom attached externally to the ring. There is complete disorder involving the external atoms. Molecules possess a crystallographic twofold symmetry axis normal to the ring and are related by the fourfold inversion axes of the tetragonal space group $P\bar{4}2_1c$. The ring has the *skew boat* conformation on account of the steric preference for large angles of torsion about S–S bonds. Three-dimensional least-squares refinement of parameters led to the mean interatomic distances P—Br = 2.07, P=S = 1.98, P—S = 2.10, and S—S = 2.03 Å.

Introduction

The known thiohalides of phosphorus[1] may be considered to belong to three classes: (I) the thiophosphoryl trihalides PSX_3, where X = F, Cl, or Br; (II) $P_4S_3I_2$, the only thioiodide; and (III) the thiobromides $P_2S_5Br_4$ and $P_2S_6Br_2$. The only molecular structures hitherto reported are for class I by electron diffraction[2] and for class II by X-ray diffraction.[3] The two compounds of class III were characterized in these laboratories by Andrews, Fergusson, and Wilkins,[1] who pointed out that S–S bonds must be present if the coordination of phosphorus with respect to sulfur is limited to four as would be expected. The high probability of the existence of this structural feature, not present in any other known crystalline compound of phosphorus and sulfur, led us to the structure analysis of $P_2S_6Br_2$, the more accessible of the two compounds in suitably crystalline form.

Experimental

Large opaque yellow needle-shaped crystals were prepared under dry carbon dioxide, following the method of Andrews, Fergusson, and Wilkins,[1] and were manipulated in a drybox.

Crystal Data.—$P_2S_6Br_2$, molecular weight 414.2, tetragonal, space group $P\bar{4}2_1c$ from systematic absences of X-ray reflections, $a = b = 9.79$ Å. ($\sigma = 0.01$ Å.), $c = 11.51$ Å. ($\sigma = 0.01$ Å.) ($\lambda = 1.5418$ Å. for Cu Kα radiation), $U = 1104$ Å.^{3}, $D_m = 2.53$

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(1) See, *e.g.*, J. M. Andrews, J. E. Fergusson, and C. J. Wilkins, *J. Inorg. Nucl. Chem.*, **25**, 829 (1963).

(2) "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958.

(3) D. A. Wright and B. R. Penfold, *Acta Cryst.*, **12**, 455 (1959).

g. cm.$^{-3}$ (by flotation),[4] $Z = 4$, $D_x = 2.58$ g. cm.$^{-3}$, $F(000) = 784$, molecular symmetry, 2. Linear absorption coefficients are 159.3 cm.$^{-1}$ for Cu Kα and 67.6 cm.$^{-1}$ for Mo Kα radiation.

The crystals were very brittle and therefore difficult to cleave to a suitable size for X-ray photography. The single sample used for all X-ray data was sealed in a Lindemann glass tube and remained in good condition for several months. Reciprocal lattice levels ($hk0 \ldots . 6$) were recorded by the equi-inclination Weissenberg method, using Cu Kα radiation, and the levels ($0 \ldots . 2kl$) with the Buerger precession camera using Mo Kα radiation. Within the Weissenberg levels, visual estimates were made of the intensities of 412 independent reflections; 56 were under the threshold of observation and these were assigned a value one-half of the minimum observable intensity for purposes of the least-squares refinement. The precession data, being of inferior quality, were used only for preliminary interlevel correlation purposes. The crystal fragment used was a needle 0.18 mm. long (parallel to the tetrad axis) with a rectangular cross section 0.065 × 0.055 mm. Corrections for absorption were applied on the assumption that the crystal was a cylinder of radius 0.03 mm. ($\mu R = 0.5$).

Structure Determination

The structure was eventually solved, but by no means readily, from the sharpened three-dimensional Patterson function. The chief difficulty was that the structure is quasi-C-face-centered, as indicated by the systematic weakness of all reflections having $(h + k)$ odd. In fact, four of the five atoms of the asymmetric unit occur as two approximately C-centered pairs. This caused coincidence of otherwise distinct symmetry peaks of the Patterson function. To make matters even more difficult, it turned out that the z coordinate of the fifth atom was close to $^1/_4$, which meant that for this atom the symmetry peak of the general type $x + y$, $x - y$, $2z$ fell on the special Patterson section $z = {}^1/_2$ and was obscured by symmetry peaks of other types derived from all atoms. Disorder among two atomic sites also greatly hindered the refinement.

The very intense (220) reflection was an aid in setting up the first trial structure. There were indications from the vector map that no atom lay close to any of the special positions of the space group, all of which have values of x and y equal to 0 or $^1/_2$ where the contribution to the (220) structure amplitude (which has no imaginary component) is maximum positive. This amplitude was therefore assumed to be negative and, because of its very high unitary structure factor ($U_{\text{obsd}} = 0.6$; $U_{\text{calcd}} = 0.8$ from final refinement), it indicated the broad regions of the unit cell where atoms could reside.

In the space group P$\bar{4}2_1$c, an atom at x, y, z is related to atoms in equivalent positions by the vectors $2x$, $2y$, 0; $x + y$, $y - x$, $2z$; $^1/_2 - 2x$, $^1/_2$, $^1/_2 - 2z$; $^1/_2 - (x - y)$, $^1/_2 + (x - y)$, $^1/_2$ and symmetry related vectors. General areas of the vector map were searched for vectors of the type $x + y$, $y - x$, $2z$, identifiable by their membership of a self-consistent set as indicated above. It should be noted that an atomic site x, y, z cannot be distinguished from $^1/_2 + x$, $^1/_2 + y$, z by this method. Eventually six atom sites, comprising three C-centered pairs, were selected for a trial structure. One of these sites was assigned to a Br atom on account of its environment, while all others, for the purposes of structure factor calculation, were assigned to S atoms. Structure factor agreement was sufficiently good to justify commencement of a least-squares refinement, but after eight cycles, using the block-diagonal approximation, the R index for all reflections remained at 0.33. One sulfur atom was then removed on the evidence of an F_{obsd} electron density map, supported by an anomalously high shift in its thermal parameter. The remaining five atoms were then consistent with the over-all chemical composition, but R was reduced only slightly. At this stage, anomalous thermal parameters for Br and for the atom related to it by the quasi-lattice centering suggested that the electron density at these two sites should be much more nearly equal. After $^2/_3$Br (*i.e.*, approximately $^1/_2$Br + $^1/_2$S) was placed at each site, refinement continued and after a further ten cycles R was 0.18. Of the three atoms being considered as "sulfur" to this point, one, according to the chemical composition, was phosphorus. This atom was readily identified by its approximately tetrahedral environment. The two equal composite atoms, each required by the composition to be ($^1/_2$Br + $^1/_2$S), formed a significantly extended region of electron density which suggested an atom separation of about 0.3 Å. Approximate distances from the phosphorus atom of points on each extended peak separated by 0.3 Å. were consistent with known lengths of P—Br and P=S bonds. Refinement was then continued after placing $^1/_2$Br and $^1/_2$S at such points. All parameters behaved normally and refined to the values listed in Table I, which also illustrates the quasi-C-centered arrangement in which all atoms except phosphorus are involved. Atomic scattering factors used were those calculated from the self-consistent field model with exchange and corrected for anomalous dispersion.[5]

TABLE I

ATOMIC PARAMETERS FOR THE PS_3Br HALF-MOLECULE[a]

	x	y	z	B, Å.^{2}
P	0.2994	0.0150	0.2423	3.5
S(1)	0.4394	0.1605	0.3050	3.9
	(0.9394)	(0.3395)	(0.1950)	
S(2)	0.4164	−0.1483	0.1781	3.9
S(3)	0.1884	0.0475	0.1145	5.7
S(4)	0.2018	−0.0115	0.3846	3.3
Br(3)	0.1898	0.0808	0.0995	4.8
	(0.6898)	(0.4192)	(0.4005)	
Br(4)	0.1921	−0.0427	0.3901	4.9

[a] Coordinate values in parentheses are related to those above them by a space group symmetry operation and illustrate the quasi-C-centered relationship between S(1) and S(2) and between composite atoms (3) and (4).

An acceleration procedure[6] was used to assist the normal least-squares process at the end of the refine-

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(4) This density value, obtained with a freshly prepared sample, is to be contrasted with the much lower value of 1.82 previously reported.[1] Aged samples were observed to dissolve partially in the flotation liquid leaving a residue of lower density. We assume that the earlier value is erroneous and may refer to decomposition products.

(5) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp. 203, 206, 214.

(6) L. I. Hodgson and J. S. Rollett, *Acta Cryst.*, **16**, 329 (1963).

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES[a]

H	K	FO	|FC|
	L = 0		
2	0	354	384
4	0	176	133
6	0	537	551
8	0	783	860
10	0	165	167
1	1	320	295
2	1	123	122
3	1	*	58
4	1	352	374
5	1	571	619
6	1	142	105
7	1	421	405
8	1	*	66
9	1	146	88
10	1	*	60
11	1	130	107
2	2	1754E	2879
3	2	379	383
4	2	504	473
5	2	251	195
6	2	653	719
7	2	539	585
8	2	342	347
9	2	146	154
10	2	193	170
11	2	103	90
3	3	237	202
4	3	131	82
6	3	191	128
7	3	*	89
8	3	*	57
9	3	*	47
10	3	•	22
11	3	84	87
4	4	568	478
5	4	361	320
6	4	422	339
6	5	*	39
7	4	287	254
8	4	*	25
8	5	•	81
9	4	352	394
10	4	195	205
11	4	109	109
5	5	438	377
7	5	*	26
9	5	171	156
10	5	*	33
11	5	76	81
6	6	573	517
7	6	236	197
8	6	225	214
9	6	167	170
10	6	100	110
11	6	*	46
7	7	496	490
8	7	*	41
9	7	*	21
10	7	48	78
8	8	70	28
9	8	*	70
	L = 1		
1	0	*	29
2	0	1276E	1538
3	0	246	289
4	0	*	44
5	0	424	372
6	0	554	509
7	0	116	93
8	0	664	686
9	0	128	88
10	0	345	355
11	0	*	3
12	0	118	132
2	1	205	264
3	1	1294E	1694
4	1	192	211
5	1	872	1023
6	1	177	139
7	1	589	500
8	1	195	176
9	1	171	106
10	1	76	69
11	1	*	43
12	1	106	117
3	2	410	323
4	2	999	1048
5	2	123	127
6	2	343	289
7	2	250	243
8	2	359	303
9	2	*	65
10	2	385	366
11	2	62	84
12	2	108	119
4	3	311	291
5	3	397	430
6	3	248	264
7	3	499	582
8	3	171	143
9	3	284	304
10	3	115	170
11	3	*	28
5	4	353	348
6	4	635	641
7	4	126	125
8	4	115	71
9	4	156	155
10	4	68	77
11	4	139	162
6	5	293	274
7	5	309	297
8	5	254	247
9	5	248	246
10	5	88	69
11	5	66	47
7	6	274	274
8	6	154	132
9	6	188	198
10	6	87	55
11	6	*	39
8	7	150	148
9	7	119	93
	L = 2		
1	0	*	76
2	0	283	265
3	0	520	531
4	0	110	62
5	0	513	575
6	0	377	269
7	0	343	291
8	0	81	20
9	0	101	152
10	0	77	27
11	0	65	80
12	0	47	50
1	1	1005E	1334
2	1	190	161
3	1	810	841
4	1	64	73
5	1	681	657
6	1	345	354
7	1	396	373
8	1	257	266
9	1	101	114
10	1	77	92
12	1	45	43
2	2	1561E	2058
3	2	162	181
4	2	375	336
5	2	531	514
6	2	506	550
7	2	190	174
8	2	153	138
9	2	*	58
10	2	178	194
11	2	62	78
3	3	1034E	1271
4	3	369	376
5	3	442	402
6	3	380	360
7	3	203	133
8	3	101	72
9	3	275	306
10	3	147	143
11	3	133	149
4	4	1431E	1704
5	4	392	416
5	5	374	298
6	4	256	262
7	4	223	206
8	4	143	85
9	4	167	93
10	4	139	129
11	4	*	19
6	5	98	109
7	5	227	193
8	5	223	230
9	5	249	313
10	5	77	70
11	5	62	83
6	6	351	370
7	6	260	259
8	6	213	189
9	6	68	58
10	6	123	120
7	7	284	346
8	7	142	99
9	7	58	29
8	8	130	157
	L = 3		
1	0	*	66
2	0	1382E	1497
3	0	97	83
4	0	66	12
5	0	244	198
6	0	820	931
7	0	•	82
8	0	•	83
9	0	163	94
10	0	191	153
11	0	149	127
12	0	53	36
2	1	262	324
3	1	1225E	1469
4	1	144	146
5	1	1189	1146
6	1	176	157
7	1	544	541
8	1	308	314
9	1	145	105
10	1	202	225
11	1	112	116
12	1	52	117
3	2	281	255
4	2	394	365
5	2	190	179
6	2	271	261
7	2	197	158
8	2	501	503
9	2	144	124
10	2	174	131
11	2	108	23
12	2	46	44
4	3	262	246
5	3	782	795
6	3	326	349
7	3	528	409
8	3	127	121
9	3	159	140
10	3	155	175
11	3	87	96
5	4	250	294
6	4	286	325
7	4	241	189
8	4	103	121
9	4	137	120
10	4	84	76
11	4	*	81
6	5	101	59
7	5	284	214
8	5	100	84
9	5	130	121
11	5	*	104
7	6	161	98
8	6	271	260
9	6	83	95
8	7	150	175
	L = 4		
1	0	*	60
2	0	*	35
3	0	105	93
4	0	164	86
5	0	160	115
6	0	*	45
7	0	187	152
8	0	370	426
9	0	144	154
10	0	*	25
11	0	*	30
1	1	815E	1336
2	1	178	178
3	1	969E	1126
4	1	134	139
5	1	1026	994
6	1	314	354
7	1	452	437
8	1	253	302
9	1	170	131
10	1	130	162
11	1	171	174
2	2	812	846
3	2	292	290
4	2	271	220
5	2	191	175
6	2	456	434
7	2	168	162
8	2	160	107
9	2	*	58
10	2	140	142
11	2	*	43
3	3	968E	1195
4	3	399	402
5	3	610	590
6	3	149	141
7	3	274	331
8	3	131	136
9	3	*	53
10	3	109	140
11	3	84	94
4	4	*	20
5	4	132	117
6	4	296	250
7	4	131	112
8	4	304	272
9	4	104	74
10	4	71	63
11	4	51	57
5	5	584	619
6	5	130	39
7	5	197	197
8	5	125	101
9	5	137	130
10	5	101	121
6	6	334	266
7	6	156	72
8	6	144	114
9	6	123	125
10	6	51	62
7	7	120	104
8	7	128	120
9	7	59	63
8	8	130	154
	L = 5		
1	0	*	137
2	0	326	344
3	0	582	603
4	0	*	139
5	0	352	365
6	0	128	121
7	0	179	181
8	0	*	36
9	0	*	22
10	0	122	104
11	0	156	168
2	1	168	212
3	1	827	838
4	1	134	108
5	1	333	379
6	1	184	171
7	1	113	93
8	1	165	210
9	1	210	201
10	1	121	142
11	1	*	17
3	2	222	248
4	2	1018E	1429
5	2	305	310
6	2	217	211
7	2	230	211
8	2	142	145
9	2	135	174
10	2	96	54
4	3	213	185
5	3	461	558
6	3	136	160
7	3	233	232
8	3	246	242
9	3	252	279
10	3	91	29
11	3	80	131
5	4	244	196
6	4	592	547
7	4	143	150
8	4	227	182
9	4	*	82
10	4	168	152
6	5	309	340
7	5	347	294
8	5	*	37
9	5	93	97
7	6	*	76
8	6	158	79
9	6	83	94
8	7	*	63
	L = 6		
1	0	48	18
2	0	125	67
3	0	283	334
4	0	693	673
5	0	183	173
6	0	248	243
7	0	221	224
8	0	244	194
9	0	131	146
10	0	278	289
11	0	100	15
1	1	605	875
2	1	342	360
3	1	800	754
3	1	800	754
4	1	223	234
5	1	333	333
6	1	163	141
7	1	281	258
8	1	*	97
9	1	131	185
10	1	111	132
11	1	80	61
2	2	660	766
3	2	*	30
4	2	106	103
5	2	313	331
6	2	345	301
7	2	140	168
8	2	279	267
9	2	*	51
10	2	171	163
11	2	*	57
3	3	217	219
4	3	231	292
5	3	561	487
6	3	169	140
7	3	401	419
8	3	*	129
9	3	124	104
4	4	404	373
5	4	167	135
6	4	140	114
7	4	*	73
8	4	266	262
9	4	143	116
5	5	544	519
6	5	*	85
7	5	274	233
8	5	125	150
6	6	309	354
7	6	182	170
7	7	163	131

[a] An asterisk indicates unobserved reflection. E indicates one of 13 reflections before application of an empirical extinction correction.

ment, and seven further cycles led to a final R value of 0.13 for all 412 reflections. Included in these reflections were all which had been unobserved and also 13 which were badly affected by extinction and to which an empirical correction had been applied. If these two classes are excluded, R is 0.11. As can be seen from Table II, which lists all reflections, those 13 which were corrected were the most intense in their respective levels and all were observed much too low. For the last four least-squares cycles, the original Hughes type weighting scheme was replaced by the two-parameter function

$$w = 1\Big/\left[1 + \left(\frac{F_{\text{obsd}} - b}{a}\right)^2\right]$$

suggested by Mills and Rollett,[7] assigning a and b the values 310 and 250, respectively. This choice of parameters had the effect of greatly down-weighting both the unobserved reflections and also the very intense reflections. No interference with the acceleration procedure was observed. The final coordinate shifts were all less than half the corresponding indicated standard errors when the refinement was terminated.

Discussion

The Crystal Structure.—The nature of the packing of $P_2S_6Br_2$ molecules is illustrated in Figure 1. This shows the layering of the structure in planes normal to the c axis. The mean plane of a molecule is, to a good approximation, parallel to (001) and includes its own pair of phosphorus atoms. Accordingly the mean heights of the two pairs of molecules which define one layer, as illustrated, are $z = 0.24$ and 0.26, respectively, relative to the $\bar{4}$ inversion centers at $z = 0$ and $^1/_2$. Molecular layers are therefore separated by about $^1/_2c$. There are no intermolecular contacts shorter than 3.55 Å. (Br–S) and, of those under 3.8 Å., most occur *between* rather than *within* molecular layers.

Molecular Structure.—The $P_2S_6Br_2$ molecule in its averaged crystal setting, as illustrated in Figure 2, possesses a two fold rotation axis, the crystal asymmetric unit being a grouping of three sulfur atoms and one bromine atom around a phosphorus in a distorted tetrahedral configuration.

Intramolecular distances and angles are listed in Table III together with standard deviations based on *twice* the coordinate errors derived from the least-squares refinement. For distances and angles within the P_2S_4 ring these estimates of error should be a safe

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[7] O. S. Mills and J. S. Rollett, "Computing Methods and the Phase Problem in X-ray Crystal Analysis," Pergamon Press, London, 1961, p. 117.

TABLE III

MOLECULAR INTERATOMIC DISTANCES AND VALENCY ANGLES, WITH STANDARD DEVIATIONS[a]

	Length, Å.	σ, Å.	Angle	Value, deg.	σ, deg.
P–S(1)	2.104	0.014	S(1)PS(2)	106.3	0.5
P–S(2)	2.101	0.014	PS(1)S(2)′	99.5	0.6
S(1)–S(2)′	2.034	0.015	PS(2)S(1)′	99.8	0.6
P–S(3)	1.856	(0.029)	S(1)PS(3)	122.5	(1.0)
P–S(4)	1.914	(0.024)	S(1)PBr(3)	113.6	(0.6)
P–Br(3)	2.066	(0.016)	S(1)PS(4)	97.1	(0.9)
P–Br(4)	2.078	(0.016)	S(1)PBr(4)	103.4	(0.7)
S(1)···S(2)	3.36		S(2)PS(3)	99.8	(1.1)
S(1)···S(1)′	3.36		S(2)PBr(3)	103.9	(0.7)
S(2)···S(2)′	3.32		S(2)PS(4)	118.0	(0.9)
S(1)···S(3)	3.47		S(2)PBr(4)	110.0	(0.7)
S(1)···Br(3)	3.49		S(3)PBr(4)	113.5	(1.2)
S(1)···S(4)	3.01		S(4)PBr(3)	117.6	(1.1)
S(1)···Br(4)	3.28				
S(2)···S(3)	3.03				
S(2)···Br(3)	3.28				
S(2)···S(4)	3.44				
S(2)···Br(4)	3.44				

[a] Atoms numbered (3) and (4) are half-atoms. Listed errors in lengths or angles involving them, although derived from the least-squares results in the same way as for the other values in the table, have only limited significance because of the lack of resolution of these atoms.

upper limit. The coordinates of the terminal half-atoms will be expected to interact strongly so that distances and angles in which these atoms are involved will be subject to errors which are hard to assess and may well be larger than those given. In fact, all distances are quite consistent internally. The same cannot be said, however, of the bond angles involving terminal atoms. The tetrahedral environment of phosphorus appears to be considerably distorted by means of a 7° twisting of the planes of X(3)-PX(4) away from the normal to the plane S(1)PS(2). It is difficult to account for such a distortion, except on grounds of intermolecular packing, as it increases the nonbonded repulsions within the molecule.

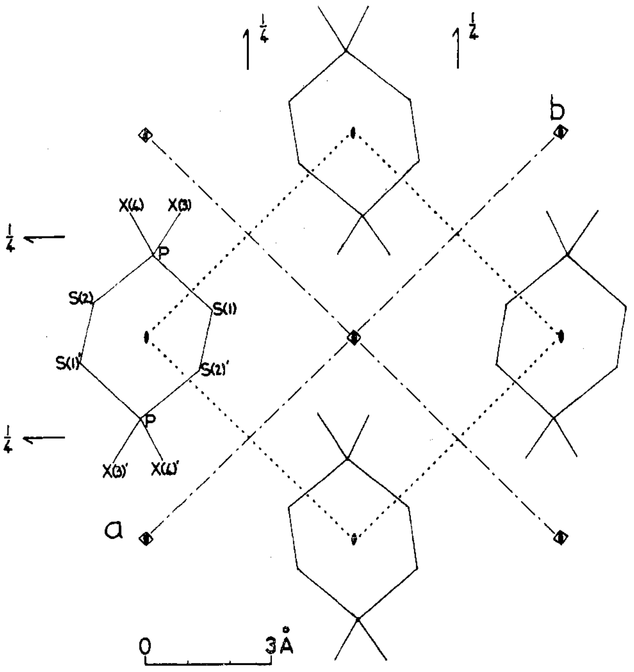


Figure 1.—The arrangement of $P_2S_6Br_2$ molecules in one layer viewed normal to the *c* axis. In this projection there is overlap with alternate layers which may be visualized as being generated by the *c* glide planes.

Both *cis* and *trans* isomers are possible with this molecular structure. The nature of the disordering means that the crystal structure is consistent with either *cis* or *trans* or a mixture of both. Whatever the nature of the geometrical isomerism, there will be equal numbers of *d* and *l* optical isomers because of the operation of the $\bar{4}$ symmetry axes.

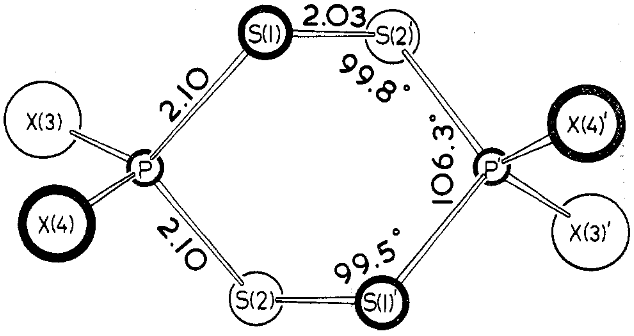


Figure 2.—The molecule $P_2S_6Br_2$ as it appears in its averaged crystal setting, dimensions of the ring portion being shown. A crystallographic twofold axis relates primed with unprimed atoms. X represents a multiple atomic site ($^1/_2$Br + $^1/_2$S).

The Six-Membered Ring.—In no other known phosphorus sulfide or thiohalide has a molecular structure been established as based on one simple ring or as containing S–S bonds. The "P_2S_4" ring in this structure is of the *skew boat* type and it is interesting to examine the reasons why this form should be preferred to the *chair* form which would be expected to minimize nonbonded repulsions within the ring. We may compare the sulfur bond angles, the lengths of S–S bonds, and the torsion angles about them, as they occur in the P_2S_4 ring, with those found in other cyclic structures and also in some noncyclic structures. Representative results of the more recent studies are listed in Table

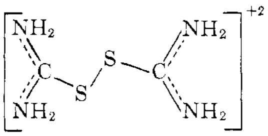
TABLE IV

DISTANCES, ANGLES, AND TORSION ANGLES ASSOCIATED WITH SULFUR–SULFUR BONDS

Compound	S–S length, Å.	Bond angle at S, deg.	Torsion angle about S–S, deg.
S_8[d]	2.06	107.9	98.9
S_6[e]	2.06	102.2	74.5
$P_2S_6Br_2$	2.03	100, 100	86
$(S_4O_6)^{2-}$ [f]	2.02[a]	104	90
Formamidinium disulfide (I)[f]	2.04[b]	102[b]	97[b]
1,2-Dithiolane-4-carboxylic acid (II)[f]	2.10	93, 97	27
4-Methyl trithione (III)[g]	2.05	91, 99	2.5[c]

[a] Length of the central bond in the four-atom sulfur chain. [b] Mean figures for the dibromide and diiodide derivatives. [c] There are a number of other examples of planar five-membered rings containing carbon and nitrogen. [d] J. Donohue, private communication referred to ref. *e*. [e] J. Donohue, A. Caron, and E. Goldish, *J. Am. Chem. Soc.*, **83**, 3748 (1961). [f] O. Foss, *et al., Acta Chem. Scand.*, **12**, 1700, 1782, 1810 (1958). [g] G. A. Jeffrey and R. Shiono, *Acta Cryst.*, **12**, 447 (1959).

IV. Fuller information is available in the reviews of Abrahams[8] and Foss.[9]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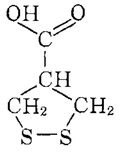
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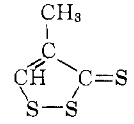
III

There is clearly a preference for a torsion angle of about 90° which has been attributed to repulsions between the unshared pπ electron pairs on adjacent sulfur atoms.[10] This preference is sacrificed only in the special case of the five-membered ring of compound II and in general with conjugated rings such as in compound III. In these cases approximate ring planarity is apparently the more pressing energetic requirement. In the $P_2S_6Br_2$ molecule there are no other such requirements apart from the condition that nonbonded atoms should be as far apart as possible. If we assume that bond lengths and bond angles are fixed within the narrow limits (2.02–2.06 Å. and 102–108°) indicated in the comparable compounds in Table IV, we may then regard the molecular conformation as being determined by the two requirements of (a) a torsion angle about S–S of 90° (±10°) and (b) a minimization of nonbonded repulsions.

Study of models shows that the inherently rigid *chair* ring such as is exhibited by S_6, the only other molecule with S–S bonds in a six-membered ring, leads to serious repulsions between terminal atoms and ring sulfur atoms in $P_2S_6Br_2$. Relief of the consequent strain would be possible only by a drastic reduction of the S–S torsion angle which would, in turn, require an accompanying large increase in the sulfur bond angles. The *skew boat* ring is, however, inherently flexible; *i.e.*, a range of torsion angles can be accommodated without large accompanying changes in bond angles. Torsion angles about P–S bonds are expected to be less critical than those about S–S bonds because the repulsion between a bond pair and a lone pair on adjacent bonded second-row atoms is less than that between two lone pairs. It is reasonable, therefore, to assume that, in $P_2S_6Br_2$, changes in the ring conformation to minimize repulsions between nonbonded atoms may be accommodated by changes in the P–S torsion angles within the ring while S–S torsion angles need not change. The small values (40 and 42°) observed for the P–S torsion angles are therefore not unexpected.

The discovery of the P_2S_4 ring in $P_2S_6Br_2$ suggests that there are likely to be other instances of this previously unknown structural feature in sulfur-rich phosphorus sulfide phases, including polymeric amorphous phases of the type found by Moedritzer and Van Wazer.[11] These authors did in fact suggest some such bonding system, but structural evidence was lacking.

This structure also leads us to compare the behavior toward sulfur of phosphorus and nitrogen. There is an extensive chemistry based on nitrogen–sulfur ring systems of various kinds,[12] nitrogen exhibiting a covalency of three and coordination numbers two or three. Phosphorus, on the other hand, prefers expansion of its valence shell. In none of the known phosphorus sulfides and thiohalides does phosphorus show coordination less than three and consequently three-dimensional cage structures are preferred to simple rings. If phosphorus is to form simple rings with sulfur, part of its valence requirements must be met externally to the ring, either as in $P_2S_6Br_2$ or by polymerization.

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(8) S. C. Abrahams, *Quart. Rev.* (London), **10**, 407 (1956).

(9) O. Foss, *Advan. Inorg. Chem. Radiochem.*, **2**, 237 (1960).

(10) L. Pauling, *Proc. Natl. Acad. Sci. U. S.*, **35**, 495 (1949).

(11) K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, **25**, 683 (1963).

(12) M. Becke-Goehring, *Progr. Inorg. Chem.*, **1**, 207 (1959).