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The Molecular and Crystal Structure of Sulphur-Deficient Tetraphosphorus Heptasulphide (β-P_4S_7)

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A three-dimensional crystal structure analysis has been carried out on the reported non-stoichiometric phosphorus sulphide phase of approximate composition $P_4S_{6.5}$. The structural units are molecules of P_4S_7 of the same type as those found in the stable phase of this composition except that in the present case the molecules possess an exact crystallographic twofold symmetry axis. There is direct crystallographic evidence for a deficiency of sulphur in the terminal positions. Molecular dimensions are as found in the stable P_4S_7 phase except that the unique P–P bond is found to have the more usual length of 2·26 Å.

Introduction

The crystal structures of the stoichiometric phosphorus sulphides P_4S_3 (Leung, Waser, van Houten, Vos, Wiegers & Wiebenga, 1957), P_4S_5 (van Houten & Wiebenga, 1957), P_4S_7 and P_4S_{10} (Vos & Wiebenga, 1955) are well established. Each molecular species is based on a cage of its own distinctive type. Rodley & Wilkins (1960) subsequently reported the existence of a new phosphorus sulphide phase of variable composition in the region of $P_4S_{6.5}$. They also reported the space group and approximate unit-cell dimensions obtained from single crystal X-ray diffraction photographs. The present structure analysis was undertaken with a view to establishing the molecular structure of the new phase and also explaining its variable composition.

Experimental

Following the method of Rodley & Wilkins (1960), the new phase was produced by slow cooling of melts of approximate overall composition P_4S_6. Single-crystal fragments were extracted from the resulting sticky yellow solid, most of them yielding X-ray diffraction patterns of poor quality. The crystals decomposed fairly readily in moist air but remained stable for several weeks inside Lindemann-glass capillaries in which they were sealed for all diffraction work.

Crystallographic data

Unit-cell parameters were determined with the aid of calibrated Weissenberg and precession photographs, assuming $\lambda = 1{\cdot}5418$ Å for Cu $K\alpha$ radiation. Uncertainties listed are three times the estimated standard errors. The crystals are orthorhombic with

$$a = 8{\cdot}14 \pm 0{\cdot}04,\ b = 11{\cdot}43 \pm 0{\cdot}03,\ c = 11{\cdot}39 \pm 0{\cdot}03\ \text{Å}\,.$$

Formula weight for $P_4S_{6.5} = 332{\cdot}3$, $U = 1059{\cdot}7$ Å^3, D_m (by flotation) $= 2{\cdot}09$ g.cm^{-3}, $Z = 4$, D_x (for $P_4S_{6.5}$) $= 2{\cdot}08$ g.cm^{-3}. Space group *Pbcn* from absences. Molecular symmetry 2 or $\bar{1}$.

Reciprocal lattice levels ($h0l$) to ($h6l$) were recorded by the equi-inclination Weissenberg method and the levels ($hk0$), (hkh) and ($0kl$) to ($2kl$) by the Buerger precession camera with Mo $K\alpha$ radiation ($\mu = 19$ cm^{-1}) in all cases. Within these levels the intensities of all observed reflexions were estimated visually. 617 independent reflexions were recorded of which 91 were unobservably weak. Angular fall-off in intensity was great, indicating a large overall temperature factor.

Two crystals were required to complete the data collection. They were of similar dimensions, $0{\cdot}4 \times 0{\cdot}15 \times 0{\cdot}2$ mm, where the greatest elongation is parallel to the *b* crystallographic axis. Absorption errors were therefore negligible and no corrections were made. The first crystal provided all the data collected by the Weissenberg method. The precession data obtained from the second crystal were used mainly for correlation purposes and the few reflexions which did not also appear on Weissenberg films were given low weight in the subsequent least-squares refinement of the structure. The two crystals were not necessarily of identical composition even though they had separated from melts of the same overall composition. The implications of this uncertainty are discussed later in the light of the established crystal structure.

Structure determination

Attempts to interpret the sharpened three-dimensional Patterson function were abandoned mainly because of the lack of computing facilities for superposition techniques, although it must be admitted that we made our task harder by initially assuming that the molecules were based on a composition P_4S_6 rather than P_4S_7.

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The structure was solved by systematic application of sign relationships between structure factors of the type $S(\mathbf{H})=S(\mathbf{H}')S(\mathbf{H}+\mathbf{H}')$ (Cochran, 1952; Cochran & Penfold, 1952). In all cases $\mathbf{H}$ was a zonal reflexion but $\mathbf{H}'$ and $(\mathbf{H}+\mathbf{H}')$ could be zonal or general. In this way, all available data were used to produce signs for $hk0$, $h0l$ and $0kl$ reflexions as a means of establishing the projected positions of the atoms down all three principal axes. Reflexions of particular use had the following values for their unitary structure factors (derived with the aid of Wilson's (1942) method): $U(4,4,0) = 0{\cdot}42$; $U(3,5,0) = 0{\cdot}88$; $U(0,10,0) = 0{\cdot}73$; $U(2,2,2) = 0{\cdot}43$; $U(0,0,10) = 0{\cdot}67$.

The three projections were solved simultaneously and sets of twenty $hk0$, nineteen $h0l$ and twenty-two $0kl$ signs were deduced, of which four, two and three respectively proved subsequently to be wrong. However the mistakes in sign involved only the smallest F values. Fourier syntheses evaluated with these sets of signs were good enough to enable the six atoms in the asymmetric unit to be located without difficulty. It was clear that, contrary to expectation, the crystal structure was based on molecules of P_4S_7 as found by Vos & Wiebenga (1955) in the stable compound of this composition. We shall refer to this stable form as α-P_4S_7, distinct from β-P_4S_7 the subject of this study. In β-P_4S_7 a crystallographic twofold rotation axis passes through one of the sulphur atoms and through the centre of the unique P–P bond.

Refinement

Preliminary refinement of atomic positional and isotropic thermal parameters was achieved in the course of several three-dimensional electron-density difference cycles. It was apparent that it would not have been possible to distinguish phosphorus from sulphur atoms from these maps. The chemical composition, together with a knowledge of the valence properties of phosphorus and sulphur, does however make the correct choice obvious, and the appropriate self-consistent field model atomic scattering factors from *International Tables for X-ray Crystallography* (1959) were used after the first cycle.

The main feature of interest in the difference maps was the fact that after all atoms appeared to be correctly placed atom S(2), the terminal sulphur atom, remained in a deep hollow which could be removed by allowing its thermal parameter to become about 5·0 Å^2 greater than the average for the other atoms. Alternatively the hollow would be removed by subtracting only seven-eighths of a sulphur atom at this position instead of a whole atom. At this stage a full least-squares refinement was commenced with the program ORFLS of Busing, Levy & Martin (1962). In two successive cycles all 31 parameters were allowed to vary. These comprised all positional and isotropic thermal parameters for the atoms, eight scale factors, and also the occupancy factor for atom S(2). All observed data were included, the ratio of observations to parameters being about 20 to 1. A weighting scheme similar to that of Hughes (1941) was used with the addition that about twenty of the most intense reflexions which were apparently suffering from extinction were treated as special cases and were assigned appropriately low weights after empirical corrections had been applied.

Examination of the correlation matrix produced by the ORFLS program showed that, as might have been anticipated, there was a large interaction (correlation coefficient 0·73) between the temperature and occupancy factors of the 'deficient' sulphur atom. The only other appreciable interactions (above 0·40) were among scale and temperature factors. Because of their particularly high interaction, contributed to by the lack of high angle diffraction data, there will be large uncertainties in these two parameters for S(2). The values of both parameters indicate, however, that there is a deficiency of electrons associated with the atom at this site. Had the occupancy factor been held at unity the thermal parameter could only have shifted to an abnormally high value in compensation for the electron deficiency. That this parameter still remained significantly higher than that of any other atom, even when the occupancy factor was 0·90, suggests strongly that the effect is real.

Finally a least-squares cycle was performed in which only the positional parameters of all atoms and the occupancy factor of S(2) were allowed to vary. The thermal parameter of S(2) was held at 5·00 Å^2, a value considered to be appropriately in excess of the mean of the other atoms for an atom which is external to the molecular cage. The behaviour of parameters during these three least-squares cycles is summarized

Table 1. *Progress of refinement by least squares*

	Cycle 1		Cycle 2		Cycle 3	
	Mean	Max.	Mean	Max.	Mean	Max.
Δx	0·011 Å	0·026 Å	0·005 Å	0·009 Å	0·002 Å	0·003 Å
Δy	0·009	0·023	0·007	0·013	0·001	0·003
Δz	0·007	0·011	0·004	0·006	0·001	0·001
ΔB	−0·9	−1·2	−0·06	−0·1	fixed	
ΔB(S(2))	(5·4 to 5·3)		(4·8 to 5·5)		fixed at 5·0	
S(2) occupancy	0·86 to 0·89		(0·89 to 0·93)		0·90 to 0·88	
σ(occupancy)	0·029		0·028		0·016	
R(discrepancy)	0·185		0·170		0·171	

Table 2. *Observed and calculated structure amplitudes on the absolute scale*

H	L	FO	FC
K= 0			
0	2	129	-105
0	4	51	60
0	6	40	-34
0	8	42	-29
0	10	83	-97
0	12	20	29
1	2	89	-98
1	4	89	-98
1	6	25	27
1	8	46	-43
1	10	27	25
1	12	16	17
2	0	22	-20
2	2	62	61
2	4	27	23
2	6	18	27
2	8	27	-25
2	10	6	-4
2	12	16	-16
3	2	43	42
3	4	34	-33
3	6	6	-10
3	8	17	14
3	10	31	-39
4	0	51	57
4	2	10	9
4	4	96	103
4	6	84	-98
4	8	15	21
4	10	32	-24
4	12	13	-6
5	2	49	40
5	4	60	-59
5	6	31	-26
5	8	6	8
5	10	6	-4
5	12	13	-12
6	0	42	54
6	2	23	23
6	4	12	-6
6	6	17	-12
6	8	6	7
6	10	30	-32
7	2	58	-62
7	4	6	-2
7	6	17	-19
7	8	31	-24
7	10	13	9
8	0	6	-2
8	2	6	-10
9	2	18	-14
10	0	20	13
K= 1			
1	0	53	-51
1	1	89	-104
1	2	43	43
1	3	77	-85
1	4	35	-29
1	5	6	0
1	6	8	12
1	7	71	-86
1	8	30	-36
1	9	8	-4
1	10	29	30
1	11	9	12
2	1	23	-24
2	2	41	48
2	3	32	-28
2	4	73	-92
2	5	20	20
2	6	19	-21
2	7	4	-3
2	8	38	40
2	9	4	-5
2	10	4	0
2	11	21	29
3	0	62	-73
3	1	19	-15
3	2	17	-18
3	3	6	-3
3	4	62	-72
3	5	81	-106
3	6	75	87
3	7	4	3
3	8	9	10
3	9	14	-9
4	1	4	3
4	2	17	16
4	3	67	-84
4	4	54	55
4	5	27	30
4	6	31	34
4	7	18	15
4	8	14	-16
4	9	4	2
4	10	13	-15
5	0	19	-18
5	1	58	54
5	2	46	47
5	3	59	-66
5	4	4	-7
5	5	4	-8
5	6	27	-25
5	7	22	-18
5	8	19	-16
5	9	4	-4
5	10	11	11
6	1	34	-31
6	2	19	-21
6	3	6	-3
6	4	8	-8
6	5	20	-16
6	6	4	0
6	7	22	20
7	0	57	-60
7	1	35	-27
7	2	21	19
7	3	9	7
7	4	6	-4
7	5	29	-24
7	6	4	7
7	7	9	9
7	8	4	-4
7	9	21	-17
7	10	19	17
8	1	29	-31
8	2	4	16
8	3	12	11
8	4	4	3
8	5	4	-5
8	6	4	-5
8	7	4	-9
8	8	13	11
8	9	17	23
8	10	26	-1
9	0	17	10
9	1	26	16
9	2	4	-1
9	3	19	-10
9	4	12	-15
9	5	4	1
9	6	17	15
10	4	4	8
10	5	13	-4
11	0	4	-2
11	1	15	-8
11	2	4	6
11	3	4	4
11	4	14	-4
11	5	4	0
11	6	4	3
K= 2			
0	0	99	-75
0	1	94	69
0	2	44	49
0	3	39	30
0	4	60	-65
0	5	23	23
0	6	27	-28
0	7	4	-8
0	8	13	11
0	9	44	49
0	10	9	6
0	11	17	-22
0	12	15	16
1	1	69	67
1	2	124	-115
1	3	84	-83
1	4	4	4
1	5	13	11
1	6	29	-34
1	7	45	44
1	8	4	13
1	9	34	-40
1	10	11	9
1	11	4	3
1	12	15	20
2	0	49	-52
2	1	83	-81
2	2	155	-192
2	3	61	55
2	4	74	82
2	5	41	35
2	6	35	-42
2	7	8	12
2	8	68	88
2	9	4	-10
2	10	11	2
2	11	10	15
2	12	19	21
3	1	44	42
3	2	8	12
3	3	44	-45
3	4	57	63
3	5	36	33
3	6	46	31
3	7	4	-4
3	8	9	-18
3	9	9	-15
3	10	12	17
3	11	4	1
3	12	17	-18
4	0	27	-27
4	1	16	18
4	2	32	-34
4	3	11	-3
4	4	7	-13
4	5	36	36
4	6	14	8
4	7	11	10
4	8	4	4
4	9	4	-8
4	10	12	14
5	1	13	-8
5	2	30	25
5	3	44	41
5	4	24	29
5	5	4	-1
5	6	4	8
5	7	21	-25
6	0	55	55
6	1	50	45
6	2	51	-49
6	3	17	18
6	4	8	4
6	5	36	-37
6	6	4	-5
6	7	32	31
7	1	16	16
7	2	4	4
7	3	4	-0
7	4	5	-1
7	5	4	-5
7	6	16	16
7	7	4	8
7	8	4	7
7	9	4	-6
7	10	4	2
8	0	4	-7
8	1	11	-5
8	2	19	-24
8	3	4	2
8	4	4	11
8	5	4	5
8	6	4	-2
9	1	10	5
9	2	18	17
9	3	4	5
9	4	11	12
9	5	3	-2
K= 3			
1	0	26	-24
1	1	4	-6
1	2	123	151
1	3	43	39
1	4	25	-23
1	5	51	62
1	6	13	-14
1	7	24	28
1	8	26	-25
1	9	8	-5
1	10	9	-8
1	11	4	7
1	12	25	-24
1	13	7	-3
2	1	24	-25
2	2	89	-111
2	3	66	75
2	4	22	18
2	5	7	-5
2	6	29	-33
2	7	37	-44
2	8	13	-19
2	9	19	23
2	10	11	22
2	11	6	-3
2	12	11	6
2	13	12	-11
3	0	30	-30
3	1	71	36
3	2	14	10
3	3	17	16
3	4	19	17
3	5	8	8
3	6	23	21
3	7	16	19
3	8	9	-8
3	9	28	37
3	10	4	6
3	11	23	-25
3	12	18	-16
3	13	12	-3
4	1	33	39
4	2	13	10
4	3	13	-9
4	4	31	31
4	5	4	-8
4	6	8	-4
4	7	18	25
4	8	18	-20
4	9	25	-27
4	10	4	3
4	11	4	-8
4	12	14	-15
4	13	12	2
5	0	37	49
5	1	41	-37
5	2	50	57
5	3	31	35
5	4	46	-46
5	5	19	19
5	6	34	34
5	7	11	13
5	8	49	-56
5	9	10	-5
6	1	22	26
6	2	9	-18
6	3	4	-1
6	4	28	-35
6	5	16	9
6	6	33	-23
7	0	25	17
7	1	10	4
7	2	20	-10
7	3	19	-15
7	4	4	-3
7	5	37	39
7	6	11	17
8	1	10	1
8	2	4	3
8	3	24	26
8	4	20	-18
9	0	30	-25
9	1	4	6
9	2	25	21
9	3	15	12
9	4	11	-8
9	5	22	-17
K= 4			
0	0	162	138
0	1	22	10
0	2	30	25
0	3	20	17
0	4	86	112
0	5	120	-153
0	6	99	-126
0	7	35	48
0	8	5	-5
0	9	24	-28
0	10	28	-20
0	11	5	-4
0	12	5	0
0	13	15	8
1	1	10	1
1	2	9	-2
1	3	25	-16
1	4	78	-84
1	5	5	-1
1	6	33	-28
1	7	5	3
1	8	18	16
1	9	17	16
1	10	20	20
1	11	13	-20
1	12	5	-10
1	13	17	16
1	14	15	12
2	0	12	10
2	1	36	34
2	2	4	-1
2	3	76	-82
2	4	5	1
2	5	17	-9
2	6	22	25
2	7	38	-34
2	8	10	10
2	9	18	-8
2	10	14	-20
2	11	5	-0
2	12	5	-3
2	13	15	11
3	1	42	-45
3	2	5	1
3	3	43	38
3	4	21	19
3	5	40	-38
4	0	88	105
4	1	76	-82
4	2	33	-31
4	3	9	5
4	4	35	25
4	5	12	-16
4	6	17	-16
4	7	28	-22
4	8	5	10
4	9	15	-16
4	10	33	-32
5	1	37	-37
5	2	34	-32
5	3	5	11
5	4	10	7
5	5	5	-2
5	6	5	6
5	7	17	-12
5	8	34	-28
5	9	25	24
5	10	5	3
5	11	16	4
6	0	10	10
6	1	5	-5
6	2	5	12
6	3	5	-5
6	4	27	29
6	5	12	-12
6	6	32	-31
6	7	13	-18
6	8	10	-6
7	1	5	-2
7	2	5	1
7	3	35	-34
7	4	31	-31
7	5	5	7
7	6	13	-18
8	0	17	7
8	1	5	-6
8	2	20	-14
9	1	5	-5
10	0	24	18
K= 5			
1	0	16	13
1	1	30	32
1	2	41	-50
1	3	33	-33
1	4	61	-68
1	5	18	-21
1	6	48	57
1	7	4	-3
1	8	4	-10
1	9	8	-4
1	10	4	14
1	11	4	-4
1	12	4	15
1	13	18	8
2	1	14	-19
2	2	29	-28
2	3	19	24
2	4	24	-20
2	5	14	-18
2	6	26	33
2	7	4	2
2	8	9	-15
3	0	167	-197
3	1	6	-14
3	2	22	14
3	3	16	-8
3	4	19	-15
3	5	12	-14
3	6	18	21
3	7	9	-10
3	8	4	3
3	9	4	-2
3	10	35	56
4	1	18	-16
4	2	61	84
4	3	12	6
4	4	18	13
4	5	11	-5
4	6	4	10
4	7	4	-1
4	8	32	38
4	9	4	12
4	10	16	-23
5	0	4	-0
5	1	4	-2
5	2	4	-0
5	3	18	-18
5	4	4	-8
5	5	17	14
5	6	20	-19
5	7	19	-24
5	8	4	10
5	9	11	7
5	10	4	0
5	11	4	-1
5	12	4	3
5	13	6	0
6	1	4	-6
6	2	9	2
7	0	38	-41
7	1	10	-11
7	2	18	15
7	3	4	2
7	4	34	-37
7	5	4	-3
7	6	27	32
8	1	4	-2
8	2	27	-17
8	3	12	-11
8	4	36	37
8	5	4	5
8	6	12	11
9	0	4	-10
9	1	4	8
9	2	4	-1
9	3	4	-6
9	4	13	9
K= 6			
0	0	66	57
0	1	5	13
0	2	5	-5
0	3	5	-2
0	4	30	28
0	5	75	110
0	6	32	-37
0	7	5	-14
0	8	26	-26
0	9	21	15
0	10	13	8
0	11	14	3
1	1	13	-4
1	2	24	22
1	3	26	28
1	4	58	-70
1	5	11	-9
1	6	23	-23
1	7	11	-2
1	8	28	35
1	9	9	-12
1	10	5	-2
1	11	14	15
2	0	31	30
2	1	28	-36
2	2	63	-73
2	3	61	84
2	4	20	13
2	5	5	-7
2	6	19	16
2	7	40	49
2	8	32	27
2	9	9	-1
2	10	5	-13
2	11	14	5
3	1	27	28
3	2	39	45
3	3	16	-11
3	4	12	-15
3	5	20	22
3	6	22	16
3	7	16	-16
3	8	5	7
3	9	5	-3
3	10	18	-13
4	0	21	15
4	1	41	50
4	2	7	-10
4	3	5	7
4	4	5	2
4	5	5	19
4	6	13	-12
4	7	21	18
4	8	15	19
4	9	16	13
4	10	11	-14
5	1	21	31
5	2	13	-15
5	3	5	-4
5	4	15	17
5	5	5	-0
5	6	14	14
5	7	14	9
5	8	22	-12
5	9	16	-21
6	0	20	-19
6	1	17	-12
6	2	9	7
6	3	21	16
6	4	27	31
6	5	5	11
6	6	35	-41
7	1	5	8
7	2	5	-1
7	3	22	24
8	0	5	3
8	1	5	0
8	2	11	-15
8	3	12	7
8	4	12	5
9	1	5	7
9	2	5	3
9	3	16	10
K= 7			
1	0	24	32
1	1	5	-3
1	2	69	74
2	1	45	38
2	2	42	-40
2	3	64	-67
2	4	5	-13
2	5	5	21
2	6	5	-17
2	7	23	25
3	0	8	-2
K= 8			
0	0	20	6
0	1	84	-100
0	2	15	15
0	3	5	6
0	4	5	0
0	5	5	-22
0	6	39	-34
1	1	24	-18
1	2	48	-44
2	0	23	-22
2	1	23	22
2	2	48	-39
2	3	26	-39
2	4	23	28
4	0	19	15
K= 9			
1	0	55	-62
1	1	32	34
3	0	34	-37
K=10			
0	0	89	109
0	1	28	36
0	2	5	-16
2	0	8	-8

Table 3. *Atomic coordinates and isotropic thermal parameters with their standard errors*

	x	σx (Å × 10^3)	y	σy (Å × 10^3)	z	σz (Å × 10^3)	B (Å^2)	σB
P(1)	0·0928	6·5	0·1804	9·0	0·3238	6·5	4·66	0·17
P(2)	0·1617	5·2	0·4003	7·0	0·1528	5·0	3·20	0·14
S(1)	0·0000		0·5082	10·5	0·2500		3·52	0·17
S(2)	0·3062	7·0	0·4992	10·0	0·0684	7·5	(5·00)	
S(3)	0·0243	5·5	0·2877	7·8	0·0476	5·6	4·03	0·15
S(4)	0·2826	5·9	0·2869	7·9	0·2627	5·8	4·38	0·16

in Table 1. The final value of the error of fit function $\sqrt{[\Sigma w(F_o-|F_c|)^2/(m-n)]}$ was 1·50 and the R index was 0·17.

A three-dimensional difference map following least-squares cycle two showed no spurious electron density maxima greater than 1·8 e.Å^{-3}. There were no indications of strongly anisotropic thermal vibrations. Final observed and calculated structure amplitudes are listed in Table 2, the original uncorrected observed values being given for those reflexions which were corrected empirically for 'extinction'.

In Table 3 are listed the final positional and thermal parameters together with their standard errors as derived directly from the inverse least-squares matrix. With due allowance for errors in unit-cell parameters, the coordinate errors led to the estimated limits of error for individual bond lengths and angles which are listed in Table 4.

Table 4. *Molecular dimensions of* α- *and* β-P_4S_7

	β-P_4S_7	3σ	α-P_4S_7*
P(1)–P(1′)	2·26 Å	0·060 Å	2·33 Å†
P(1)–S(3)	2·13	0·045	2·104
P(1′)–S(4)	2·08	0·045	2·105
P(2)–S(3)	2·08	0·040	2·090
P(2)–S(4)	2·05	0·040	2·072
P(2)–S(1)	2·12	0·040	2·110
P(2)–S(2)	1·89	0·045	1·915

	β-P_4S_7	α-P_4S_7*
S(1)P(2)S(2)	107·7°	107·4°
S(1)P(2)S(3)	109·1	109·5
S(1)P(2)S(4)	110·2	108·9
S(3)P(2)S(4)	102·6	102·9
S(2)P(2)S(3)	114·2	114·0
S(2)P(2)S(4)	112·9	114·1
P(1)S(3)P(2)	101·5	102·8
P(1′)S(4)P(2)	102·5	102·1
S(3)P(1)P(1′)	102·3	102·3
S(3)P(1)S(3′)	103·0	103·6
S(4)P(1′)P(1)	104·2	103·1
P(2)S(1)P(2′)	108·7	109·9†

* Mean values from Vos & Wiebenga (1964).

† Single value.

The molecular structure

A diagram illustrating the P_4S_7 molecule on which the crystal structure is based is shown in Fig. 1 and a view down the b axis of the contents of a unit cell is shown in Fig. 2. Within limits of error the molecule possesses symmetry mm (C_{2v}) in its crystal setting of symmetry 2. This is as found by Vos & Wiebenga for α-P_4S_7, the molecules of which are in an unsymmetrical crystal environment. The detailed molecular dimensions of the two forms are compared in Table 4. The figures for α-P_4S_7, kindly supplied by Dr. A. Vos, resulted from a recent three-dimensional leasts-quares refinement (Vos & Wiebenga, 1964) which included allowance for individual anisotropic thermal parameters. The estimated standard deviation in the length of an individual bond is 0·007 Å. The only significant difference between the two forms is in the length of the unique P–P bond. The unusually large value of 2·329 Å, observed for the α form, is to be compared with 2·26 Å for the β form, a value which is not significantly different from those reported for

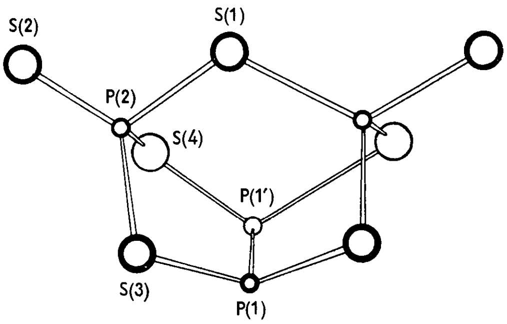

Fig. 1. A representation of the P_4S_7 molecule. A crystallographic twofold rotation axis passes through S(1) and through the mid point of the bond P(1)–P(1′).

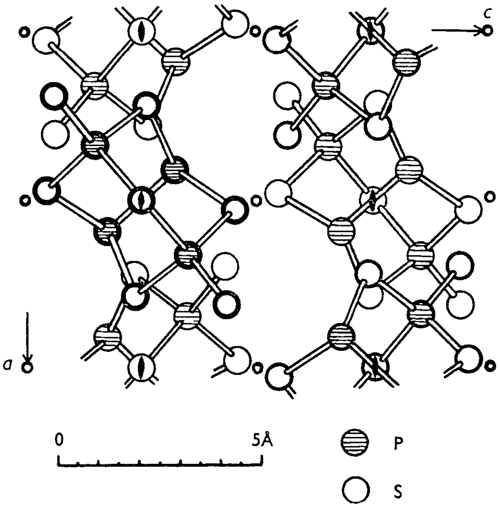

Fig. 2. The crystal structure of β-P_4S_7 viewed down the b axis.

black phosphorus and for the remaining phosphorus sulphides. (For a summary see Wright & Penfold, 1959.)

In the β-P_4S_7 structure itself, there is a possibly significant difference (1% level) between the lengths of the bonds P(1)S(3) (2·13 Å) and P(2)S(4) (2·05 Å) which involve tricovalent and pentacovalent phosphorus respectively. This difference is not, however, paralleled by the chemically similar pair, P(1)S(4) and P(2)S(3) (both 2·08 Å), and we do not attach chemical significance to it. Intermolecular contacts are typical of those found in the other phosphorus sulphides, the shortest of 3·35 Å involving P(1) and S(2).

Molecular stoichiometry

We have established that there is a deficiency of electrons associated with the double bonded S(2) atom even though the interaction between temperature and occupancy factors is large; we have demonstrated that the temperature factor becomes unreasonably large when the occupancy is held at unity. While there remains some uncertainty as to the extent of the effect, this electron deficiency of S(2) does provide a necessary structural interpretation of the analytical and X-ray powder diffraction evidence of Rodley & Wilkins. With crystals containing the P_4S_7 unit there must, on the average, be some deficiency of sulphur relative to this formula. In other words, in some fraction of the molecules, one or more sulphur atoms must be missing altogether. If an internal cage sulphur S(1), S(3) or S(4) were missing, the whole molecular cage would be disrupted, but the absence of the terminal S(2) would simply reduce the covalence of P(2) from five to three and would allow P(2) to maintain the same distribution of its bonds to the remaining sulphur atoms. If we accept the crystallographic occupancy factor of 0·88, the overall molecular composition is $P_4S_{6\cdot76}$ and the lower sulphur content reported for some of Rodley & Wilkins's samples would correspond simply to a lower occupancy factor for S(2). In the light of this structural basis for the variable composition, it can be seen that the possibly different sulphur content of the two crystals used for producing the X-ray data would not seriously affect the actual atomic positions.

We are led to consider the nature of the small fraction of molecules which are sulphur-deficient. The terminal sulphur atoms could be absent from molecules singly or in pairs, although on the average, because of the crystallographic symmetry, both terminal positions must be equally deficient. We are left then with molecules of P_4S_6 or P_4S_5. No stoichiometric phase P_4S_6 has yet been established and the known P_4S_5 phase has a molecular structure different from that of the cage portion of P_4S_7. This suggests therefore that two terminal sulphur atoms are required to impart stability to this basic cage. One further comment is that, if our structural explanation for the non-stoichiometry of β-P_4S_7 is correct, there is no reason why the other phosphorus sulphides which contain terminal double-bonded sulphur atoms should not also be sulphur-deficient.

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