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The Crystal Structure of P_4S_5

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The crystal structure of P_4S_5 has been determined by X-ray diffraction. Space group $P2_1$, 2 molecules per unit cell. Approximate coordinates were found from a three-dimensional Patterson synthesis. The coordinates were refined by means of successive Fourier syntheses of the three projections. The crystal consists of molecules of P_4S_5, which have an unexpected structure. The P–S distances vary from 2·08 to 2·19 Å, the average P–P distance is 2·21 Å and the P=S distance is 1·94 Å.

Introduction

Phosphorus and sulphur form the compounds P_4S_3, P_4S_5, P_4S_7 and P_4S_{10} (Stock, 1910; Treadwell & Beeli, 1935; Pernert & Brown, 1949). The structures of these compounds have been investigated in our laboratory during recent years (Vos & Wiebenga, 1955; van Houten, Vos and Wiegers, 1955); that of P_4S_3 has also been determined independently by Leung, Waser & Roberts (1955). The structure determination of P_4S_5, being the last compound investigated, is described in the present paper.

Experimental

Materials

P_4S_5 is formed when a solution of P_4S_3, sulphur and some iodine in dry carbon disulphide is exposed to diffuse daylight for three days (Boulouch, 1904). The reaction has to take place in a closed vessel in an atmosphere of carbon dioxide to prevent the oxidation of P_4S_3. The substance can be purified by recrystallization from carbon disulfide. The X-ray photographs were made from crystals having a diameter of approximately 0·1 mm. perpendicular to the axis about which the photographs were taken. The crystals were mounted in capillaries of borosilicate glass.

Space group and lattice constants

Weissenberg photographs showed the crystals to be monoclinic. The systematic absences are those required by the space groups $P2_1$ or $P2_1/m$. The pyroelectricity of the crystals indicated the space group $P2_1$, which was confirmed by the result of the structure determination.

The lattice constants were measured on Weissenberg and oscillation photographs about the three axes. With $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å the following values for the lattice constants were obtained:

$$a = 6{\cdot}41 \pm 0{\cdot}03,\quad b = 10{\cdot}94 \pm 0{\cdot}04,\quad c = 6{\cdot}69 \pm 0{\cdot}03 \text{ Å}\,,\quad \beta = 111{\cdot}7 \pm 0{\cdot}4^\circ\,.$$

The inaccuracies listed are estimated standard deviations. With two molecules per unit cell the density was calculated to be 2·15 g.cm.$^{-3}$; the experimental value is 2·17 g.cm.$^{-3}$ at 25° C. (Treadwell & Beeli, 1935).

Structure factors

The intensities of 738 independent reflexions hkl were estimated visually on equi-inclination Weissenberg photographs about the a axis, using Ni-filtered Cu radiation. Use was made of the multiple-film technique. The crystals were twins with common b^* and c^* axes; therefore two sets of reflexions were available on all but the zero layer lines. A correction for absorption was applied. The intensity data observed on different layer lines were related by $h0l$ and $hk0$ reflexions from integrated equiinclination Weissenberg photographs (Wiebenga & Smits, 1950) about the b and c axes respectively. In the course of the structure determination the scale factors thus obtained were somewhat adjusted, using the calculated structure factors.

Determination of the structure

Interpretation of the Patterson synthesis

After some unsuccessful attempts to solve the structure by means of inequalities, a three-dimensional Patterson synthesis was computed. Peaks around the origin at distances of about 2 Å give the vectors between bonded atoms. These peaks were all very low, suggesting that there are no parallel bonds in the molecule.

The location of some of these peaks, combined with those of other general peaks in the three-dimensional Patterson synthesis, gave an indication of the relative positions of four atoms, lying at the vertices of a trigonal pyramid. The location of this pyramid in the cell could be found by making use of the information obtained from the Harker section. An atom at the position (x, z) relative to any one of the four independent screw axes of the cell is represented in the Harker section $y = \frac{1}{2}$ by a peak at $(2x, 2z)$ relative to the origin. Therefore, a set of four Harker sections, reduced to half scale and put with their origins on the four screw axes, will represent four superimposed projections of the structure (Fig. 1). The projection of the trigonal pyramid could now be put on peaks in Fig. 1, giving the x and z coordinates of four atoms. The positions of the other atoms were deduced from the other peaks in the Harker section, combined with the information obtained from peaks in the section $y = 0$ and from peaks around the origin.

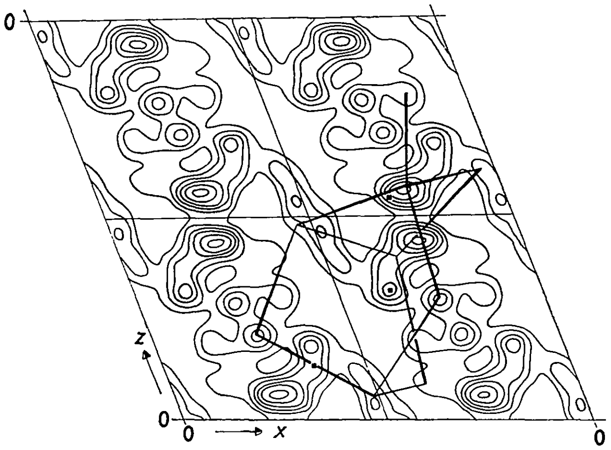

Fig. 1. A set of four Harker sections, reduced to half scale and put with their origins on the four independent screw axes of the unit cell. One of the two molecules is shown. Contour lines are on an arbitrary scale. Squares indicate non-Harker maxima.

The molecules appeared to have an unexpected asymmetric structure, shown in Fig. 3. Phosphorus and sulphur are distinguished by chemical arguments only.

Refinement of the parameters

The coordinates were refined by successive Fourier syntheses of the three projections, applying 'back-shift' corrections (Booth, 1946) in the later stages of the refinement. Using a temperature factor $\exp(-B \sin^2 \theta/\lambda^2)$ the values of the disagreement index R for the three projections are:

	B (Å^2)	R (%)
[001]	2·37	8·0
[010]	2·69	11·7
[100]	2·88	7·5

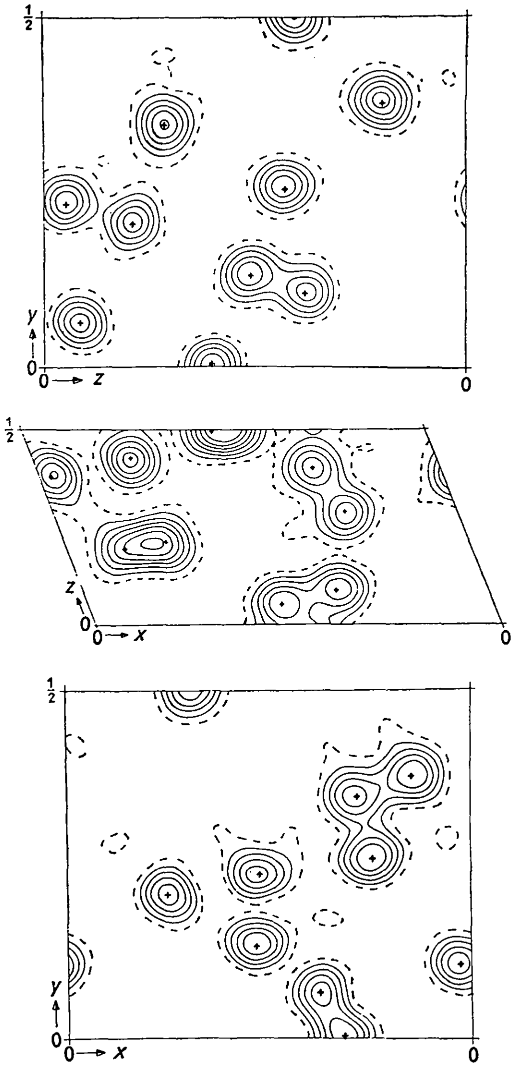

Fig. 2. Final electron-density maps of the three projections. Contour lines are at intervals of 4 e.Å^{-2}; the broken line is at 4 e.Å^{-2}. Crosses indicate final atomic coordinates.

Table 4 shows the agreement between observed and calculated F values. With these structure amplitudes and phases the final Fourier syntheses were computed (Fig. 2). As final coordinates (Table 1) the average values of each coordinate obtained from two projections were taken. The structure factors were not recalculated with these final coordinates.

Table 1. *Final atomic coordinates*

Atom	x	y	z
P_1	0·684$_5$	0·004	0·401
P_2	0·470	0·132	0·495
P_3	0·758	0·259	0·575
P_4	0·480	0·237$_5$	0·052
S_1	0·627	0·065	0·088
S_2	0·251	0·209	0·212
S_3	0·722$_5$	0·349	0·288
S_4	0·970	0·106	0·622$_5$
S_5	0·856	0·378	0·805

Discussion

Accuracy

The accuracy of the final coordinates was estimated by comparing the final values of the coordinates obtained from different projections. The standard deviation of the coordinates thus obtained was 0·016 Å in each direction. Since the refinements of the coordinates in the three projections were not entirely independent, this value must be considered to be a lower limit for the standard deviation. As the standard deviation calculated from Cruickshank's formula (1949, 1954) was about 0·02 Å, the standard deviation in the final coordinates was assumed to be $0{\cdot}02/\sqrt{2}$ Å, giving a standard deviation of 0·02 Å in the atomic distances. Since the effect of the inaccuracies in the lattice constants on the standard deviation in the atomic distances is about 0·01 Å, the bond lengths are subject to a total standard deviation of $[(0{\cdot}02)^2+(0{\cdot}01)^2]^{\frac{1}{2}} = 0{\cdot}025$ Å. The corresponding standard deviation in the bond angles is about 1° (Cruickshank & Robertson, 1953).

Description and discussion of the structure

The crystal structure consists of molecules of P_4S_5, shown in Fig. 3. Their structure is asymmetric; P_4S_5 is therefore expected to be optically active. The bond lengths and angles are listed in Table 2. With the exception of the value 2·19 Å for S_4–P_1, the differences in the P–S bond lengths and that of the two P–P bond lengths are not significant. Many bond angles, however, show significant differences. The distances

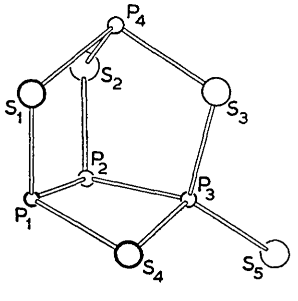

Fig. 3. Molecule of P_4S_5.

Table 2. *Bond lengths and angles in the* P_4S_5 *molecule*

P_1–P_2	2·20 Å	S_1–P_4–S_2	100°	S_3–P_3–S_4	111°
P_2–P_3	2·21	S_1–P_4–S_3	105	S_3–P_3–S_5	108
S_1–P_1	$2{\cdot}09_5$	S_2–P_4–S_3	99	S_5–P_3–S_4	114
S_1–P_4	2·09	P_1–S_1–P_4	108	S_5–P_3–P_2	128
S_2–P_2	2·08	P_2–S_2–P_4	99	P_1–P_2–P_3	85
S_2–P_4	$2{\cdot}13_5$	P_3–S_3–P_4	102	P_2–P_3–S_4	88
S_3–P_3	2·09	S_1–P_1–P_2	101	P_3–S_4–P_1	88
S_3–P_4	2·14	S_1–P_1–S_4	108	S_4–P_1–P_2	86·5
S_4–P_1	2·19	S_2–P_2–P_1	106		
S_4–P_3	2·11	S_2–P_2–P_3	101		
S_5–P_3	1·94	S_3–P_3–P_2	106		

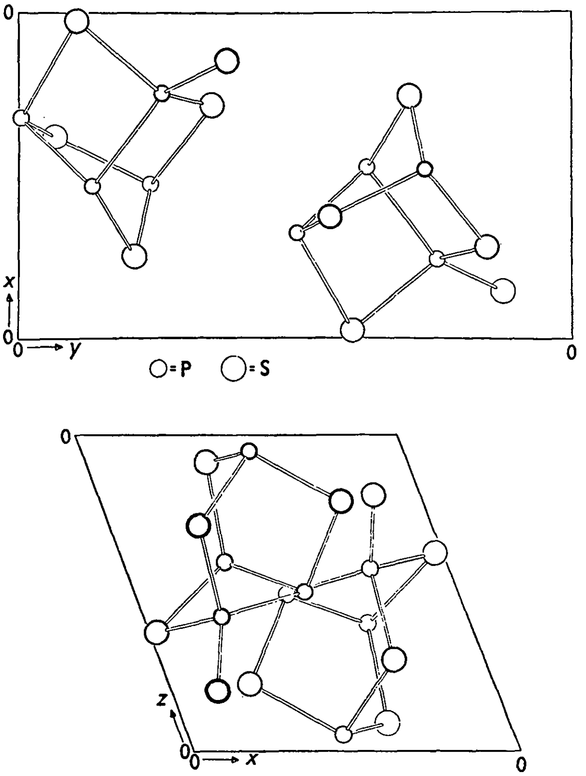

Fig. 4. P_4S_5 structure. (*a*) Projection along [001] on the (001) plane; (*b*) projection along [010] on the (010) plane.

Table 3. *Atomic distances in some phosphorus compounds*

(The inaccuracies listed are estimated standard deviations.)

	P–P (Å)	P–S (Å)	P=S (Å)	Method*	Ref.†
P_4S_3	2·235±0·005	2·090±0·005	—	*X*	1
P_4S_5	2·21 ±0·025	2·08–2·19±0·025	1·94 ±0·02	*X*	—
P_4S_7	2·35 ±0·01	2·08 ±0·01	1·95 ±0·02	*X*	2, 3
P_4S_{10}	—	$2{\cdot}08_5$ ±0·01	$1{\cdot}95_5$ ±0·015	*X*	2
P_2I_4	2·21 ±0·06	—	—	*X*	4
P_4‡	2·21 ±0·02	—	—	*E*	5

* *X*: X-ray diffraction; *E*: electron diffraction.

† 1: Leung *et al.*, 1957.
2: Vos & Wiebenga, 1955.
3: Vos & Wiebenga, 1956.
4: Leung & Waser, 1956.
5: Maxwell *et al.*, 1935.

‡ Tetrahedral.

Table 4. *Observed and calculated structure amplitudes and calculated phases*

hkl	F_o	F_c	α (°)
020	48	48	134
040	24	22	113
060	32	34	124
080	51	51	328
0,10,0	6	7	140
0,12,0	< 6	1	75
100	36	40	180
110	41	40	356
120	28	28	293
130	82	85	294
140	32	31	180
150	< 6	4	98
160	6	5	227
170	13	14	180
180	8	4	240
190	23	24	21
1,10,0	23	24	329
1,11,0	27	26	231
1,12,0	19	17	111
1,13,0	8	6	341
200	25	21	180
210	37	36	65
220	51	53	75
230	20	23	98
240	31	33	180
250	20	19	184
260	40	42	237
270	21	26	184
280	7	8	15
290	11	10	16
2,10,0	13	14	91
2,11,0	13	15	10
2,12,0	12	12	246
300	5	6	0
310	17	16	241
320	39	40	18
330	29	29	36
340	26	30	77
350	9	9	304
360	13	11	349
370	25	22	73
380	16	19	215
390	25	26	170
3,10,0	12	11	344
3,11,0	13	16	6
3,12,0	13	16	45
400	38	37	0
410	31	32	311
420	45	48	157
430	12	10	321
440	19	19	313
450	8	6	162
460	14	14	249
470	8	7	233
480	23	22	318
490	20	21	290
4,10,0	17	19	98
500	12	19	180
510	14	16	142
520	9	14	63
530	13	7	212
540	9	7	117
550	27	23	91
560	16	17	196
570	9	9	251
580	15	16	174
600	< 6	6	0
610	19	22	291
620	19	16	11
630	19	19	80
640	9	9	159
650	23	21	49
660	< 6	5	316
001	33	33	180
002	10	9	0
003	10	11	180
004	< 6	2	180
005	14	13	0
006	15	15	180
007	10	11	180
003	5	5	180
011	34	32	131
012	50	50	140
013	28	28	53
014	40	37	210
015	19	20	151
016	9	5	70
017	< 5	5	197
020	48	46	134
021	23	23	243
022	58	50	84
023	8	8	316
024	27	29	204
025	8	7	228
026	< 5	2	264
027	15	15	273
031	27	25	25
032	43	40	288
033	26	27	135
034	19	21	100
035	6	9	215
036	29	30	343
037	13	12	297
040	24	21	113
041	13	16	344
042	28	29	18
043	21	19	54
044	22	22	236
045	23	22	321
046	21	23	199
047	9	9	33
051	22	25	109
052	54	55	218
053	24	22	126
054	13	11	218
055	< 6	2	41
056	22	23	146
057	6	7	279
060	32	35	127
061	48	48	114
062	42	40	240
063	6	6	283
064	9	11	32
065	9	7	115
066	9	9	312
067	7	7	341
071	35	34	215
072	24	25	316
073	< 5	6	135
074	29	25	313
075	14	11	301
076	< 4	5	136
080	51	52	331
081	31	32	193
082	20	20	52
083	14	11	263
085	14	12	359
091	20	17	79
092	6	7	353
093	8	8	269
094	22	21	220
095	9	9	96
0,10,0	6	7	142
0,10,1	11	12	228
0,10,2	11	13	136
0,10,3	< 5	5	238
0,10,4	10	10	141
0,10,5	15	16	356
0,11,1	11	10	334
0,11,2	11	11	307
0,11,3	< 5	6	243
0,11,4	15	13	12
0,12,0	5	3	149
0,12,1	16	16	262
0,12,2	11	12	322
0,12,3	13	13	32
0,12,4	7	8	199
0,13,1	5	8	0
0,13,2	6	6	243
0,13,3	11	15	81
0,14,0	5	6	333
001	33	31	180
002	10	10	0
003	10	9	180
004	< 6	2	180
005	14	15	0
006	15	15	180
007	10	14	180
008	5	5	180
100	36	38	180
101	32	29	180
102	62	59	180
103	16	16	0
104	23	21	0
105	23	23	0
106	13	10	180
$\bar{1}01$	6	7	180
$\bar{1}02$	41	36	180
$\bar{1}03$	8	7	180
$\bar{1}04$	68	66	180
$\bar{1}05$	32	33	0
$\bar{1}06$	23	25	0
$\bar{1}07$	20	15	0
200	25	23	180
201	34	34	180
202	43	41	0
203	< 5	5	180
204	6	5	0
205	16	13	180
206	5	6	0
$\bar{2}01$	68	62	0
$\bar{2}02$	57	58	0
$\bar{2}03$	29	26	0
$\bar{2}04$	9	10	180
$\bar{2}05$	20	22	180
$\bar{2}06$	25	25	0
$\bar{2}07$	26	26	180
$\bar{2}08$	5	10	0
300	5	4	0
301	16	17	180
302	4	5	0
303	25	29	0
304	35	35	180
305	7	7	0
306	7	9	180
$\bar{3}01$	18	15	180
$\bar{3}02$	28	29	180
$\bar{3}03$	22	24	0
$\bar{3}04$	14	16	180
$\bar{3}05$	8	7	180
$\bar{3}06$	19	22	180
$\bar{3}07$	14	13	0
$\bar{3}08$	14	17	0

Table 4 (*cont.*)

hkl	F_o	F_c	α (°)	*hkl*	F_o	F_c	α (°)	*hkl*	F_o	F_c	α (°)
400	38	38	0	500	12	15	180	602	25	27	0
401	12	11	180	501	12	5	180	$\bar{6}01$	11	5	0
402	9	4	0	502	7	5	0	$\bar{6}02$	12	19	180
403	< 7	10	0	503	20	20	180	$\bar{6}03$	< 6	1	180
404	< 7	7	0	$\bar{5}01$	18	19	0	$\bar{6}04$	10	12	180
405	7	9	0	$\bar{5}02$	8	10	180	$\bar{6}05$	6	6	180
$\bar{4}01$	39	51	180	$\bar{5}03$	27	34	0	$\bar{6}06$	< 6	1	0
$\bar{4}02$	7	7	0	$\bar{5}04$	16	19	180	$\bar{6}07$	16	16	180
$\bar{4}03$	< 6	9	180	$\bar{5}05$	14	14	0	700	< 6	1	180
$\bar{4}04$	16	18	0	$\bar{5}06$	6	9	0	$\bar{7}01$	6	5	180
$\bar{4}05$	< 6	7	180	$\bar{5}07$	8	12	180	$\bar{7}02$	6	9	180
$\bar{4}06$	< 6	2	180	600	< 6	6	0	$\bar{7}03$	< 6	4	0
$\bar{4}07$	< 6	1	180	601	< 6	1	180	$\bar{7}04$	18	21	0

between the non-bonded atoms P_2 and S_4, and between P_1 and P_3, are very short (about 3·00 Å).

The arrangement of the molecules in the crystal is shown in Fig. 4. The shortest distance between atoms of different molecules is 3·68 Å.

The bond lengths found may be compared with those in the other phosphorsulfides and some other phosphorus compounds (Table 3). The P–P, P–S and P=S distances in these compounds are mutually very similar, with the exception of the remarkably long P–P distance in P_4S_7.

We wish to thank Mr G. A. Wiegers for his help during the early stages of the structure determination. The assistance of Miss A. M. Zweens and Mr H. Schürer during the calculations is also gratefully acknowledged. The Patterson and Fourier syntheses were computed on IBM machines, which were generously put at our disposal by Theodorus Niemeyer N.V.; our thanks are due to Mr M. R. van de Velde and Miss G. E. Veldman for operating these machines. The work was supported by the Netherlands Organization for Pure Research (Z. W. O.).

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