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The Crystal Structures of P_4S_{10} and P_4S_7

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P_4S_{10} and P_4S_7 belong to the space groups $P\bar{1}$ and $P2_1/n$ with 2 and 4 molecules per unit cell respectively. Approximate coordinates were found from three-dimensional Patterson syntheses; the coordinates were refined by computing Fourier syntheses of projections. The structures consist of molecules of P_4S_{10} and P_4S_7. The intermolecular distances are approximately 3·4 Å. In both molecules two types of P–S bonds may be distinguished with bond lengths of 2·08 and 1·95 Å respectively. The e.s.d. is approximately 0·01 Å for the former and $0{\cdot}01_5$ Å for the latter. The symmetry of the P_4S_{10} molecule is $\bar{4}3m$; the S–P–S and P–S–P angles show no significant deviation from 109·5°. In P_4S_7 some S–P–S bond angles are significantly different from 109·5°; the molecule has the symmetry $mm2$ and contains a remarkably long P–P bond (2·37 Å with an e.s.d. of 0·04 Å).

Introduction

Phosphorus and sulfur form the compounds P_4S_3, P_4S_5, P_4S_7 and P_4S_{10} (Stock, 1910*a*, *b*, *c*; Treadwell & Beeli, 1935; Pernert & Brown, 1949). The only direct information available on the structures of these compounds was an electron-diffraction study of P_4S_3 (Hassel & Pettersen, 1941). For P_4S_{10} molecules in solution a structure was postulated (Pernert & Brown, 1949) analogous to that of P_4O_{10} molecules, as determined by Hampson & Stosick (1938) by electron diffraction. Though this structure for the molecule in solution is very probable, this does not imply that solid P_4S_{10} should also consist of these molecules. For P_4O_{10}, for example, three solid modifications were reported, only one form containing molecules of P_4O_{10} (de Decker & MacGillavry, 1941; de Decker, 1941; MacGillavry, de Decker & Nijland, 1949). The structures proposed for P_4S_7 and P_4S_5 (Pernert & Brown, 1949) are far less certain than that suggested for P_4S_{10} and did not find general acceptance.

Our X-ray examination of crystalline P_4S_{10} and P_4S_7 shows these compounds to consist of molecules of P_4S_{10} and P_4S_7. The structure reported for the P_4S_{10} molecule confirms that proposed by Pernert & Brown; that observed for P_4S_7 is different from all structures postulated previously for this compound.

The crystal structures of P_4S_5 and P_4S_3 are now being investigated in our laboratory.

Materials

P_4S_{10} and P_4S_7 were prepared by melting a mixture of phosphorus and sulfur (*Organic Synth.*, 1932). After solidification of the melt, crystals could be obtained by a slow continuous extraction with CS_2. As the crystals are not stable in moist air, they were transferred into a boron silicate glass capillary in which they could be kept for a long time. Perpendicular to the crystal axis, about which the X-ray photographs were made, their diameter was approximately 0·1 mm.

P_4S_{10}

Unit cell and space group

Optical goniometric measurements and a construction of the reciprocal lattice from oscillation, rotation and Weissenberg photographs about the *a* axis showed the crystals to be triclinic. With $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}5418$ Å the following lattice constants were obtained:

$$a = 9{\cdot}07,\ b = 9{\cdot}18,\ c = 9{\cdot}19\ \text{Å};$$
$$\alpha = 92{\cdot}4,\ \beta = 101{\cdot}2,\ \gamma = 110{\cdot}5^\circ.$$

With a density of 2·09 g.cm.$^{-3}$ (Stock, 1910*c*) the number of molecules per cell was calculated to be 1·98. Wilson's statistical method (Wilson, 1949) and the absence of piezoelectricity indicated the space group $P\bar{1}$, which was confirmed during the structure analysis.

Structure factors

The intensities of most reflexions ***hkl*** were measured on integrated oscillation photographs (Wiebenga & Smits, 1950; Boswijk, 1954, p. 35) about the *a* axis, taking an inclination angle of 20°. The photographs were taken with Zr-filtered Mo radiation, using three films of different speed during each exposure. The oscillation range was 20° with an overlap of 5° for two successive photographs. The indices of the reflexions *hkl* were determined graphically from the reciprocal lattice. The intensities of the reflexions on different photographs were put on the same scale by comparing the intensities of the reflexions which successive photographs had in common. The maximum deviation of these scaling factors from those derived from the exposure times of the different photographs was 14%.

No absorption correction had to be applied, because of the small crystals used. A correction for oblique incidence was made (Cox & Shaw, 1930) as well as a correction for the Lorentz and polarization factors. Use was made of a general expression for the Lorentz factor (Boswijk, 1954, p. 36). The relative intensities of approximately 900 reflexions were measured. They were put on an approximate absolute scale using Wilson's statistical method (Wilson, 1949). The scaling factor thus obtained later appeared to show a difference of approximately 9% from the final one, derived from a comparison of observed and calculated structure factors.

Determination of the approximate structure

With the F^2 values obtained, a three-dimensional Patterson synthesis was computed. This vector map shows an interesting regular arrangement of high peaks. At a distance of about 2 Å the origin is tetrahedrically surrounded by only four peaks, $A-D$ (Fig. 1), of a weight corresponding to eight coincident atomic distances. This suggests that the eight phosphorus atoms in the unit cell are tetrahedrically surrounded by sulfur atoms and that these PS_4 tetrahedra are either parallel or centrosymmetrically oriented. A centrosymmetrical arrangement of two P_4S_{10} molecules of a general shape shown in Fig. 2 satisfies this condition. Such a structure would lead to additional peaks in the Patterson map of weights corresponding to ten coincident atomic distances and at positions corresponding to the edges of the PS_4 tetrahedra. Since these peaks were actually observed in the Patterson synthesis (peaks $E-J$ in Fig. 1) a structure of P_4S_{10} molecules was assumed. The orientation of these molecules could be taken from the vector map; the approximate location relative to the centre of symmetry was determined by trial and error making use of the reflexions *h*00, 0*k*0 and 00*l*.

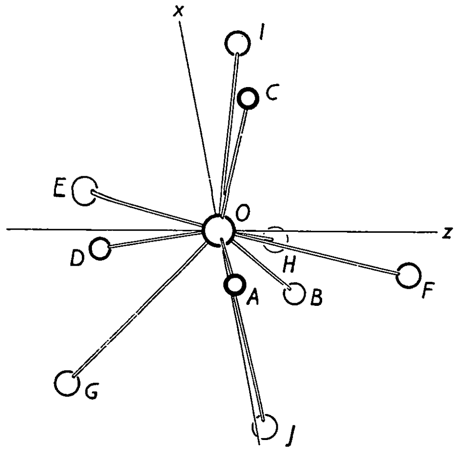

Fig. 1. Some high peaks from the three-dimensional Patterson synthesis of P_4S_{10}, shown schematically in [010] projection.

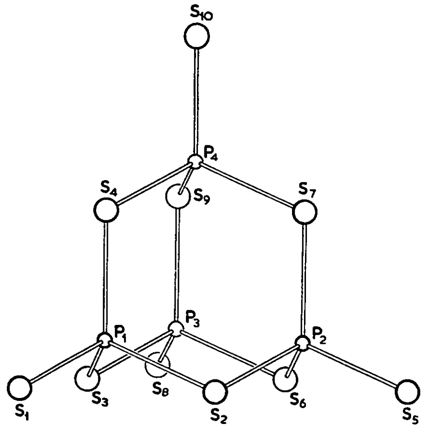

Fig. 2. Molecule of P_4S_{10}.

Refinement of the structure

[010] *projection.*—With the approximate coordinates, the structure factors for the reflexions *h*0*l* were calculated. The agreement between F_c and F_o was sufficient to determine the signs of 72 out of the 74 observed structure factors. With these structure factors a Fourier synthesis of the [010] projection was computed. The fourteen (independent) atoms appeared to be fairly well resolved in this projection and it was possible to determine their *x* and *z* coordinates from the contour map. These coordinates were refined by consecutive Fourier syntheses and corrected for series termination by Booth's backshift method (Booth, 1946). The final electron-density map is shown in Fig. 3(*a*). The final value of the disagreement index $R \equiv \Sigma_{hl}||F_o|-|F_c|| \div \Sigma_{hl}|F_o|$ is 0·11, including the observed reflexions only.* Temperature factor:

$$\exp\left(-2{\cdot}36 \sin^2 \theta/\lambda^2\right) .$$

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* A table of observed and calculated structure factors has been deposited as Document No. 4489 with the ADI Auxiliary, Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting $ 1·25 for photoprints, or $ 1·25 for 35 mm. microfilm. Advance payment is required. Make cheques or money orders payable to: Chief, Photoduplication Service, Library of Congress.

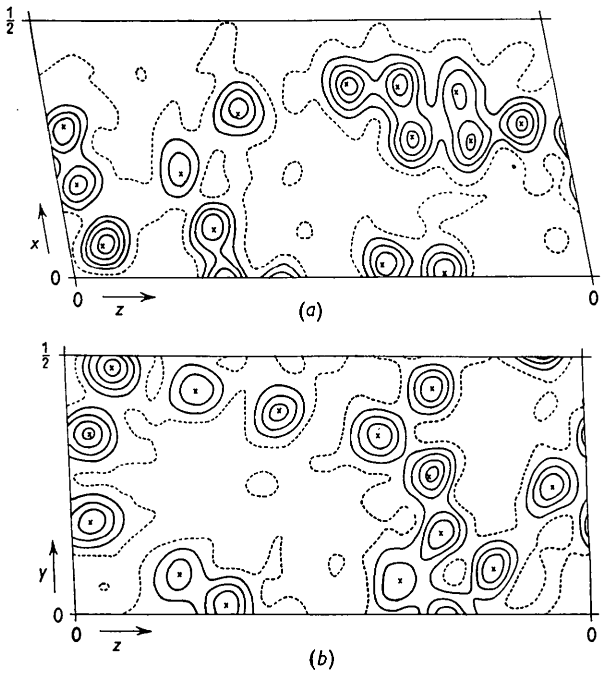

Fig. 3. (a) P_4S_{10}: final electron-density projection along [010] on the (010) plane. Contours at intervals of 6 e./1·08 Å^2, the 3 e./1·08 Å^2 line being broken.

(b) P_4S_{10}: final electron-density projection along [100] on the (100) plane. Contours at intervals of 6 e./1·10 Å^2, the 3 e./1·10 Å^2 line being broken.

[100] *projection*.—Starting from the approximate structure, the signs of 64 out of the 76 observed reflexions could be determined. The coordinates were refined in the same way as reported for the [010] projection. Fig. 3(*b*) shows the final electron-density map; $R = 0{\cdot}11$.* Temperature factor:

$$\exp\left(-2{\cdot}36 \sin^2 \theta/\lambda^2\right).$$

[001] *projection*.—Since only three atoms were well resolved in this projection a refinement of the coordinates by the Fourier method was not attempted. Using the coordinates and the temperature factor as determined from the other projections, a disagreement index $R = 0{\cdot}12$ was calculated for the observed *hk*0 reflexions.*

The final values for the atomic coordinates are listed in Table 1.

Table 1. P_4S_{10}: *final atomic coordinates*

	(*a*) [100] projection		(*b*) [010] projection	
	y	*z*	*x*	*z*
P_1	0·087	−0·190	0·259	−0·187
P_2	0·153	−0·289	−0·090	−0·288
P_3	0·435	−0·297	0·267	−0·297
P_4	0·345	0·034	0·178	0·037
S_1	−0·074	−0·195	0·357	−0·197
S_2	−0·014	−0·285	0·008	−0·284
S_3	0·265	−0·308	0·367	−0·308
S_4	0·176	0·033	0·288	0·030
S_5	0·065	−0·374	−0·316	−0·372
S_6	0·343	−0·405	0·024	−0·403
S_7	0·245	−0·066	−0·062	−0·062
S_8	0·609	−0·407	0·375	−0·406
S_9	0·526	−0·079	0·298	−0·080
S_{10}	0·430	0·237	0·199	0·245

Final *z* coordinates are derived from (*a*) and (*b*) by taking the average values.

Accuracy of the atomic coordinates

An estimate of the accuracy of the final coordinates was obtained by comparing the 14 *z* coordinates as determined independently from the [010] and [100] projections respectively. Their r.m.s. deviation is 0·026 Å, corresponding to $\sigma(z) = 0{\cdot}018$ Å. This is approximately twice as large as the r.m.s. average for the standard deviations calculated for the *z* coordinates of the different atoms by applying Cruickshank's formula (Cruickshank, 1949). This discrepancy is probably due to incomplete corrections for series termination. The backshifts were rather large (0·03 Å on an average) because of the partial overlap of some atoms and the lack of some fairly weak reflexions which could not be measured on the oscillation photographs; moreover, they were, especially for some atoms, very sensitive to small variations of the coordinates on which the F_c syntheses were based. The 'experimental' standard deviation $\sigma = 0{\cdot}018$ Å was assumed for all coordinates. For the atomic distances this corresponds to a standard deviation $\sigma(d) = \sqrt{2} \times 0{\cdot}018 = 0{\cdot}026$ Å, resulting from inaccuracies in the intensities and imperfections of the backshift corrections. Apart from these errors, the atomic distances are subject to errors due to inaccuracies in the unit-cell dimensions and angles. Their influence was estimated to be represented by a standard deviation of approximately 0·02 Å in the atomic distances. The total standard deviation in the bond lengths thus amounts to approximately $(0{\cdot}026^2 + 0{\cdot}02^2)^{\frac{1}{2}} = 0{\cdot}03$ Å. The corresponding standard deviation in the bond angles (Cruickshank & Robertson, 1953) is 1·2°.

Discussion

The structure consists of molecules of P_4S_{10} separated by shortest intermolecular distances of approximately 3·4 Å. The [010] and [100] projections are shown in Fig. 4. The molecule is shown in Fig. 2; its bond lengths and angles are listed in Table 2. Since no distinction between phosphorus and sulfur atoms could be made from the Fourier maps, their distinction is entirely based on chemical arguments. From Table 2 and Fig. 2 it is seen that the P–S distances range from 2·02 to 2·13 Å when the sulfur atoms are connected to two phosphorus atoms, and from 1·91 to 1·98 Å when they are connected to one phosphorus atom only.

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* See footnote p. 218.

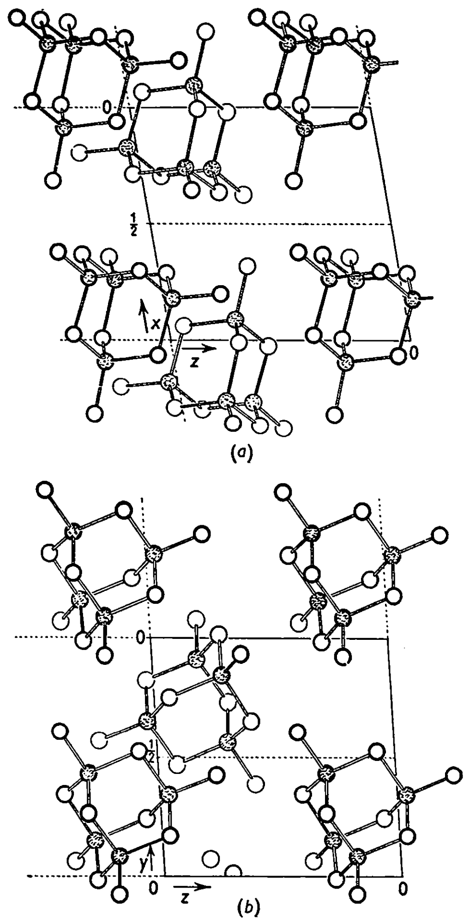

Fig. 4. (*a*) P_4S_{10}: projection along [010] on the (010) plane. (*b*) P_4S_{10}: projection along [100] on the (100) plane.

Table 2. P_4S_{10}: *intramolecular bond lengths and angles*

P_1–S_1	1·97 Å	S_1–P_1–S_2	110°	S_4–P_4–S_7	110°
P_1–S_2	2·12	S_1–P_1–S_3	109	S_4–P_4–S_9	107
P_1–S_3	2·07	S_1–P_1–S_4	111	S_4–P_4–S_{10}	111
P_1–S_4	2·08	S_2–P_1–S_3	109	S_7–P_4–S_9	111
P_2–S_2	2·02	S_2–P_1–S_4	108	S_7–P_4–S_{10}	108
P_2–S_5	1·91	S_3–P_1–S_4	110	S_9–P_4–S_{10}	109
P_2–S_6	2·13	S_2–P_2–S_5	111	P_1–S_2–P_2	110
P_2–S_7	2·13	S_2–P_2–S_6	113	P_1–S_3–P_3	109
P_3–S_3	2·07	S_2–P_2–S_7	108	P_1–S_4–P_4	110
P_3–S_6	2·08	S_5–P_2–S_6	110	P_2–S_6–P_3	107
P_3–S_8	1·98	S_5–P_2–S_7	107	P_2–S_7–P_4	110
P_3–S_9	2·06	S_6–P_2–S_7	108	P_3–S_9–P_4	108
P_4–S_4	2·12	S_3–P_3–S_6	110		
P_4–S_7	2·04	S_3–P_3–S_8	109		
P_4–S_9	2·10	S_3–P_3–S_9	112		
P_4–S_{10}	1·96	S_6–P_3–S_8	107		
		S_6–P_3–S_9	111		
		S_8–P_3–S_9	108		

The conclusion may be drawn that two essentially different bond lengths can be distinguished in the molecule: one, with an average value of $2{\cdot}08_5$ Å, corresponding to a 'single' P–S bond; and another, with a mean value of $1{\cdot}95_5$ Å, corresponding to a 'double' P–S bond. It was shown by a many-parameter significance test (Cruickshank & Robertson, 1953) that the observed deviations from this model are not significant. Assuming for all atomic coordinates a standard deviation of $0{\cdot}03/\sqrt{2}$ Å, a value of 15·1 for T_o^2 was obtained corresponding, for 14 degrees of freedom, to $P \approx 0{\cdot}4$ (Cruickshank & Robertson's notation is used). If, on the other hand, all bond lengths were supposed to be essentially equal, with an average value of 2·05 Å, the deviations from this model were highly significant ($P < 0{\cdot}001$), showing that the latter interpretation of the experimental results is not correct.

The bond angles range from 107 to 113°. The deviations from 109·5° are not significant. Hence it may be concluded that each phosphorus atom is tetrahedrically surrounded by four sulfur atoms. The averages of the observed bond lengths, $2{\cdot}08_5$ and $1{\cdot}95_5$ Å, which are subject to an estimated standard deviation of 0·01 Å and $0{\cdot}01_5$ Å respectively, may be compared with Pauling's values (Pauling, 1945, p. 164) for the lengths of a single (2·14 Å) and double (1·94 Å) bond between phosphorus and sulfur.

P_4S_7

Unit cell and space group

The cell dimensions were obtained from rotation and Weissenberg photographs about the three crystal axes. With $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}5418$ Å and $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}7107$ Å, the following values for the lattice constants of the monoclinic crystals were obtained:

$$a = 8{\cdot}87 \pm 0{\cdot}02,\ b = 17{\cdot}35 \pm 0{\cdot}03,\ c = 6{\cdot}83 \pm 0{\cdot}02\ \text{Å};\quad \beta = 92{\cdot}7 \pm 0{\cdot}4^\circ.$$

With a density of 2·19 g.cm.$^{-3}$ (Stock, 1910*b*), the number of molecules per unit cell was calculated to be 4·00. The systematic absences indicate the space group $P2_1/n$.

Structure factors

The intensities of most reflexions *hkl* were measured on integrated equi-inclination Weissenberg photographs about the *c* axis, taken with Ni-filtered Cu radiation (Wiebenga & Smits, 1950; Smits & Wiebenga, 1953). In addition to this, integrated Mo data were available for the 0*kl* and *hk*0 reflexions. Weak reflexions 0*kl* and *hk*0 were estimated visually on ordinary Weissenberg photographs of long exposure time, using both Ni-filtered Cu and Zr-filtered Mo radiation. Use was made of the multiple-film technique, with three films of different speed for the Mo photographs. No absorption correction had to be applied to the Mo data; the Cu data were roughly corrected for absorption. The intensities measured on *c*-axis Weissenberg photographs of different layer lines were correlated by zero-layer-line Weissenberg photographs about the *a* and *b* axes.

Determination of the approximate structure

After some unsuccessful applications of phase relationships between the structure factors 0*kl* and *hk*0

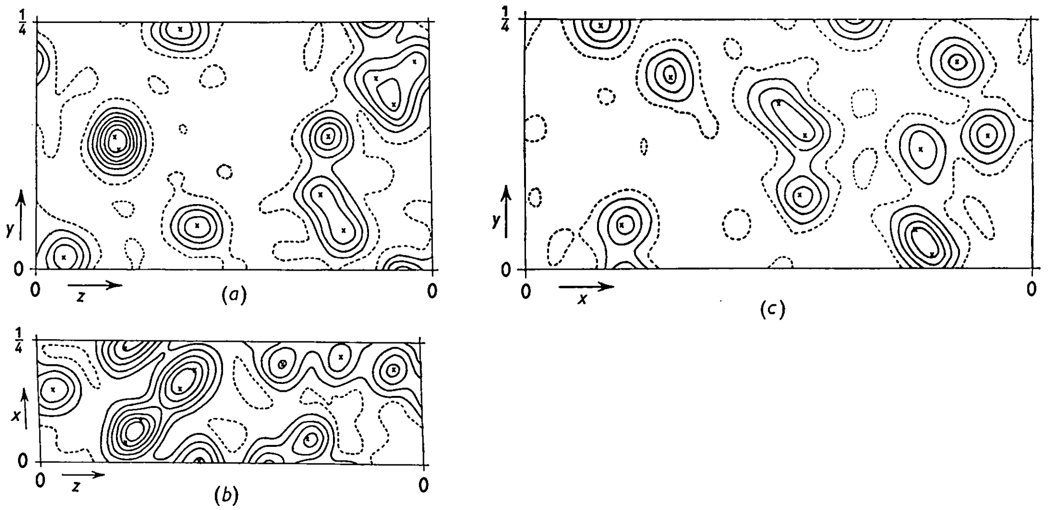

Fig. 5. P_4S_7: final electron-density projection (*a*) along [100] on the (100) plane, (*b*) on (010), (*c*) along [001] on the (001) plane. Contours at intervals of 6 e.Å^{-2}, the 3 e.Å^{-2} line being broken.

respectively, a three-dimensional Patterson synthesis was computed. It appeared that, at a distance of approximately 2 Å, the origin was tetrahedrically surrounded by four somewhat blurred, independent peaks; this was considered as an indication of the presence of approximately parallel PS_4 tetrahedra. An interpretation of the Harker section $(x, \frac{1}{2}, z)$ was difficult because of the many 'non-Harker maxima' and the ambiguity connected with the presence of two independent screw axes in the unit cell. The information obtained from the section $(x, \frac{1}{2}, z)$ can be combined however, with that obtained from the zero section $(x, 0, z)$, the Harker line $(\frac{1}{2}, y, \frac{1}{2})$, general peaks in the three-dimensional Patterson synthesis and the relative intensities of reflexions $h0l$ with h and l even, as was extensively described by Albrecht & Corey (1939). In this way, keeping in mind the information obtained from the maxima around the origin, the approximate positions of two phosphorus and seven sulfur atoms could be determined. These phosphorus atoms are tetrahedrically surrounded by sulfur atoms, the two tetrahedra having one sulfur atom in common. The coordinates of the remaining two phosphorus atoms were determined less directly, combining chemical evidence with the positions of some Harker maxima which had not been used yet. The molecule is shown in Fig. 7.

Refinement of the structure

With the approximate coordinates the structure factors of the reflexions $0kl$, $h0l$ and $hk0$ were calculated. The agreement between observed and calculated values was sufficient to determine the signs of 61, 39 and 67 out of the 86, 51 and 84 observed, independent, structure factors for the [100], [010] and [001] projections respectively. Some atoms proved to be poorly resolved in the projections, as is shown in Fig. 5. A Fourier refinement of the coordinates was possible by comparing the 'observed' electron-density maps with 'calculated' ones, combining the information from the three projections. The coordinates were corrected for the finite-series effect by the application of Booth's backshift method (Booth, 1946). The final coordinates are listed in Table 3. The disagreement indices R amount to 0·08, 0·13 and 0·10 for the observed $0kl$, $h0l$ and $hk0$ reflexions respectively.* Temperature factor: $\exp(-2{\cdot}47 \sin^2\theta/\lambda^2)$.

Accuracy of the atomic coordinates

The effect of inaccuracies in the measured intensities was estimated by applying Cruickshank's formula (Cruickshank, 1949). The r.m.s. average of the estimated standard deviations for the coordinates was approximately the same for all directions and equal to approximately 0·014 Å.

Attempts were also made to estimate the errors due to an imperfect correction for series termination by comparing the backshifts obtained from F_c syntheses of the [001] projection, based on slightly different

Table 3. P_4S_7: *final atomic coordinates*

	x	y	z
P_1	0·281	0·379	0·709
P_2	0·353	0·293	0·463
P_3	0·271	0·461	0·274
P_4	0·003	0·335	0·409
S_1	0·043	0·425	0·220
S_2	0·307	0·544	0·094
S_3	−0·212	0·308	0·363
S_4	0·305	0·487	0·569
S_5	0·413	0·367	0·239
S_6	0·150	0·245	0·366
S_7	0·052	0·366	0·697

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* See footnote on p. 218.

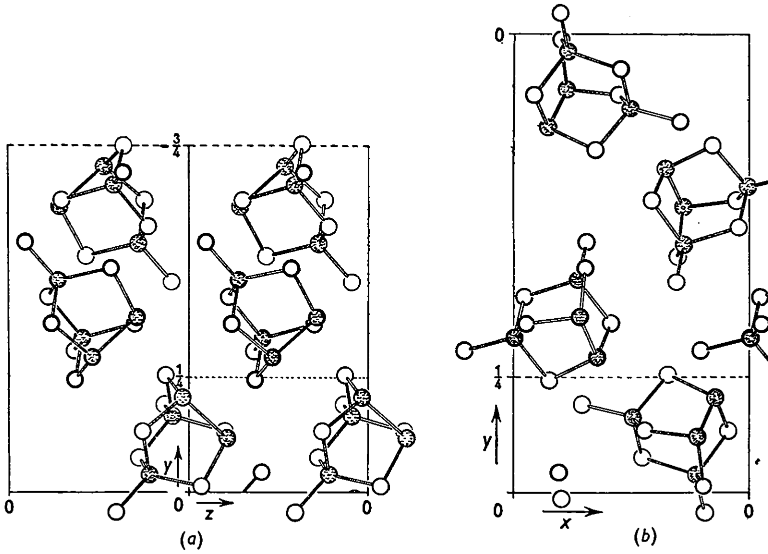

Fig. 6. P_4S_7: projection (a) along [100] on the (100) plane, (b) along [001] on the (001) plane.

coordinates. These coordinates were all close to the final ones. Two of such comparisons were made, the r.m.s. average $\{\overline{(\Delta q)^2}\}^{\frac{1}{2}}$ of the differences of the coordinates being $0{\cdot}02_9$ and $0{\cdot}01_4$ Å respectively. In both cases the mean backshifts obtained, $(\overline{b^2})^{\frac{1}{2}}$, are approximately the same and equal to $0{\cdot}02_5$ Å for the two F_c syntheses involved; the backshift for each individual coordinate, however, appeared in general to be different in both F_c syntheses. The r.m.s. average $\{\overline{(\Delta b)^2}\}^{\frac{1}{2}}$ of these backshift differences are $0{\cdot}01_1$ and 0·007 Å for the two sets of F_c syntheses respectively, being almost one-half of the mean differences, $\{\overline{(\Delta q)^2}\}^{\frac{1}{2}}$, of the coordinates on which the corresponding set of F_c syntheses were based. This means that the backshift corrections involve an inaccuracy, even if these corrections are taken from a F_c synthesis based on the 'final' coordinates. Denoting the standard deviation of the coordinates due to inaccuracies in the intensities by σ_i and that due to the imperfect backshift correction by σ_b, the combined standard deviation σ_{ib} is given by $\sigma_{ib} = (\sigma_i^2+\sigma_b^2)^{\frac{1}{2}}$ if it is assumed that no direct correlation exists between the two sources of error. When σ_i is known, σ_{ib} may be calculated from

$$\sigma_b = f\sigma_{ib} = f(\sigma_i^2+\sigma_b^2)^{\frac{1}{2}} \text{ or } \sigma_{ib} = (1-f^2)^{-\frac{1}{2}}\sigma_i\,,$$

in which $f \equiv \{\overline{(\Delta b)^2}\}^{\frac{1}{2}}/\{\overline{(\Delta q)^2}\}^{\frac{1}{2}}$.

With $\sigma_i = 0{\cdot}014$ Å and $f = 0{\cdot}5$ a value of 0·016 Å for σ_{ib} is calculated. With this standard deviation in the coordinates, a standard deviation of $\{(0{\cdot}016\sqrt{2})^2+0{\cdot}01^2\}^{\frac{1}{2}} = 0{\cdot}025$ Å in the bond lengths is obtained when the error due to inaccuracies in the cell dimensions is represented by a standard deviation of 0·01 Å for bond lengths of approximately 2 Å. The corresponding standard deviation in the bond angles is 1·0° (Cruickshank & Robertson, 1953).

Discussion

The structure consists of molecules of P_4S_7 separated by shortest intermolecular distances of approximately 3·4 Å. The [100] and [001] projections are shown in Fig. 6. The general shape of the molecule (Fig. 7) does not correspond to any of the structures suggested for P_4S_7 previously; from the valencies of phosphorus and sulfur, it was concluded that apart from two phos-

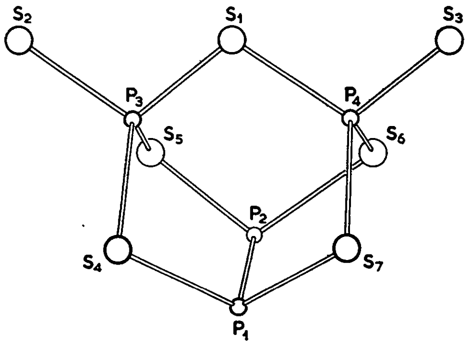

Fig. 7. Molecule of P_4S_7.

Table 4. P_4S_7: *intramolecular bond lengths and bond angles*

P_1–P_2	2·37 Å	S_2–P_3–S_1	107°	P_3–S_5–P_2	103°
P_1–S_4	2·12	S_3–P_4–S_1	106	P_4–S_7–P_1	103
P_1–S_7	2·04	S_2–P_3–S_4	116	P_4–S_6–P_2	101
P_2–S_5	2·08	S_2–P_3–S_5	113	P_3–S_1–P_4	108
P_2–S_6	2·06	S_3–P_4–S_7	112	S_4–P_1–P_2	102
P_3–S_1	2·13	S_3–P_4–S_6	114	S_5–P_2–P_1	103
P_3–S_2	1·93	S_4–P_3–S_1	110	S_7–P_1–P_2	101
P_3–S_4	2·08	S_5–P_3–S_1	109	S_6–P_2–P_1	103
P_3–S_5	2·09	S_7–P_4–S_1	111	S_4–P_1–S_7	102
P_4–S_1	2·07	S_6–P_4–S_1	111	S_5–P_2–S_6	105
P_4–S_3	1·97	S_4–P_3–S_5	103		
P_4–S_6	2·07	S_7–P_4–S_6	103		
P_4–S_7	2·06	P_3–S_4–P_1	104		

phorus atoms, each surrounded by four sulfur atoms, the molecule contains two directly linked phosphorus atoms at a distance of 2·37 Å. The distances P_3–S_2 and P_4–S_3 are 1·93 and 1·97 Å respectively. The other P–S distances range from 2·04 to 2·13 Å (Table 4). A many-parameter significance test (Cruickshank & Robertson, 1953) showed these observations to be in agreement with the assumption of only two different types of bonds in the molecule: 'double' bonds, between P_3–S_2 and P_4–S_3, and 'single' bonds, the lengths of these bonds being equal to the average values of $1{\cdot}95_0$ and $2{\cdot}08_0$ Å respectively. In the significance test a value of $T_o^2 = 12{\cdot}1$, corresponding to $P = 0{\cdot}2$ for ten degrees of freedom, was obtained.

The following types of bond angles may be distinguished in the molecule: $S_2P_3S_1$, $S_2P_3S_4$, $S_4P_3S_1$, $S_4P_3S_5$, $P_3S_4P_1$, $P_3S_1P_4$, $S_4P_1P_2$ and $S_4P_1S_7$. The average value for these angles is 106·6, 113·7, 110·1, 103·0, 102·8, 107·8, 102·2 and 103·6° respectively, the largest deviations from the mean value being twice the standard deviation. Consequently the mutual differences between the individual bond lengths and angles of the same type do not indicate a significant deviation from a symmetry $mm2$ of the molecule. In this molecule the PS_4 tetrahedra are distorted since the average bond angles of the types $S_2P_3S_1$, $S_2P_3S_4$ and $S_4P_3S_5$ show a significant deviation from 109·5°.

The average values for the two P–S bond types, namely $2{\cdot}08_0$ and $1{\cdot}95_0$ Å with an estimated standard deviation of 0·01 and 0·02 Å respectively, agree very well with the corresponding values ($2{\cdot}08_5$ and $1{\cdot}95_5$ Å respectively) in the P_4S_{10} molecule. The standard deviation of the atomic distance P_1–P_2 is somewhat larger than $0{\cdot}02_5$ Å, as these atoms are not very well resolved in the projections, and was estimated to be 0·04 Å. The P–P distance, 2·37 Å, is remarkably large in comparison with P–P distances known from other structures. In black phosphorus the shortest P–P distances are 2·18 Å (Hultgren, Gingrich & Warren, 1935) and P_4 tetrahedra in the vapour phase show a P–P distance of 2·21 Å (Maxwell, Hendricks & Mosley, 1935).

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