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α-Tetraphosphorus Tetrasulphide

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Abstract. P_4S_4, monoclinic, $C2/c$, $a = 9{\cdot}771\ (8)$, $b = 9{\cdot}047\ (7)$, $c = 8{\cdot}746\ (6)$ Å, $\beta = 102{\cdot}67\ (6)°$, $U = 754{\cdot}3$ Å^3, $Z = 4$, $D_x = 2{\cdot}22$ g cm^{-3}, μ (Mo $K\alpha$) $= 18{\cdot}4$ cm^{-1}. The structure was determined by direct methods and refined to an R of 0·035 for 1121 unique diffractometer data. A crystallographic twofold axis passes through two of the S atoms, and the molecule possesses $\bar{4}2m$ (D_{2d}) symmetry within experimental error. Mean bond lengths and angles are: P—P, 2·350 (1); P—S, 2·108 (2) Å; P—P—S, 100·4 (1); S—P—S, 95·1 (1); P—S—P, 98·9 (1)°. Librational corrections increase both these bonds by 0·010 Å.

Introduction. The single-line ^{31}P NMR spectrum of α-P_4S_4 indicates a highly symmetrical structure, and is consistent with either the realgar structure (a square of S atoms bisecting a tetrahedron of As atoms in As_4S_4) or the inverted realgar structure adopted by S_4N_4, Se_4N_4 and Te_4N_4. Although α-P_4S_4 was first reported recently by Griffin, Minshall & Sheldrick (1976), a theoretical study by Gleiter (1970) had predicted a D_{2d} realgar structure with long P—P bonds compared with those found in other phosphorus sulphides.

A single crystal was prepared by slow cooling of a saturated solution in *o*-dichlorobenzene, and sealed in a Lindemann-glass capillary tube. 2524 reflexions were measured with a Syntex $P2_1$ four-circle diffractometer, Mo $K\alpha$ radiation and a graphite monochromator. After application of Lp and absorption corrections, equivalent reflexions were merged to give 1121 unique reflexions with $F > 4\sigma(F)$ based on counting statistics. Cell dimensions were obtained from diffractometer measurements of 15 reflexions. The full structure was located by multisolution Σ_2 sign expansion, and refined by full-matrix least squares with anisotropic atoms, complex neutral-atom scattering factors, and the weighting scheme $w = 1/[\sigma^2(F) + 0{\cdot}000119F^2]$ to a final R' $(=\Sigma\, w^{1/2}\Delta/\Sigma\, w^{1/2}|F_o|)$ of 0·029; the corresponding unweighted R was 0·035. A final difference electron density synthesis did not show any features greater than 0·5 e Å^{-3}, and an analysis of variance in terms of $|F_o|$ and $\sin\theta$ did not show any systematic trends. Atomic coordinates are given in Table 1, and

Table 1. *Fractional coordinates* ($\times 10^4$)

	x	y	z
P(1)	−17 (1)	2024 (3)	5666 (6)
P(2)	1501 (3)	3861 (5)	8700 (9)
S(1)	0	5380 (6)	7500
S(2)	0	508 (6)	7500
S(3)	1960 (3)	2945 (4)	6657 (7)

Table 2. *Bond lengths* (Å)

P(1)—P(2′)	2·350 (1)	P(2)—S(1)	2·112 (1)
P(1)—S(2)	2·108 (1)	P(1)—S(3)	2·108 (1)
P(2)—S(3′)	2·106 (1)		

Table 3. *Bond angles* (°)

P(2)—P(1)—S(2)	100·6 (1)	P(2)—P(1)—S(3)	100·4 (1)
P(1)—P(2)—S(1)	100·3 (1)	P(1)—P(2)—S(3′)	100·3 (1)
S(2)—P(1)—S(3)	95·2 (1)	S(1)—P(2)—S(3′)	95·1 (1)
P(2)—S(1)—P(2′)	98·9 (1)	P(1)—S(2)—P(1′)	98·8 (1)
P(1)—S(3)—P(2′)	99·1 (1)		

Table 4. *Shortest non-bonded distances* (Å)

Symmetry code: (i) $0·5 + x, y - 0·5, z$; (ii) $-x, y, 1·5 - z$; (iii) $-x, -y, 1 - z$; (iv) $-x, 1 - y, 1 - z$; (v) $0·5 - x, 0·5 - y, 1 - z$.

Intermolecular		Intramolecular	
S(3)···S(1^{i})	3·713	P(2)···P(2^{ii})	3·210
S(2)···P(1^{iii})	3·596	S(1)···S(3)	3·110
P(1)···P(1^{iii})	3·845	S(2)···P(2)	3·433
S(1)···P(1^{iv})	3·635		
S(2)···S(3^{v})	3·392		

the resulting interatomic distances and angles in Tables 2–4.*

Discussion. Atoms S(1) and S(2) lie in special positions on the crystallographic twofold axis which passes through the molecule. The molecular dimensions given in Tables 2 and 3 are consistent with $\bar{4}2m$ (D_{2d}) molecular symmetry within experimental error. The molecular structure is analogous to that found for As_4S_4 in the mineral realgar (Ito, Morimoto & Sadanaga, 1952) rather than the inverted geometry adopted by S_4N_4. α-P_4S_4 is almost isostructural with a second crystalline modification of As_4S_4 (Porter & Sheldrick, 1972), though there are significant differences in cell dimensions and atomic coordinates arising because the As—As bond is appreciably longer [2·593 (6) Å] than the P—P bond.

The anisotropic temperature factors were found to be in excellent agreement with the rigid-body-motion model of Schomaker & Trueblood (1968): $R_g = (\Sigma \Delta^2/\Sigma U_{ij}^2)^{1/2}$ for the agreement between the observed and calculated U_{ij} was 0·019. Librational tensors, with respect to axes parallel to x^*, y and z, were: L_{11} 47 (1), L_{12} 0, L_{13} 9 (1), L_{22} 39 (1), L_{23} 0, L_{33} 44 (1) ($\times 10^{-4}$ rad^2); S_{11} −15 (1), S_{12} 0 (1), S_{13} 15 (1), S_{22} 23 (1), S_{23} 0 (1), S_{33} 8 (1) ($\times 10^{-4}$ rad Å); T_{11} 232 (4), T_{12} 0, T_{13} −16 (3), T_{22} 277 (3), T_{23} 0, T_{33} 238 (4) ($\times 10^{-4}$ Å^2); these were relative to an origin at (0,0·2839,0·75) which makes **S** symmetric. These values were used in calculating the mean librationally corrected bond lengths given in Fig. 1.

As predicted by Gleiter (1970), the P—P bond is longer than those previously found in phosphorus sulphides [the longest being 2·326 (7) Å in P_4S_7; Vos, Olthof, van Bolhuis & Botterweg, 1965]. In order to gain some insight into the P—P distances, it is instructive to consider the five-membered $\overline{PPSP'S}$ rings in P_4S_7, β-P_4S_5 (Griffin & Sheldrick, 1975) and α-P_4S_4; we compare mean librationally corrected bond lengths, estimated in the case of P_4S_7. The P—S bonds involving trivalent P are remarkably similar, falling within the range 2·116 to 2·118 Å. The sum of the internal ring angles is 512·8 in β-P_4S_5 and 513·0° in P_4S_7, so these rings probably deviate from planarity to about the same extent. The P—P bond in P_4S_7 [2·334 (8) Å] is longer than that in β-P_4S_5 [2·295 (5) Å] and this can be attributed to the increase in S—P′—S ring angle [102·8 (3) and 97·6 (2)° respectively], consistent with the increase in P *s*-orbital character in the P′—S (ring) bonds resulting from the extra terminal S atom. In α-P_4S_4 the removal of the S atom linking the two P′ atoms causes the five-membered rings to deviate more from planarity (sum of internal angles = 493·7°). The valence angles at S and P′ are smaller than those found in other phosphorus sulphides, and they would be even

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33245 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

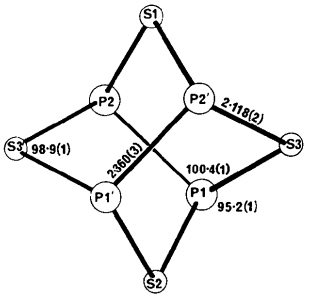

Fig. 1. The molecule of α-P_4S_4, showing mean librationally corrected bond lengths (Å) and angles (°).

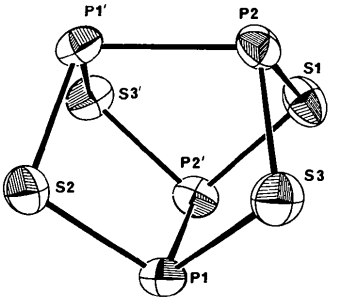

Fig. 2. *ORTEP* plot of α-P_4S_4, showing 50% probability ellipsoids.

smaller were it not for the long P—P bond. The S—P—S angle of 95·1 (1)° in α-P_4S_4 is much smaller than the corresponding angles in β-P_4S_5 [104·6 (1)°] and P_4S_7 [103·9 (3)°]; this is likely to direct the hybridized atomic orbitals away from the line joining the two P atoms, reducing the overlap and weakening the P—P bond. Kinetic factors arising from the high molecular symmetry presumably account for the stability of α-P_4S_4 at room temperature; NMR studies show that it is a very minor component of fused P/S mixtures, suggesting that it is thermodynamically unstable with respect to other phosphorus sulphides. Fig. 2 is an *ORTEP* plot of the molecule.

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Potassium Tetrachloroaluminate

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Abstract. $KAlCl_4$, monoclinic, $P2_1$ (non-standard setting with unique axis *a*), a = 10·481 (9), b = 7·183 (5), c = 9·273 (5) Å, α = 93·10 (3)°, Z = 4, D_c = 1·98 g cm^{-3}. The structure was refined to an R of 0·035 for 1501 counter reflections with $I > 3\sigma(I)$. The salt contains discrete $AlCl_4^-$ anions and K^+ cations. The $AlCl_4^-$ tetrahedra are distorted (average Al—Cl = 2·129 Å). The structure is a slight deformation of that of $NOAlCl_4$ ($BaSO_4$ type).

Introduction. In the alkaline and pseudo-alkaline tetrachloroaluminates the Rb^+, Cs^+ (Gearhart, Beck & Wood, 1975), NO^+ (Barbier, Mairesse, Wignacourt & Baert, 1976) and NH_4^+ (Mairesse, Barbier, Wignacourt, Rubbens & Wallart, 1977) salts crystallize in the space group *Pnma*. For the Na^+ salt, symmetry decreases to $P2_12_12_1$ (Baenziger, 1951) and for Li^+ to $P2_1/c$ (Mairesse, Barbier, Wignacourt & Baert, 1977). In most tetrahedral compounds such as tetrafluoroborates (Clark & Lynton, 1969) or perchlorates (Johansson & Lindqvist, 1977), the K^+ is always isostructural with the Rb^+ and NH_4^+ salts, whereas in the tetrachloroaluminates, a preliminary study showed that $KAlCl_4$ crystallized in a monoclinic system. The crystal structure of $KAlCl_4$ was determined to gain an understanding of the structural evolution of this family.

Single crystals were prepared and isolated by a method previously described (Barbier & Mairesse, 1971). The highly hygroscopic crystals were mounted in quartz capillaries.

We used a pear-shaped crystal with numerous faces and maximum dimensions 0·25 × 0·25 × 0·30 mm. The cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections centered on a Philips PW 1100 automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ = 0·7107 Å). Owing to the similarity of the cell parameters with those of $NOAlCl_4$ [a = 10·411 (8), b = 7·055 (3), c = 9·461 (5) Å], we ascribed a non-standard setting to the unit cell, with the twofold screw axis coincident with **a**. In this setting, systematic absences were $h00$: h odd, possible space groups $P2_1$ or $P2_1/m$. Data were collected on the diffractometer with an ω–2θ scan technique, a scan width of 1·60°, a scan speed of 0·03° s^{-1}, and background counts at each extremity for half the scan time. 2247 independent reflections were obtained. No absorption correction was applied (μ = 22·6 cm^{-1}).