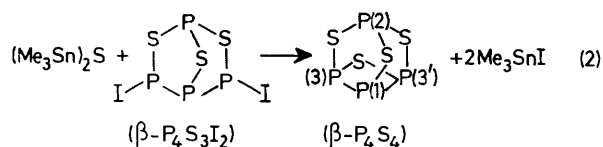
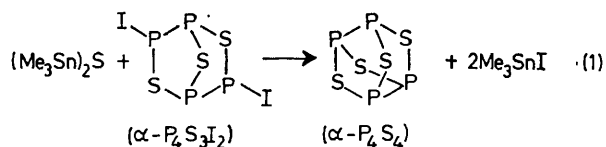


Two New Molecular Phosphorus Sulphides: α -P₄S₄ and β -P₄S₄; X-Ray Crystal Structure of α -P₄S₄

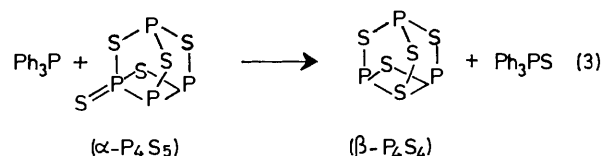
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Summary α -P₄S₄ and β -P₄S₄ are formed quantitatively by the action of (Me₃Sn)₂S on α -P₄S₃I₂ and β -P₄S₃I₂ respectively; X-ray crystal structure analysis shows that α -P₄S₄ possesses *D*_{2d} molecular symmetry in the crystal.

FOURIER transform phosphorus n.m.r. spectra indicate that at least five previously unreported molecular binary phosphorus sulphides are present in fused P₄S₃-P₄S₇ mixtures.¹ We find that two of these species, both of composition P₄S₄, are formed quantitatively by the action of an excess of (Me₃Sn)₂S on the two isomers of P₄S₃I₂ in CS₂ solution [equations (1) and (2)].



The mass spectra of both isomers exhibit molecular ions, though there appears to be some disproportionation of β -P₄S₄ on the probe; neither possesses an i.r. absorption in the region 600–700 cm⁻¹, suggesting that no terminal P=S units are present. α -P₄S₄ is stable indefinitely in CS₂ solution, and gives a single line phosphorus n.m.r. spectrum (δ -89.4 p.p.m. from external P₄O₆), consistent with the molecular structure found in the crystal by X-ray diffraction. The phosphorus spectrum of β -P₄S₄ was assigned as an AMX₂ spin system, with *J*_{1,2} 50.4(2), *J*_{1,3} 168.4(2), and *J*_{2,3} 18.2(2) Hz, and δ ₁ +26.96(1), δ ₂ -62.09(1), and δ ₃ -94.97(1) p.p.m. N.m.r. spectra show that the initial products of the reaction of triphenylphosphine with α -P₄S₅



in CS₂ are triphenylphosphine sulphide and β -P₄S₄ [equation (3)]. After several days some P₄S₃ and α -P₄S₄ are also formed, possibly *via* disproportionation of β -P₄S₄. The structure proposed for β -P₄S₄ is based on the spectroscopic evidence and the two methods of preparation; it is difficult

to isolate a sample uncontaminated with α - P_4S_4 , and we have not yet obtained crystals suitable for X-ray structure determination.

The crystals of α - P_4S_4 are monoclinic, space group $C2/c$, $a = 9.771(8)$, $b = 9.047(7)$, $c = 8.746(6)$ Å, $\beta = 102.67(6)^\circ$, $Z = 4$, $U = 754.3$ Å³, $D_c = 2.22$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 36.91$ cm⁻¹. 2524 data were measured with a Syntex P2₁ 4-circle diffractometer with graphite monochromated Mo-K α radiation, and were corrected for absorption. Equivalent reflections were averaged to give 1121 unique observed reflections [$F > 4\sigma(F)$]. The structure was solved by multi-solution Σ -2 sign expansion and refined anisotropically to R_w 0.029. The molecule possesses D_{2d} ($42m$) symmetry within experimental error, and a two-fold crystallographic axis which passes through S-1 and S-2. The observed temperature factors give good agreement with the rigid body model of molecular libration; the librational corrected dimensions averaged for D_{2d} symmetry are given in the Figure. The uncorrected bond lengths are ca. 0.010 Å shorter. Even the uncorrected P-P distance is significantly longer than the longest P-P bond in other phosphorus sulphides [2.326(7) Å in P_4S_7];³ it is likely that kinetic rather than thermodynamic factors are responsible for the stability of α - P_4S_4 .

It is difficult to reconcile these results with the report⁴ by Vincent and Vincent-Forat that a P-S melt of composition 1:1 consists of a compound P_4S_4 with a proposed structure different from either of the isomers reported here. Their

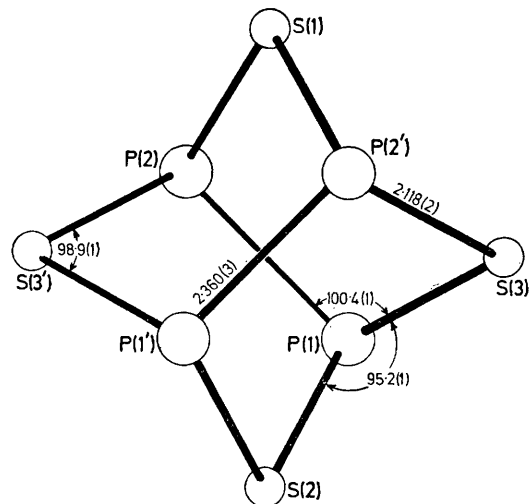


FIGURE. X-Ray structure of α - P_4S_4 ; distances in Å.

i.r. spectrum, however, is entirely consistent with the mixture of components of such melts revealed by n.m.r. spectroscopy.

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⁴ H. Vincent and C. Vincent-Forat, *Bull. Soc. chim. France*, 1973, 499.