# Crystal and Molecular Structure of Tetraphenylcyclotetraphosphine Monosulphide

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*Summary* The title compound, $(C_6H_5P)_4S$, has been structurally characterised by a single crystal X-ray study, and contains a 5-membered $P_4S$ ring.

PENTAPHENYLCYCLOPENTAPHOSPHINE $Ph_5P_5$ reacts with sulphur to give $Ph_3P_3S_3$,[1] from which tributylphosphine abstracts sulphur to form $Ph_4P_4S$; various structural formulae have been suggested for both sulphides.[2-4] We have

also prepared the monosulphide from phenyldichlorophosphine and potassium sulphide, and by the reaction of phenylphosphonothioic dichloride with phenylphosphine. The preparative reactions are structurally uninformative, and we have therefore determined the structure of the

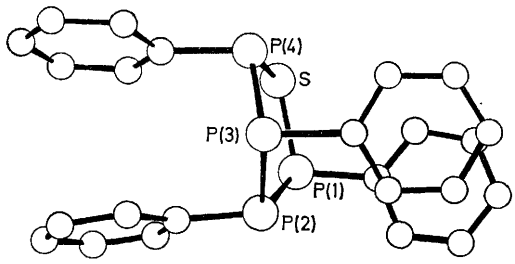


FIGURE. *The structure of tetraphenylcyclotetraphosphine monosulphide.*

phenyl monosulphide. Crystals of $Ph_4P_4S$ are orthorhombic, $a = 24{\cdot}700(6)$, $b = 13{\cdot}508(3)$, $c = 13{\cdot}410(2)$ Å, $Z = 8$, space group *Pbca*. The structure was determined with Mo-$K_\alpha$ diffractometer data by direct methods, and was refined by full-matrix least-squares methods to $R = 0{\cdot}083$ for 1475 observed reflections. The structure of the molecule is based on a five-membered $P_4S$ ring, as shown in the Figure, and not a four-membered $P_4$ ring, as suggested previously.[5] Mean bond lengths are: P–P, 2·190(5); P–S, 2·116(5); P–C, 1·831(22); C–C, 1·382(16) Å. The $P_4S$ ring is significantly nonplanar, deviations from the mean plane being: P(1), 0·19; P(2), −0·24; P(3), 0·24; P(4), −0·15; S, −0·02 Å. The phenyl groups are nearly perpendicular to the mean plane, the pairs on the same side of the ring being roughly parallel to each other, but perpendicular to the other pair. The endocyclic angles at phosphorus range from 104·2(2)° to 105·9(2)°, mean 105·2°, and the angle at sulphur is 110·4(2)°. The near equality of the angles at phosphorus is to be contrasted with the variability of those in $Ph_5P_5$,[6] in which the angles range from 94·1° to 107·2°, mean 100°. The stability of the monosulphide, indicated by the variety of synthetic methods and the difficulty of removing the remaining sulphur with tributylphosphine, may be due in part to the larger and more regular angles at phosphorus, themselves a result of reduced steric repulsions of the phenyl groups.

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