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Structure of Tetra-*tert*-butylcyclotetraphosphane Monosulfide, (C₄H₉P)₄S

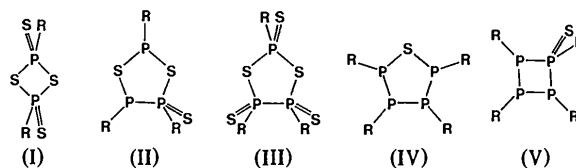
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Abstract. C₁₆H₃₆P₄S, *M_r* = 384.3, monoclinic, *P*2₁/*m*, *a* = 9.542 (2), *b* = 11.324 (2), *c* = 10.518 (4) Å, β = 101.84 (1)°, *V* = 1112 (1) Å³, *Z* = 2, *D_x* = 1.15, *D_m* = 1.16 (1) g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 4.2 cm⁻¹, *F*(000) = 416, *T* = 293 K, *R* = 0.030 for 1399 reflections with *F_o*² > 3σ(*F_o*²). The molecule has a non-planar ring of four P atoms; each is bonded to one *tert*-butyl group and one is bonded to an exocyclic S atom. The P–P distances are 2.214 (1) to 2.222 (1) Å, the P–P–P angles range from 86.46 (2) to 90.17 (2)°, and the P–P–P–P torsion angles average 20.05 (5)°. The P–C distances average 1.885 (5) Å and the P=S distance is 1.954 (1) Å.

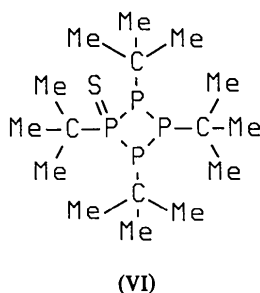
Introduction. Four different stoichiometries are well established for molecules composed of sulfur and organophosphorus (P–R, R = aryl or alkyl) moieties: (PR)₂S₄ (I), (PR)₃S₃ (II), (PR)₃S₅ (III), and (PR)₄S (IV) or (V). As shown, these molecules have been found to be cyclic with either four- or five-membered rings.



The four-membered-ring structure shown for (I) has been verified by X-ray structure determinations of the methyl (Wheatley, 1962; Daly, 1964) and *tert*-butyl (Shore, Pennington, Noble & Cordes, 1988) molecules. The (PR)₃S₃ molecule was first reported as a tetramer (Maier, 1963); the asymmetric structure (II) of R₃P₃S₃ (R = aryl) rather than the initially assumed six-membered P₃S₃ ring is the conclusion of two independent NMR studies (LeGeyt & Paddock, 1975; Baudler, Koch, Vakraatsas, Tolls & Kipker, 1975). The (PR)₃S₅ stoichiometry has only been reported (Burg & Parker, 1970) for R = CF₃; structure (III) is proposed on the basis of NMR spectral analysis. Structure (V) was

originally proposed for $\text{Ph}_4\text{P}_4\text{S}$ (Maier, 1963), but an X-ray structure determination (Calhoun & Trotter, 1974) showed the correct structure to be the five-membered ring of (IV); structure (IV) has also been used to rationalize the NMR spectrum of $\text{Ph}_4\text{P}_4\text{S}$ in solution (Hoffman & Caulton, 1975).

These molecules have been prepared by a wide variety of reactions which employ simple, chloro, linear anion, or cyclic organophosphines as the P-R source, and S, H_2S , or S_xCl_2 ($x = 1, 2,$ or 3) as the sulfur source. In this paper we report that $R_4\text{P}_4\text{S}$ ($R = \textit{tert}$ -butyl) (VI), as prepared by a photochemical reaction of tetra-*tert*-butylcyclotetraphosphane with elemental sulfur, was found to be the first example of a type (V) structure; this is in contrast to the five-membered ring (type IV) of the phenyl analogue.



Experimental. Title compound prepared by 40 min irradiation of CS_2 solution of $(\text{C}_4\text{H}_9\text{P})_4$ and sulfur in a quartz tube under nitrogen with 254 nm Hg lamps. Product purified by sublimation (0.01×10^5 Pa, 393 K) and crystals obtained from ethanol/diethyl ether (6:1) solution. Pale-yellow parallelepiped crystal ($0.30 \times 0.36 \times 0.42$ mm) used for data collection mounted with epoxy on a glass fiber. Data collected with an Enraf-Nonius CAD-4 diffractometer and graphite-monochromated $\text{Mo K}\alpha$ radiation using ω - 2θ scans of 4 to $16^\circ \text{ min}^{-1}$ in θ . Density measured by suspension in aqueous zinc chloride solution. Unit cell determined from least-squares analysis of angle data for 25 reflections with $16 < 2\theta < 20^\circ$. Data collected to $(\sin\theta)/\lambda$ of 0.70 \AA^{-1} , $0 < h < 10$, $-12 < k < 12$, $-11 < l < 11$. Three standard reflections (107, 520, 017) decayed less than 1.6% over 57.0 h of data collection. 3117 reflections measured, 1542 unique ($R_{\text{int}} = 0.010$), 143 reflections with $I < 3\sigma(I)$. The analytical absorption correction ranged from 0.62 to 1.00. No extinction correction was made. Solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier methods. Full-matrix least squares minimized $\sum w(|F_o| - |F_c|)^2$. H-atom positional parameters [except H(32)] were refined with fixed isotropic B of 1.2 times the B value of the attached C atoms. Because H(32) did not refine to a reasonable position it was constrained to an idealized position. All non-H

atoms refined anisotropically for 158 parameters. $R = 0.030$, $wR = 0.044$, $S = 3.4$, where non-Poisson $w^{-1} = [\sigma^2(I) + (0.015I)^2]/4F^2$. Final $(\Delta/\sigma)_{\text{max}} < 0.12$, $\Delta\rho_{\text{max}} = 0.26$ (5) and $\Delta\rho_{\text{min}} = -0.30$ (5) e \AA^{-3} on final difference map. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974) and programs used were those of Enraf-Nonius (1982) *SDP*.* Table 1 gives the atomic coordinates and Table 2 selected bond distances and angles. Fig. 1 shows the molecule with the numbering scheme.

Discussion. The photochemical aspects of the synthesis apparently involve activation of the phosphane ring since it has an absorption peak at 257 nm and prolonged irradiation of the phosphane alone converts it to $(\text{C}_4\text{H}_9\text{P})_3$. The CS_2 solvent is not the source of the sulfur in the product as verified by a non-productive irradiation of $(\text{C}_4\text{H}_9\text{P})_4$ in CS_2 .

The structure of $(\text{C}_4\text{H}_9\text{P})_4\text{S}$ reveals a P_4 ring with an exocyclic S atom. The molecule has lattice-imposed C_s symmetry and the central P_4 ring is nonplanar with torsion angles of 20.10 (3) and 20.00 (3) $^\circ$ [dihedral angles of fold of 151.1 (1) to 151.9 (1) $^\circ$]. The $\text{P}=\text{S}$ distance of 1.954 (1) \AA falls within the normal range found for this linkage: 1.921 (1) \AA for the *tert*-butyl (Shore *et al.*, 1988) and 1.945 (5) \AA for the methyl (Daly, 1964) derivatives of $\text{R}_2\text{P}_2\text{S}_4$, and 1.978 (2) \AA for $\text{P}_4\text{S}_8^{4-}$ (Falius, Krause & Sheldrick, 1981). There are no unusual intermolecular contacts. The variations in the $\text{P}-\text{P}$ distances indicate that steric factors outweigh the

* Tables of H-atom coordinates, distances and angles involving H atoms, anisotropic temperature factors, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51324 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

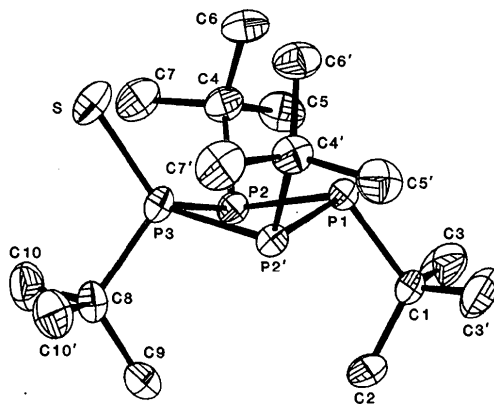


Fig. 1. ORTEP (Johnson, 1976) drawing and numbering scheme. The ellipsoids are drawn at the 30% probability surface and the H atoms have been omitted for figure clarity.

Table 1. Final fractional coordinates and B_{eq} thermal factors for non-H atoms

E.s.d.'s in parentheses are in the units of the least-significant digit.

$$B_{eq} = \frac{4}{3} \sum_i \sum_j b_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j)$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
P(1)	0.21289 (8)	0.750	0.43381 (7)	3.52 (2)
P(2)	0.30693 (5)	0.88842 (5)	0.32839 (5)	3.59 (1)
P(3)	0.32239 (8)	0.750	0.18221 (7)	3.65 (2)
S	0.1946 (1)	0.750	0.01128 (8)	6.00 (2)
C(1)	0.3295 (3)	0.750	0.6022 (3)	4.25 (7)
C(2)	0.4872 (4)	0.750	0.6072 (4)	7.0 (1)
C(3)	0.2904 (3)	0.8585 (3)	0.6692 (2)	8.18 (9)
C(4)	0.1519 (2)	0.9894 (2)	0.2612 (2)	4.63 (5)
C(5)	0.1416 (3)	1.0710 (2)	0.3742 (3)	6.28 (7)
C(6)	0.1965 (3)	1.0581 (3)	0.1519 (3)	6.62 (7)
C(7)	0.0084 (3)	0.9290 (2)	0.2131 (3)	5.93 (6)
C(8)	0.5148 (3)	0.750	0.1656 (3)	4.65 (7)
C(9)	0.6166 (3)	0.750	0.2964 (4)	5.68 (9)
C(10)	0.5372 (3)	0.8605 (3)	0.0906 (2)	7.20 (7)

Table 2. Selected bond distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

P(1)–P(2)	2.214 (1)	C(1)–C(3)	1.501 (2)
P(1)–P(3)	2.222 (1)	C(4)–C(5)	1.524 (2)
P(1)–P(3)	3.038 (1)	C(4)–C(6)	1.519 (2)
P(2)–P(2')	3.135 (1)	C(4)–C(7)	1.521 (2)
P(3)–S	1.954 (1)	C(8)–C(9)	1.513 (3)
P(1)–C(1)	1.888 (2)	C(8)–C(10)	1.518 (2)
P(2)–C(4)	1.888 (2)	C–H (av.)	0.94
P(3)–C(8)	1.880 (2)	C–H (range)	0.86–0.99
C(1)–C(2)	1.495 (3)		
P(1)–P(2)–P(3)	86.46 (2)	P(2)–C(4)–C(7)	115.8 (1)
P(2)–P(3)–P(2')	89.75 (2)	P(3)–C(8)–C(9)	111.9 (1)
P(2)–P(1)–P(2')	90.17 (2)	P(3)–C(8)–C(10)	107.0 (1)
P(2)–P(3)–S	121.28 (2)	C(2)–C(1)–C(3)	109.2 (1)
P(1)–P(2)–C(4)	104.45 (5)	C(5)–C(4)–C(6)	110.6 (1)
P(2)–P(1)–C(1)	104.39 (4)	C(3)–C(1)–C(3')	109.9 (2)
P(3)–P(2)–C(4)	109.04 (4)	C(6)–C(4)–C(7)	110.6 (1)
P(2)–P(3)–C(8)	105.61 (4)	C(5)–C(4)–C(7)	109.5 (1)
C(8)–P(3)–S	110.57 (6)	C(9)–C(8)–C(10)	109.9 (1)
P(1)–C(1)–C(2)	115.3 (1)	C(10)–C(8)–C(10')	111.1 (2)
P(1)–C(1)–C(3)	106.6 (1)	C–C–H (range)	106–115
P(2)–C(4)–C(5)	104.2 (1)	H–C–H (range)	102–115
P(2)–C(4)–C(6)	105.9 (1)		

Primed atoms are related to the unprimed by $x, 1.5-y, z$.

effects due to the two different oxidation states of P: the P^V atom has P–P distances of 2.222 (1) \AA compared to the others at 2.214 (1) \AA . The crowded environment at the oxidized P atom has the *exo*-bonded S atom at the van der Waals contact distance of 2.80 (2) \AA to H atoms of the C(7) methyl groups on adjacent P atoms. As a result of these contacts these *tert*-butyl groups are bent away from the S atom: P(3)–P(2)–C(4) is 109.04 (4) $^\circ$ whereas the other P–P–C angles are 104.39–105.61 $^\circ$, and the P–P(3)–S angles have opened to 121.28 (2) $^\circ$ while the P–P(3)–C and S–P(3)–C angles are closer to tetrahedral values. In all of the $(RP)_4$ organophosphanes reported the P–C–X ($X = C, F, \text{ or } H$) angle involving the X group oriented toward the ring center is significantly larger than the

other P–C–X angles even though all cross-ring contacts are longer than the sum of the appropriate van der Waals radii, and that is the case in the present structure also: the P–C–C angles range from 111.9 to 115.8 $^\circ$ for those oriented toward the ring center and from 104.2 to 107.0 $^\circ$ for the others. For cyclophosphanes with P_4 rings the P–P distances are relatively insensitive to electronegativity and steric differences in the *exo* groups: the value of 2.218 (4) \AA in this report compares to the 2.224 (2) \AA value for $(C_6H_{11}P)_4$ (Bart, 1969), to 2.213 (5) \AA for $(CF_3P)_4$ (Palenik & Donohue, 1962), to 2.211 (2) \AA for $(C_4H_9P)_4$ (Weigand, Cordes & Swepston, 1981), and to 2.283 (4) \AA for $P_4S_8^{4-}$ (Falius *et al.*, 1981). Perhaps the largest difference in the ring parameters of these molecules is the approach to planarity of the P_4 ring; P–P–P–P torsion angles vary from 34 $^\circ$ for $(CF_3P)_4$ to 0 $^\circ$ for $P_4S_8^{4-}$. In this regard it is interesting to note that the addition of one *exo* S atom to the *tert*-butyl tetramer decreases the P–P–P–P torsion angles from 24.51 (4) to 20.05 (5) $^\circ$ as an approach to the planarity found for $P_4S_8^{4-}$.

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