Preparation and Crystal Structures of Two Phosphorus–Sulphur Rings: $(PhP)_3S_3$ and $(PhP)_2S_4$ †

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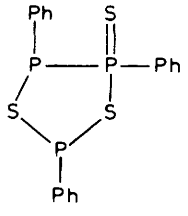
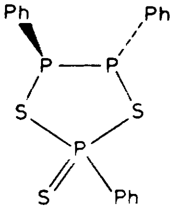
The 1 : 1 reaction between $PPhCl_2$ and $(SnMe_3)_2S$ in CS_2 provides a convenient direct route to $(PhP)_3S_3$ (1), which reacts with elemental sulphur to give $(PhP)_2S_4$ (2). Both structures have been determined by *X*-ray diffraction using twinned crystals. Compound (1) is monoclinic, space group $P2_1$ with a = 8.884(2), b = 13.713(2), c = 8.309(2) Å, β = 106.61(2)°, Z = 2, and R = 0.051 for 1 938 unique observed reflections. The structure contains an unsymmetrical five-membered ring with one exocyclic sulphur, and does not agree with a previous proposal based on n.m.r. data. Compound (2) is monoclinic, space group $P2_1/c$, with a = 6.624(1), b = 14.438(3), c = 7.667(2) Å, β = 95.31(2)°, Z = 2, and R = 0.060 for 880 unique observed reflections. The four-membered ring with two *trans* exocyclic sulphurs possesses a crystallographic centre of symmetry.

The compound of empirical formula $(PhP)_3S_3$ (1) has been reported by a number of authors. A very thorough study by Baudler *et al.*[1] showed that various reaction conditions all led to the same isomer, to which the structure (1a) was assigned on the basis of spectroscopic evidence, in particular the ABX proton-decoupled ^{31}P n.m.r. spectrum. Structure (1b), which with *trans* phenyl groups attached to the two trivalent phosphorus atoms should also give an ABX spectrum, was rejected because the ^{31}P chemical shifts did not appear to be consistent with the structure. In the course of our work on the reactions of organotin sulphides with phosphorus–halogen bonds, which enable phosphorus sulphides and their derivatives to be prepared under very mild conditions, we have synthesised a compound which is analytically and spectroscopically identical to that studied by Baudler *et al.*[1] Since the assignment of the n.m.r. spectrum appeared ambiguous to us, we attempted to grow single crystals for *X*-ray analysis. In common with previous work,[1,2] all our attempts yielded twinned crystals, so we eventually decided to determine the structure using data from a twinned crystal.

Reaction of (1) with sulphur yields the known[3] $(PhP)_2S_4$ (2). We also determined the structure of (2) from *X*-ray data from a twinned crystal.



(1a)



(1b)

Experimental

Phosphorus-31 n.m.r. spectra were measured on a Bruker WP 80SY Fourier-transform spectrometer with 85% H_3PO_4 as external standard and mass spectra by electronic ionisation at 70 eV on a Varian CH5 spectrometer. Solvents were dried and distilled before use. Elemental analyses were performed by Beller in Göttingen. Light petroleum used had b.p. 40—60 °C.

Preparation of $(PhP)_3S_3$ (1).—$(SnMe_3)_2S$ (6 g, 16.7 mmol) in CS_2 (50 cm^3) was added dropwise to a stirred solution of $PPhCl_2$ (3 g, 16.7 mmol) in CS_2 (100 cm^3) at −30 °C. The solvent and trimethyltin chloride were removed under reduced pressure at 50 °C. Compound (1) remained as a white powder (1.65 g, 70% yield) (Found: C, 50.6; H, 3.85; P, 22.2; S, 21.3. $C_{18}H_{15}P_3S_3$ requires C, 51.4; H, 3.60; P, 22.1; S, 22.9%). Crystals for *X*-ray examination were grown from a 1 : 1 : 2 CS_2–toluene–light petroleum mixture at −20 °C. The proton-decoupled ^{31}P n.m.r. spectrum was analysed as an ABX spin system, yielding the parameters: J_{AX} ± 7.5, J_{BX} ± 13.0, and J_{AB} 263.4 Hz; δ(A) 76.12, δ(B) 88.05, and δ(X) 157.61 p.p.m. in CS_2. Mass spectrum: m/e 420 (relative intensity 1.2%, M), 388 (16, $M - S$), 356 (8, $M - 2S$), 344 (6.2, $Ph_2P_2S_4$), 324 (6.8, Ph_3P_3), 249 (19.8, Ph_2PS_2), 248 (99, Ph_2P_2S), 217 (18, Ph_2PS), 185 (100, Ph_2P), 183 [93, $(C_6H_4)_2P$], 172 (40, $PhPS_2$), 171 (27, PhP_2S), 140 (19, PhPS), 107 (61, C_6H_4P), 77 (33, Ph), and 63 (49, PS).

Preparation of $(PhP)_2S_4$ (2).—Compound (1) (1.75 g, 4.16 mmol) was refluxed in CS_2 (50 cm^3) with excess sulphur (0.4 g, 12.5 mmol). Compound (2) was obtained as white crystals on the addition of light petroleum, yield 1.3 g (3.8 mmol, 61%) (Found: C, 42.1; H, 3.05; P, 17.7; S, 37.2. $C_{12}H_{10}P_2S_4$ requires C, 41.9; H, 2.95; P, 18.0; S, 37.2%). The proton-decoupled ^{31}P n.m.r. spectrum gave a single peak at δ(^{31}P) = 15.16 p.p.m. in CS_2. Mass spectrum: m/e 344 (relative intensity 55%, M), 248 (32, Ph_2P_2S), 216 (14, Ph_2P_2), 172 (100, $PhPS_2$), 171 (58, PhP_2S), 139 (7.8, PhP_2), 108 (14, PhP), and 63 (28, PS).

Crystal Data for (1).—$C_{18}H_{15}P_3S_3$, M = 420.42, monoclinic, space group $P2_1$, a = 8.884(2), b = 13.713(2), c = 8.309(2) Å, β = 106.61(2)°, Z = 2, U = 970.1 Å^3, D_c = 1.439 g cm^{-3}, $F(000)$ = 432, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 6.09 cm^{-1}, crystal dimensions 0.5 × 0.25 × 0.05 mm.

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† 2,4,5-Triphenyl-2-thioxo-1,3,2λ^5,4,5-dithiatriphospholane and 2,4-diphenyl-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane respectively.

Supplementary data available (No. SUP 23838, 21 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Atom co-ordinates (× 10⁴) for (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
P(1)	5 800(2)	5 000	4 878(2)
P(2)	3 671(2)	4 078(2)	3 980(2)
P(3)	6 949(2)	2 628(1)	5 130(2)
S(2)	4 621(2)	2 734(2)	3 525(2)
S(1)	7 361(2)	3 978(2)	6 381(2)
S(3)	7 355(2)	1 598(2)	6 789(2)
C(11)	6 445(7)	5 120(5)	2 976(8)
C(12)	5 364(9)	5 237(5)	1 405(9)
C(13)	5 887(11)	5 388(6)	6(11)
C(14)	7 451(11)	5 419(5)	149(11)
C(15)	8 535(11)	5 301(6)	1 697(14)
C(16)	8 061(9)	5 143(6)	3 134(12)
C(21)	3 177(7)	3 933(5)	5 961(8)
C(22)	3 605(8)	3 129(5)	7 046(9)
C(23)	3 061(10)	3 072(6)	8 445(11)
C(24)	2 134(9)	3 805(6)	8 807(10)
C(25)	1 735(8)	4 591(5)	7 753(9)
C(26)	2 253(7)	4 659(5)	6 331(9)
C(31)	8 137(7)	2 517(4)	3 707(8)
C(32)	7 634(8)	2 773(6)	2 018(10)
C(33)	8 611(11)	2 645(7)	1 008(11)
C(34)	10 069(12)	2 290(5)	1 669(13)
C(35)	10 621(10)	2 037(6)	3 299(14)
C(36)	9 655(8)	2 160(5)	4 364(11)

Table 2. Bond lengths (Å) and angles (°) for (1)

P(1)–P(2)	2.219(2)	P(1)–S(1)	2.111(2)
P(1)–C(11)	1.836(8)	P(2)–S(2)	2.106(3)
P(2)–C(21)	1.832(7)	P(3)–S(2)	2.121(2)
P(3)–S(1)	2.103(3)	P(3)–S(3)	1.934(3)
P(3)–C(31)	1.803(8)	C(11)–C(12)	1.391(9)
C(11)–C(16)	1.405(10)	C(12)–C(13)	1.385(13)
C(13)–C(14)	1.361(14)	C(14)–C(15)	1.378(13)
C(15)–C(16)	1.392(16)	C(21)–C(22)	1.405(10)
C(21)–C(26)	1.381(10)	C(22)–C(23)	1.383(13)
C(23)–C(24)	1.387(12)	C(24)–C(25)	1.369(11)
C(25)–C(26)	1.388(11)	C(31)–C(32)	1.391(10)
C(31)–C(36)	1.391(9)	C(32)–C(33)	1.380(14)
C(33)–C(34)	1.345(13)	C(34)–C(35)	1.347(15)
C(35)–C(36)	1.408(15)		

P(2)–P(1)–S(1)	100.0(1)	P(2)–P(1)–C(11)	102.0(2)
S(1)–P(1)–C(11)	104.8(2)	P(1)–P(2)–S(2)	102.3(1)
P(1)–P(2)–C(21)	99.2(2)	S(2)–P(2)–C(21)	106.1(2)
S(2)–P(3)–S(1)	104.6(1)	S(2)–P(3)–S(3)	116.6(1)
S(1)–P(3)–S(3)	108.7(1)	S(2)–P(3)–C(31)	104.0(2)
S(1)–P(3)–C(31)	110.3(2)	S(2)–P(3)–C(31)	112.4(2)
P(2)–S(2)–P(3)	108.4(1)	P(1)–S(1)–P(3)	107.4(1)
P(1)–C(11)–C(12)	121.1(6)	P(1)–C(11)–C(16)	119.0(5)
C(12)–C(11)–C(16)	119.9(8)	C(11)–C(12)–C(13)	119.8(8)
C(12)–C(13)–C(14)	120.7(8)	C(13)–C(14)–C(15)	120.1(10)
C(14)–C(15)–C(16)	121.1(9)	C(11)–C(16)–C(15)	118.4(7)
P(2)–C(21)–C(22)	124.8(6)	P(2)–C(21)–C(26)	115.6(5)
C(22)–C(21)–C(26)	119.5(7)	C(21)–C(22)–C(23)	119.2(7)
C(22)–C(23)–C(24)	120.9(8)	C(23)–C(24)–C(25)	119.5(8)
C(24)–C(25)–C(26)	120.6(7)	C(21)–C(26)–C(25)	120.2(7)
P(3)–C(31)–C(32)	124.1(5)	P(3)–C(31)–C(36)	117.1(6)
C(32)–C(31)–C(36)	118.7(7)	C(31)–C(32)–C(33)	120.3(7)
C(32)–C(33)–C(34)	119.9(8)	C(33)–C(34)–C(35)	122.3(11)
C(34)–C(35)–C(36)	119.3(8)	C(31)–C(36)–C(35)	119.5(7)

Table 3. Atomic co-ordinates (× 10⁴) for (2) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
S(1)	6 468(3)	5 581(1)	1 230(2)
P	3 380(2)	5 209(1)	1 105(2)
S(2)	1 464(3)	6 210(1)	971(2)
C(2)	1 215(10)	4 266(4)	3 453(8)
C(6)	4 689(10)	3 794(4)	3 443(8)
C(3)	904(11)	3 585(5)	4 646(9)
C(1)	3 095(9)	4 369(4)	2 814(7)
C(5)	4 359(12)	3 128(5)	4 673(9)
C(4)	2 483(12)	3 024(5)	5 257(8)

Table 4. Bond lengths (Å) and angles (°) for (2); a prime denotes atoms generated by the centre of symmetry 1 − *x*, 1 − *y*, −*z*

S(1)–P	2.108(2)	S(1)–P′	2.133(2)
P–S(2)	1.920(2)	P–C(1)	1.808(6)
C(2)–C(1)	1.388(9)	C(2)–C(3)	1.371(9)
C(6)–C(5)	1.378(9)	C(6)–C(1)	1.394(9)
C(5)–C(4)	1.368(11)	C(3)–C(4)	1.370(10)

P–S(1)–P′	86.9(1)	S(1)–P–S(2)	116.3(1)
S(1)–P–C(1)	107.7(2)	S(2)–P–C(1)	115.5(2)
S(1)–P–S(1′)	93.1(1)	S(2)–P–S(1′)	116.1(1)
C(1)–P–S(1′)	105.4(2)	C(3)–C(2)–C(1)	120.5(6)
C(1)–C(6)–C(5)	119.3(6)	C(2)–C(3)–C(4)	119.7(7)
P–C(1)–C(2)	119.0(4)	P–C(1)–C(6)	121.6(5)
C(2)–C(1)–C(6)	119.3(5)	C(6)–C(5)–C(4)	120.5(6)
C(3)–C(4)–C(5)	120.7(6)		

Weissenberg photographs revealed that the crystal used for data collection (and all others examined) was twinned by reflection in (0 0 1). The identification of reflections required to derive an initial orientation matrix on the diffractometer was performed by hand on the basis of the photographic data, in order to ensure that all the reflections used belonged to the same twin component. Data were collected for $7 < 2\theta < 45°$ on a Stoe-Siemens 4-circle diffractometer using a profile fitting procedure,[4] and Lorentz, polarisation but not absorption corrections applied. Since the two twin components overlapped exactly for the *hk*0 reflections, an appropriate correction for the twin ratio (*ca.* 4 : 1) was applied initially, and separate scale factors were refined for batches based on $|I|$ at the isotropic stage of the structure refinement. 2 520 Unique data were measured, of which 1 938 with $F > 4\sigma(F)$ were used for all calculations, which were performed on a Data General Eclipse S-250 minicomputer using the SHELXTL program (written by G. M. S.). The structure was solved by multi-solution direct methods and refined with riding isotropic hydrogen atoms (C–H = 0.96 Å on external C–C–C bisectors), remaining atoms anisotropic, complex neutral-atom scattering factors, and weights $w^{-1} = [\sigma^2(F) + 0.0003\ F^2]$ to $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o| = 0.042$ ($R = \Delta\Sigma/\Sigma|F_o| = 0.051$). Refinement with the polar axis direction inverted gave *R* indices 0.005 higher. The final atomic co-ordinates are given in Table 1 and bond lengths and angles in Table 2.

Crystal Data for (2).—$C_{12}H_{10}P_2S_4$, $M = 344.40$, monoclinic, space group $P2_1/c$, $a = 6.624(1)$, $b = 14.438(3)$, $c = 7.667(2)$ Å, $\beta = 95.31(2)°$, $Z = 2$, $U = 730.1$ Å³, $D_c = 1.566$ g cm⁻³, $F(000) = 352$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 8.20$ cm⁻¹, crystal dimensions 0.3 × 0.05 × 0.05 mm.

The data collection and processing were performed as for (1), with the difference that (2) was twinned by reflection in (1 0 0). 1 667 Data with $7 < 2\theta < 50°$ were reduced to 1 258 unique reflections, of which 880 with $F > 4\sigma(F)$ were used for structure solution by direct methods and refinement with riding isotropic hydrogen atoms [C–H = 0.96 Å on external C–C–C bisectors, $U(\text{H}) = 1.2\ U_{\text{eq.}}(\text{C})$], the remaining atoms anisotropic, and $w^{-1} = [\sigma^2(F) + 0.003\ F^2]$. Refinement converged to $R' = 0.053$ and $R = 0.060$. Final atomic co-

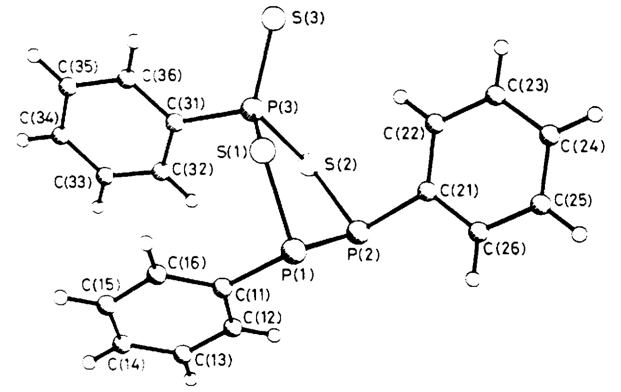

Figure 1. The molecule of $(PhP)_3S_3$ (1)

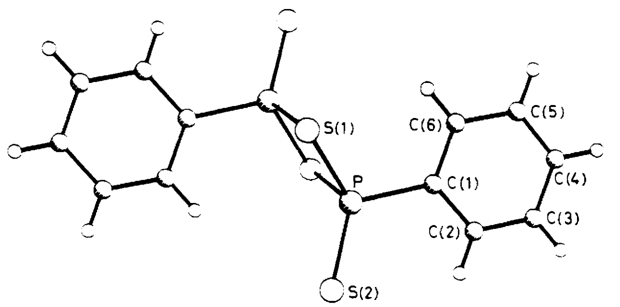

Figure 2. The molecule of $(PhP)_2S_4$ (2), with unique atoms labelled

ordinates are given in Table 3 and bond lengths and angles in Table 4.

Results and Discussion

Despite the use of twinned crystals, there were no serious problems in solving or refining the structures, and there is no evidence of systematic error in the results. A detailed *X*-ray photographic examination of the crystals was crucial to the success of the analysis. The molecular structures of (1) [≡(1b)] and (2) are shown in Figures 1 and 2 respectively. Whereas (1) possesses no symmetry, (2) lies on a crystallographic centre of symmetry, which obliges the exocyclic sulphur atoms to be *trans*. The conformation of (2) is similar to that reported[5] for $(MePS_2)_2$ (3). However, the P–S bonds in the four-membered ring of (2) are significantly different [2.108(2) and 2.133(2) Å], whereas in (3) they are equal [2.141(6) Å][5] as a result of space-group symmetry. Compound (1) possesses a slightly puckered five-membered ring, and also shows some variation of endocyclic P–S bond lengths. The phenyl groups on the trivalent phosphorus atoms are arranged *trans* to one another; since the environments of these two phosphorus atoms are almost identical, they can be assigned to the AB part of the ABX spin system. The chemical shifts of the ^{31}P atoms in the –S–P(S)Ph–S– groups in (1) and (2) thus differ by *ca.* 140 p.p.m., which underlines the danger of making structural assignments on the basis of ^{31}P chemical shifts in such molecules.

Acknowledgements

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