Preparation and Crystal Structures of two Phosphorus–Sulphur Rings: $(RPS)_4$ and $(RPS_2)_2$ ($R = C_6H_2Me_3$-2,4,6) †

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The 1 : 1 reaction between $PRCl_2$ ($R = C_6H_2Me_3$-2,4,6) and $(Me_3Si)_2S$ in toluene yields $(RPS)_4$ (1) which slowly disproportionates under mild conditions (35—40 °C, 3 d) to $(RPS_2)_2$ (2). Both structures have been determined by *X*-ray diffraction. Compound (1) is monoclinic, space group *Cc*, with a = 2 299.3(7), b = 1 167.9(3), c = 1 937.8(6) pm, β = 130.65(2)°, and Z = 4; R = 0.050 for 3 209 unique observed reflections. The eight-membered $(PS)_4$ ring adopts the crown conformation but is disordered. Compound (2) is monoclinic, space group $P2_1/c$, with a = 890.1(2), b = 1 845.2(12), c = 641.3(1) pm, β = 98.74(1)°, and Z = 2; R = 0.062 for 904 unique observed reflections. The four-membered ring with two *trans* exocyclic sulphurs possesses a crystallographic centre of symmetry.

Very few phosphorus–sulphur ring compounds of the type $(RPS)_n$ are described in the literature: $(PhPS)_3$ has been shown [1,2] to contain a five-membered ring, with one exocyclic P=S, and Lappert and co-workers [3] reported a six-membered $(RPS)_3$ ring with $R = C_6H_2Bu^t_3$-2,4,6. In the course of our study [2] of the reactions of organosilicon and organotin sulphides with phosphorus–halogen bonds, which enable phosphorus sulphides to be prepared under very mild conditions, we have synthesised a compound with the composition $(RPS)_x$ (1; $R = C_6H_2Me_3$-2,4,6 = mesityl). The molecular ion peak could not be observed in the mass spectrum and the proton-decoupled ^{31}P n.m.r. spectrum showed only a single line, so a crystal structure determination was required to establish the size of the PS ring. On warming a solution of compound (1), white crystals of $(RPS_2)_2$ (2; $R = C_6H_2Me_3$-2,4,6) separated, which were also employed for *X*-ray structure elucidation.

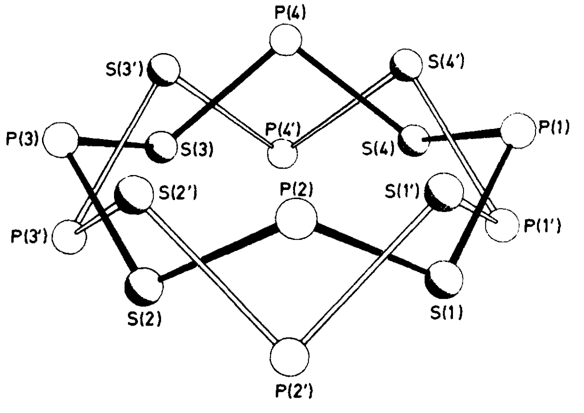

Figure 1. The $(PS)_4$ ring in compound (1), illustrating the disorder. The major [78.7(2)%] component corresponds to the shaded atoms and filled bonds

Experimental

Phosphorus-31 n.m.r. spectra were recorded on a Bruker WP 80 SY Fourier-transform spectrometer with 85% H_3PO_4 as external standard, mass spectra by electronic ionisation (e.i.) and field desorption (f.d.) at 70 eV (1.12×10^{-17} J) on a Varian CH5 spectrometer. Solvents were dried and distilled before use. Elemental analyses were performed by Beller in Göttingen.

Preparation of $(2,4,6\text{-}Me_3C_6H_2PS)_4$ (1).—Bis(trimethylsilyl) sulphide (5.5 g, 31 mmol) in toluene (50 cm^3) was added dropwise to a stirred solution of mesitylphosphorus dichloride (6.8 g, 31.0 mmol) in toluene (100 cm^3). The solvent and trimethylsilyl chloride were removed under reduced pressure. Compound (1) remained as a white powder (5.2 g, 92% yield) (Found: C, 59.25; H, 6.05; P, 16.85; S, 17.45. $C_{36}H_{44}P_4S_4$ requires C, 59.30; H, 6.10; P, 17.00; S, 17.60%). Crystals for *X*-ray examination were grown from a solution in toluene by slowly condensing in pentane at −30 °C. The proton-decoupled ^{31}P n.m.r. spectrum in toluene showed one single peak at δ = 85.87 p.p.m. Mass spectrum: f.d., *m/e* 332 (R_2P_2S); e.i., *m/e* 332 (relative intensity 59.4%, R_2P_2S), 299 (19.6, R_2P_2 − H), 214 (34.8, RPS_2), and 181 (100, RPS − H) ($R = C_6H_2Me_3$-2,4,6).

Preparation of $(2,4,6\text{-}Me_3C_6H_2PS_2)_2$ (2).—White crystals of compound (2) formed slowly when a solution of (1) (1.5 g, 2.0 mmol) in toluene was allowed to stand. After 3 d at 35 °C the yield was 0.31 g (0.7 mmol, 35%) (Found: C, 51.30; H, 5.25; P, 14.10; S, 29.15. $C_{18}H_{22}P_2S_4$ requires C, 50.45; H, 5.15; P, 14.45; S, 29.90%). The proton-decoupled ^{31}P n.m.r. spectrum in toluene exhibited a single peak at δ = 11.47 p.p.m. Mass spectrum: f.d., *m/e* 428 (relative intensity 1.9%, *M*), 396 (10.4, *M* − S), 364 (4.5, *M* − 2S), 332 (100, R_2P_2S), 214 (66.9, RPS_2), and 182 (18.2, RPS) ($R = C_6H_2Me_3$-2,4,6).

Crystal Data for Compound (1).—$C_{36}H_{44}P_4S_4$, M = 728.88, monoclinic, space group *Cc*, a = 2 299.3(7), b = 1 167.9(3), c = 1 937.8(6) pm, β = 130.65(2)°, U = 3.948 nm^3, Z = 4, D_c = 1.226 Mg m^{-3}, $F(000)$ = 1 536, λ(Mo-K_α) = 71.069 pm, μ(Mo-K_α) = 0.41 mm^{-1}, crystal dimensions 0.5 × 0.5 × 0.4 mm.

Data were collected for $2\theta < 50°$ on a Stoe-Siemens four-

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† Cyclotetra(mesitylphosphathiane) and cyclodi[mesityl(thio)-λ^5-phosphathiane].

Supplementary data available (No. SUP 56050, 7 pp.): H-atom co-ordinates, thermal parameters, full bond lengths and angles for compound (1). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Atom co-ordinates (× 10^4) for compound (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
P(1)	5 022(1)	4 145(2)	5 008(1)
P(2)	5 537(1)	4 770(2)	6 919(1)
P(3)	4 103(1)	6 359(2)	6 001(1)
P(4)	3 587(1)	5 751(2)	4 064(1)
P(1′)	4 730(4)	3 675(6)	4 889(4)
P(2′)	5 278(3)	4 295(5)	6 854(3)
P(3′)	3 816(3)	5 886(5)	5 870(3)
P(4′)	3 298(3)	5 268(5)	3 963(3)
S(1)	5 194(1)	3 289(2)	6 093(1)
S(2)	4 672(1)	5 047(2)	6 996(1)
S(3)	3 177(1)	5 551(2)	4 768(1)
S(4)	3 831(1)	4 091(2)	3 887(1)
S(1′)	5 661(3)	4 503(6)	6 110(4)
S(2′)	5 018(3)	5 995(5)	6 994(4)
S(3′)	3 631(3)	6 764(4)	4 777(3)
S(4′)	4 194(3)	5 017(5)	3 907(4)
C(11)	5 309(3)	3 041(4)	4 607(3)
C(12)	5 100(3)	1 898(5)	4 427(3)
C(13)	5 394(3)	1 206(6)	4 135(4)
C(14)	5 904(3)	1 616(6)	4 044(4)
C(15)	6 104(3)	2 749(6)	4 233(3)
C(16)	5 830(3)	3 483(5)	4 520(3)
C(12′)	4 550(3)	1 347(6)	4 509(4)
C(14′)	6 226(5)	876(8)	3 723(5)
C(16′)	6 067(4)	4 701(5)	4 672(4)
C(21)	6 270(3)	4 142(4)	8 036(3)
C(22)	6 967(3)	4 720(4)	8 547(3)
C(23)	7 600(3)	4 292(5)	9 384(3)
C(24)	7 561(3)	3 292(5)	9 729(3)
C(25)	6 879(3)	2 736(4)	9 242(3)
C(26)	6 215(2)	3 129(4)	8 401(3)
C(22′)	7 047(3)	5 863(5)	8 227(4)
C(24′)	8 277(3)	2 845(6)	10 657(3)
C(26′)	5 483(3)	2 461(5)	7 926(4)
C(31)	3 554(3)	7 012(4)	6 306(3)
C(32)	3 063(3)	6 475(5)	6 389(3)
C(33)	2 706(3)	7 129(5)	6 626(3)
C(34)	2 848(3)	8 250(6)	6 828(3)
C(35)	3 348(3)	8 770(5)	6 768(4)
C(36)	3 704(3)	8 178(5)	6 511(3)
C(32′)	2 864(4)	5 226(6)	6 231(4)
C(34′)	2 494(4)	8 952(8)	7 140(5)
C(36′)	4 250(4)	8 783(6)	6 453(5)
C(41)	2 661(2)	6 030(4)	2 875(3)
C(42)	1 977(3)	5 383(4)	2 414(3)
C(43)	1 333(3)	5 793(5)	1 571(3)
C(44)	1 349(3)	6 763(5)	1 167(3)
C(45)	2 044(3)	7 318(5)	1 633(3)
C(46)	2 688(3)	6 975(4)	2 486(3)
C(42′)	1 883(3)	4 311(5)	2 749(4)
C(44′)	638(4)	7 199(7)	277(4)
C(46′)	3 423(3)	7 656(5)	2 926(3)

Table 2. Selected bond lengths (pm) and angles (°) for compound (1)

P(1)–S(1)	211.9(1)	P(1)–S(4)	211.4(1)
P(1)–C(11)	183.6(1)	P(2)–S(1)	212.8(1)
P(2)–S(2)	211.4(1)	P(2)–C(21)	182.0(1)
P(3)–S(2)	211.9(1)	P(3)–S(3)	212.2(1)
P(3)–C(31)	186.9(1)	P(4)–S(3)	211.5(1)
P(4)–S(4)	210.8(1)	P(4)–C(41)	188.6(1)
S(1)–P(1)–S(4)	106.6(1)	S(1)–P(1)–C(11)	101.7(1)
S(4)–P(1)–C(11)	97.2(1)	S(1)–P(2)–S(2)	105.8(1)
S(1)–P(2)–C(21)	99.8(1)	S(2)–P(2)–C(21)	99.3(1)
S(2)–P(3)–S(3)	106.0(1)	S(2)–P(3)–C(31)	98.7(1)
S(3)–P(3)–C(31)	98.6(1)	S(3)–P(4)–S(4)	106.3(1)
S(3)–P(4)–C(41)	100.6(1)	S(4)–P(4)–C(41)	99.7(1)
P(1)–S(1)–P(2)	95.8(1)	P(2)–S(2)–P(3)	95.7(1)
P(3)–S(3)–P(4)	97.8(1)	P(1)–S(4)–P(4)	96.3(1)

circle diffractometer by a profile-fitting procedure,[4] and Lorentz, polarisation but no absorption corrections applied. 4 063 Unique data were measured of which 3 209 with $F > 4\sigma(F)$ were used for all calculations. The structure was solved by multisolution direct methods. After some cycles of refinement, difference electron-density syntheses indicated an alternative ring orientation and all further refinement was thus based on a disordered model (Figure 1). The minor component [21.3(2)%] was refined with isotropic P and S, but its C and H atoms could not be located separately (the mesityl groups of the two components overlap extensively). All P–S and all P–C bond lengths were restrained to be equal with a weight based on an estimated standard deviation (e.s.d.) of 1 pm; they refined to 212.7 (P–S) and 186.4 pm (P–C). The P, S, and C atoms of the major component were refined anisotropically, with a riding model for aromatic H [C–H 96 pm on external C–C–C bisectors, $U(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{C})$], rigid methyl groups [C–H 96 pm, H–C–H 109.5°, $U(\mathrm{H}) = 1.5\ U_{\mathrm{eq}}(\mathrm{C})$], complex neutral-atom scattering factors, and weights $w^{-1} = [\sigma^2(F) + 0.000\,25\ F^2]$. Refinement converged to $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o| = 0.047$ and $R = \Sigma\Delta/\Sigma|F_o| = 0.050$.

Table 3. Atomic co-ordinates (× 10^4) for compound (2) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
P(1)	4 685(2)	5 675(1)	977(3)
S(1)	6 049(3)	6 241(1)	2 932(3)
S(2)	4 487(3)	4 592(1)	1 864(3)
C(11)	2 810(8)	6 054(4)	238(10)
C(12)	2 599(8)	6 570(4)	−1 392(11)
C(13)	1 130(8)	6 846(4)	−2 018(11)
C(14)	−83(8)	6 627(4)	−1 088(12)
C(15)	189(8)	6 157(4)	616(11)
C(16)	1 614(8)	5 871(4)	1 325(11)
C(2)	3 850(9)	6 888(4)	−2 444(13)
C(4)	−1 650(9)	6 931(5)	−1 824(14)
C(6)	1 792(10)	5 413(5)	3 315(12)

Table 4. Bond lengths (pm) and angles (°) for compound (2); 'a' denotes atoms generated by the centre of symmetry $1 - x$, $1 - y$, $-z$

P(1)–S(1)	191.7(1)	P(1)–S(2)	209.3(1)
P(1)–C(11)	180.5(1)	P(1)–S(2a)	212.5(1)
S(2)–P(1a)	212.5(1)	C(11)–C(12)	140.5(1)
C(11)–C(16)	139.9(1)	C(12)–C(13)	140.4(1)
C(12)–C(2)	150.7(1)	C(13)–C(14)	137.1(1)
C(14)–C(15)	138.8(1)	C(14)–C(4)	151.1(1)
C(15)–C(16)	138.5(1)	C(16)–C(6)	151.9(1)
S(1)–P(1)–S(2)	114.4(1)	S(1)–P(1)–C(11)	115.4(1)
S(2)–P(1)–C(11)	109.2(1)	S(1)–P(1)–S(2a)	114.8(1)
S(2)–P(1)–S(2a)	93.8(1)	C(11)–P(1)–S(2a)	107.0(1)
P(1)–S(2)–P(1a)	86.2(1)	P(1)–C(11)–C(12)	118.1(1)
P(1)–C(11)–C(16)	121.3(1)	C(12)–C(11)–C(16)	120.5(1)
C(11)–C(12)–C(13)	118.1(1)	C(11)–C(12)–C(2)	125.0(1)
C(13)–C(12)–C(2)	116.7(1)	C(12)–C(13)–C(14)	122.0(1)
C(13)–C(14)–C(15)	118.1(1)	C(13)–C(14)–C(4)	120.4(1)
C(15)–C(14)–C(4)	121.4(1)	C(14)–C(15)–C(16)	122.5(1)
C(11)–C(16)–C(15)	118.2(1)	C(11)–C(16)–C(6)	124.2(1)
C(15)–C(16)–C(6)	117.4(1)		

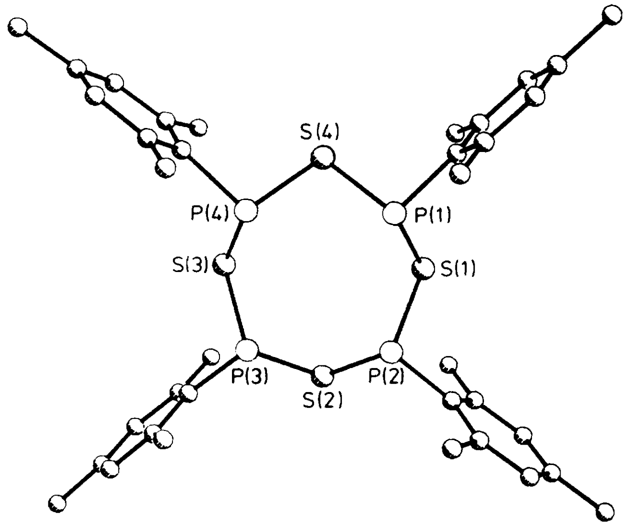

Figure 2. The molecule of $(2,4,6\text{-}Me_3C_6H_2PS)_4$ (1), with the P and S atoms labelled. Only the predominant component is shown

The final atomic co-ordinates are given in Table 1, bond lengths and angles in Table 2.

Crystal Data for Compound (2).—$C_{18}H_{22}P_2S_4$, $M = 428.56$, monoclinic, space group $P2_1/c$, $a = 890.1(2)$, $b = 1\,845.2(12)$, $c = 641.3(1)$ pm, $\beta = 98.74(1)^\circ$, $U = 1.041$ nm^3, $Z = 2$, $D_c = 1.367$ Mg m^{-3}, $F(000) = 448$, $\lambda(\text{Mo-}K_\alpha) = 71.069$ pm, $\mu(\text{Mo-}K_\alpha) = 0.59$ mm^{-1}, crystal dimensions 0.3 × 0.1 × 0.2 mm.

The data collection was performed as for compound (1). 1 417 Data with $2\theta < 45^\circ$ were reduced to 1 354 unique reflections, of which 904 with $F > 4\sigma(F)$ were used for structure solution by direct methods. The structure was refined with riding aromatic H and rigid methyl groups as for (1), with the remaining atoms anisotropic and $w^{-1} = [\sigma^2(F) + 0.0008\ F^2]$. Refinement converted to $R' = 0.060$ and $R = 0.062$. Final atomic co-ordinates are given in Table 3, bond lengths and angles in Table 4. All calculations were performed using programs written by G. M. S.

Results and Discussion

The molecular structures of compounds (1) and (2) are displayed in Figures 2 and 3. Compound (1) appears to be the first structure containing an eight-membered $(PS)_4$ ring with trivalent phosphorus, although bridged rings of this type are found in the cage molecules $\alpha\text{-}P_4S_4$ [5] and $\beta\text{-}P_4S_5$.[6] The mean P–S bond length of 212.7 pm in (1) is only slightly greater than the mean values in $\alpha\text{-}P_4S_4$ (210.9) and $\beta\text{-}P_4S_5$ (212.1 pm), and the librational correction is likely to be larger for the two cages. The mean P^{III}–S distance in $[(PhP)_3S_3]$ [2] is 210.9 pm. Compound (1) adopts the crown conformation as in the molecule S_8; the six-membered ring in $(2,4,6\text{-}Bu^t_3C_6H_2PS)_3$ has the chair form.[3] The mesityl groups in (1) lie approximately perpendicular to the plane of the ring.

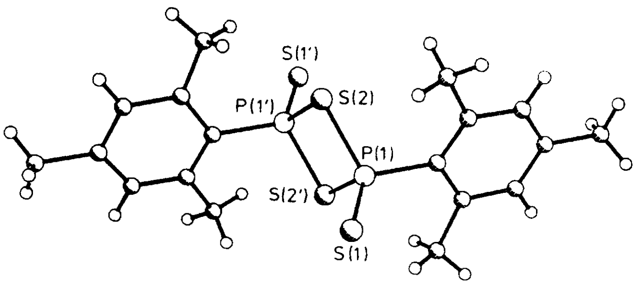

Figure 3. The molecule of $(2,4,6\text{-}Me_3C_6H_2PS_2)_2$ (2), with the P and S atoms labelled

The four-membered $(PS)_2$ ring in compound (2) lies on a crystallographic inversion centre, which obliges the exocyclic sulphur atoms to be *trans*. The endocyclic P–S bonds are significantly different (209.3 and 212.5 pm), as found also in $(PhPS_2)_2$ [2] but not $(MePS_2)_2$.[7] This might be considered as a small step along the reaction pathway for the dissociation into two monomer units; $2,4,6\text{-}Bu^t_3C_6H_2PS_2$ is monomeric.[8]

Acknowledgements

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References

1 M. Baudler, D. Koch, Th. Vakrasas, E. Tolls, and K. Kipker, *Z. Anorg. Allg. Chem.*, 1975, **413**, 239.
2 C. Lensch, W. Clegg, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 723.
3 B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, 1982, 691.
4 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
5 P. C. Minshall and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1978, **34**, 1326.
6 A. M. Griffin and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1975, **31**, 2738.
7 J. J. Daly, *J. Chem. Soc.*, 1964, 4065.
8 R. Appel, F. Koch, and H. Kunze, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 1004.

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