

X-Ray Crystal Structure of 2,4,6-Tris(*p*-methoxyphenyl)-1,3,5,2,4,6-trioxatriphosphinane 2,4,6-Trisulphide, a Co-product in $P=O \rightarrow P=S$ Thionation with Lawesson's Reagent

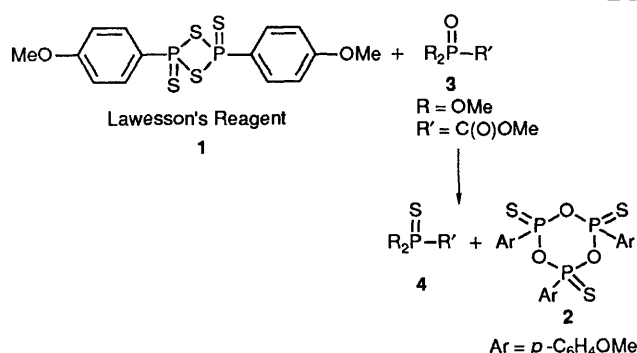
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2,4,6-Tris(*p*-methoxyphenyl)-1,3,5,2,4,6-trioxatriphosphinane 2,4,6-trisulphide **2**, obtained from trimethyl phosphonoformate ester **3** and Lawesson's reagent **1** in acetonitrile, has been structurally characterized by X-ray diffraction.

Lawesson's reagent **1**, the dimer of *p*-methoxyphenyl thiono-phosphine sulphide, thionates a wide range of carbonyl compounds,¹ thiooxidizes P^{III} to P^V derivatives,^{2,3} and can also convert the $P=O$ group in some organophosphorus compounds to a $P=S$ group.⁴⁻⁷ In some of these thio-transfer reactions a byproduct was isolated,⁵⁻⁷ and identified on spectroscopic grounds as the trimer **2** (see Scheme 1), which has been cited as evidence favouring a betaine mechanism.¹ The trimer **2** was also identified as a co-product from the reaction of **1** with several trialkyl phosphites to form the corresponding thiophosphates.^{5,6} We report here the single crystal X-ray structure of **2**, obtained by treatment of **3** with **1** in a synthesis of trimethyl thiophosphonoformate **4**.⁸

Single crystal X-ray structural analysis† of **2** as prepared by our method‡ confirms that it is a six-membered ring of alternating $P=S$ and O atoms (Fig. 1). The trimer consists of three $R-P=S$ units ($R = p$ -anisyl) connected by oxygen atoms to give a slightly puckered six-membered ring. The structure is similar to that of the phenyl analogue, $[PhP(S)O]_3$, prepared from the reaction of $PhP(O)Cl_2$ with H_2S and NEt_3 .^{9,10} As in



Scheme 1

† Crystal data for $C_{21}H_{21}O_6P_3S_3$ **2**: Triclinic, space group $P\bar{1}$, $a = 12.258(11)$, $b = 20.657(14)$, $c = 9.761(6)$ Å, $\alpha = 94.20(5)$, $\beta = 97.52(6)$, $\gamma = 85.44(6)^\circ$ and $V = 2437.6(3)$ Å³. A white diamond-shaped crystal ($1.3 \times 0.8 \times 0.3$ mm) was mounted on a four-circle Siemens/Nicolet/Syntex $P2_1$ automated diffractometer, and 5266 unique reflections were measured at room temperature using Cu-K α radiation ($\lambda = 1.5418$ Å) giving 2566 reflections with $I < 3\sigma(I)$ which were employed for all calculations. Data processing was carried out using Lorentz, polarization and empirical absorption corrections. The structure was solved by direct methods¹¹ which revealed the positions of the six sulphur and six phosphorus atoms as discrete ($P-S$) bonding pairs unconnected to each other. Subsequent difference-Fourier maps gradually revealed the positions of the remaining non-hydrogen atoms and the structure was refined to a final agreement factor of $R = 0.0721$. The two independent molecules in the unit cell are, for all intents and purposes, identical. The central $-(P-O)-$ ring is close to being planar: four atoms [$P(4)$, $P(5)$, $P(6)$, $O(7)$; see Fig. 1] are coplanar within ± 0.02 Å, with one oxygen atom displaced in one direction [$O(8) + 0.23$ Å] and the other in the opposite direction [$O(9) - 0.40$ Å]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Preparative details and spectroscopic data: Lawesson's reagent **1** (26.40 g, 65.45 mmol) was added to a solution of trimethyl phosphonoformate **3** (22.0 g, 130.9 mmol) in 375 ml of acetonitrile under Ar. After 2 h at room temperature, the mixture was refluxed at 82°C for 6 h, during which time **1** gradually dissolved, resulting in a dark-yellow solution. On cooling to room temperature, the mixture deposited the title compound **2** as a white powder, which was collected by suction filtration (9.186 g). The pale-yellow filtrate was washed three times with dimethyl ether (20 ml portions). After 1 day at room temperature, the combined filtrates deposited a second crop of $[(p\text{-anisyl})P(S)O]_3$ **2**. The first crop was purified by column chromatography on silica gel (hexane:EtOAc, 6:1). Air evaporation of the main fraction of **2** (one day) provided single crystals of X-ray quality. M.p. (uncorr): 158–159°C; TLC: (hexane:EtOAc, 6:1, $R_f = 0.14$); 1H NMR ($CDCl_3$): δ 3.85 (s, 6H), 3.87 (s, 3H), 6.95–7.08 (m, 6H); 8.03–8.30 (m, 6H); ^{31}P NMR ($CDCl_3$): δ 72; IR ν_{max}/cm^{-1} (KBr pellet, inc.): 610(s), 680(m), 695(m), 750(s), 805–840 (grp 4, ms); 930 cm^{-1} [$\nu(P-O)$]; 1500, 1600 (s, aromatic bands).

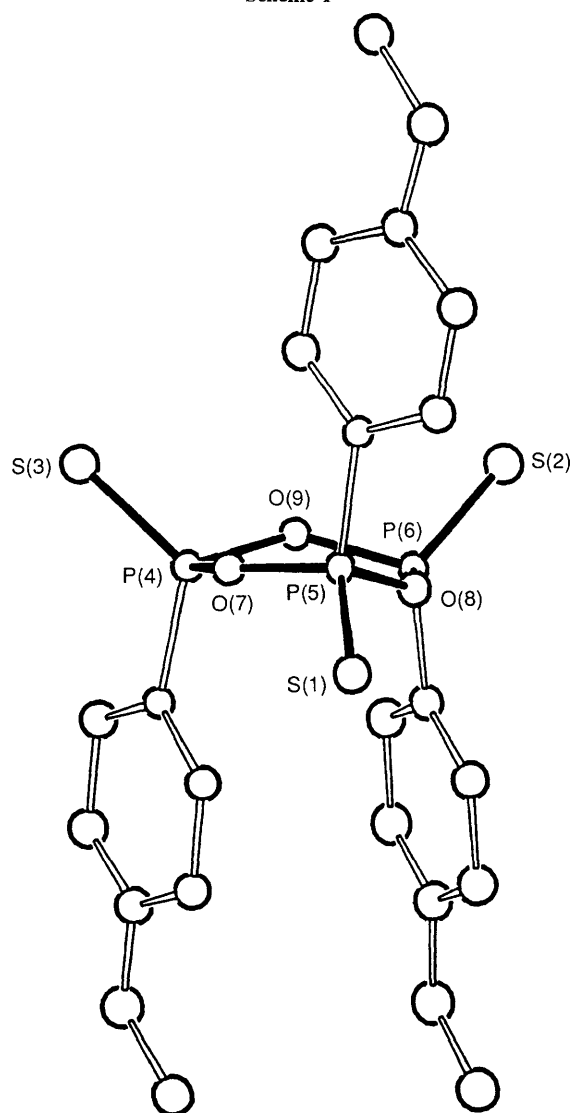


Fig. 1 Structure of 2,4,6-tris(*p*-methoxyphenyl)-1,3,5,2,4,6-trioxatriphosphinane 2,4,6-trisulphide

the case of $[\text{PhP}(\text{S})\text{O}]_3$, a notable feature of this structure is that two aromatic rings are oriented on one side of the $-(\text{P}-\text{O})_3-$ ring in a stacked fashion, with the third anisyl group similarly oriented on the opposite side (Fig. 1).

Distances and angles are normal, with selected mean values being P–S (1.892 Å), P–O (1.613 Å), P–C (1.782 Å) and the bond angles P–O–P (136°), O–P–O (100°), S–P–O (110–116°) and S–P–C (117°). This structure provides unambiguous proof of earlier conclusions^{4–7} that a trimeric by-product is produced in some reactions of Lawesson's reagent.[§]

§ Identity of **2** characterized in this work with the trimer co-product (TCP) from Lawesson's reagent thionation reactions involving other substrates: TCP formed in a synthesis of thiocarboxamides had: m.p. 160°C; ¹H NMR δ 3.8, 6.8–9.2, 7.8–8.3; IR $\nu_{\text{max}}/\text{cm}^{-1}$ 807, 930.⁷ TCP isolated from thionation of several dialkyl phosphites and of an alkyl phenylphosphinate had: m.p. 155–156°C, ³¹P NMR δ 71;⁵ from thionation of a trialkyl phosphite, m.p. 154–155°C, ³¹P NMR δ 72.⁴ In an extension of the latter study, the TCP obtained had (no m.p. obtd.): ¹H NMR, δ 2.63, 5.87–8.07; ³¹P NMR, δ 71; IR $\nu_{\text{max}}/\text{cm}^{-1}$ (inc.) 670, 680, 930–950, 1500, 1590.⁶

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