

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

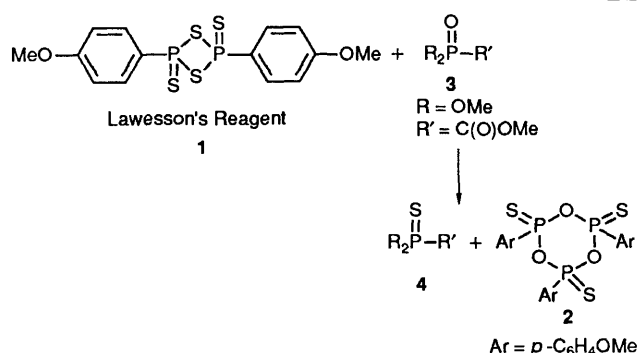
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2,4,6-Tris(*p*-methoxyphenyl)-1,3,5,2,4,6-trioxatriphosphinane 2,4,6-trisulphide **2**, obtained from trimethyl phosphonoformate ester **3** and Lawesson's reagent **1** in acetonitrile, has been structurally characterized by X-ray diffraction.

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



† *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 $-(P-O)_3-$ 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); ³¹P 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} [s, $\nu(P-O)$]; 1500, 1600 (s, aromatic bands).

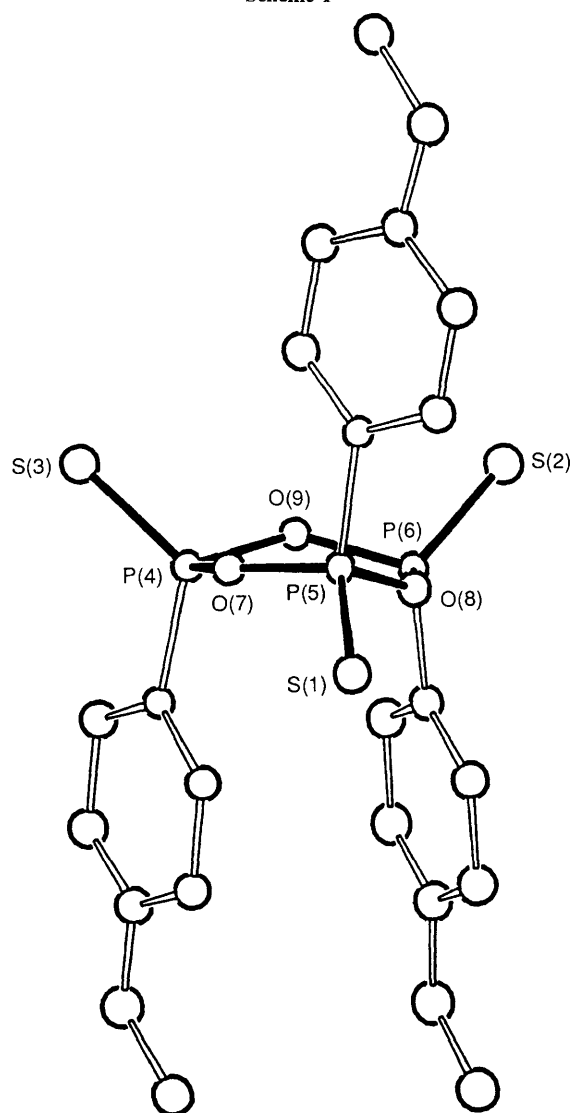


Fig. 1 Structure of 2,4,6-tris(*p*-methoxyphenyl)-1,3,5,2,4,6-trioxatriphosphinane 2,4,6-trisulphide

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

We thank the National Institutes of Health (Grant No. AI-25697 to C. E. M.) for financial support.

Received, 26th March 1991; Com. 1/01454D

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