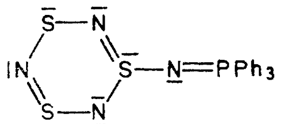
The Crystal and Molecular Structure of the Intermediate in the Reaction between Triphenylphosphine and Tetrasulphur Tetranitride

By E. M. Holt and S. L. Holt*

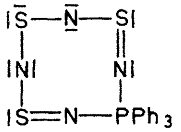
(*Department of Chemistry, University of Wyoming, Laramie, Wyoming* 82070)

Summary In crystalline form, $Ph_3PS_3N_4$, the isolable intermediate of the reaction of S_4N_4 and triphenylphosphine, exists as a triphenylphosphine group bonded through nitrogen to an S_3N_3 ring, five members of which are planar.

Fluck, Becke-Goehring, and Dehoust[1] have reported that the reaction of tetrasulphur tetranitride with triphenylphosphine produces a bright-red intermediate which may be isolated from solution. Fron analytical data this intermediate was assigned the formula $Ph_3PS_3N_4$, with structure (**1**) or (**2**). To determine which of these structures is correct and to provide information for both kinetic and electronic structure investigations, we have determined the crystal structure of this intermediate.



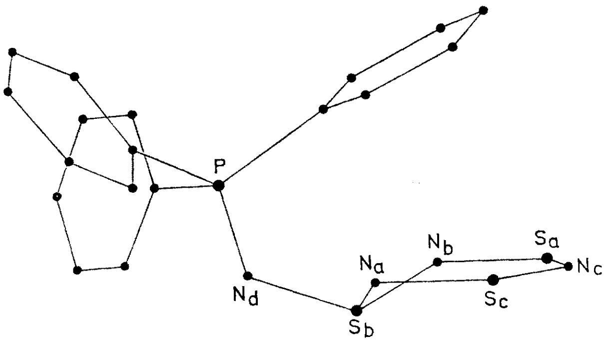
(1)



(2)

Crystal data: $Ph_3PS_3N_4$, M 414, monoclinic, a = 14·987, b = 13·107, c = 11·587 Å, β = 124·89°, V_c = 1865·89 Å^3, D_o = 1·45, Z = 4, D_c = 1·473 g cm^{-3}, space group $P2_1/a$. Intensities were recorded on a Picker diffractometer, for 2106 reflections, 1952 being non-zero, using Mo radiation. The structure was refined by least-squares to an R value of 8·7% ignoring hydrogens and using anisotropic temperature factors for all 26 atoms.

The structure shows (Figure) five members of the S_3N_3 ring lying in a plane (within the limits of experimental error) with the remaining sulphur 139° out of that plane. This partial planarity of the sulphur nitrogen ring is unexpected considering the full planarity of the sulphur–nitrogen ring of $S_4N_3(NO_3)$[2] and the non planar or puckered rings observed in S_4N_4[3] and other six- and eight-membered sulphur–nitrogen ring compounds prepared from it: $S_4N_4H_4$,[4] $S_4N_4F_4$,[5] $S_3N_3Cl_3$,[6] and $S_3N_3O_3Cl_3$.[7]



Figure

The sulphur–nitrogen bond-lengths fall into two groups: (i) S_b–N_a = 1·647(9), S_b–N_b = 1·679(8), S_c–N_a = 1·656(9), S_c–N_c = 1·619(9) Å; (ii) S_a–N_c = 1·576(11), S_a–N_b = 1·561(9) Å. All these bond lengths are shorter than the sulphur–nitrogen single-bond length of 1·76 Å. The two shorter sulphur–nitrogen bonds (which are adjacent) are close to the sulphur–nitrogen double-bond length of 1·55 Å.

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[1] E. Fluck, M. Becke-Goehring, and G. Z. Dehoust, *Z. anorg. Chem.*, 1961, **312**, 60.

[2] A. W. Cordes, R. Kruh, and E. K. Gordon, *Inorg. Chem.*, 1965, **4**, 681.

[3] B. D. Sharma and J. Donohue, *Acta. Cryst.*, 1963, **16**, 891.

[4] R. L. Sass and J. Donohue, *Acta. Cryst.*, 1958, **14**, 497.

[5] C. A. Wiegers and A. Voss, *Acta Cryst.*, 1961, **14**, 562.

[6] C. A. Wiegers and A. Voss, *Proc. Chem. Soc.*, 1962, 387.

[7] A. J. Banister and A. C. Hazell, *Proc. Chem. Soc.*, 1962, 282.