The Thermal Decomposition of Triphenylphosphinimino-cyclotrithiazene; Preparation and Crystal Structure of $Ph_3P{=}NSNSS$, a Sulphur–Nitrogen Chain with a Terminal Sulphur–Sulphur Bond

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Summary The thermal decomposition of $Ph_3P{=}N{-}S_3N_3$ leads to the open-chain derivative $Ph_3P{=}NSNSS$; an *X*-ray crystallographic analysis of the latter shows that the five atom N–S–N–S–S sequence exists in a nearly planar, *cis–trans* conformation.

RECENTLY we reported the smooth thermal interconversion of the three binary S–N anions $S_4N_5^-$, $S_3N_3^-$, and S_4N^-, and showed that the last had a planar, *cis–trans* chain structure with nitrogen in the middle of four sulphur atoms.[1] In a continuation of our studies on the thermal degradation of S–N compounds we have found that $Ph_3P{=}N{-}S_3N_3$ (**1**) decomposes in boiling acetonitrile to yield $Ph_3PNSNSS$ (**2**), a neutral S–N chain with a terminal sulphur–sulphur bond. We describe here the preparation and *X*-ray structural determination of (**2**).

When (**1**) (2·00 g), prepared from S_4N_4 and $Me_3SiN{=}PPh_3$,[2] is heated at reflux in dry acetonitrile (200 ml), a deep red colour is rapidly generated. After 4 h, chromatography of the reaction mixture on a Bio-Beads S-X8 column eluted with toluene, and recrystallization of the main product fraction from acetonitrile affords deep red crystals (with a green metallic lustre) of (**2**) (m.p. 116—118 °C) in 35% yield. The u.v.–visible spectrum of (**2**) (in CH_2Cl_2) shows bands at 314 (ϵ *ca.* $2{\cdot}3 \times 10^3$) and 491 nm (ϵ *ca.* $1{\cdot}4 \times 10^4$ l mol^{-1} cm^{-1}).

Crystals suitable for an *X*-ray structural determination were obtained from acetonitrile. *Crystal data:* $C_{18}H_{15}N_2PS_3$,

M = 386·49, monoclinic, space group $P2_1/c$, a = 12·573(1), b = 11·170(1), c = 14·816(2) Å, β = 115·96(1)°, U = 1872·2 Å^3, Z = 4, D_c = 1·37 g cm^{-3}. A total of 1772 reflections [$I \geqslant 3\sigma(I)$] were collected with a manual GE XRD-5 diffractometer employing the θ—2θ technique with Ni-filtered Cu-K_α radiation. The structure was solved by direct methods and refined by Fourier and full-matrix least-squares techniques and all atoms were refined anisotropically to give a final unweighted R-factor of 0·040.†

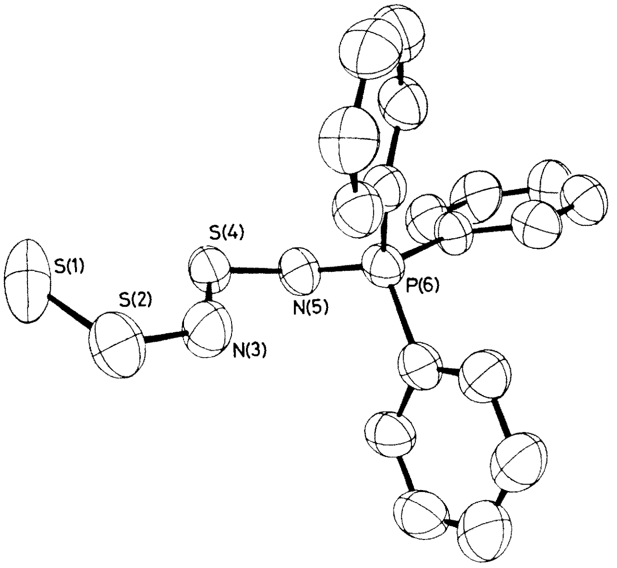
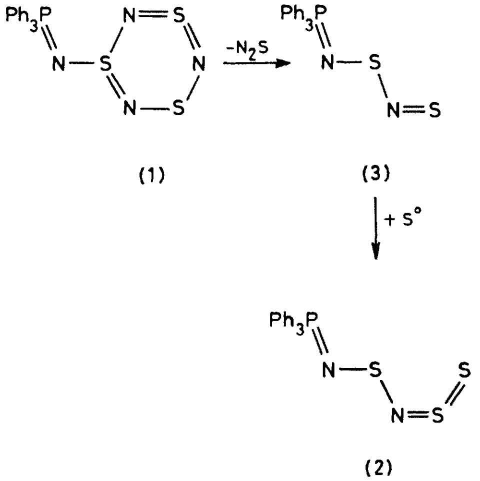


FIGURE. ORTEP drawing of $Ph_3PNSNSS$ showing the atomic numbering scheme. The atoms are represented by their thermal ellipsoids drawn to enclose 50% of their electron density. Principal bond distances (e.s.d.'s in parentheses) are: S(1)–S(2), 1·908(2); S(2)–N(3), 1·592(4); N(3)–S(4), 1·587(4); S(4)–N(5), 1·607(4); N(5)–P(6), 1·598(3); S(1)–S(4), 3·131(2) Å. Principal bond angles are: S(1)–S(2)–N(3), 111·4(2); S(2)–N(3)–S(4), 120·9; N(3)–S(4)–N(5), 107·7; S(4)–N(5)–P(6), 124·0(2)°.

The structure of (**2**) is shown in the Figure. The unusual arrangement of the S(1)–S(2)–N(3)–S(4) fragment is similar to the sickle-shaped structure of S_4N^- ion.[1] The five atoms of the SSNSN chain are coplanar to within 0·04 Å, but the phosphorus atom is twisted out of this plane so that the N(3)–S(4)–N(5)–P(6) torsion angle is 136·4(3)°. The S(1)–S(2) bond length of 1·908 Å is remarkably short, indicating a bond order significantly greater than one [*cf.* mean length of 1·91 Å for terminal S–S bonds in S_4N^-,[1] and d(S–S) = 1·86 Å in $S{=}SF_2$[3]]. However, in contrast to the S_4N^- ion, where the two S–N bond lengths [1·667(5) and 1·521(5) Å] are markedly different,[1] the S(2)–N(3) and S(4)–N(3) bonds in (**2**) are equal within experimental error. The environment at phosphorus is not unusual, but the P(6)–N(5) distance of 1·598(3) Å is slightly shorter than the corresponding bond in $Ph_3P{=}N{-}S_3N_3$ [d(P–N) = 1·645(10) Å].[4]



We suggest that the formation of (**2**) involves the loss of N_2S from (**1**) (Scheme),‡ as observed in the thermal conversion of $S_4N_5^-$ to $S_3N_3^-$ [1] and of $C_6F_5SNSNSC_6F_5$ to $C_6F_5SSC_6F_5$.[7] Rapid disproportionation of N_2S followed by the reaction of sulphur with $Ph_3P{=}NSNS$ (**3**) then gives (**2**). It is interesting, and not inconsistent with our findings, that a 1:2:3:2:1 five-line e.s.r. signal, assigned to the $N_2S^{\cdot -}$ radical anion, has been observed in the solid state decomposition of (**1**).[2]

The ready formation of (**2**) from (**1**) suggests that the controlled thermal decomposition of other sulphur nitride derivatives may provide a useful route to new SN compounds. The structure of (**2**) stresses the importance of the terminal S–N–S–S unit as a structural feature in open-chain SN species.§

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Although the existence of N_2S has been postulated,[5] and *ab initio* MO calculations favour a linear, unsymmetrical structure,[6] no confirmatory experimental evidence for this molecule has been reported.

§ Note added in the press. Since the submission of this communication, a report of the X-ray structural determination of a compound containing the –S–N=S=S unit bonded to a substituted piperidine ring has come to our attention (C. Tamura, K. Aiba, S. Sato, T. Hata, S. Morimura, and T. Yoshioka, *Acta Cryst.*, 1977, **B33**, 3918). No details of the synthesis of this compound were given.

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