Thermal Decomposition of Binary Sulphur–Nitrogen Anions; Preparation and *X*-Ray Crystal Structure of $(Ph_3P)_2N^+$ S_4N^-

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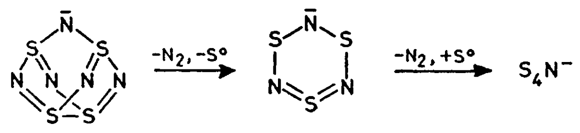
Summary The thermal decomposition of $(Ph_3P)_2N^+$ $S_4N_5^-$ in acetonitrile leads, sequentially, to the corresponding salts of the $S_3N_3^-$ and S_4N^- anions; an *X*-ray crystallographic analysis of $(Ph_3P)_2N^+$ S_4N^- shows that the anion is a planar, *cis–trans* chain with nitrogen in the middle of four sulphur atoms.

The only binary S–N anions to be structurally characterized are the planar, cyclic $S_3N_3^-$ anion[1] and the bicyclic, cage anion, $S_4N_5^-$.[2] In common with other nitrogen-rich sulphur nitride species, salts of these anions, particularly with alkali metal cations, exhibit a tendency to explode.[3] We have discovered, however, that the thermal decomposition of salts of $S_4N_5^-$ and $S_3N_3^-$ can be controlled when the reaction is carried out in acetonitrile.[4] The final product from both anions is the dark blue S_4N^- anion, previously characterized as the $Bu^n{}_4N^+$ salt but of uncertain structure.[5] We describe here the preparation of PPN^+ S_4N^- [(**3**); PPN = $(Ph_3P)_2N^+$] by thermolysis of PPN^+ $S_4N_5^-$ (**1**) (see Scheme)† and we report the crystal structure of (**3**) which contains the first example of an acyclic binary S–N anion to be structurally characterized.



(1) (2) (3)

Scheme

Compound (**1**) can be prepared by cation exchange of $[C_5H_{10}NH_2][S_4N_5]$[6] with PPN^+Cl^- in water. When a solution of (**1**) (1·37 mmol) is heated to reflux in dry, oxygen-free acetonitrile (30 ml) for 24 h, a gradual colour change from yellow through green to very deep blue is observed. After cooling the mixture to room temperature and filtering it to remove *ca.* 10 mg of cyclo-S_8, the solution is further cooled to −10 °C, whereupon small rectangular plates of (**3**) (0·69 mmol, 50%) are obtained. Crystals of (**3**) (m.p. 154—158 °C) are dark purple with a metallic copper-like lustre, but the powdered solid has a deep blue colour. Compound (**3**) is stable in air as a solid, but oxidizes rapidly (with decolourization) in solution. The

† For convenience, the $S_4N_5^-$ and $S_3N_3^-$ ions are represented by valence bond structures. These structures are not intended to imply formal bond orders for individual bonds.

u.v.–visible spectrum (in CH_2Cl_2, λ_{max} 582 nm, ϵ *ca.* 1·6 × 10^4 l mol^{-1} cm^{-1} and 364 nm, ϵ *ca.* 10^3 l mol^{-1}) and i.r. spectrum (in Nujol, excluding cation bands, 894w, 598m, 572s, and 418w cm^{-1}) both show bands attributable to the S_4N^- anion.[5,7]

Crystals suitable for an *X*-ray structural determination were obtained from acetonitrile. *Crystal data:* $C_{36}H_{30}N_2P_2S_4$, M = 680·86, triclinic, space group $P\bar{1}$, a = 11.220(2), b = 16·860(3), c = 9·862(2) Å, α = 99·17(1), β = 98·04(1), γ = 71·56(1)°, U = 1739·2(9) Å^3, Z = 2, D_c = 1·300 g cm^{-3}. A total of 5454 independent reflections [$I \geqslant 3\sigma(I)$] were collected with an Enraf-Nonius CAD4 diffractometer employing the θ–2θ technique with graphite-monochromated Mo-K_α radiation. The structure was solved by direct methods and Fourier techniques. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions in the final cycles of refinement to give an unweighted R-factor of 0·064.‡

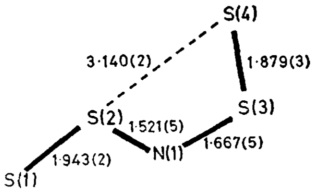


FIGURE. Structure of the S_4N^- anion in $PPN^+S_4N^-$ (**3**) showing the atomic numbering scheme and principal bond distances in Å (e.s.d.'s in parentheses). Principal bond angles are: ∠S(1)–S(2)–N(1) = 110·4(2); S(2)–N(1)–S(3) = 120·8(3); S(4)–S(3)–N(1) = 110·6(2)°.

The structure of the S_4N^- anion in (**3**) (see Figure) consists of a nearly planar (deviations from mean plane through all five atoms <0·05 Å) *cis–trans* chain, with nitrogen as the central atom. The sickle shape of the anion is in marked contrast to the *cis–cis* structure of the isoelectronic cation, $NS_2Cl_2^+$,[8] and the staggered conformation found for S_5^{2-}.[9] As a result of the orientation of the S(3)–S(4) bond, the S(2)–S(4) distance (3·14 Å) is significantly shorter than the van der Waals' separation (3·7 Å) for two sulphur atoms. The linear arrangement of S(1), S(2), and S(4) is reminiscent of a similar structural feature in thiathiophthenes.[10] The S–S bond lengths [S(3)–S(4) = 1·879(3) and S(1)–S(2) = 1·943(2) Å] are remarkably short compared to the corresponding distances in polysulphide anions, *e.g.* in S_5^{2-}, *d*(S–S) *ca.* 2·06 Å,[9] and suggest that S(3)–S(4) is best represented as being close to a S=S double bond *cf.* *d*(S–S) = 1·860 in S=SF_2[11] and 1·884 Å in S=SO.[12] The marked inequality of the S(3)–N(1) [1·667(5) Å] and S(2)–N(1) [1·521(5) Å] bonds, despite the equal bond angles (*ca.* 110°) at S(2) and S(3),[13] further reflects the asymmetry of the electronic structure of the anion. The shorter S–N bond is adjacent to the longer S–S bond. Thus, valence bond structures are obviously inadequate representations of the electron distribution in S_4N^- and do not account for the remarkably intense 582 nm transition. The P–N distances of 1·573(3) and 1·562(3) Å and the bond angle of 143·1(2)° at nitrogen in the PPN^+ cation are unexceptional.[14]

Although the formation of the S_4N^- ion by the deprotonation of S_7NH[5,7] and the reaction of cyclo-S_8 with sodium[15] or tetra-alkylammonium[16] azides have been reported, the synthesis described here provides a novel example of the controlled thermal conversion of one binary sulphur nitride species to another. While the mechanism of the transformations shown in the Scheme is not fully understood, the intermediacy of the $S_3N_3^-$ in the decomposition of $S_4N_5^-$ has been established by the isolation of (**2**) when the thermolysis is stopped immediately after the formation of the blue colour (6—7 h). Crystals of (**2**), mixed with cyclo-S_8, were obtained on cooling the solution to −10 °C and were identified by comparison of spectral properties with an authentic sample prepared from $PPN^+N_3^-$ and S_4N_4.[3] When a solution of pure (**2**) in acetonitrile is heated to reflux, it too decomposes rapidly to give (**3**).

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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.

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