The Oxidation of the Trisulphur Trinitride Anion $S_3N_3^-$ by Molecular Oxygen; Preparation and the Crystal and Molecular Structure of $[(Ph_3P)_2N]^+[S_3N_3O]^-$

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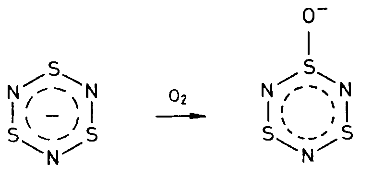
Summary The oxidation of $S_3N_3^-$ with molecular oxygen yields the novel oxyanion $S_3N_3O^-$, the structure of which {as its $[(Ph_3P)_2N]^+$ salt} has been determined by *X*-ray crystallography.

The trisulphur trinitride anion $S_3N_3^-$ is a species of current interest. Its role in the nucleophilic degradation of S_4N_4 has been established,[1] and the interpretation of its electronic structure in terms of a 6-orbital 10 π-electron system has received both theoretical[2] and experimental[3] verification. During our synthetic studies involving this anion we had often noted its sensitivity to oxidation;[1,†] we have therefore examined its reaction with molecular oxygen. We find that, under carefully controlled conditions, solutions of $S_3N_3^-$ can be oxidized to the monoxyanion $S_3N_3O^-$ [equation (1)]. We report here the preparation and the *X*-ray crystal structure determination of $[(Ph_3P)_2N]^+S_3N_3O^-$. The electronic structure of the novel $S_3N_3O^-$ anion is described in terms of the expected perturbation of the parent $S_3N_3^-$ system.



(1)

When O_2 is bubbled into a solution of $[(Ph_3P)_2]^+S_3N_3^-$ (2·9 mmol) in 30 ml anhydrous acetonitrile for 30 min at a flow rate of 20 ml min^{-1} and the mixture then cooled to -20 °C, deep red crystals of $[(Ph_3P)_2N]^+S_3N_3O^-$ can be obtained in a 42% yield (1·3 mmol). Crystals suitable for *X*-ray work were obtained by recrystallization from acetonitrile. *Crystal data:* $C_{36}H_{30}N_4OP_2S_3$, $M = 692{\cdot}8$, monoclinic, space group $P2_1/c$, $a = 17{\cdot}161(2)$, $b = 9{\cdot}970(1)$, $c = 20{\cdot}591(2)$ Å, $\beta = 104{\cdot}45(1)°$, $U = 3411{\cdot}7$ Å^3, $Z = 4$, $D_c = 1{\cdot}35$ g cm^{-3}. A total of 3030 observed reflections $[I \geqslant 3\sigma(I)]$ was collected with a manual G.E. XRD-5 diffractometer employing the θ–2θ technique ($2\theta_{max} = 100°$)

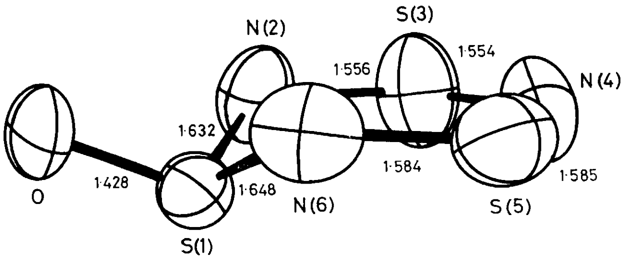


Figure 1. ORTEP drawing (30% probability ellipsoids) and bond distances (e.s.d.s 0·7 Å) of the $S_3N_3O^-$ anion, showing the atom numbering scheme. Ring bond angles are 105·4(3) at S(1), 119·2(1) at N(2), 116·4(4) at S(3), 124·2(3) at N(4), 113·3(3) at S(5), and 118·7(2)° at N(6). The N(2)–S(1)–O and N(6)–S(1)–O angles are 105·5(3) and 106·3(3)°.

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† Highly coloured solutions are produced in the electrolytic reduction of S_4N_4. U.v.–visible spectroscopic analysis of these solutions indicates the presence of $S_3N_3^-$ and $S_3N_3O^-$.

with Ni-filtered Cu-K_α radiation. The structure was solved by direct methods and refined by Fourier and full-matrix least-squares techniques to give a final unweighted *R*-factor of 0·053.‡

The structure of the $S_3N_3O^-$ anion is shown in Figure 1. As in the related structures S_3N_3–N=PPh_3[4] and S_3N_3–N=$AsPh_3$[5] the S_3N_3 ring has a half-chair conformation with the exocyclic ligand lying in a pseudo-equatorial position. The 5-atom sequence, N(2)–S(3)–N(4)–S(5)–N(6), is planar to within ±0·04 Å, and the S(1) atom is displaced from this plane by 0·67 Å, producing a dihedral angle [with the N(2)–S(1)–N(6) plane] of 43°. The S–N bonds to the oxidized sulphur are longer [mean 1·64(1) Å] than those found in $S_3N_3^-$ (1·60 Å), while the S–N bonds to S(3) and S(5) are slightly shorter [mean 1·57(2) Å]. The geometry at S(1) (sum of all angles = 317·2°) is similar to that of the substituted sulphur atoms in S_3N_3–N=PPh_3 (318·6°) and S_3N_3–N=$AsPh_3$ (318·8°).

The structural resemblance of $S_3N_3O^-$ and the S_3N_3–N=EPh_3 (E = P, As) derivatives is complemented by the similarity of their electronic spectra. Solutions of $S_3N_3O^-$ exhibit two absorption maxima in the visible region [in CH_2Cl_2, λ_{max} 509 (ϵ *ca.* 8 × 10^3 dm^3 mol^{-1} cm^{-1}) and 340 nm (ϵ *ca.* 2 × 10^3 dm^3 mol^{-1} cm^{-1})]. By analogy with the S_3N_3–N=EPh_3 derivatives, whose magnetic circular dichroism have recently been analysed,[6] we assign these two absorptions to $\pi^* \rightarrow \pi^*$ transitions originating from the formally degenerate H.O.M.O. of $S_3N_3^-$ which is split by the perturbation at one sulphur (see Figure 2).

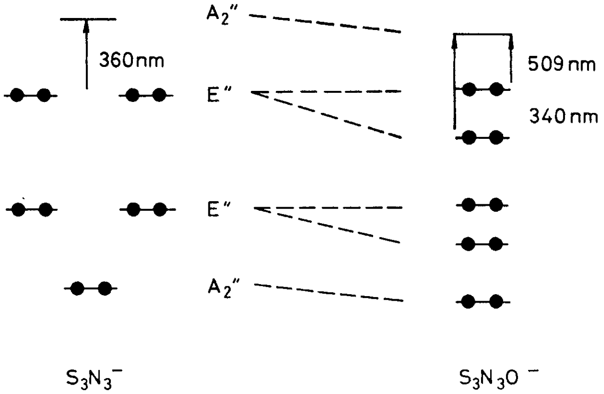

FIGURE 2. π-Energy level diagram of $S_3N_3^-$ and $S_3N_3O^-$, showing the splitting of the degenerate H.O.M.O. of $S_3N_3^-$ upon oxidation, and the expected $\pi^* \rightarrow \pi^*$ transitions of the two systems.

The results reported here suggest that studies of the oxidation of $S_3N_3^-$ with other reagents, *e.g.* halogens, should lead to other S_3N_3X derivatives whose spectroscopic properties and molecular structures will be similar to those observed for the $S_3N_3O^-$ anion. Such reactions are being investigated.

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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 Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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