Synthesis of the Trisulphur Trinitride Anion, $S_3N_3^-$†

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Summary Reaction of caesium or tetra-alkylammonium azides with tetrasulphur tetranitride in ethanol produces salts of the trisulphur trinitride anion, $S_3N_3^-$, which, on the basis of vibrational spectra, has a cyclic structure.

Banister has described binary sulphur–nitrogen species with $(4n+2)\pi$ electrons as 'electron-rich aromatics'.[1] Examples of such Hückel systems include the neutral molecules S_2N_2 (6π) and S_4N_2 (10π) and the cations $S_4N_3^+$ (10π) and $S_5N_5^+$ (14π). We now report the synthesis of a sulphur–nitrogen anion, $S_3N_3^-$, a potentially aromatic (10π) system according to the postulates of Banister.

We found earlier that the reaction of sodium azide with S_4N_4 in ethanol provides a convenient synthesis of salts of the $S_4N_5^-$ ion,[2] first described by Scherer and Wolmershäuser.[3] A detailed investigation of the reaction of alkali metal or tetra-alkylammonium azides with S_4N_4 has revealed that the product isolated is markedly dependent on the size of the cation. Whereas lithium, sodium, and potassium azides produce the $S_4N_5^-$ ion exclusively, caesium and tetra-alkylammonium azides (R = Me, Et, Pr^n, or Bu^n) yield salts of the novel $S_3N_3^-$ ion, and rubidium azide gives a mixture of $Rb^+S_4N_5^-$ and $Rb^+S_3N_3^-$. For example, $Me_4N^+S_3N_3^-$ is obtained in 40% yield by the addition of n-pentane (100 ml) to the orange solution obtained, after decantation, when approximately equimolar amounts of tetramethylammonium azide and S_4N_4 are stirred in ethanol (35 ml) for 1 day. Soxhlet extraction with n-pentane removes the other solid product, elemental sulphur,[2] from $Me_4N^+S_3N_3^-$. Complete elemental analyses were in excellent agreement with the calculated values for $Me_4N^+S_3N_3^-$ and $Et_4N^+S_3N_3^-$, and the i.r. spectra of the other $S_3N_3^-$ salts showed all the bands attributed to the anion in the R_4N^+ salts (R = Me or Et) (*vide infra*).

By analogy with isoelectronic species, the most likely structural alternatives for $S_3N_3^-$ are: (a) a six-membered ring, *cf.* S_4N_2,[4] or (b) a five-membered ring with exocyclic nitrogen, *cf.* $S_3N_2Cl^+$ [5] or S_3N_2O.[6] The i.r. spectrum of $Cs^+S_3N_3^-$ (Nujol) showed bands at 957w, 928s, 694w, 640vs, 589w, 372s, and 168m cm^{-1}. All these bands are observed in the i.r. spectra of the tetra-alkylammonium salts, but the band at 372 cm^{-1} is shifted to *ca.* 382 cm^{-1}. The Raman spectrum of $Cs^+S_3N_3^-$ had bands at 953m, 928s, 700w, 648w, 588vs, and 371 cm^{-1}. The small number of observed vibrational frequencies, the absence of a band above *ca.* 950 cm^{-1} ($>S{=}N-$), and the lack of a strong band in the Raman spectrum attributable to an S–S stretching frequency[7] rules out structure (b). The calculated number of fundamental vibrational modes for a six-membered ring are shown in the Table. The observed vibrational spectra are clearly in best agreement with a C_{3v} structure for $S_3N_3^-$, which thus bears a close structural resemblance to $S_4N_5^-$.[8]

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† *Caution:* The $S_3N_3^-$ salts, like those of $S_4N_5^-$,[2,3] are explosive under the influence of heat or pressure. For example, during the determination of the Raman spectrum of $Cs^+S_3N_3^-$ the capillary tube disintegrated in the laser beam.

TABLE. Calculated number of fundamental vibrational modes for cyclic $S_3N_3^-$

Structure[a]	Symmetry	I.r.-active modes	Raman-active modes	Coincidences
Planar ..	.. D_{3h}	4	6	3
Puckered ..	.. C_{3v}	7	7	7
Boat or chair	.. C_s	12	12	12
Experimental spectra	..	7	6	6

[a] Assuming alternating S and N atoms.

Significantly, solutions of $Et_4N^+S_3N_3^-$ in ethanol show a single absorption band at 360 nm in the u.v.–visible spectrum. We[9] and others[10] have previously observed the formation of a 360 nm-species from the reaction of S_4N_4 with secondary amines[9] or liquid ammonia[10]‡ and after the controlled potential electrolysis of S_4N_4 at $-0{\cdot}7$ V *vs.* standard calomel electrode, which consistently gave *n* values in the range 1·3—1·4.[9] Thus it appears that the characterization of the $S_3N_3^-$ ion will be a key step towards understanding the behaviour of S_4N_4 towards nucleophiles and on reduction.

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‡ Professor O. J. Scherer has informed us that he has identified $NH_4[S_4N_5]$ as one of the products of the reaction of S_4N_4 with ammonia. I.r. spectra of the ether-insoluble product from the reaction of S_4N_4 in liquid ammonia (obtained by I. Drummond in 1973) reveal the presence of $S_3N_3^-$ in addition to $S_4N_5^-$.

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