Preparation and *X*-Ray Crystal Structure of $(S_3N_2)_2NAsF_6$, containing the Bis(thiodithiazyl)aminylium(1+) Cation †

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Crystalline $(S_3N_2)_2NAsF_6$ was prepared in *ca.* 60% yield from a 1 : 1 mixture of S_4N_4 and S_2NAsF_6 in liquid SO_2 at 0 °C, and its structure determined by *X*-ray crystallography. The compound crystallises in the monoclinic space group *C*2/*c* with unit-cell dimensions $a = 17.343(6)$, $b = 17.103(6)$, $c = 16.737(9)$ Å, $\beta = 98.29(3)°$, and $Z = 16$. The structure was solved by direct methods and refined by least-squares techniques to a final *R* of 0.11 for 2 308 observed reflections. $(S_3N_2)_2NAsF_6$ is essentially ionic with sulphur–fluorine cation–anion contacts. The $(S_3N_2)_2N^+$ cation is the first example of a monobridged bicyclic sulphur–nitrogen cation, and consists of two thiodithiazyl (S_3N_2) groups connected together by a bridging nitrogen atom attached to a sulphur atom of each S_3N_2 ring. The S_3N_2 rings are *cis* with respect to the bridging nitrogen atom, and are essentially eclipsed with respect to the SNS bridge. $(S_3N_2)_2NAsF_6$ reacts with CsN_3 in liquid SO_2 solution yielding impure poly(sulphur nitride) and $CsAsF_6$. Solutions of $(S_3N_2)_2NAsF_6$ in liquid SO_2 slowly disproportionate to $S_4N_3AsF_6$ and S_4N_4. The i.r. spectrum of $(S_3N_2)_2NAsF_6$ is also reported.

The recent synthesis of S_2NAsF_6[1] provides a readily available source of the S_2N^+ cation, a potential building block in the systematic synthesis of sulphur–nitrogen species. The $SbCl_6^-$ [2] and $AlCl_4^-$ [3] salts of S_2N^+ have also been prepared but in unspecified yield. The utility of S_2N^+ as a building block is illustrated by the reaction of S_2NAsF_6 and S_4N_4, in sulphur dioxide solution at 0 °C, leading to $(S_3N_2)_2NAsF_6$ containing the $(S_3N_2)_2N^+$ cation and is the subject of this paper. The binary sulphur–nitrogen cations SN^+,[4] S_2N^+,[1-3] $S_3N_2^+$,[5] $S_4N_3^+$,[6] $S_4N_4^{2+}$,[7] $S_4N_5^+$,[8] $S_5N_5^+$,[9] and $S_6N_4^{2+}$,[5,10] have linear, ring, and cage structures. The cation $(S_3N_2)_2N^+$ is the first example of a monobridged bicyclic sulphur–nitrogen cation. The recent syntheses of these sulphur–nitrogen cations attest to the rich diversity of this area of non-metal chemistry, which has recently been reviewed.[11] Interest in sulphur–nitrogen chemistry is also illustrated by the many investigations [11-13] of the anisotropic conducting metal-like polymer, poly(sulphur nitride) $(SN)_x$. We report herein the reaction of $(S_3N_2)_2NAsF_6$ with CsN_3 to give impure poly(sulphur nitride) and $CsAsF_6$.

Experimental

Except where stated, the apparatus and chemicals were as previously described.[14-16] The salt S_2NAsF_6 was prepared according to ref. 1. Sulphur dioxide (Matheson) was dried and stored over CaH_2 and CsN_3 (Eastman) was vacuum dried before use. The CCl_4 and CH_3CN (Fischer Scientific) were dried and stored over 3 Å molecular sieves. The S_4N_4 was prepared as described by Villena-Blanco and Jolly,[17] with some modifications.[18]

Preparation of $(S_3N_2)_2NAsF_6$.—Sulphur dioxide (11.64 g, 182 mmol) was condensed onto a mixture of ground S_4N_4 (0.50 g, 2.69 mmol) and a slight excess of S_2NAsF_6 (0.76 g, 2.86 mmol) in one bulb of a two-bulbed vessel incorporating a coarse sintered glass frit. The mixture was stirred for 4 d at 0 °C during which time a yellow precipitate formed below a red solution. Sulphur dioxide was slowly condensed into the second bulb until a small amount of liquid remained above the solids. This mixture was then filtered into the second bulb and the yellow solid was then washed twice with small amounts of SO_2. The volatiles were removed and CCl_4 (5.54 g) was condensed onto the yellow solid and the solution filtered into the second bulb. The solvent was recondensed back onto the solid and the purification process repeated several times in order to remove S_4N_4. The yield of the purified yellow solid was 0.70 g [1.55 mmol, 58% based on equation (1)] [Found: N, 15.45; S, 42.25. $(S_3N_2)_2NAsF_6$ requires N, 15.50; S, 42.65%]. The i.r. spectrum (Nujol mull, KBr plates) is given in Table 1. The impure fraction (0.56 g) was largely $(S_3N_2)_2NAsF_6$, with small amounts of S_4N_4 and $S_4N_3AsF_6$ (i.r.).

$$S_2NAsF_6 + S_4N_4 \xrightarrow{SO_2} (S_3N_2)_2NAsF_6 \qquad (1)$$

A reaction mixture that was allowed to stand at room temperature (r.t.) for 1 month yielded $S_4N_3AsF_6$ and S_4N_4 essentially quantitatively (i.r.), according to equation (2). Solid $(S_3N_2)_2NAsF_6$ stored under nitrogen in sealed glass tubes at 0 °C showed no sign of decomposition after 6 months (i.r.).

$$2(S_3N_2)_2NAsF_6 \xrightarrow{SO_2} 2S_4N_3AsF_6 + S_4N_4 \qquad (2)$$

Single crystals suitable for *X*-ray analyses were formed in a similar unstirred reaction in which less SO_2 was used and the reaction time was 1 week.

Reaction of $(S_3N_2)_2NAsF_6$ *and* CsN_3.—Sulphur dioxide (13.75 g, 215 mmol) was condensed onto a frozen ‡ mixture of $(S_3N_2)_2NAsF_6$ (0.49 g, 1.08 mmol) and CsN_3 (0.19 g, 1.08 mmol) in one bulb of a two-bulbed vessel, as described above. On warming to 0 °C with stirring, a dark blue precipitate formed as well as a thin bronze film on the sides of the bulb in the now orange-red solution. After 30 min the solution was filtered into the second bulb, and the insoluble material washed several times with SO_2. The SO_2, N_2 (0.02 g, 0.66 mmol), and a small amount of an unidentified dark red liquid (S_4N_2?) were removed by pumping. Acetonitrile (4.62 g, 30.0 mmol) was then condensed into the vessel and the dark

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† Nitrilobis(cyclotrithiadiazole) monocation.

Supplementary data available (No. SUP 23765, 27 pp.): structure factors, anisotropic thermal parameters, bond distance and angle data for AsF_6^-. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

‡ **CAUTION**: The CsN_3 must be frozen down to −196 °C before any SO_2 is introduced into the vessel as it will ignite in the presence of SO_2 vapours at room temperature.

Table 1. Infrared spectrum and tentative assignments of $(S_3N_2)_2NAsF_6$, by comparison to the S–N and S–S frequencies of $S_3N_2NC(O)CF_3$, S_3N_2O, and $[(CH_3)_2S]_2N^+$

$(S_3N_2)_2NAsF_6$ (Nujol mull)	$S_3N_2NC(O)CF_3$ [a]	S_3N_2O [a]	$[(CH_3)_2S]_2N^+$ [b]	Assignments	$CsAsF_6$ [c]	
					I.r.	Raman [d]
996m	995ms	981s		ν(SN) ring		
929m	927s	910s		ν(SN) ring		
865s			920vs	$\nu_{asym}(S_2N)$		
751w	757w			ν(SN) ring or		
738ms	734s	734s	725m	$\nu_{sym}(S_2N)$		
700vs				$\nu_3(AsF_6^-)$	699s	
685 (sh)				$\nu_1(AsF_6^-)$		685 (10)
674 (sh)	678s	663s		ν(SN) ring		
597w	576w	583m		δ(NSN) ring		
580m				δ(NSN) ring and $\nu_2(AsF_6^-)$?		576 (2.3)
498m	477s			δ(NSN) ring		
398m				$\nu_4(AsF_6^-)$	392m	
381m	377mw			ν(SS)		
	350mw					
368vw				$\nu_5(AsF_6^-)$		372 (2.6)
347vw	325vw			ν(SS)		

[a] Ref. 30. [b] Ref. 34. [c] Ref. 33. [d] Relative intensities are in parentheses.

blue insoluble product was washed several times. The soluble material (0.42 g) was identified as S_4N_4 and $CsAsF_6$ (i.r.). The dark blue insoluble material [0.24 g, 5.21 mmol, 80% based on equation (3)] was identified as $(SN)_x$ (i.r.)[13] containing a small amount of an unidentified impurity.

$$(S_3N_2)_2NAsF_6 + CsN_3 \longrightarrow \tfrac{6}{x}(SN)_x + CsAsF_6 + N_2 \quad (3)$$

Crystal Data.—$(S_3N_2)_2NAsF_6$, $M = 451.3$, monoclinic, space group $C2/c$, $a = 17.343(6)$, $b = 17.103(6)$, $c = 16.737(9)$ Å, $\beta = 98.29(3)°$, $U = 4\,913$ Å^3, $Z = 16$, $D_c = 2.44$ Mg m^{-3}, $F(000) = 3\,488$, $\mu = 3.80$ mm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, crystal size = $0.54 \times 0.40 \times 0.27$ mm.

A suitable crystal was mounted under dry nitrogen, in a rigorously dried (evacuated at 250 °C) capillary tube. Preliminary precession photographs provided space group information and approximate unit-cell dimensions after which the crystal was mounted on a Picker FACS-I diffractometer equipped with graphite-monochromated Mo-K_α radiation. Unit-cell parameters and an orientation matrix were refined by least squares using the centred co-ordinates of 12 Friedel pairs of reflections with $30 \leqslant 2\theta \leqslant 45°$. Intensity data were collected using the ω—2θ scan technique at a scan rate of $2°(2\theta)$ min^{-1}. Backgrounds were estimated by standing counts of $\frac{1}{10}$ scan-time at each end of the scan. If the reflection had a significant intensity $[I > 2\sigma(I)]$ the profile of the peak was analysed and those portions of the scan that were not part of the peak were included in the background estimate. Data were collected in the range $5 \leqslant 2\theta \leqslant 45°$ resulting in 3 182 unique reflections of which 2 308 were considered observed $[I \geqslant 2\sigma(I)]$ and included in the subsequent calculations. Three standard reflections monitored every 100 reflections throughout the data collection showed no significant deviations from their mean values. The structure was solved in the space group $C2/c$ using a version of the direct methods program MULTAN[19] adapted for the PDP8 computer. After correction of the data for absorption (transmission coefficients in the range 0.36—0.41), the structure was refined by least-squares techniques minimising the function $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme was of the form $w = 1/[\sigma(F)^2 + p|F|^2]$ where $\sigma(F)$ was derived from counting statistics and a value of $p = 0.005$ was determined from the standards. The final refinement cycle resulted in $R = (\Sigma|\Delta F|/\Sigma|F|) = 0.11$ and $R' = (\Sigma w\Delta|F|^2/\Sigma w|F|^2) = 0.16$ (0.13 and 0.19 respectively including all reflections) for 326 variables. An attempt to refine the structure in the space group Cc did not improve the agreement. The fluorine thermal parameters indicated some libration of the anions which is the probable cause of the relatively large agreement factors. The programs used were those of Larson and Gabe,[20] for the PDP8/A computer. Table 2 gives the final atomic co-ordinates.

Results and Discussion

Preparation and Azide Reaction of $(S_3N_2)_2NAsF_6$.—Crystalline $(S_3N_2)_2NAsF_6$ was prepared in *ca.* 60% yield by the reaction of S_4N_4 and S_2NAsF_6 in a 1 : 1 ratio at 0 °C for 4 d in liquid sulphur dioxide according to equation (1). A similar reaction carried out at r.t. for 1 month yielded $S_4N_3AsF_6$ and S_4N_4. It is likely that $(S_3N_2)_2NAsF_6$ was formed, but slowly disproportionates according to equation (2).

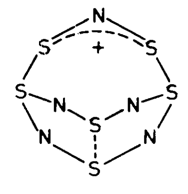
Banister and Hauptman,[21] and Hey[22] also obtained the $FeCl_4^-$ salt of $(S_3N_2)_2N^+$ from the reaction of $S_3N_2Cl_2$ (0.65 g) and iron powder (1.16 g) (6 h with agitation) in liquid sulphur dioxide at r.t. Elemental analyses and i.r. spectra of the filtrate corresponded to a 1 : 1 mixture of $(S_3N_2)_2NFeCl_4$ and $S_4N_3FeCl_4$. During recrystallisation from liquid SO_2 disproportionation occurred to give $S_4N_3FeCl_4$ and S_4N_4 consistent with equation (2). Hey[22] also obtained impure $(S_3N_2)_2NAsF_6$ from the reactions of $S_8(AsF_6)_2$ and $Se_4(AsF_6)_2$ with S_4N_4 (1 : 2 ratio in liquid SO_2), which also gave elemental analyses for a 1 : 1 mixture of $(S_3N_2)_2NAsF_6$ and $S_4N_3AsF_6$.

The reaction of S_4N_4 and S_2N^+ may proceed by donation of electrons from the highest occupied molecular orbital (h.o.m.o) of S_4N_4[23–25] into the lowest unoccupied molecular orbital (l.u.m.o.) of S_2N^+, which are a pair of π^* orbitals that are antibonding with respect to the S–N bond. (S_2N^+ is isoelectronic and isostructural with CO_2.[26]) There are two ways this may occur depending on which is the h.o.m.o. of S_4N_4. Salaneck *et al.*[23] have stated that the $4b_2$ h.o.m.o. of S_4N_4 contains almost 70% of its charge density in the S–S bonding portion of the molecular orbital. If this is true, then the S_2N^+ cation could possibly add across the S–S interaction of S_4N_4, leading to an intermediate (1) which is structurally related to the basket-like cage of the electronically similar species

Table 2. Atomic co-ordinates for both $(S_3N_2)_2NAsF_6$ units

Atom	*x*	*y*	*z*
As(1)	0.328 58(10)	0.093 27(10)	0.434 95(11)
F(11)	0.362 8(6)	0.110 8(5)	0.535 5(6)
F(12)	0.333 5(11)	0.184 7(7)	0.413 1(8)
F(13)	0.238 8(7)	0.102 7(10)	0.455 4(7)
F(14)	0.294 1(8)	0.075 0(7)	0.336 7(6)
F(15)	0.417 2(7)	0.078 9(11)	0.413 8(9)
F(16)	0.323 7(10)	−0.000 8(7)	0.455 5(8)
As(2)	0.418 90(10)	0.337 77(9)	0.058 72(10)
F(21)	0.385 6(5)	0.358 8(6)	−0.040 5(6)
F(22)	0.452 0(7)	0.315 9(6)	0.156 5(6)
F(23)	0.330 0(7)	0.341 1(9)	0.084 6(7)
F(24)	0.407 5(8)	0.242 9(6)	0.039 0(7)
F(25)	0.431 3(10)	0.430 9(6)	0.079 1(8)
F(26)	0.509 6(6)	0.332 2(9)	0.036 1(7)
S(1)	0.052 7(3)	0.105 6(2)	0.391 8(3)
S(2)	0.128 3(3)	0.152 1(3)	0.269 6(3)
S(3)	0.078 7(2)	0.229 4(2)	0.396 1(2)
S(4)	−0.156 2(3)	0.320 5(3)	0.382 5(3)
S(5)	−0.111 9(3)	0.422 7(3)	0.275 2(3)
S(6)	−0.031 0(2)	0.340 1(2)	0.399 8(2)
N(1)	0.082 5(8)	0.089 5(7)	0.307 4(8)
N(2)	0.136 9(7)	0.224 8(7)	0.326 5(7)
N(3)	−0.002 3(7)	0.265 7(7)	0.351 5(7)
N(4)	−0.176 3(8)	0.372 2(7)	0.300 9(8)
N(5)	−0.035 8(8)	0.413 2(7)	0.336 5(8)
S(11)	0.302 8(3)	0.355 7(2)	0.388 3(3)
S(12)	0.387 2(3)	0.415 6(3)	0.279 7(3)
S(13)	0.324 7(2)	0.479 7(2)	0.405 7(2)
S(14)	0.216 0(2)	0.591 1(2)	0.405 9(2)
S(15)	0.122 6(3)	0.665 0(3)	0.283 3(3)
S(16)	0.093 5(2)	0.565 8(3)	0.401 3(3)
N(11)	0.341 6(9)	0.347 1(8)	0.307 1(8)
N(12)	0.388 9(8)	0.483 8(7)	0.343 0(8)
N(13)	0.244 8(7)	0.516 6(7)	0.357 3(7)
N(14)	0.204 2(8)	0.661 1(7)	0.338 3(8)
N(15)	0.062 8(8)	0.612 1(8)	0.321 0(8)

S_5N_6 (2).[27] Replacement of X in $N(SX)_2^+$ (X = Cl or Br)[28] by two sulphur atoms of S_4N_4 leads to structure (1). This may then be followed by the breaking of two S–N bonds in the S_4N_4 ring with subsequent recyclisation to give the observed structure. However, experimental work and *ab initio* calculations[8,24,25] have led to the conclusion that the h.o.m.o. of S_4N_4 is largely located on the nitrogen atoms. This is consistent with the fact that all known structures of $S_4N_4{\cdot}L$ adducts are nitrogen bonded to the acceptor L.[25] If the S_2N^+ cation concertedly added onto two of the adjacent nitrogen atoms of S_4N_4 an intermediate species (3) would be formed, similar to the neutral (2) except all the sulphur atoms of (2) have been replaced by nitrogen atoms in (3) and *vice versa*. This species may then rearrange to give the observed structure.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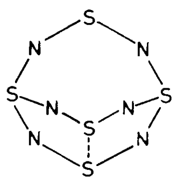
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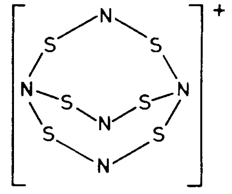
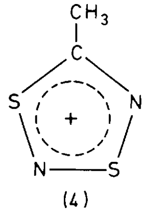

(3)

This pathway to $(S_3N_2)_2N^+$ may not occur, as the concerted addition of S_2N^+ to two adjacent nitrogen atoms of the S_4N_4 cage is symmetry forbidden. [The h.o.m.o. of S_4N_4 (*cf.* the $4a_1$ molecular orbital of Salaneck *et al.*[23]) is antisymmetric, while the l.u.m.o. of S_2N^+ (or CO_2[26]) is symmetric.] The simple addition of S_2N^+ to two transannular nitrogen atoms is ruled out on steric grounds. One plausible pathway may involve the donation of electrons from one nitrogen atom of S_4N_4 into that part of the π^* l.u.m.o. of S_2N^+ located on one of its sulphur atoms. This may be followed by addition of the other sulphur atom of S_2N^+ to an adjacent sulphur atom of S_4N_4, thus forming one S_3N_2 ring. The subsequent breaking of an adjacent S–N bond of the S_4N_4 ring may then occur, followed by recyclisation to yield the observed structure illustrated in the Scheme. This step is supported by the observation that the sulphur–nitrogen bonds adjacent to the nitrogen–ligand bonds in $S_4N_4{\cdot}L$ (L = acceptor)[25] adducts are weaker than the other bonds of the S_4N_4 ring. The observed structure (see below) of the $(S_3N_2)_2N^+$ cation with its two five-membered S_3N_2 rings is not altogether surprising, as various reactions of S_4N_4 have led to species containing an S_3N_2 ring, *e.g.* $S_3N_2^+$,[5] $(S_3N_2^+)_2$,[5,10] $(S_3N_2^+)_2 2Cl^-$,[10] $S_3N_2Cl^+Cl^-$,[29] $S_3N_2NC(O)CF_3$,[30] and $S_3N_2NSO_2F$.[31] Whatever the mechanism of the addition of S_4N_4 to S_2N^+, it is possible that it is in fact ' simple ' although caution must be exercised in drawing definite conclusions in the absence of substantial and convincing evidence in the light of the complexity of other reactions of sulphur–nitrogen compounds (ref. 11, p. 10). Nevertheless, in this reaction, S_2N^+ is acting as a building block in the synthesis of a more complex species. Other examples of S_2N^+ acting as a building block include the reaction of S_2NAsF_6 with chlorine and bromine to form $(SX)_2NAsF_6$ (X = Cl or Br),[28] XeF_2 to give $(SF_2)_2NAsF_6$,[28] and CsN_3 to give $(SN)_x$ and $CsAsF_6$.[13] In addition, S_2NAsF_6 reacts with CH_3CN, HCCH, and CH_3CCH leading to the AsF_6^- salts of 5-methyl-1,3,2,4-dithiadiazolium (4), 1,3,2-dithiazolium (5), and 4-methyl-1,3,2-dithiazolium (6)[32] cations respectively. All these reactions are essentially quantitative.

The $(S_3N_2)_2NFeCl_4$ salt[21] disproportionates more readily than $(S_3N_2)_2NAsF_6$ in solution. It is possible that dissociation is initiated by formation of a neutral S_6N_5X (X = F or Cl), formed more readily in the case of the chloride from the more basic $FeCl_4^-$ salt (*i.e.* $FeCl_4^-$ is a better halide-ion donor than AsF_6^-).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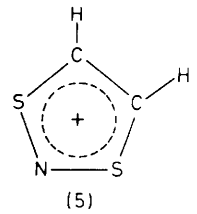
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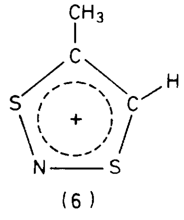
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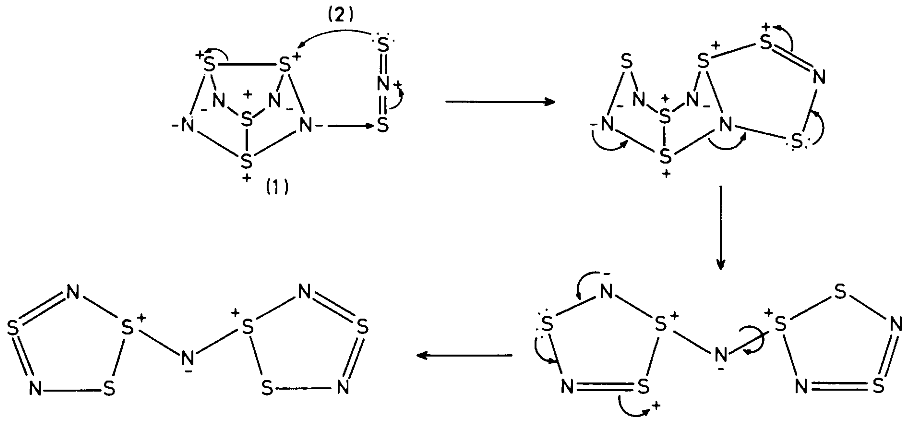


Scheme.

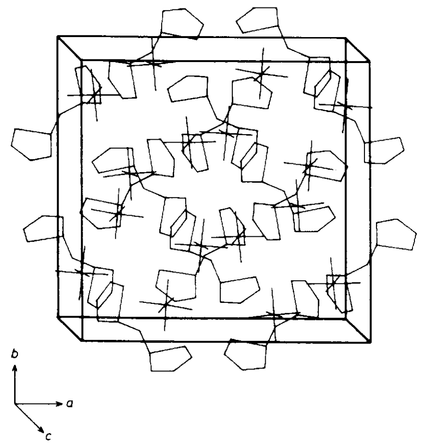


Figure 1. Unit-cell contents of $(S_3N_2)_2NAsF_6$

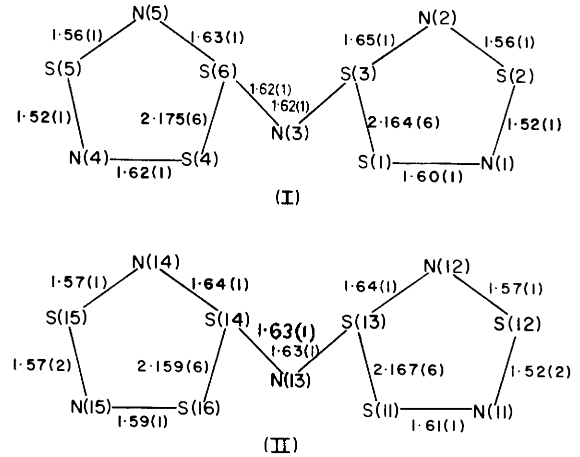


Figure 3. Bond distances (Å) for the two $(S_3N_2)_2N^+$ cations

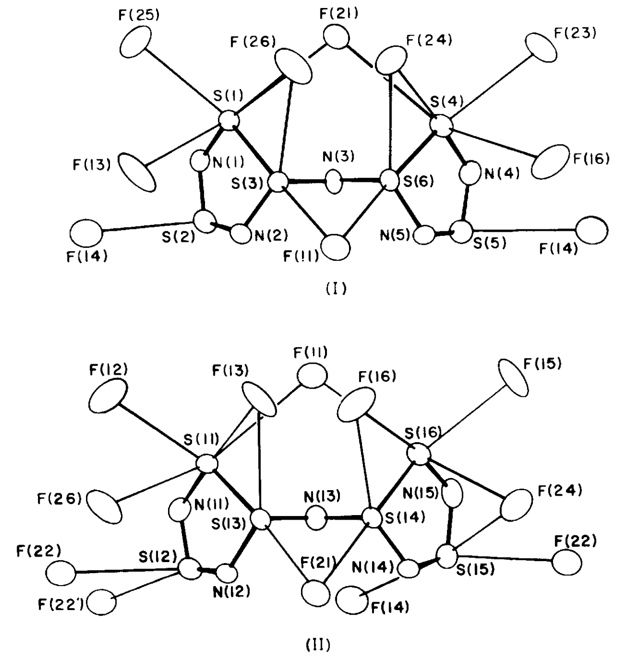


Figure 2. Structures of the two $(S_3N_2)_2N^+$ cations including anionic fluorine contacts (S · · · F ⩽ 3.37 Å)

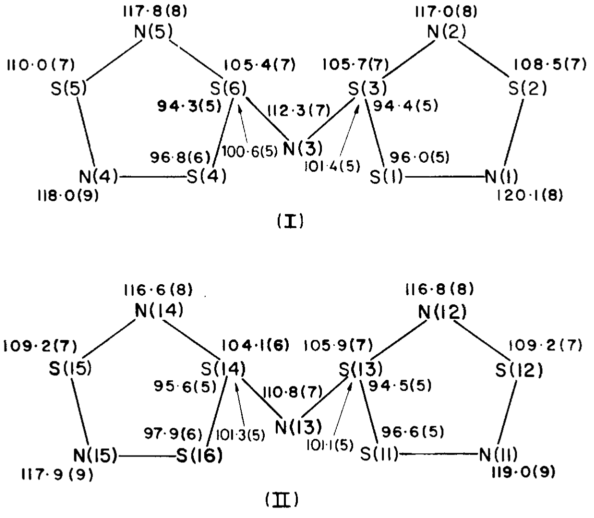
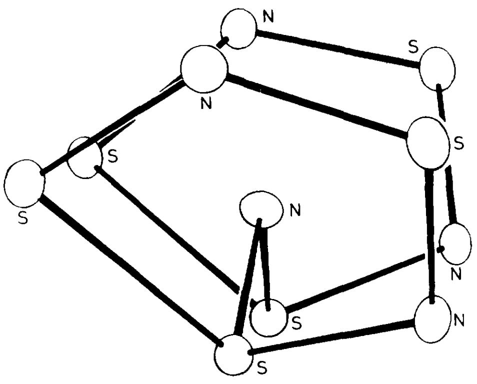


Figure 4. Bond angles (°) for the two $(S_3N_2)_2N^+$ cations

The i.r. spectrum of $(S_3N_2)_2NAsF_6$ is consistent with the presence of AsF_6^-,[33] S_3N_2 rings,[30] and an S–N–S bridging group [34] (see Table 1).

In the hope of preparing a new neutral sulphur–nitrogen



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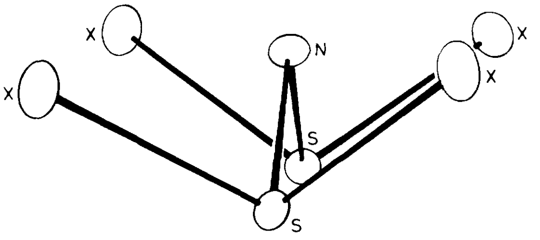


(8)

Table 3. Intraionic and interionic contact distances (Å) * and selected angles (°) for $(S_3N_2)_2NAsF_6$ with estimated standard deviations in parentheses

Cation (I)		Cation (II)	
(*a*) Intraionic			
S(3)-S(6)	2.691(5)	S(14)-S(13)	2.681(5)
N(2)-N(3)	2.61(2)	N(12)-N(13)	2.61(2)
N(5)-N(3)	2.59(2)	N(14)-N(13)	2.58(2)
S(1)-N(3)	2.95(1)	S(11)-N(13)	2.95(1)
S(4)-N(3)	2.94(1)	S(16)-N(13)	2.95(1)
(*b*) Interionic			
S(1)-F(25)	3.03(1)	S(11)-F(12)	2.99(1)
S(1)-F(26)	2.84(1)	S(11)-F(13)	2.90(1)
S(1)-F(13)	3.25(1)	S(11)-F(26)	3.34(1)
S(1)-F(21)	3.32(1)	S(11)-F(11)	3.36(1)
S(2)-F(14)	3.21(1)	S(12)-F(22)	3.02(1)
		S(12)-F(22′)	3.31(1)
S(3)-F(26)	2.97(1)	S(13)-F(13)	3.06(1)
S(3)-F(11)	3.08(1)	S(13)-F(21)	3.05(1)
S(6)-F(11)	3.08(1)	S(14)-F(21)	3.07(1)
S(6)-F(24)	3.05(1)	S(14)-F(16)	2.95(1)
S(4)-F(24)	2.90(1)	S(16)-F(16)	2.84(1)
S(4)-F(23)	3.16(1)	S(16)-F(15)	3.10(1)
S(4)-F(16)	3.33(1)	S(16)-F(24)	3.19(1)
S(4)-F(21)	3.36(1)	S(16)-F(11)	3.25(1)
S(5)-F(14)	3.31(1)	S(15)-F(14)	3.05(1)
		S(15)-F(22)	3.12(1)
		S(15)-F(24)	3.37(1)
(*c*) Angles			
F(25)-S(1)-S(3)	160.8(4)	F(12)-S(11)-S(13)	156.1(4)
F(26)-S(1)-N(1)	167.6(6)	F(13)-S(11)-N(11)	166.8(7)
F(26)-S(3)-N(2)	153.7(5)	F(13)-S(13)-N(12)	149.3(6)
F(11)-S(3)-S(1)	159.6(3)	F(21)-S(13)-S(11)	166.8(3)
F(11)-S(6)-S(4)	165.1(3)	F(21)-S(14)-S(16)	164.3(3)
F(24)-S(6)-N(5)	149.5(5)	F(16)-S(14)-N(14)	154.8(5)
F(24)-S(4)-N(4)	166.2(6)	F(16)-S(16)-N(15)	168.4(7)
F(23)-S(4)-S(6)	156.7(3)	F(15)-S(16)-S(14)	163.2(4)
F(14)-S(2)-N(1)	93.5(6)	F(22)-S(12)-N(11)	91.9(6)
F(14)-S(5)-N(4)	86.8(6)	F(14)-S(15)-N(14)	83.9(5)
(*d*) Torsional angles			
S(3),S(1)-S(6),S(4)	9.0(5)	S(13),S(11)-S(14),S(16)	6.9(5)
S(3),N(2)-S(6),N(5)	7.0(5)	S(13),N(12)-S(14),N(14)	6.6(5)

* All contacts shown for $S \cdots S < 3.60$, $S \cdots N < 3.35$, $N \cdots N < 3.00$, and $S \cdots F \leqslant 3.37$ Å; $S \cdots S$ and $S \cdots N$ contacts within the rings are omitted.

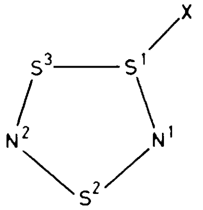
species, we reacted $(S_3N_2)_2NAsF_6$ with CsN_3 in liquid SO_2 at 0 °C, but instead obtained the known $(SN)_x$ in high yield (80%) according to equation (3). The $(SN)_x$ obtained was in the form of a blue-black powder and contained the same impurities (i.r.) as the $(SN)_x$ obtained from the reaction of S_2NAsF_6 and CsN_3 in liquid SO_2.[13] The direct chemical synthesis of $(SN)_x$ in solution has been recently reported from the reactions of $S_3N_3Cl_3$, $S_3N_2Cl_2$, S_3N_2Cl, and S_2Cl_2 with NaN_3 and/or $SiMe_3N_3$, as well as the reaction of S_2NAsF_6 with CsN_3.[13] The initial species formed in the $(S_3N_2)_2N^+/N_3^-$ reaction may be an open-chain form of S_6N_6 which may polymerize or dissociate to species ($2 \times S_3N_3$ or $3 \times S_2N_2$) [13] that polymerise to $(SN)_x$.

Crystal Structure of $(S_3N_2)_2NAsF_6$.—The crystal packing in $(S_3N_2)_2NAsF_6$ is shown in Figure 1. The structure consists of two identical, but crystallographically different, discrete $(S_3N_2)_2N^+$ cations and AsF_6^- units with some cation–anion interaction. The two $(S_3N_2)_2N^+$ cations with interionic fluorine contacts are illustrated in Figure 2, and bond distances and angles in the two cations are compared in Figures 3 and 4 respectively. The corresponding bond distances and angles in the two crystallographically different cations are essentially the same. Interionic and intraionic bond angles and distances are given in Table 3.

The $(S_3N_2)_2N^+$ cation can be regarded as a bicyclic derivative of $S_3N_2^+{-}N^-{-}R$ ($R = P_3N_3F_5$,[35,36] $P_4N_4F_7$,[36] $P_5N_5F_9$,[36] or $C_3N_3F_2$[36]) with $R = S_3N_2^+$, or alternatively as $(S_3N_2^+)_2$[5,10] with one of the long sulphur–sulphur contacts bridged by N^-. It is noted that $(S_3N_2)_2N^+$ and the neutral S_5N_6[27] [see (2)] are isoelectronic but not isostructural. Usually, isoelectronic species have similar structures. The reason why $(S_3N_2)_2N^+$ and S_5N_6 are different may be mechanistic (see above), or the thermodynamic stability of the $S_3N_2^+$ rings in $(S_3N_2)_2N^+$ may provide the driving force for the formation of this isomer.

The two S_3N_2 rings of the $(S_3N_2)_2N^+$ cation are essentially eclipsed when viewed along the axis of the bridgehead sulphur atoms [see (7)]. The average torsion angles between the disulphide groups of each ring and the adjacent bridgehead sulphur–nitrogen bonds are 7.9 and 6.8°, respectively. Similar geometries are found in $(SX_2)_2N^+$ ($X = F$[28] or CH_3[37]) depicted in (8). Such a geometry would minimise lone-pair repulsions in the plane of the bridging SNS atoms, and also maximise $p\pi$–$d\pi$ bonding between the bridging atoms. The $(S_3N_2)_2N^+$ structure may be viewed as being represented by two canonical forms $(S_3N_2){=}N{-}(S_3N_2)^+$ and $(S_3N_2)^+{-}N{=}(S_3N_2)$ and with a lesser contribution from $(S_3N_2)^+{-}N^-{-}(S_3N_2)^+$, consistent with the average bridging S–N bond distance of 1.624(5) Å, corresponding to a bond order of 1.47

Table 4. Bond lengths (Å) about various S_3N_2 rings



Compound	S^1-N^1	N^1-S^2	S^2-N^2	N^2-S^3	S^1-S^3	S^1-X	Average S–N	Deviation (Å) of S^1 from $N^1S^2N^2S^3$ plane
$(S_3N_2)_2NAsF_6$ [a]	1.640(7)	1.567(9)	1.535(26)	1.603(16)	2.166(7)	1.624(5)	1.586	0.37(3)
$S_3N_2NSO_2F$ [b]	1.644(3)	1.578(3)	1.565(3)	1.635(3)	2.200(2)	1.603(3)	1.605	0.31
$S_3N_2NC(O)CF_3$ [c]	1.641(4)	1.589(3)	1.551(2)	1.633(2)	2.206(1)	1.600(2)	1.603	0.38
$S_3N_2NP_3N_3F_5$ [d]	1.647(4)	1.572(4)	1.540(4)	1.629(4)	2.221(2)	1.555(4)	1.597	0.31
$(S_3N_2O)_2{\cdot}SnCl_4$ [e]	1.622(6)	1.575(7)	1.544(7)	1.611(7)	2.174(3)	1.494(5)	1.588	0.38
$Ag(S_3N_2O)_2AsF_6$ [f]	1.659(6)	1.557(6)	1.553(8)	1.628(9)	2.210(3)	1.439(8)	1.599	0.47
$S_3N_2Cl^+Cl^-$ [g]	1.581(5)	1.617(5)	1.543(5)	1.615(5)	2.136(5)	2.168(5)	1.589	0.26
$S_3N_2AsF_6$ [h]	1.595(9)	1.572(12)	1.557(12)	1.611(10)	2.143(5)	—	1.584	0.00
$S_6N_4(SO_3F)_2$ [h]	1.613(3)	1.569(3)	1.566(2)	1.613(3)	2.145(1)	—	1.590	0.00

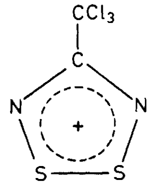
[a] Average of four S_3N_2 rings from two crystallographically different $(S_3N_2)_2N^+$ cations [quoted standard deviations = $\sqrt{\Sigma(x - \bar{x})^2/(n - 1)}$] where x = individual bond length and $\bar{x}$ and n are the average and number of such lengths. [b] Ref. 31. [c] Ref. 30. [d] Refs. 35 and 36. [e] H. W. Roesky, M. Kuhn, and J. W. Bats, *Chem. Ber.*, 1982, **115**, 3025. (Bond lengths of the two S_3N_2O molecules are averaged. The oxygen atom of S_3N_2O is bonded to the tin atom.) [f] H. W. Roesky, M. Thomas, J. Schimkowiak, M. Schmidt, M. Noltemeyer, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1982, 790. (The S_3N_2O molecule is mainly nitrogen bonded, with some oxygen bonding to the silver atom.) [g] Ref. 29. [h] Ref. 5.

as calculated using the relationship of Nyburg [38] between SN bond distance and bond order. The disulphide bonds of each ring are also eclipsed, *i.e.* the cation has idealised symmetry, C_s rather than C_2. This may arise mechanistically; as a result of fluorine interactions from the anion (see Figure 2), or from weak interactions between the two disulphide groups (or S_3N_2 rings) although the two bridgehead sulphur atoms and the adjacent sulphur atoms are separated by an average of 2.69 and 5.14 Å, respectively (twice the van der Waals radius of sulphur is 3.60 Å[39]).

The four S_3N_2 rings of the two $(S_3N_2)_2N^+$ cations are similar in geometry to one another (see Figures 3 and 4) and to those of other S_3N_2X species, whether they are cationic or neutral and whatever the substituent (see Table 4). Small differences, however, are observed. Those rings with a strongly interacting substituent have slightly weaker S–S bonds and S–N bonds adjacent to the substituent and also slightly weaker average S–N bond lengths. In addition, the neutral rings have a slightly longer average S–N bond distances than the cationic rings. The bonding in S_3N_2X rings has been discussed by various authors.[11,40–43]

The average bridging S–N bond distances and bridging nitrogen bond angle in $(S_3N_2)_2N^+$ [1.624(5) Å, 111.6(3)°] are not significantly different from those in $[S(CH_3)_2]_2N^+$ [1.635(5) Å, 110.8(2.0)° [37]] and both are consistent with Banister's [43,44] empirical formula relating the mean S–N bond length (pm) to the angle (degrees) about the central nitrogen atom ($d_{NS} = 177.47 - 0.1421\hat{N}$) for an unstrained species. The bond lengths and angles about the S_3N_2 rings are also consistent with Banister's relationship for a strained system ($d_{NS} = 284.8 - 1.053\hat{N}$ and $d_{NS} = 213.14 - 0.4816\hat{S}$).

The anionic fluorine contacts with the sulphur atoms of the S_3N_2 rings in the $(S_3N_2)_2N^+$ cations (see Figure 2) are very similar to those interionic contacts in various $S_6N_4{}^{2+}$ [5,10] salts and $S_3N_2AsF_6$.[5] Other related systems that contain a disulphide group in the ring such as $S_4N_3{}^+$ [6] and 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride (9),[45] also possess an interionic contact that bridges this disulphide bond. These interionic contacts, as Gillespie *et al.*[5] have pointed out, and others have shown,[46] are in such directions as to avoid non-bonding and bonding electron density about the sulphur atoms. Therefore these contacts are approximately collinear with one of the bonds in the S_3N_2 ring and/or perpendicular to others in the ring (see Figure 2 and Table 3). The number of S ··· F interactions is not significantly different between the individual S_3N_2 rings in $(S_3N_2)_2N^+$, and $S_6N_4(AsF_6)_2$ or $S_3N_2AsF_6$, but the average strength of the S ··· F contacts in $(S_3N_2)_2N^+$ (*ca.* 3.12 Å) is significantly weaker than the average seen in $S_3N_2AsF_6$ (*ca.* 3.068 Å) and $S_6N_4(AsF_6)_2$ (*ca.* 2.980 Å).[5] This reflects the lower charge per S_3N_2 ring (+0.5) in $(S_3N_2)_2N^+$. The extra fluorine contacts to sulphur atoms S(12) and S(15) in the $(S_3N_2)_2N^+$ cation (II), that are not present in cation (I), do not lead to observable bond length differences within the cations.



(9)

The geometries about the two $AsF_6{}^-$ anions are that of a distorted octahedron, but due to high fluorine thermal parameters no significant correlation can be made between the length of the As–F bonds and the strength or number of contacts that an anionic fluorine makes with the sulphur atoms of the $(S_3N_2)_2N^+$ cations.

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