The Reaction of S_2NAsF_6 with Halogens: Preparation and *X*-Ray Crystal Structure of Bis(difluorothio)nitronium Hexafluoroarsenate(v), $(SF_2)_2NAsF_6$; † Preparation of $(SBr)_2NAsF_6$, and Vibrational Spectrum and Normal-co-ordinate Analysis of the $(SX)_2N^+$ (X = Cl or Br) Cations

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Solutions of S_2NAsF_6 in liquid SO_2 react with elemental chlorine and bromine yielding $(SX)_2NAsF_6$ (X = Cl or Br), essentially quantitatively. No reaction was detected with iodine. The vibrational spectrum of $(SBr)_2N^+$ was similar to that of $(SCl)_2N^+$ of known structure, implying a similar structure for the bromine derivative. This conclusion was supported by a normal-co-ordinate analysis of $(SX)_2N^+$. The analysis was consistent with some positive interaction between the halogen atoms in $(SX)_2N^+$, possibly accounting for the *cis* planar geometry of these cations. Attempts to prepare $(SF)_2NAsF_6$ were unsuccessful. However, $(SF_2)_2NAsF_6$ was synthesised by the reaction of S_2NAsF_6 and XeF_2 in liquid SO_2F_2, essentially quantitatively. The structure of $(SF_2)_2NAsF_6$ was determined by *X*-ray diffraction. The crystals are orthorhombic with a = 14.909(1), b = 9.843(4), c = 12.113(1) Å, and Z = 8. The structure was refined in space group *Pbca* to a conventional R factor of 0.076 for 902 independent reflections with $I \geqslant 2\sigma(I)$. It consists of discrete $(SF_2)_2N^+$ and AsF_6^- with some cation–anion interactions. The $(SF_2)_2N^+$ cation has approximate C_{2v} symmetry with essentially eclipsed fluorine–sulphur bonds as viewed along the sulphur–sulphur axis. The average S–N and S–F distances are 1.551(10) and 1.523(8) Å, and the average FSF and FSN bond angles are 94.0(5) and 100.2(6)°. The SNS bond angle is 121.1(6)°. The vibrational spectrum of $(SF_2)_2NAsF_6$ is reported.

We recently described [1] a convenient synthesis of S_2NAsF_6 containing the dithionitronium cation, S_2N^+, previously prepared in unspecified yield as the $SbCl_6^-$ salt.[2] The S_2N^+ cation is a potentially useful building block in sulphur–nitrogen chemistry and in this paper we report its systematic reaction with the halogens and the mild fluorinating agents ClF and XeF_2. The new compounds $(SBr)_2NAsF_6$ and $(SF_2)_2NAsF_6$ were subsequently prepared. In order to establish the geometry of $(SBr)_2N^+$, its vibrational spectrum was compared with that of $(SCl)_2N^+$, and a normal-co-ordinate analysis undertaken of both cations. The structure of $(SF_2)_2NAsF_6$ was established by *X*-ray crystallography. Other chemistry of S_2NAsF_6 includes its reaction with CsN_3 in SO_2 solution to give poly(sulphur nitride),[3] and with S_4N_4 leading to $(S_3N_2)_2NAsF_6$.[4]

Experimental

General Procedures.—Techniques and reagents, unless otherwise specified, have been described in refs. 5—8.

The SO_2, Cl_2 (Matheson), Br_2 (Fisher Scientific), and SO_2ClF (Aldrich) were stored over CaH_2, P_4O_{10}, and NaF respectively. The Xe and F_2 (Matheson) used to prepare XeF_2,[9] ClF (Ozark-Mahoning), SO_2F_2 (Matheson), BF_3 (ICN Pharmaceuticals), and $SiMe_3Cl$ (Petrarch) were used directly. The S_2NAsF_6 was prepared as in ref. 1. Unless otherwise specified, reactions were carried out in two bulbed glass vessels incorporating a medium sintered frit and a Teflon-stemmed glass J. Young valve.

Infrared spectra were obtained of powdered solids and Nujol mulls using KBr windows as previously described.[5] In addition, spectra were recorded in the region 700—120 cm^{-1} using a Nicolet 7 199 Fourier-transform i.r. spectrometer using polyethylene plates. Mass spectra were obtained using the direct inlet method.[5]

Preparation of $(SCl)_2NAsF_6$.—In a typical reaction, SO_2 (4.06 g, 63.3 mmol) and an excess of Cl_2 (0.28 g, 3.96 mmol) relative to equation (1) (see Results and Discussion section) were consecutively condensed onto S_2NAsF_6 (0.58 g, 2.16 mmol) in one of the bulbs of a two-bulbed vessel. The mixture was warmed to room temperature (r.t.) with shaking, and after 1 h the yellow solution was quantitatively transferred into the second bulb through the sintered glass frit. Sulphur dioxide was condensed back into the first bulb, held at 0 °C, from the solution containing the product. Volatiles were removed by evacuation, and the yellow needle-shaped crystals obtained were identified as $(SCl)_2NAsF_6$ from their i.r. and Raman spectra (Table 1). The yield of $(SCl)_2NAsF_6$ (0.73 g, 2.15 mmol) was 99% based on equation (1) [Found: As, 21,85; Cl, 20.8; N, 4.05; S, 18.55. Calc. for $(SCl)_2NAsF_6$: As, 22.15; Cl, 21.0; N, 4.15; S, 19.0%].

Thermal Decomposition of $(SCl)_2NAsF_6$.—Powdered $(SCl)_2NAsF_6$ (0.41 g, 1.20 mmol) was subjected to a dynamic vacuum at r.t. for 20 h, with no weight loss. The same material (0.35 g) was heated in a similar manner at 130 °C for 48 h with a weight loss of 0.01 g. Small quantities of a yellow liquid slowly condensed into the −196 °C cold trap. The i.r. spectrum of the remaining solid only showed peaks attributable to $(SCl)_2NAsF_6$. The mass spectrum of $(SCl)_2NAsF_6$ at 130 °C showed peaks attributable to AsF_4^+ (m/e = 151, intensity 90%), SN^+ (m/e = 46, 54%), and weaker peaks attributable to S_2Cl^+ (m/e = 101 and 99, 8 and 20% respectively), and their breakdown products.

Preparation of $(SBr)_2NAsF_6$.—In a typical reaction, SO_2 (9.58 g, 150 mmol) and an excess of Br_2 (0.85 g, 5.34 mmol) relative to equation (1) were consecutively condensed onto S_2NAsF_6 (1.30 g, 4.88 mmol). The reaction mixture was treated as described above, yielding orange-red needle-shaped crystals which were identified as $(SBr)_2NAsF_6$ from their i.r. and Raman spectra (Table 1). The yield of $(SBr)_2NAsF_6$ (2.08 g, 4.87 mmol) was 99% based on equation (1) [Found: As,

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† *Supplementary data available* (No. SUP 23634, 13 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

17.65; Br, 37.4; N, 3.25; S, 14.65. Calc. for $(SBr)_2NAsF_6$: As, 17.55; Br, 37.45; N, 3.30; S, 15.0%].

Thermal Decomposition of $(SBr)_2NAsF_6$.—Powdered $(SBr)_2NAsF_6$ (0.50 g, 1.18 mmol) was subjected to a dynamic vacuum at r.t. for 115 h. A dark red liquid (Br_2) slowly condensed into the −196 °C glass cold trap. The solid product contained $(SBr)_2NAsF_6$ and S_2NAsF_6 (i.r.), and was 0.04 g lighter than the starting material. Pure material stored in sealed glass tubes at 0 °C for several months showed (i.r.) no detectable signs of decomposition. The mass spectrum of $(SBr)_2NAsF_6$ obtained at 80 °C showed peaks attributable to Br_2^+ (m/e = 162, 160, and 158; intensity 50, 100, and 53% respectively), and weaker peaks attributable to S_2N^+ (m/e = 78, 1.3%) and AsF_4^+ (m/e = 151, 1.0%), and their breakdown products.

Attempted Preparation of $(SI)_2NAsF_6$.—Sulphur dioxide (3.89 g, 60.7 mmol) was condensed onto I_2 (0.34 g, 1.34 mmol) in one bulb of a two-bulb glass vessel. On warming to r.t. a red-purple solution formed, but a large proportion of the I_2 remained undissolved. The SO_2 was then condensed onto S_2NAsF_6 (0.31 g, 1.17 mmol) in the second bulb, and the yellow solution was transferred onto the I_2 through the frit. The solution became reddish in colour, but a large proportion of the I_2 remained undissolved. The SO_2 was slowly evaporated from the solution yielding yellow and black (I_2) crystals; the latter sublimed from the vessel on evacuation. The yellowish product (0.31 g) was identified (i.r.) as S_2NAsF_6.

Attempted Preparations of $(SF)_2NAsF_6$.—(*a*) Sulphuryl chloride fluoride (5.31 g, 44.8 mmol) and ClF (0.16 g, 2.85 mmol) were consecutively condensed onto $(SCl)_2NAsF_6$ (0.48 g, 1.43 mmol) in a Teflon vessel (outside diameter 12 mm) equipped with a stainless-steel 1KS4 Whitey valve and a brass Swagelok reducing junction. On warming to r.t. a yellow gas collected above the stirred yellow solution. After 5 h the volatiles containing SO_2ClF, SF_4, SF_5Cl, and a trace of OSF_2 (i.r.) were removed. The pale yellow solid (0.55 g) that remained contained unreacted $(SCl)_2NAsF_6$ and SF_3AsF_6 (i.r.).[10]

(*b*) Sulphuryl fluoride (15.38 g, 150.7 mmol) and XeF_2 (0.49 g, 2.89 mmol) were consecutively condensed onto S_2NAsF_6 (0.73 g, 2.73 mmol) in a well dried and fluorinated Monel reaction vessel (35 cm^3) equipped with a removable top and Teflon gasket. The mixture was held at 0 °C, with agitation, for 1 h. The volatiles containing SO_2F_2 and a trace of SiF_4 (i.r.) were removed after 2 h at r.t. The remaining yellow and white solid mixture (0.80 g) contained S_2NAsF_6 and $(SF_2)_2NAsF_6$ (i.r.).

(*c*) Sulphuryl fluoride (6.28 g, 61.5 mmol) and F_2 (0.03 g, 0.73 mmol) were consecutively transferred into a Monel vessel containing S_2NAsF_6 (0.19 g, 0.71 mmol) at −196 °C and then stirred for 4 h while held at −78 °C. After 20 h of stirring at r.t. the volatiles containing SO_2F_2 and SF_6 (i.r.), as well as a non-condensable gas, were removed. The pale yellow solid product (0.18 g) contained S_2NAsF_6, SF_3AsF_6, and $(SF_2)_2NAsF_6$ (i.r.).

Preparation of $(SF_2)_2NAsF_6$.—In a typical reaction, a preweighed excess of XeF_2 (0.96 g, 5.67 mmol) * was quantitatively condensed from a weighed vessel *via* a Monel U-tube onto a frozen mixture of S_2NAsF_6 (0.62 g, 2.32 mmol) and SO_2F_2 (9.41 g, 92.2 mmol) in a Monel vessel. In order to facilitate a quicker transfer of XeF_2, a hot-air gun was used to warm the XeF_2 containing vessel and the connecting U-tube. The mixture was stirred and shaken at 0 °C for 0.5 h to transfer the XeF_2 adhering to the walls of the vessel into the solution, and to effect good mixing. After further stirring for 12 h at r.t. the volatiles containing SO_2F_2 and a trace of SF_6 (i.r.) were removed (3 h of pumping to evacuate excess of XeF_2). The white solid powder was characterised as $(SF_2)_2NAsF_6$ by its i.r. and Raman spectra (Table 2). The yield of $(SF_2)_2NAsF_6$ (0.79 g, 2.30 mmol) was 99% based on equation (3).

The $(SF_2)_2NAsF_6$ (0.59 g, 1.72 mmol) was separated from impurities derived from the Monel vessel and traces of XeF_2 by dissolving it in SO_2 (5.04 g, 78.7 mmol) in a two-bulb glass vessel and filtering the pale yellow solution through a finely sintered glass frit into the second bulb. The solution was then manipulated in a manner similar to that described for $(SCl)_2NAsF_6$, to yield 0.59 g of a colourless microcrystalline material. Colourless crystals suitable for *X*-ray structure analysis were obtained by recrystallisation from an SO_2 (3.64 g)-SO_2ClF (2.05 g) mixture, m.p. 122—123 °C (decomp.). ^{19}F N.m.r. spectrum of $(SF_2)_2NAsF_6$ (20% by weight) in SO_2 solution (p.p.m. relative to CCl_3F): δ + 23.2 (s), $W_{\frac{1}{2}}$ = 5 Hz, $(SF_2)_2N^+$; *ca.* −57.5 (s), $W_{\frac{1}{2}}$ = 1 300 Hz, AsF_6^- [Found: As, 21.35; F, 60.45; N, 4.0; S, 18.7. Calc. for $(SF_2)_2NAsF_6$: As, 21.85; F, 55.4; N, 4.1; S, 18.7%]. Other reactions of XeF_2 and S_2NAsF_6 using CH_2Cl_2 and CCl_4 as solvents led to extensive fluorination of the solvent and no detectable amounts of $(SF_2)_2NAsF_6$.

Thermal Decomposition of $(SF_2)_2NAsF_6$.—Powdered $(SF_2)_2NAsF_6$ (0.06 g, 0.17 mmol) was placed in the bottom of a right-angled Monel side arm attached to a prefluorinated stainless-steel i.r. cell (10 cm) equipped with AgCl windows. The vessel was evacuated and the side arm was slowly heated at a steady rate, while i.r. spectra were recorded. The concentration of SF_4 increases with temperature (to 225 °C), and was first observed at *ca.* 140 °C.

Similar experiments in glass gave volatiles containing large amounts of SiF_4, OSF_2, SF_4, and SO_2F_2 (i.r.). The yellowish solid residue contained $(SF_2)_2NAsF_6$ (i.r.) as well as a small amount of an unidentified species.

Reactions of $(SF_2)_2NAsF_6$.—(*a*) *With* CsF. Caesium fluoride (0.24 g, 1.58 mmol) and $(SF_2)_2NAsF_6$ (0.40 g, 1.17 mmol) were each thoroughly ground and placed in a dry Monel vessel (28 cm^3) containing three nickel balls (diameter 1 cm). The vessel was shaken on a mechanical agitator for 24 h at room temperature. The volatiles contained SF_4, NSF, as well as a small amount of OSF_2 and NSF hydrolysis products (i.r.), and a non-condensable gas. The remaining whitish solid (0.45 g) contained $CsAsF_6$ (i.r.).

(*b*) *With* F_2. Fluorine (0.03 g, 0.68 mmol) was expanded into a Monel vessel containing SO_2F_2 (6.09 g, 59.7 mmol) and $(SF_2)_2NAsF_6$ (0.07 g, 0.20 mmol) held at −196 °C. The mixture was held at −78 °C, with stirring, for 3 h. After stirring for 20 h at r.t. the volatiles containing SO_2F_2, traces of SF_6 (i.r.), and a non-condensable gas were removed. The remaining while solid (0.07 g) was $(SF_2)_2NAsF_6$ (i.r.).

Attempted Preparation of $(SCl_2)_2NAsF_6$.—Chlorotrimethylsilane (1.37 g, 12.6 mmol) was condensed onto $(SF_2)_2NAsF_6$ (0.38 g, 1.11 mmol) in a Teflon vessel. On warming to 0 °C the stirred slurry turned yellow with evolution of a gas. After 1 h the gas evolution had stopped, and the volatiles containing $SiMe_3Cl$ and $SiMe_3F$ (i.r.) were removed leaving a yellow solid identified as $(SCl)_2NAsF_6$ (i.r.).

Crystal Data.—$(SF_2)_2NAsF_6$, M = 343.03, Orthorhombic, space group *Pbca*, a = 14.909(1), b = 9.843(4), c = 12.113(1)

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* **CAUTION**: A violent reaction occurred on mixing solid XeF_2 and S_2NAsF_6 at r.t. without a moderating solvent.

Å, $U = 1\,778$ Å^3, $Z = 8$, $D_c = 2.563$ g cm^{-3}, $F(000) = 1\,296$, $\mu(\text{Mo-}K_\alpha) = 4.39$ mm^{-1}, $\lambda = 0.710\,69$ Å.

A well formed crystal of $(SF_2)_2NAsF_6$ of dimensions $0.56 \times 0.14 \times 0.06$ mm was mounted and sealed, under dry nitrogen, in a rigorously dried glass capillary tube as previously described.[11] An initial photographic investigation was made using precession techniques after which the crystal was transferred to a Picker FACS-I diffractometer equipped with a graphite monochromator and Mo-K_α radiation.

The diffractometer was controlled by a FORTRAN IV control program;[12] cell parameters and an orientation matrix were refined by least squares using the centered co-ordinates of 19 reflections and their Friedel opposites. Data were collected using an ω–2θ scan during which a profile of the peak was accumulated in the computer. The background level was estimated by a stationary count for 1/10 of the scan time at each end of the scan. If the net intensity was significant $[I > 2\sigma(I)]$ an analysis of the profile was performed to determine the limits of the peak and those parts of the scan on either side were included in the background estimate. The intensities of three standard reflections, monitored every 100 reflections, showed no significant deviation from their mean values.

After reduction of the intensity data the structure was solved by multiple-solution direct methods using the computer program MULTAN.[13] The E map phased by the solution with the highest 'combined figure of merit' yielded the positions of all the non-fluorine atoms. The fluorines were located in a subsequent difference synthesis. After correction of the data for absorption (transmission coefficients 0.33—0.62) the structure was refined by block-matrix least squares using anisotropic thermal parameters for all atoms. The function minimised was $\Sigma w(\Delta F)^2$ with $w = 1/[\sigma^2(F) + pF^2]$ the factor p was determined from the measurements of the standards to be 0.002. Scattering factors were taken from ref. 14 and corrected for anomalous dispersion. The final values of $R(=\Sigma|\Delta F|/\Sigma|F_o|)$ and $R'[=(\Sigma w|\Delta F|^2/\Sigma w|\Delta F_o|^2)^{\frac{1}{2}}]$ were 0.076 and 0.108 (0.094 and 0.117 including unobserved reflections) respectively. The final positional parameters are given in Table 3. The program system used was that of Larson and Gabe[12] for the PDP8/E computer.

Results and Discussion

Preparations of $(SX)_2NAsF_6$ *(X = Cl or Br), and Attempted Preparations (X = F or I).*—Dichloro- and dibromo-dithionitronium hexafluoroarsenate(V) are readily prepared in essentially quantitative yields by the addition of a slight excess of chlorine or bromine to S_2NAsF_6 in liquid sulphur dioxide at room temperature according to equation (1) (X = Cl or Br). Various $(SCl)_2N^+$ salts[15-18] have been prepared by other routes, including $(SCl)_2NAsF_6$.[18,19] This is the first report of a $(SBr)_2N^+$ salt, and of a bromine-containing sulphur-nitrogen cation, although the carbon-containing cation in $CS_3N_2Br^+Br_3^-$ has been described.[20]

$$S_2NAsF_6 + X_2 \xrightarrow{SO_2} (SX)_2NAsF_6 \qquad (1)$$

Attempts to prepare $(SI)_2NAsF_6$ from S_2NAsF_6 and iodine were unsuccessful. The $(SBr)_2NAsF_6$ dissociates under dynamic vacuum at r.t. to S_2NAsF_6 and Br_2 [*i.e.* reverse of equation (1)], while $(SCl)_2NAsF_6$ did not dissociate under similar conditions. At 130 °C $(SCl)_2NAsF_6$ decomposes or dissociates into products that include sulphur chlorides but not Cl_2. Thus the stabilities of $(SX)_2NAsF_6$ (X = I, Br, or Cl) towards dissociation into S_2NAsF_6 and halogen appear to be related to the relative strength[21,22] of the sulphur-halogen bonds. The non-existence of $(SI)_2NAsF_6$ under these conditions is reflected in the instability of solid binary sulphur iodides at room temperature;[23] HSI is, however, stable in the gas phase,[21] and S_2I_2 at -90 °C,[24] and the salts $S_2I_4(AsF_6)_2$,[25] $(S_7I)_4S_4(AsF_6)_6$,[26] $(S_7I)_2I(SbF_6)_3{\cdot}2AsF_3$,[27] and S_7IMF_6 (M = As or Sb)[28] containing stable sulphur iodine cations have been prepared and characterised.

Attempts to prepare $(SF)_2NAsF_6$ by the reaction of S_2NAsF_6 with elemental fluorine or XeF_2, in a 1 : 1 ratio, in SO_2F_2 diluent were unsuccessful and led instead to products that included $(SF_2)_2NAsF_6$. A similar reaction of $(SCl)_2NAsF_6$ and ClF gave products that included SF_3AsF_6. These reactions are inhomogeneous and $(SF)_2NAsF_6$ may be initially formed on the various surfaces and preferentially react further to give the observed product.

Vibrational Spectra and Normal-co-ordinate Analysis of $(SCl)_2N^+$ *and* $(SBr)_2N^+$.—The vibration spectra of $(SX)_2NAsF_6$ with tentative assignments of frequencies are given in Table 1. It is noted that the relative intensities of the Raman lines of $(SCl)_2NAsF_6$ obtained with the exciting lines 6 328 and 5 145 Å were not identical, presumably due to some partial resonance-enhancement effect. The similarity of the vibrational spectra (Table 1) of $(SCl)_2N^+$ and $(SBr)_2N^+$ indicates that the two must have the same general *cis* planar conformation. Therefore, for our vibrational analysis we developed a provisional $(SBr)_2N^+$ structure as follows. First we averaged the available data[19] for $(SCl)_2N^+$ to give C_{2v} symmetry. Then keeping the identical S–N–S geometry to that in $(SCl)_2N^+$, we assumed S–Br distances to be 0.15 Å[29] greater than the S–Cl distance[19] in $(SCl)_2N^+$ and the Br $\cdots$ Br distance to be 3.3% less than twice the bromine van der Waals distance, since that is the case for the Cl $\cdots$ Cl distance[19] in $(SCl)_2N^+$ (van der Waals distances[30] Cl $\cdots$ Cl 3.50 Å and Br $\cdots$ Br 3.70 Å). The geometries of both cations are given in Table 4. The vibrational analysis is insensitive to changes in the Br $\cdots$ Br distance of ± 0.1 Å.

Our assignment of in-plane vibrations of $(SCl)_2N^+$ differs from those proposed by Glemser *et al.*[19] and Schnepel,[31] most notably for the two lowest frequencies. One of the difficulties in this case is that there are several middle-range frequencies that cannot easily be assigned to particular motions. Thus the assignments in Table 1 are the ones we prefer, but there are not yet sufficient data to make them definitive.

The vibrational analysis used the Wilson F and G matrix method[32] and a least-squares fitting procedure to find a set of force constants for the $(SX)_2N^+$ cations, treated as isolated ions. The constants include a halogen–halogen stretching constant, because: (*a*) the short Cl $\cdots$ Cl distance (and by inference Br $\cdots$ Br) implies at least a very weak interaction; (*b*) the lack of evidence for non-planar or less symmetrical forms in solution (see Table 1) is most easily explained by halogen–halogen interactions; and (*c*) this constant greatly accelerates and improves the fitting. This may also explain why the $(SCl)_2N^+$ cation does not fit Banister's[33] empirical formula for the correlation of the mean S–N bond length (in pm) with the bond angle (in degrees) at the nitrogen for an unstrained species, as given in equation (2). The $\hat{N}$ angle is calculated by equation (2) to be 174° (observed 151°). Presumably $\hat{N}$ is reduced from its strain-free value of 174° by the interaction of the two Cl atoms.

$$d_{NS} = 177.47 - 0.1421\hat{N} \qquad (2)$$

The values of the force constants are given in Table 5 and the calculated and observed frequencies in Table 6. These values are best for the assumptions and constraints we have chosen, but the values are not very sensitive to small changes in the geometry. The large values of the off-diagonal terms are

Table 1. Vibrational spectra (cm^{-1}) of $(SCl)_2NAsF_6$ and $(SBr)_2NAsF_6$

$(SCl)_2NAsF_6$ [a]				$(SBr)_2NAsF_6$			
	Raman				Raman		
I.r. (Nujol)	solid, 6 328 Å	solid, 5 145 Å	SO_2 soln., 5 145 Å	I.r. (Nujol)	solid, 6 328 Å	SO_2 soln., 5 145 Å	Tentative assignment
1 128m		*ca.* 1 133 ?vvw		1 126m			$\nu_{asym.}(NS_2)$
1 091w		*ca.* 1 077 ?vvw		1 089w			
817w				811w			AsF_6^- ? [b]
718 ? (sh)	728(60)	728(100)	721(100)p		716(100)	714(100)p	$\nu_{sym.}(NS_2)[+\ \delta_{sym.}(SNS)]$ [c]
698vs				698vs			$\nu_3(AsF_6^-)$ [d]
	681(25)	684(9)	679(9)p		680(19)		$\nu_1(AsF_6^-)$ [d]
660mw	661(65)	664(17)	659(57)p	664mw	647(70)	645(18)p	$\delta_{sym.}(SNS)(+$ SX or SN$)$ [c]
574w	576(6)	578(1)		570vw	575(4)		$\nu_2(AsF_6^-)$ [d]
529ms	530(30)	525(7)	527(18)p [e]	461ms	461(2)	465(1)	$\nu_{asym.}(SX)(+\ SN)$ [c]
512m	518 (sh)						
455w	457(17)	458(2)	452(10)p	413 ? (sh)	414(20)	414(2)	$\nu_{sym.}(SX)(+\ SN)$ [c]
	405(3)	407(1)	405(1)	346vw	[f]	341(3)dp ?	$2\delta_{asym.}(NSX)$
390s				393s			$\nu_4(AsF_6^-)$ [d]
356w	370(8)	372(2)	371(1)	362vw	369(35)	365(4)p	$\nu_5(AsF_6^-)$ [d]
	227(14)	226(8)	218(7)p			165(6)dp ?	$\nu_{sym.}(X \cdots X)$
203mw	204(100)	204(4)	202(13)dp ?	155 ?mw	155(100)		$\delta_{asym.}(NSX)$
	129(18)						$\tau_{sym.}$ or lattice mode

[a] Frequencies quoted in substantial agreement with those quoted in ref. 19. [b] Peaks are seen in other unrelated salts, *e.g.* $OSClF_2AsF_6$.[8] [c] Mode may be mixed. [d] G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212. [e] Includes a peak attributable to SO_2 solvent (519 cm^{-1}). [f] Peaks may be hidden under that at 369 cm^{-1}.

typical of small-ring systems with delocalised bonds and strained angles. Small differences in values are not significant. However, the constants suggest that the bromide tends toward a separation into S–N–S and Br–Br (S–Cl is stronger than S–Br, but N–S and $X \cdots X'$ are stronger in the bromide), which is consistent with its behaviour on dissociation.

In conclusion, the vibrational data and the normal-co-ordinate analysis support the proposal that the structure of the bromine derivative is similar to the known structure of the chloride, and that there are real halogen–halogen constants in $(SX)_2N^+$ (X = Cl or Br) which are probably responsible for the *cis*, planar geometries.

Preparation of Bis(*difluorothio*)*nitronium Hexafluoroarsenate*(v).—The compound $(SF_2)_2NAsF_6$ is prepared in essentially quantitative yield by the reaction of S_2NAsF_6 and a slight excess of XeF_2 in liquid sulphuryl fluoride according to equation (3).

$$S_2NAsF_6 + 2XeF_2 \xrightarrow{SO_2F_2} (SF_2)_2NAsF_6 + 2Xe \quad (3)$$

The product was characterised by elemental analyses, vibrational spectra (Table 2), ^{19}F n.m.r., and by the determination of its *X*-ray crystal structure (below). The typical ^{19}F chemical shift range for $R{-}N{=}SF_2$ compounds is between +16.7(2) ($FNSF_2$) and +69.9(1) p.p.m. ($CH_3{-}NSF_2$).[34] The $(SF_2)_2N^+$ cation, as may be expected,[34] with its positive charge, lies in the high end of this range, at +23.2(5) p.p.m.*

Solid caesium fluoride and $(SF_2)_2NAsF_6$ agitated together at r.t., yielded SF_4 and NSF in the volatile products. No evidence was found for the sought after F_3SNSF_2 species, under our experimental conditions, related to $(CH_2)_nSBrNSPh_2$ (n = 4 or 5).[35] Attempts to prepare $NS_2F_n^+$ ($n > 4$), by the fluorination of $(SF_2)_2NAsF_6$ with elemental fluorine and an excess of XeF_2, were unsuccessful.

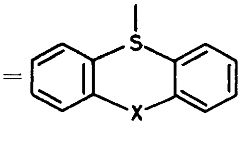
Cations of the type $(SX_2)_2N^+$ have been previously prepared, and include $(S_3N_2)_2N^+$,[4] $(SMe_2)_2N^+$,[36-38] $(SPh_2)_2N^+$,[39,40] $[(CH_2)_5SNSPh_2]^+$,[35] $[SMe(CH_2Cl)]_2N^+$,[40] and R_2N^+ (R = ; X = O, S, NPh, or NMe).[41] An attempt to prepare the analogous tetrachloro-derivative, $(SCl_2)_2N^+$, from the reaction of $(SF_2)_2NAsF_6$ with $SiMe_3Cl$

Table 2. Vibrational spectra (cm^{-1}) of $(SF_2)_2NAsF_6$

I.r. (Nujol)	Raman (solid, 5 145 Å)	Tentative assignment [a]
1 226 (sh)		$\nu_{asym.}(NS_2)$
1 187s		
1 015vw		overtones and/or combination bands
969vw		
903mw	900(70)	$\nu_{sym.}(SF_2)$ or $\nu_{sym.}(NS_2)$
851 (sh)	848(80)	$\nu_{asym.}(SF_2)$ or $\nu_{asym.}(SF_2)$ or $\nu_{asym.}(SF_2)$
833vs	835(85)	
711vs [b,c]	703(20)	$\nu_{sym.}(NS_2)$ or $\delta_{asym.}(SNS)$
699 (sh)		$\nu_3(AsF_6^-)$ [c]
	c,d	$\nu_1(AsF_6^-)$ [c]
676mw	674(100)	$\delta_{sym.}(SNS)$
576 (sh)	577(6)	$\nu_2(AsF_6^-)$ [c] $\delta_{sym.}(NSF_2)$ or $\nu_2(AsF_6^-)$ [c]
564mw	563(15)	
507m	507(6)	$\delta_{asym.}(NSF_2)$ or $\delta_{sym.}(NSF_2)$
472mw	471(35)	$\delta_{sym.}(SF_2)$
392s		$\nu_4(AsF_6^-)$ [c]
368vw	368(15)	$\nu_5(AsF_6^-)$ [c]
	322(7)	$\delta_{asym.}(SF_2)$
	306(70)	$\tau_{sym.}$
	274(2)	$\tau_{asym.}$

[a] Made by comparison with $(SCl)_2N^+$; $(SBr)_2N^+$; OSF_2 and SO_2F_2 (T. Shimanouchi, *J. Phys. Chem. Ref. Data*, 1977, **6**, 993 and refs. therein); and SF_3^+ (M. Arzein, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, 1969, **47**, 4159; ref. 10). [b] Major component is the very strong $\nu_3(AsF_6^-)$ mode at 699 cm^{-1}. [c] G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212. [d] $\nu_1(AsF_6^-)$ mode hidden under peak at 674 cm^{-1}.

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* Signs of chemical shifts are given as recommended by IUPAC (*Pure Appl. Chem.*, 1972, **29**, 627; 1976, **45**, 217).

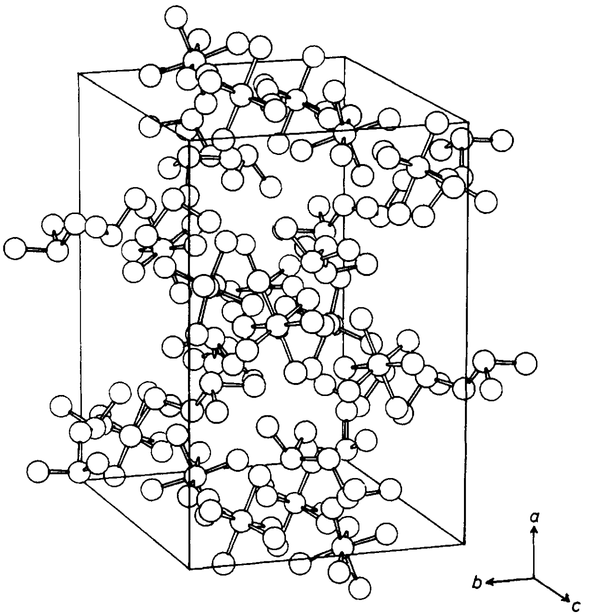


Figure 1. Contents of $(SF_2)_2NAsF_6$ unit cell

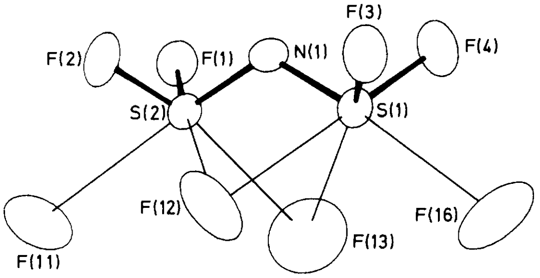


Figure 2. The $(SF_2)_2N^+$ cation with anion contacts

yielded $(SCl)_2NAsF_6$ and chlorine. The instability of $(SCl_2)_2NAsF_6$ may be similar to that of SCl_4, which dissociates to SCl_2 and Cl_2 at r.t.[42]

The Crystal Structure of $(SF_2)_2NAsF_6$.—The structure consists of discrete $(SF_2)_2N^+$ and AsF_6^- ions, with interionic interactions, arranged as shown in the packing diagram (Figure 1). The $(SF_2)_2N^+$ cation, with the strongest of its contacts with AsF_6^-, is illustrated in Figure 2. Appropriate bond distances and angles are given in Tables 7 and 8 respectively.

The $(SF_2)_2N^+$ cation has essentially C_{2v} symmetry. The two SN bond distances, and four SF bond distances, are not significantly different from one another and have average values of 1.551(10) (d_{SN}) and 1.523(8) Å (d_{SF}) respectively. Similarly the four NSF angles and two FSF angles are also essentially equal with average values of 100.2(6) (NSF) and 94.0(5)° (FSF).

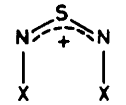
The average SN bond distance of 1.551(10) Å in $(SF_2)_2N^+$ is significantly less than those in $S_3N_3Cl_3$ [1.605(5) Å][43] and $S_3N_3F_3$ (1.593 Å)[44] which have formal bond orders of *ca.* 1.5. Using Nyburg's[45] relationship between SN bond order and bond distance, a bond order of 1.85 is derived for the SN bond in $(SF_2)_2N^+$. The bonding in $(SF_2)_2N^+$ may be represented by valence-bond structures (I) and (II), with lesser contributions from (III) and (IV).

As viewed along the sulphur-sulphur bond, the sulphur-fluorine bonds are nearly eclipsed, as shown in structure (V).

Table 3. Final atomic positional parameters for $(SF_2)_2NAsF_6$, with estimated standard deviations in parentheses

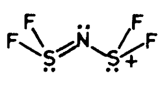
Atom	*x*	*y*	*z*
As(1)	0.422 32(9)	0.230 19(14)	0.393 95(11)
F(11)	0.442 4(9)	0.300 4(21)	0.508 4(12)
F(16)	0.378 2(14)	0.097 5(16)	0.448 4(13)
F(13)	0.458 2(16)	0.367 3(18)	0.331 9(17)
F(12)	0.527 4(9)	0.179 9(19)	0.365 0(9)
F(15)	0.318 4(9)	0.301 4(17)	0.396 7(15)
F(14)	0.393 6(14)	0.160 5(24)	0.269 1(14)
S(1)	0.665 0(2)	0.012 6(3)	0.333 8(2)
F(4)	0.748 0(7)	−0.076 8(9)	0.325 3(7)
F(3)	0.705 0(6)	0.102 8(9)	0.424 7(6)
N(1)	0.679 5(6)	0.106 1(11)	0.232 2(8)
S(2)	0.601 0(2)	0.141 3(4)	0.153 4(3)
F(1)	0.644 6(6)	0.116 2(9)	0.043 4(5)
F(2)	0.611 7(8)	0.296 1(8)	0.146 6(8)

Table 4. Interatomic distances (Å) and angles (°) in

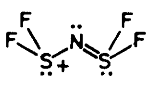


	X = Cl[a]	X = Br[b]
r(N–S)	1.528	1.528
S–N–S	151	151
r(S–X)	1.992	2.142
r(X · · · X)	3.385	3.578
S–N–X	110.65	112.81

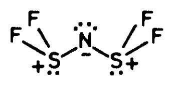
[a] From ref. 19, averaged to C_{2v} symmetry. [b] Estimated, see text.



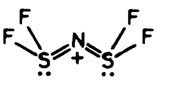
(I)



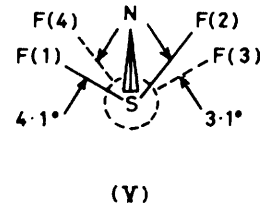
(II)



(III)



(IV)



(V)

The SNS angle of 121.1(6)° is consistent with nitrogen sp^2 hybridisation. The three lone pairs in the cation therefore lie in the SNS plane. The eclipsed geometry of the cation minimises lone pair-lone pair repulsions and maximises p_π–d_π bonding in, and perpendicular to, the SNS plane relative to other rotational isomers. The related $(SMe_2)_2N^+$[37] and $(S_3N_2)_2N^+$[4] have similar geometries, as has $(PCl_3)_2N^+$[46] with two P–Cl bonds lying approximately parallel to one another in the PNP plane in similar positions to the sulphur lone pairs depicted in structures (I)—(IV). The analogous phenyl derivative, $(PPh_3)_2N^+$,[47] does not have this eclipsed structure

Table 5. Force constants (N m^{-1}) [a]

Co-ordinate	$(SCl)_2N^+$	$(SBr)_2N^+$	Values for comparison
Diagonal constants			
N–S	657	676	625 [b]; 852, NS [c]; 1 149, NS^+ [c]; 826, NS_2^+ [d]
S–X	300	276	232 [b]; 375, SCl [e]; 361, SBr [e]; 199, SCl_2 [f]; 140, SBr_2 [f]
X · · · X	44	69	323, Cl_2 [c]; 246, Br_2 [c]
S–N–S	44	68	42 [b]; 237, NS_2^+ [d]
N–S–X	50	38	18.4 [b]
Interaction constants			
N–S/N–S	155	169	169 [b]; 66, NS_2^+ [d]
N–S/S–X	189	133	11 [b]
N–S/S–N–S	60	99	68 [b]
N–S/N–S–X	69	57	29 [b]

[a] All bending co-ordinates include weighting by the root-mean-square of the two bond lengths. [b] $(SCl)_2N^+$. This set includes N–S–Cl/N–S–Cl interaction.[31] [c] K. P. Huber and G. Herzberg, 'Constants of Diatomic Molecules,' Van Nostrand-Reinhold, New York, 1979. [d] Calculated from frequencies given in ref. 2. [e] M. Feuerhahn, R. Minkwitz, and G. Vahl, *Spectrochim. Acta, Part A*, 1980, **36**, 183. [f] C. A. Frenzel and K. E. Blick, *J. Chem. Phys.*, 1971, **55**, 2715.

Table 6. Observed and calculated in-plane vibrational frequencies (cm^{-1})

	$(SCl)_2N^+$		$(SBr)_2N^+$		
	Obs.	Calc.	Obs.	Calc.	Principal motion
A_1					
ν_1	721	721	714	715	N–S, S–N–S, mixed
ν_2	659	658	645	644	
ν_3	452	453	414	407	S–X
ν_4	218	218	165? *	179	X · · · X
B_1					
ν_5	1 128	1 128	1 126	1 129	N–S
ν_6	527	528	465	469	S–X
ν_7	202	202	155	155	N–S–X

* This frequency was not included in the vibrational analyses.

Table 7. Bond lengths (Å) for $(SF_2)_2NAsF_6$ with estimated standard deviations in parentheses

$(SF_2)_2N^+$		AsF_6^-	
N–S(1)	1.552(10)	As–F(11)	1.577(13)
N–S(2)	1.550(10)	As–F(12)	1.681(11)
S(1)–F(3)	1.534(8)	As–F(13)	1.635(16)
S(1)–F(4)	1.522(9)	As–F(14)	1.716(14)
S(2)–F(1)	1.502(7)	As–F(15)	1.701(13)
S(2)–F(2)	1.534(9)	As–F(16)	1.604(13)
Intraionic contacts *		Interionic contacts *	
S(1) · · · S(2)	2.701(4)	N · · · F(12)	2.874(15)
N · · · F(1)	2.347(11)	S(1) · · · F(12)	2.657(12)
N · · · F(2)	2.366(14)	S(1) · · · F(13)	3.074(20)
N · · · F(3)	2.362(12)	S(1) · · · F(16)	2.923(14)
N · · · F(4)	2.357(13)	S(2) · · · F(11)	3.001(13)
		S(2) · · · F(12)	2.815(11)
		S(2) · · · F(13)	2.844(19)

* Includes all contacts less than the sum of van der Waals radii (S · · · S 3.60, S · · · F 3.27, and N · · · F 3.02 Å; ref. 30).

Table 8. Bond angles (°) for $(SF_2)_2NAsF_6$ with estimated standard deviations in parentheses

$(SF_2)_2N^+$		AsF_6^-	
S(1)–N–S(2)	121.1(6)	F(11)–As–F(12)	97.8(7)
N–S(1)–F(3)	99.9(5)	F(11)–As–F(13)	88.9(11)
N–S(1)–F(4)	100.1(6)	F(11)–As–F(14)	175.9(11)
N–S(2)–F(1)	100.5(5)	F(11)–As–F(15)	88.6(8)
N–S(2)–F(2)	100.2(6)	F(11)–As–F(16)	94.2(10)
F(3)–S(1)–F(4)	93.9(5)	F(12)–As–F(13)	80.9(10)
F(1)–S(2)–F(2)	94.1(5)	F(12)–As–F(14)	86.1(9)
		F(12)–As–F(15)	167.2(8)
Intraionic contacts *		F(12)–As–F(16)	103.2(10)
F(1) · · · N · · · F(3)	176.1(6)	F(13)–As–F(14)	90.4(11)
F(2) · · · N · · · F(4)	177.2(6)	F(13)–As–F(15)	88.1(10)
		F(13)–As–F(16)	174.5(11)
Dihedral angles		F(14)–As–F(15)	87.4(10)
F(3)–S(1) · · · S(2)–F(2)	3.11	F(14)–As–F(16)	86.3(9)
F(4)–S(1) · · · S(2)–F(1)	4.05	F(15)–As–F(16)	87.4(10)

* Includes all contacts less than the sum of van der Waals radii (S · · · S 3.60, S · · · F 3.27, and N · · · F 3.02 Å; ref. 30).

Table 9. Comparison of the NSF_2 units in $(SF_2)_2N^+$ to other related compounds

	$(SF_2)_2N^+$	$ClNSF_2$ [a]	$Hg(NSF_2)_2$ [b]	SF_3^+ [c]
d_{SF}/Å	1.523(8)	1.596(2)	1.595(13)	1.496(2)
d_{NS}/Å	1.551(10)	1.476(3)	1.439(14)	—
F–S–F/°	94.0(5)	89.3(2)	88.3	97.5(1)
N–S–F/°	100.2(6)	111.2(1)	110.5	—

[a] Ref. 49. [b] Ref. 50. [c] Ref. 10.

(average C–P–P–C torsional angle *ca.* 42°), probably due to steric interactions and/or solid-state effects, whereas $Ph_2SNPPh_3^+$ has an eclipsed structure (C–S–P–C torsional angles of 4 and 9°),[48] with the third phenyl group attached to the phosphorus atom lying in the S–N–P plane.

The nitrogen atom in $(SF_2)_2N^+$ lies 0.021 Å above the plane of the four adjacent fluoride atoms, with an average N · · · F distance of 2.358 Å, approximately 18% less than the sum of the appropriate van der Waals radii (N · · · F 3.02 Å).[30] It is possible that the charge on the nitrogen atom is slightly positive as in structure (IV), and the long N · · · F contacts may be attractive, favouring the eclipsed geometry.

Average parameters for the NSF_2 fragment in $(SF_2)_2N^+$ are compared with those for $ClNSF_2$,[49] $Hg(NSF_2)_2$,[50] and SF_3^+ [10] in Table 9. The NS bond distances are proportional to formal S–N bond orders of *ca.* 1.5 in $(SF_2)_2N^+$ [as per (I) and (II)] and *ca.* 2 in $Hg(NSF_2)_2$ and $ClNSF_2$, and the SF bond distances are shorter the larger is the formal charge on sulphur. Relative bond angles are consistent with a valence-shell electron-pair repulsion (V.S.E.P.R.) model.[51]

The geometries of $(SF_2)_2N^+$ and the $(PF_2)_2N$ portion of $P_3N_3F_6$ [52] are very similar and are compared in Table 10. The sulphur lone pairs in structures (I) and (II) can be regarded as occupying the same positions as PN bonds in $P_3N_3F_6$, but may have greater steric activity, thus accounting for the smaller angles about sulphur.[51] The bond distances are essentially the same in both species. Shorter bonds to sulphur would be expected on the grounds that a partially positive sulphur atom is smaller than a neutral phosphorus atom [*e.g.* S–F in SF_3^+, 1.496(2) Å; [10] and P–F in PF_3,[53] 1.570(1) Å]. On the other hand the lone pairs on each of the S^{IV} atoms may be expected to lengthen adjacent bonds. The close similarity of the SNS and PNP geometries in $(SF_2)_2N^+$ and $P_3N_3F_6$ [52] suggests that the p_π–d_π system in the sulphur cation may be

Table 10. Comparison of average bond distances (Å) and bond angles (°) in $(SF_2)_2NAsF_6$ and $(PNF_2)_3$

$(SF_2)_2NAsF_6$		$(PNF_2)_3$ *	
S–N	1.551(10)	P–N	1.560(10)
S–F	1.523(8)	P–F	1.521(10)
S–S	2.701(4)	P–P	2.71
S–N–S	121.1(6)	P–N–P	120.3(8)
F–S–N	100.2(6)	F–P–N	109.0(6)
F–S–F	94.0(5)	F–P–F	99.3(6)

* Ref. 52.

analogous to one of the three-centre islands of delocalisation that Dewar envisaged to account for the π bonding in the cyclic phosphonitriles.[54]

The mean S–N distance and angle about the nitrogen in $(SMe_2)_2N^+$ agrees with Banister's [33] empirical equation (2), but for $(SF_2)_2N^+$ a much larger nitrogen bond angle (157.4°) is calculated given the observed NS bond distance. The $(SF_2)_2N^+$ data fit equation (4) [33] which accommodates strained four- or five-membered planar, or close to planar $S-N-S^{IV}$ containing rings (calc. $d_{NS} = 1.57$ Å for the observed angle of 121.1°).

$$d_{NS} = 248.8 - 1.053\,\hat{N} \qquad (4)$$

The two sulphur atoms of the $(SF_2)_2N^+$ cation are bridged by two anionic fluorine atoms (see Figure 2). These contacts are stronger than the third sulphur fluorine cation–anion contact [*cf.* 2.657(12), 3.074(20) *vs.* 2.923(14); and 2.844(19), 2.815(11) *vs.* 3.001(13) Å] and may cause some compression of the SNS angle. Alternatively, it could be that the fluorine atoms of $(SF_2)_2N^+$, and the partial charge on each sulphur atom [see (I)—(III)] lead to σ strengthening in the SNS bonds relative to related compounds. Banister's approach assumes that the SNS bond angle is related to π-bond strength and also a consistency of σ-bond strength, and therefore this model may not be altogether applicable in this case. A third possibility is that there may be some sulphur–sulphur bonding analogous to the phosphorus–phosphorus bonding suggested in cyclic phosphonitriles.[55]

There are significant cation–anion contacts and these are illustrated in Figure 2, with corresponding bond distances and angles in Tables 7 and 8. The approximate co-ordination of each sulphur atom is AX_3Y_3E when the anion contacts are included. The overall geometry of each sulphur atom is then similar to that in F_5SOSF_5,[56] and $(SF_5)_2NX$ (X = H or F).[57] It is noted that all sulphur–fluorine bonds and contacts in $(SF_2)_2NAsF_6$, F_5SOSF_5,[56] and $(SF_5)_2NX$ [57] are eclipsed when viewed along the sulphur–sulphur bond.

The AsF_6^- anion (Tables 7 and 8) is of essentially octahedral symmetry and there is no obvious direct correlation between the strength of interionic contacts and the relative As–F distances.

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