Infrared Spectra, Structures, and Force Constants of the Matrix-isolated Thiazyl Halides ClSN and BrSN

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Pyrolysis of the tetrathiatriazyl halide $S_4N_3^+X^-$ at low pressures furnishes the corresponding thiazyl halide XSN where X = Cl or Br but not where X = I. Infrared spectra of both ClSN and BrSN suspended in argon matrices at 15 K are reported. Isotopic variations at all three atomic positions in ClSN and at two positions in BrSN verify the molecular identity and indicate, through normal co-ordinate analysis, that both molecules are bent with $\angle$ClSN = 117 ± 3° and $\angle$BrSN = 118 ± 3° (allowance being made for anharmonicity corrections). The force constant k_{SN} diminishes from 1070·9 N m^{-1} for FSN through 1009·5 N m^{-1} for ClSN to 987·5 N m^{-1} for BrSN. This trend, together with the relatively small k_{SX} values for all three molecules, is rationalised in a simple molecular orbital treatment which invites comparisons with molecules in the series XNO and XEEX (E = O or S).

THE infrared spectra of gaseous thiazyl fluoride FSN[1] and thiazyl chloride ClSN[2] have been the focus of earlier investigations. With FSN the frequencies have been used in conjunction with the parameters of the microwave spectrum[3] to compute a complete valence force field.[4] In the case of ClSN, only two of the three *a'* vibrational fundamentals were disclosed by the infrared spectrum reported for the vapour,[2] though the position of the third fundamental ν_3 was deduced from the frequencies of bands attributed to the overtone $2\nu_3$ and the combination $\nu_2 + \nu_3$; on this basis the potential constants of an approximate (diagonal) force field were calculated. In addition, the dimensions of the gaseous ClSN molecule have lately been established by an analysis of its microwave spectrum,[5] whence also sufficient information about vibrational–rotational interactions has been gleaned to specify up to four potential constants of a more general force field.

Recently we have extended the series of known thiazyl halides to include the bromide BrSN.[6] Here we describe an attempt to investigate how the nature of the halogen X influences the potential constants and bond angle in the series of molecules XSN. Such a comparison necessitates the calculation of a complete valence force field for each member of the series. We have therefore exploited the matrix-isolation technique to secure vibrational frequencies for a variety of isotopic versions of the molecules ClSN and BrSN with the ambition of specifying completely the $n(n + 1)/2 = 6$ force constants for each molecule, and of treating the bond angle as an additional unknown variable. The matrix-isolation technique is particularly apposite to the present study since all of the thiazyl halides are thermally unstable at room temperature, association occurring typically to yield the oligomer $(XSN)_x$.[7,8]

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EXPERIMENTAL

Thiazyl chloride and thiazyl bromide were prepared by controlled pyrolysis of the corresponding tetrathiatriazyl halide $S_4N_3^+X^-$:

$$2S_4N_3^+X^- \longrightarrow S_4N_4 + 2XSN + 2S$$

The details of this reaction, which represents a new small-scale approach to the preparation of S_4N_4, S_2N_2, and XSN, will be described elsewhere.[6] In the preparation of the ^{15}N-enriched ClSN and BrSN, the parent tetrathiatriazyl halide was prepared by the reaction of 30% ^{15}N-enriched NH_4Cl (Prochem) with S_2Cl_2 following the method of Logan and Jolly.[9] It was found possible to convert the resulting chloride $S_4N_3^+Cl^-$ into the bromide $S_4N_3^+Br^-$ in 90—100% yields by mixing ice-cold aqueous solutions of the chloride and potassium bromide, followed by rapid filtration and drying of the orange bromide so precipitated. The brick-red iodide may be prepared similarly using ice-cold potassium iodide solution. Like the chloride and bromide, the iodide is moisture-sensitive; unlike the other halides, however, it is also thermally unstable at room temperature. Accordingly, after its preparation, the material was transferred to sealed glass ampoules which were stored at liquid-nitrogen temperatures.

In the matrix-isolation experiments which we report, the thiazyl halides ClSN and BrSN were prepared *in situ* by carefully controlled pyrolysis of $S_4N_3^+Cl^-$ and $S_4N_3^+Br^-$ in a small Pyrex glass furnace. For the chloride pyrolysis temperatures were typically in the order of 120 °C, whereas for the bromide temperatures in the region of 90 °C were employed. The volatile pyrolysis products were passed through a packed Pyrex furnace maintained at 120 °C in each case in order to promote the decomposition of oligomeric sulphur–nitrogen species like S_4N_4 and $(XSN)_3$. The vapour was mixed with a stream of pure, dry (B.O.C. Grade 'X') argon prior to condensation on a caesium iodide window cooled to 15 K, the triple point of hydrogen, by means of a two-stage Joule–Thomson refrigerator (Air Products AC-2-109 'Cryotip'). Ar : XSN ratios were estimated by measurement of argon pressures and $S_4N_3^+X^-$ weights before and after each experiment. Typical ratios were in the order of 800 : 1 for complete isolation. The rate of deposition of the matrix gas was normally 3 to 5 mmol/h, and for the more dilute matrices deposition times of *ca.* 5 h were needed to secure reasonable intensities for all the absorptions attributable to the XSN species.

Spectra of the matrices were recorded in the range 4000—200 cm^{-1} on a Perkin-Elmer model 225 double-beam grating infrared spectrophotometer. Calibration was accomplished by reference to the positions of sharp lines in the spectrum of atmospheric H_2O and CO_2; in favourable circumstances an accuracy of $\pm 0{\cdot}1$ cm^{-1} was attainable, but, in the event of incomplete resolution of individual isotopic features or of broadening due to other causes, the definition of frequencies inevitably deteriorated, approaching $\pm 0{\cdot}3$ cm^{-1} for the lowest-frequency fundamental of ClSN and BrSN.

Diffusion studies were carried out at temperatures in the region of 30 K. For photolysis experiments, radiation from a medium-pressure mercury lamp was transmitted *via* a silica window and focused on the matrix.

Attempts were also made to prepare thiazyl iodide ISN by thermal decomposition of $S_4N_3^+I^-$. Here the relative instability of the parent compound dictated the use of pyrolysis temperatures in the range 0—30 °C. No spectroscopic evidence was obtained for even transitory formation of ISN. The identifiable products of the reaction were S_4N_4 and I_2. The decomposition is therefore thought to be represented by the equation

$$4S_4N_3^+I^- \longrightarrow 3S_4N_4 + 2I_2 + 4S$$

RESULTS

Both FSN and ClSN have been shown by microwave studies to be bent triatomic molecules with sulphur as the central atom,[3,5] a conclusion consistent with Walsh's rules.[10] A non-linear triatomic molecule XSN (point group C_s) gives rise to three fundamental vibrations of which ν_1 corresponds most closely to N–S stretching, ν_2 to S–X stretching, and ν_3 to the N–S–X bending mode. All three vibrations are common to the a' symmetry class, being responsive both to i.r. absorption and to Raman scattering.

ClSN. Table 1 lists the frequencies of the three fundamental modes of thiazyl chloride for the isotopic species $^{35}Cl^{32}S^{14}N$, $^{35}Cl^{32}S^{15}N$, $^{35}Cl^{34}S^{14}N$, $^{35}Cl^{34}S^{15}N$, $^{37}Cl^{32}S^{14}N$, and $^{37}Cl^{32}S^{15}N$. The frequency of each mode for the $^{35}Cl^{32}S^{14}N$ molecule isolated in argon is within 3% of the value defined by the gas-phase spectrum.[2] Other bands observed in the matrix-isolation experiments arose from traces of the less volatile S_4N_4. These could be removed completely by photolysis of the matrix; since no other bands appeared, the products of photolysing matrix-isolated S_4N_4 are presumed to be sulphur and nitrogen. Photolysis of ClSN suspended in argon at 15 or 20 K for periods of up to 1 h produced no significant change in the spectrum. However, diffusion induced by allowing the matrix to warm to *ca.* 30 K caused an enhancement in the intensity of absorptions adjacent to the monomer fundamentals ν_1 and ν_2 at the expense of the bands arising from the isolated monomer. These extra bands are thought to be due to aggregates of ClSN since they are also observed following deposition in experiments employing low matrix ratios (Ar : ClSN in the order of 50 : 1). In order to rule out the possible implication of site effects, reference was made to the spectra of ClSN at varying matrix ratios using nitrogen, krypton, and xenon as the matrix gases. Irrespective of the nature of the matrix, the two extra bands invariably appeared at low matrix ratios or on diffusion of the well-isolated monomer, their respective locations being (i) the high-frequency side of ν_1(monomer) and (ii) the low-frequency side of ν_2(monomer). The bands bear no relation to the infrared spectrum which we have measured for the cyclic trimer $(ClSN)_3$ [formula (i)] trapped in a nitrogen matrix, nor do they correspond with any of the

TABLE 1

Observed and calculated[a] frequencies (cm^{-1}) for ClSN in an argon matrix at 15 K

Isotopic species	ν_1 obs.	ν_1 calc.	ν_2 obs.	ν_2 calc.	ν_3 obs.	ν_3 calc.
$^{35}Cl^{32}S^{14}N$	1327·3	1327·3	403·75	403·7	267·4	267·4
$^{37}Cl^{32}S^{14}N$		1327·3	400·5	400·7	265·0	265·2
$^{37}Cl^{32}S^{15}N$		1296·6	399·3	399·4	260·3	260·4
$^{35}Cl^{34}S^{14}N$	1315·5	1315·4		397·1		265·3
$^{35}Cl^{34}S^{15}N$	1284·3	1284·3		392·4		261·0
$^{35}Cl^{32}S^{15}N$	1296·6	1296·7	402·55	402·6	262·6	262·6

[a] Assuming ∠ClSN = 118°.

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[9] N. Logan and W. L. Jolly, *Inorg. Chem.*, 1965, **4**, 1508.

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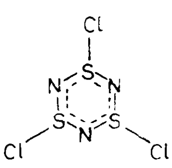
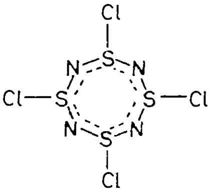
absorptions tentatively identified with the cyclic tetramer $(ClSN)_4$ [formula (ii)].[11] Evidently characterised by weak intermolecular binding, the aggregates responsible for the extra bands may assume a variety of forms, *viz* (iii)—(v), which satisfy the spectroscopic implication that electron-transfer occurs to the S–Cl but not to the S···N unit.

Species	Most prominent i.r. bands: frequencies/cm^{-1}
ClSN in Ar matrix, 15 K	1327m; 404s; 267mw
$(ClSN)_x$ in Ar matrix, 15 K	1342, 1331·5m,sh; 391, 387, 384s,br
$(ClSN)_3$ in N_2 matrix, 15 K	1025, 1021s; 708mw; 525ms
$(ClSN)_4$ in CS_2 solution, 303 K[11]	1083m; 983w; 956s; 548w; 464m

s = Strong; m = medium (intensity); w = weak; sh = sharp; br = broad.


(i)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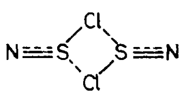
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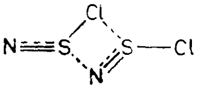
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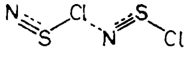
(v)

Analogy with the structure of crystalline ClCN [12] might be taken to favour the mode of interaction represented in (v), but otherwise we have insufficient information to specify the precise nature of the aggregates.

BrSN. The infrared spectra of the matrix-isolated products issuing from the pyrolysis of $S_4N_3^+Br^-$ embody, in addition to features attributable to traces of S_4N_4, no more than three well-defined bands having the following frequencies (in cm^{-1}) and intensities (s = strong, m = medium, w = weak): 1313m, 346s, and 226mw. That the relative intensities were invariant, irrespective of the experimental conditions, establishes that the three bands originate from a single molecule. Clear notice of molecular identity is served by the simplicity of the spectrum and, *a fortiori*, by the doublet splitting pattern arising from the isotopic pairs $^{14}N/^{15}N$ and $^{32}S/^{34}S$ (see Figure 1). Hence we deduce the formation of thiazyl bromide, BrSN. Table 2 lists the frequencies of the three fundamental modes for the isotopic versions $Br^{32}S^{14}N$, $Br^{32}S^{15}N$, $Br^{34}S^{14}N$, and $Br^{34}S^{15}N$. Bands due to the ^{79}Br and ^{81}Br isotopes were not satisfactorily resolved for any of the fundamental modes, although the absorption associated with ν_2, the mode entailing most motion of the bromine atom, had a half-width noticeably greater than those associated with ν_1 and ν_3. Even ν_2 is expected to suffer a shift of no more than 1 cm^{-1} with the exchange of one naturally occurring bromine isotope for the other, and with components as closely spaced as this, almost indistinguishable in intensity (corresponding to the natural abundances ^{79}Br, 50·54% and ^{81}Br, 49·46%), there could be little likelihood of resolving properly the doublet structure originating in the isotopic pair $^{79}Br/^{81}Br$. In order to check the identity of the molecule, an approximate normal co-ordinate analysis was performed using values for the principal force constants taken from calculations for S_2Br_2 [13] and ClSN (this work). The calculated frequencies lie within 7% of the measured values for all three modes. This, together with the close fit achieved between the measured and calculated isotopic splitting for each of the four isotopic versions of the molecule, provides cogent evidence for the validity of the vibrational assignments in terms of the hitherto unknown BrSN molecule. As expected, there is a strong resemblance between the appearance of the spectrum of ClSN and that of BrSN. Extra bands were again observed in the spectra of matrix-isolated BrSN to high frequency of ν_1(monomer) and to low frequency of ν_2(monomer); since these increased in intensity on diffusion of the monomer and were most prominent in experiments using low matrix ratios, they are ascribed to aggregates of BrSN. Otherwise photolysis experiments using conditions similar to those described for ClSN evoked no change in the spectrum of matrix-isolated BrSN.

TABLE 2

Observed and calculated [a] frequencies (cm^{-1}) for BrSN in an argon matrix at 15 K

Isotopic species	ν_1 obs.	ν_1 calc.	ν_2 obs.	ν_2 calc.	ν_3 obs.	ν_3 calc.
$Br^{32}S^{14}N$	1312·9	1312·9	346·1	346·1	226·2	226·2
$Br^{34}S^{14}N$	1301·0	1301·0		339·3		224·6
$Br^{32}S^{15}N$	1282·7	1282·8	344·2	344·2	222·0	221·9
$Br^{34}S^{15}N$	1270·5	1270·5		337·5		220·6

[a] Assuming ∠BrSN = 122°. In the absence of resolvable features associated with the individual isotopes ^{79}Br and ^{81}Br, the atomic mass of Br is taken to be that of the naturally occurring element, *viz*. 79·904.

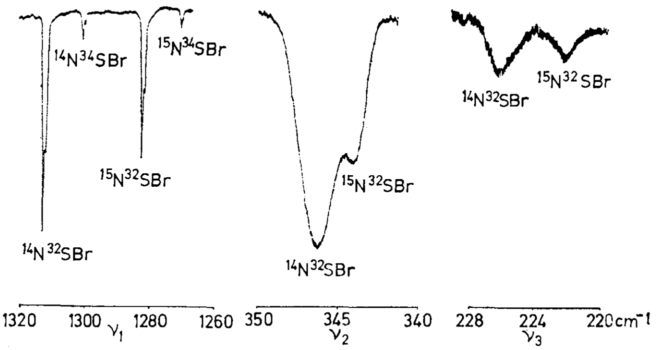

FIGURE 1 The infrared spectrum of BrSN isolated in an argon matrix at 15 K illustrating the effects (i) of ^{15}N-enrichment ($^{15}N : {}^{14}N = 3 : 7$) and (ii) of isotopic variation at sulphur ($^{34}S : {}^{32}S = 0{\cdot}044 : 1$ in natural abundance)

Product Rule Calculations.—Calculations have been performed using the Product Rule and encompassing a range of possible bond angles for both ClSN and BrSN. The experimental ratios of the frequency products for the pairs of molecules $^{35}Cl^{32}S^{14}N$, $^{35}Cl^{32}S^{15}N$ and $Br^{32}S^{14}N$, $Br^{32}S^{15}N$ are then compared with the calculated ratios based on a series of assumed values for the X–S–N bond angle. The experimental ratios were: ClSN, 0·9565;

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[11] J. Nelson and H. G. Heal, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 429.

[12] H. A. Bent, *Chem. Rev.*, 1968, **68**, 598.

[13] C. A. Frenzel and K. E. Blick, *J. Chem. Phys.*, 1971, **55**, 2715.

BrSN, 0·9536. The expected effect of anharmonicity is to cause the calculated harmonic ratio (heavy isotopes/light isotopes) to be smaller than the experimental ratio. Thus, negative deviations (calculated ratio − experimental ratio) are normally obtained. This is the case for both molecules within the range $\angle$X–S–N = 100 to 140°, limits which are thus taken to specify the bond angle of each molecule. Furthermore, the calculations give persuasive endorsement to the assignment of the observed infrared absorptions to the three fundamental modes of the bent triatomic species ClSN and BrSN.

Normal Co-ordinate Analysis.—With the assumption of a general valence force field, force constants have been computed to fit the twelve distinct frequencies measured for the six isotopic versions of ClSN and the eight distinct frequencies derived from the four isotopic versions of BrSN. For ClSN the dimensions established by microwave studies[5] have been employed, *viz.* S–Cl = 2·161 Å and S–N = 1·450 Å; the corresponding distances assumed in the first instance for BrSN were, by analogy with S_2Br_2 and ClSN, S–Br = 2·24 Å and S–N = 1·45 Å. In addition, a series of ten values between 100 and 140° was considered initially for the X–S–N bond angle of each molecule. Using the Wilson *FG* matrix method, we have solved the secular equation $\det(G\cdot F - E\lambda) = 0$ for a variety of trial *F*-matrices to arrive in each case at the best fit to the observed frequencies; this has been accomplished on an ICL 1906A digital computer with the aid of a programme engineered by Becher and Mattes following the general approach outlined by Sawodny, Fadini, and Ballein.[14] For the chloride the best fit is obtained assuming a bond angle of 118 ± 7°. The appropriate potential constants are listed in Table 3. For BrSN the best fit with the measured frequencies is realised for a bond angle of 122 ± 8°; the corresponding potential constants appear in Table 3.

TABLE 3

Force constants (N m^{-1}) for the thiazyl halides XSN (X = F, Cl, or Br)

Force constant	FSN [a] (α = 116° 52′)	ClSN [b] (α = 118°)	BrSN [b] (α = 122°)
F_{11} (k_{N-S})	1070·9	1009·5	987·5
F_{22} (k_{S-X})	287·1	138·0	129·4
F_{33} (k_{α})	41·09	27·2	22·0
F_{12} ($k_{N-S/S-X}$)	9·5	10·5	1·0
F_{13} ($k_{N-S/\alpha}$)	−4·4	0·6	7·6
F_{23} ($k_{S-X/\alpha}$)	1·9	−3·7	−3·2

[a] *F*-Matrix values taken from ref. 4. [b] Force constants calculated from measured (anharmonic) frequencies.

The major part of the quoted uncertainty in the bond angles originates in the discrepancy between measured and harmonic frequencies, which was assumed to be ⩽3% for the purposes of the preceding calculations. In view of the potential importance of anharmonicity terms in calculations of bond angles,[15] we have sought to gain a better definition of the bond angles of ClSN and BrSN through a second series of calculations based on the estimated harmonic frequencies of the molecules. This has been attempted by assuming that each observed frequency ν_i is related to its harmonic counterpart ω_i by the expression $\nu_i = \omega_i(1 - \alpha_i)$ and by setting a rough value to α_i, the anharmonicity correction, based on the known anharmonic properties of related diatomic and triatomic molecules. Thus, the anharmonicity coefficients for the diatomic molecules Cl_2 (α_e = 0·0048),[16] SiCl (α_e = 0·0043),[16] ClBr (α_e = 0·0036),[16] SiBr (α_e = 0·0035),[16] and SN (α_e = 0·0062)[16] have been used to correct the measured frequencies ν_1 and ν_2 of ClSN and BrSN for anharmonicity effects. For the bending fundamental ν_3 a value of α_3 = *ca.* 0·01 is favoured by analogy with the bending modes of other triatomic molecules, *e.g.* ClCN (α = 0·0086)[17] and NO_2 (α = 0·010).[15] To secure *F*-matrices giving the best fit with the sets of approximately harmonic frequencies thus derived, we found it necessary to assign the following values to the bond angles of the XSN molecules: ClSN, 117 ± 3°; BrSN, 118 ± 3°.

DISCUSSION

The most striking features concerning the valence force field of the molecules XSN are: (i) the high value of k_{SN} for all three molecules [higher than that for SN($X^2\Pi$) itself, where k_{SN} = 853 N m^{-1}];[16,18] (ii) the diminishing value of k_{SN} with decreasing electronegativity of the substituent X; and (iii) the relatively small value of k_{SX}; thus, k_{SF} = 287·1 N m^{-1} for FSN is to be compared with the following values of k_{SF} (in N m^{-1}) for other sulphur fluorides: SSF_2, 450;[19] SF_4 (equatorial bonds), 480;[20] SF_6, 504;[21] likewise, k_{SCl} = 138·0 N m^{-1} for ClSN is little more than half the corresponding parameter for SCl_2 (k_{SCl} = 268 N m^{-1}).[22]

The decrease in k_{SN} with decreasing electronegativity of the substituent X in the species XSN parallels the situation presented by the series of molecules XSSX (X = F,[23] Cl,[13] Br,[13] or H[24]), where k_{SS} decreases (with a slight break at BrSSBr) from 372 N m^{-1} for FSSF to 258 N m^{-1} for HSSH. The ostensible trends in the k_{SS} force constants and S–S bond lengths of these molecules and in the k_{OO} force constants and O–O bond lengths for molecules of the type XOOX (X = F or H) have been rationalised in terms of supplementation of the bonding in varying degrees by ionic contributions of the type $X^-E{=}EX^+$.[25] An alternative explanation entails the concept of two electron-three centre molecular orbitals derived from the antibonding π^* orbitals of O_2 or S_2 and the *s*- or *p*-orbitals of the ligands.[25,26] Again, for the

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[14] H. Bürger and K. Burczyk, personal communication; H.-J. Becher and R. Mattes, *Spectrochim. Acta*, 1967, **23A**, 2449; W. Sawodny, A. Fadini, and K. Ballein, *ibid.*, 1965, **21**, 995.

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[19] R. D. Brown, G. P. Pez, and M. F. O'Dwyer, *Austral. J. Chem.*, 1965, **18**, 627.

[20] I. W. Levin and C. V. Berney, *J. Chem. Phys.*, 1966, **44**, 2557.

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[22] H. Siebert, 'Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie,' Springer-Verlag, 1966.

[23] R. D. Brown and G. P. Pez, *Spectrochim. Acta*, 1970, **26A**, 1375.

[24] V. P. Morozov and N. T. Storchai, *Russ. J. Phys. Chem.*, 1967, **41**, 45.

[25] R. H. Jackson, *J. Chem. Soc.*, 1962, 4585.

[26] R. D. Spratley and G. C. Pimentel, *J. Amer. Chem. Soc.*, 1966, **88**, 2394.

XOOX molecules, Linnett has interpreted the results within the framework of his ' double quartet ' scheme.[27] Each of the three theories also offers a basis for explaining the attenuation of the E–X bonds and the relatively meagre force constants k_{EX} in the molecules XEEX ($E = O$, $X = F$; $E = S$, $X = F$ or Cl).

In attempting to fathom the force constants for the XSN molecules ($X = F$, Cl, or Br), we favour a simple qualitative MO treatment which may be extended to encompass the species XSSX, XOOX, and XNO.[26] The principal aspects of the model are illustrated in the MO scheme of Figure 2. Interaction of X with SN occasions partial delocalisation into a bonding S–X molecular orbital of the single electron initially located in the antibonding $p\pi^*$ orbital of the SN radical in its electronic ground state ($^2\Pi$). The degree of such delocalisation depends primarily on the electronegativity of the halogen X. Thus, with the highly electronegative fluorine atom, the bonding S–F molecular orbital lies much lower than the $p\pi^*$ orbital of SN, being more nearly comparable in energy with the p_z atomic orbital of the fluorine from which it is derived; occupancy of the bonding orbital is therefore tantamount to a significant ionic contribution to the resulting S–F bond. Accordingly, the bond is characterised by a relatively inferior stretching force constant k_{SF}, whereas the partial removal of an electron from the antibonding $p\pi^*$ MO of the SN radical has the effect of enhancing the magnitude of k_{SN}. By contrast, the interaction of a less electronegative halogen finds the p_z orbital more nearly compatible in energy with the $p\pi^*$ orbital of SN, the result being a *proportionately* greater discrimination between the energies of the S–X MO and the halogen p_z AO (see Figure 2). The ' ionic character ' of the S–X bond is therefore reduced, and the degree to which the antibonding electron of the SN radical is delocalised in the S–X bond is also reduced. Conventional estimates of the electronegativities of the halogens, *viz.* F, 4·0; Cl, 3·0; Br, 2·8, suggest that there should be a significant drop in k_{SN} when fluorine in FSN is replaced by chlorine, and a much smaller drop when chlorine is replaced by bromine. This is indeed found to be the case (see Figure 3).

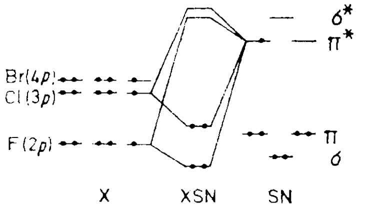

FIGURE 2 Schematic MO diagram appropriate to the thiazyl halide molecules FSN, ClSN, and BrSN

Similar arguments are applicable to the nitrosyl halides FNO, ClNO, and BrNO whose force constants [28,29] follow a pattern analogous to that set by the corresponding thiazyl halides XSN. Moreover, the effect of a further diminution in the electronegativity of the ligand X in molecules of the type XNO is manifest in the singularly low values of k_{NO} for matrix-isolated HNO ($1050\ N\ m^{-1}$) [30] and LiON ($800\ N\ m^{-1}$).[31] Here the interaction of the relatively high-energy *ns*-function of the ligand with the $p\pi^*$ molecular orbital of NO brings the bonding molecular orbital progressively closer in energy to the $p\pi^*$ level, a development logically culminating in the formation of the NO^- anion. Molecules of the types XOOX and XSSX also lend themselves to a similar rationale, with the difference that two substituents are now implicated in the delocalisation of the two antibonding electrons of the O_2 and S_2 units. In no case does the force constant k_{EE} ($E = O$ or S) here exceed the value for the parent diatomic molecule in its ground state, although it does not fall far short of this limit for the difluorides FEEF. Again the predicted pattern of force constants is observed, as exemplified by molecules in the series XSSX (see Figure 3); whether the slight discontinuity in the normal trend exhibited by BrSSBr arises from unwarranted approximations in the normal co-ordinate analysis or whether it represents the effect of significant bromine–bromine interaction cannot be judged on the evidence available.

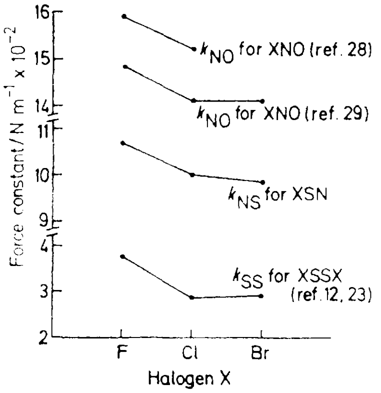

FIGURE 3 Variations of NO, SN, and SS stretching force constants as a function of the halide substituent X in molecules of the types XNO, XSN, and XSSX

Values of k_{SN} for several sulphur–nitrogen compounds are listed in Table 4. The highest values noted are for the species NSF_3 [1,29] and SN^+.[32] In both cases it may be assumed that complete, or virtually complete, removal of the single electron in the $p\pi^*$ orbital of the SN radical has been accomplished to furnish an unusually strong S–N bond. It is entirely consistent with

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our model that k_{SN} for the thiazyl halides XSN should lie approximately midway between the limits set by $k_{SN}[SN^+]$ and $k_{SN}[SN]$. Not surprisingly, the effect of association of SN units to give S_2N_2 and S_4N_4 is to produce values for k_{SN} significantly lower than that for the parent SN radical.[33-35] It is also understandable that, although the value assumed by k_{SCl} in ClSN (138·0 N m^{-1}) is markedly inferior to the corresponding parameters of ClSCl (198·5 N m^{-1})[13] and SCl_2 (268 N m^{-1}),[22] k_{SBr} differs but little for the molecules BrSN (129·4 N m^{-1}) and BrSSBr (139·8 N m^{-1}).[13] Those internuclear distances which have been measured for certain molecules, *e.g.* FSN and ClSN, are less expressive but reflect, none the less, the same general view of the bonding as do the potential constants. The solutions of the vibrational secular equation for XSN molecules are relatively insensitive to the internuclear distances assumed in the calculations; we have therefore been able to use the measured dimensions of molecules like SN, ClSN, and S_2Br_2, in conjunction with the empirical relationships advanced by Herschbach and Laurie,[36] to evaluate the approximate bond lengths for BrSN specified in Table 4.

TABLE 4

Force constants (N m^{-1}) and bond lengths (Å) for various sulphur–nitrogen species

Species	S–N stretching force constant, k_{SN}	S–N bond length	S–X stretching force constant, k_{SX}	S–X bond length	Ref.
NSF_3	1255	1·416	449	1·552	1, 29
NS^+	1185	[1·43]			32 [a]
NSF	1070·9	1·446	287·1	1·646	3, 4
NSCl	1009·5	1·450	138·0	2·161	5, this work
NSBr	987·5	[1·45]	129·4	[2·26]	this work [a]
NS ($X^2\Pi$)	853	$1{\cdot}495_7$			16, 18
S_4N_4	411	1·62			33
	295				34
S_2N_2	254				33
	283	[1·62]			35 [a]

[a] Values in parentheses deduced empirically from the relevant stretching force constants (± 0·02 Å; see ref. 36).

The bond angle of ClSN defined by normal co-ordinate analysis (117—118°) is in excellent agreement with the value deduced from microwave studies (117° 46′).[5] On the basis of the known bond angles of FSN (116° 52′) and ClSN, one might predict an angle of *ca.* 119° for BrSN. The value suggested by normal co-ordinate analysis of the measured vibrational frequencies (122°) is just a few degrees larger, but application of approximate anharmonicity corrections prompts a value (118 ± 3°) more closely in line with the expected trend for the thiazyl halides. Hence, bearing in mind the uncertainties (i) about the anharmonicity corrections and (ii) about possible matrix perturbation of the molecular geometry,[37] we can adduce no evidence of a significant departure from the normal pattern of bond angles, *viz.* FSN < ClSN < BrSN, suggested, for example, by the Valence-Shell-Electron-Pair-Repulsion Theory.[38]

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