Rings, Radicals, and Synthetic Metals: The Chemistry of SNS+

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The ONO+ cation was first identified in ONO[ClO₄] and in solutions of concentrated HNO₃ and H₂SO₄ (used for the nitration of benzene) by Ingold and co-workers in 1946.[1] SNS+, the sulfur-containing analog of ONO+, was first prepared and identified by Gillespie and co-workers in 1978[2] and might have been expected to possess a rather similar chemistry. In fact SNS+ chemistry is substantially different, and in this Account we give a short review of the synthesis, characterization, and known reactions of salts of SNS+.

Our understanding of sulfur–nitrogen chemistry has grown substantially over the last 15 years.[3] In the past, developments in this area were hampered by the baffling nature of the chemistry of many binary sulfur–nitrogen compounds, their frequent thermal instability, and the lack of a convenient spectroscopic probe. With today's ready access to X-ray crystallography, multinuclear NMR, ESR, and molecular orbital calculations, progress has become much more rapid. Nevertheless, in spite of several notable and elegant exceptions,[4] much of sulfur–nitrogen chemistry remains nonquantitative, mechanistically obscure, and, when viewed in the context of modern organic chemistry, poorly understood.
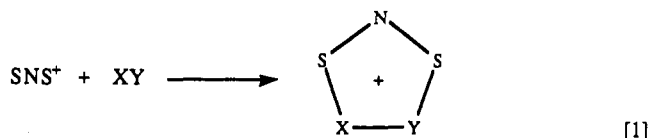
Other than SN+, SNS+ is the simplest isolable binary sulfur–nitrogen species. In contrast to neutral binary S–N compounds (e.g., $\Delta H_f[S_4N_4] = 469$ kJ mol⁻¹), it is thermally stable ($\Delta H_f[\text{SNSAsF}_6] = -1413.8$ kJ mol⁻¹),[5] and its reaction chemistry is quantitative and relatively easy to understand. We have shown,[6] for example, that its reactions with nitriles and alkynes (forming RCN-SNS+ and RCSNSCR+ salts, respectively, specific examples of the generalized cycloaddition with the unsaturated entity XY shown in eq 1), are among the simplest cycloadditions known and constitute a textbook example of the importance of orbital interactions in cycloaddition reactions.

Discovery of SNS+

Interest in SNS+ chemistry at the University of New Brunswick was initiated by a discussion in 1977 between Arthur Banister of Durham University and one of us

$$\text{SNS}^+ + \text{XY} \longrightarrow \quad [1]$$

(J.P.), over the nature of the long sulfur–sulfur interactions in S₈²⁺ and between SNSNS•+ units in S₆N₄²⁺ (Figure 1a,b). We concluded that as preparative chemists we would contribute toward a solution to the problem by preparing S₇N+, which is isovalent with S₈²⁺ (cf. the structural and electronic congruence of cyclic S₄²⁺ and S₂N₂). A NATO collaborative grant was subsequently obtained to undertake the project, and we began a fruitful collaboration.
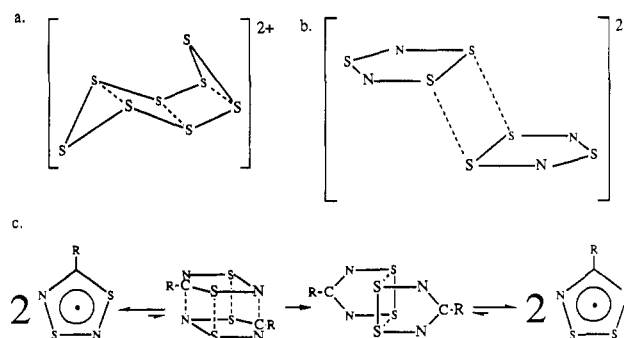

Figure 1. Some π*–π* complexes; see ref 7b. (a) S₈²⁺, illustrating transannular π*–π* bond formation: S⋯S bond lengths 2.83, 2.94, and 3.01 Å (AsF₆⁻ salt). (b) (S₃N₂•+)₂, illustrating inter-ring π*–π* bond formation: S⋯S bond length ca. 3.00 Å. (c) The mechanism of the photochemically allowed rearrangement of RCNSNS• to RCNSSN• via the π*–π* complex (RCNSNS)₂.

Previous results from our laboratory had shown that S₈²⁺ reacted quantitatively with KI to give S₇I+, KAsF₆, and ¹/₈S₈,[7a] and so Richard Hey, a graduate student from Banister's group, while at the University of New Brunswick working on the joint project, attempted the analogous reaction of S₈(AsF₆)₂ and NaN₃, in a 1:1 mole ratio. He obtained not the expected S₇NAsF₆, but yellow SNSAsF₆ in about 20% yield, which we identified

Simon Parsons was born in Huntingdonshire, England, in 1965. After receiving his B.Sc. from the University of Durham in 1987, he took his Ph.D. as a Commonwealth Scholar at the University of New Brunswick under the supervision of Prof. Passmore. Having pursued postdoctoral research as a SERC fellow with Dr. A. J. Downs at the University of Oxford, he has recently moved to the University of Edinburgh to perform postdoctoral research in X-ray crystallography with Drs. A. J. Blake and R. O. Gould.

Jack Passmore was born in Barnstaple, Devon, England, and received his B.Sc. and D.Sc. from the University of Bristol, England, and his Ph.D. degree (with Dr. Neil Bartlett) from the University of British Columbia in Vancouver. He did postdoctoral work during the year 1968–1969 at MacMaster University, Hamilton, Ontario, Canada (with Dr. Ronald J. Gillespie). He then joined the faculty at the University of New Brunswick in 1969, where he is presently Professor of Chemistry.

(1) Gillespie, R. J.; Graham, J.; Hughes, E. D.; Ingold, C. K.; Peeling, E. R. A. *Nature* 1946, *158*, 480. Goddard, D. R.; Hughes, E. D.; Ingold, C. K. *Nature* 1946, *158*, 480. Ingold, C. K.; Millen, D. J.; Poole, H. G. *Nature* 1946, *158*, 480.
(2) Faggiani, R.; Gillespie, R. J.; Lock, C. J. L.; Tyrer, J. D. *Inorg. Chem.* 1978, *17*, 2975.
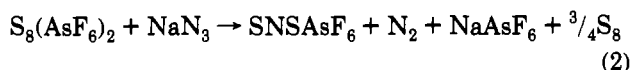(3) Chivers, T. *Chem. Rev.* 1985, *85*, 341. Oakley, R. T. *Prog. Inorg. Chem.* 1988, *36*, 299.
(4) For example: Bestari, K. T.; Boeré, R. T.; Oakley, R. T. *J. Am. Chem. Soc.* 1989, *111*, 1579.
(5) O'Hare, P. A. G.; Awere, E. G.; Parsons, S.; Passmore, J. *J. Chem. Thermodyn.* 1989, *21*, 153.
(6) Parsons, S.; Passmore, J.; Schriver, M. J.; Sun, X. *Inorg. Chem.* 1991, *30*, 3342.
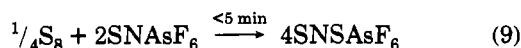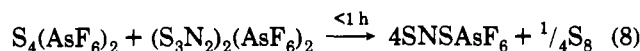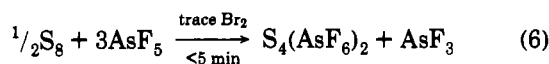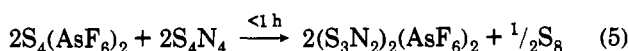
by a comparison of its IR spectrum to that of SCS and AsF_6^-.

$$S_8(AsF_6)_2 + NaN_3 \rightarrow SNSAsF_6 + N_2 + NaAsF_6 + {}^3/_4S_8 \tag{2}$$

As it happened, the very next day a paper by Gillespie appeared in *Inorganic Chemistry*[2] describing the synthesis of $SNSSbCl_6$, presumably in low yield, by the reaction of S_7NH with $SbCl_5$, and its characterization by vibrational spectroscopy and X-ray crystallography. This might have been the end of the road in terms of our interest in SNS^+ were it not for roughly concurrent discovery that trace amounts of bromine facilitated the oxidation of S_8 to S_4^{2+} by AsF_5 (without traces of Br_2, the oxidation proceeds only to S_8^{2+}).[7a,d] In the light of this, the reaction of S_8, S_4N_4, and AsF_5 in the presence of a trace of bromine appeared to be a possible route to large quantities of SNS^+ in high yield. A major breakthrough in the chemistry of SNS^+ was made at UNB by Greg MacLean, who showed[8a] that this reaction proceeded as anticipated (eq 3), and since then we have used this "one pot" synthesis to obtain over 10 g (ca. 40 mmol) of pure, yellow, crystalline $SNSAsF_6$ in over 90% isolated yield.[8b] This reaction has been shown to

$$S_8 + 2S_4N_4 + 12AsF_5 \rightarrow 8SNSAsF_6 + 4AsF_3$$
$$\Delta H = -418 \text{ kJ mol}^{-1} \tag{3}$$
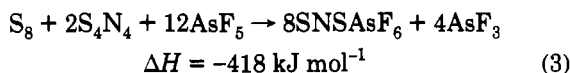
proceed[8b] via the rapid formation of S_4^{2+}, which then reacts with S_4N_4 to give $(S_3N_2)_2(AsF_6)_2$, which is subsequently oxidized in solution to SNS^+ and SN^+ (although in the solid state this exists as $S_3N_2(AsF_6)_2$; see below). The SN^+ formed reacts rapidly with S_8 to give more SNS^+:

$$S_8 + 6AsF_5 \xrightarrow[\substack{\text{trace } Br_2 \\ <5 \text{ min}}]{SO_2} 2S_4(AsF_6)_2 + 2AsF_3 \tag{4}$$

$$2S_4(AsF_6)_2 + 2S_4N_4 \xrightarrow{<1 \text{ h}} 2(S_3N_2)_2(AsF_6)_2 + {}^1/_2S_8 \tag{5}$$

$${}^1/_2S_8 + 3AsF_5 \xrightarrow[<5 \text{ min}]{\text{trace } Br_2} S_4(AsF_6)_2 + AsF_3 \tag{6}$$

$$(S_3N_2)_2(AsF_6)_2 + 3AsF_5 \xrightarrow[<1 \text{ h}]{\text{trace } Br_2} 2SNSAsF_6 + 2SNAsF_6 + AsF_3 \tag{7}$$

$$S_4(AsF_6)_2 + (S_3N_2)_2(AsF_6)_2 \xrightarrow{<1 \text{ h}} 4SNSAsF_6 + {}^1/_4S_8 \tag{8}$$

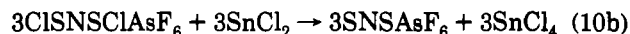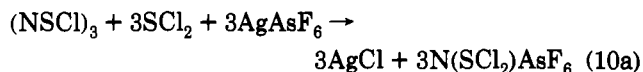$${}^1/_4S_8 + 2SNAsF_6 \xrightarrow{<5 \text{ min}} 4SNSAsF_6 \tag{9}$$
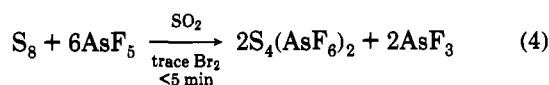
Banister[9] has published several routes to various SNS^+ salts which avoid the use of potentially explosive S_4N_4

(7) (a) Passmore, J.; Sutherland, G. W.; White, P. S. *J. Chem. Soc., Chem. Commun.* 1980, 330. (b) Klapötke, T.; Passmore, J. *Acc. Chem. Res.* 1989, 22, 234 and references cited therein. (c) Burford, N.; Passmore, J.; Sanders, J. C. P. In *From Atoms to Polymers: Isoelectronic Analogies*; Liebman, J. F., Greenburg, A., Eds.; VCH: Deerfield Beach, FL, 1989 and references cited therein. (d) Murchie, M. P.; Passmore, J.; Sutherland, G. W.; Kapoor, R. *J. Chem. Soc., Dalton Trans.* 1992, 503. (e) Murchie, M. P.; Johnson, J. P.; Passmore, J.; Sutherland, G. W.; Tajik, M.; Whidden, T. K.; White, P. S.; Grein, F. *Inorg. Chem.* 1992, 31, 273.
(8) (a) Banister, A. J.; Hey, R. G.; MacLean, G. K.; Passmore, J. *Inorg. Chem.* 1982, 21, 1679. (b) Awere, E. G.; Passmore, J. *J. Chem. Soc., Dalton Tran.* 1992, 1343.

and toxic AsF_5. In addition,[9] $SNSAsF_6$ has been prepared in a two-step synthesis in 90% overall yield, according to eqs 10a,b, providing a safer alternative to eq 3. Equation 10b has also been applied to the

$$(NSCl)_3 + 3SCl_2 + 3AgAsF_6 \rightarrow$$
$$3AgCl + 3N(SCl_2)AsF_6 \tag{10a}$$

$$3ClSNSClAsF_6 + 3SnCl_2 \rightarrow 3SNSAsF_6 + 3SnCl_4 \tag{10b}$$

syntheses of other SNS^+ salts including $AlCl_4^-$, $FeCl_4^-$, $CF_3SO_3^-$, and $SbCl_6^-$, although these tend to be insoluble, and/or their reactions complicated, possibly as a result of anionic participation.[9]

Characterization of the SNS⁺ Cation

X-ray crystal structures have been determined for $SNSAsF_6$,[10a] $SNSSbCl_6$,[2] and $SNSAlCl_4$,[10b] and all show discrete, linear SNS^+ cations, consistent with the VSEPR model. The SN bond length does not vary significantly between the salts when librational effects are taken into account, and their average (1.51 Å) is consistent with a formal SN bond order of 2. Empirical measures of the SN bond strength, such as the force constant (8.256 mdyn Å⁻¹)[11] and the bond energy term (473 kJ mol⁻¹, obtained[12] following the determination of $\Delta H_f[SNSAsF_6]$ (−1413.8 kJ mol⁻¹ by fluorine combustion calorimetry[5]), similarly attest to the importance of π bonding, and this is confirmed by MO calculations at all levels of theory. While this suggests that SNS^+ can reasonably be represented by the resonance form $S=N^+=S$, anionic contacts in these salts are formed exclusively to the sulfur atoms. Presumably the positive charge is delocalized onto the sulfur atoms in SNS^+ through polarization effects, although the weakness of the contacts implies that this may not be extreme as indicated by SCF calculations (CNDO and STO-3G charges: N, −0.32; S, +0.66).

The isoelectronic and isostructural relationships between SNS^+ and SCS are reflected by the similarity of their vibrational spectra,[8b] which show the two Raman bands (ν_s(SNS), 688 cm⁻¹, and δ(SNS), 374 cm⁻¹) and one IR band (ν_{as}(SNS), 1498 cm⁻¹) expected from $D_{\infty h}$ symmetry. The SNS^+ cation has also been characterized in SO_2 and AsF_3 solution by ¹⁴N NMR,[13] exhibiting a resonance at −91 ppm (relative to neat MeNO₂); the cylindrical charge density around the nitrogen nucleus give rise to a relatively narrow line width (8 Hz), so that SNS^+ can be readily identified in solutions using this technique, which can therefore be used to follow the course of its reactions *in situ* and was used, for example, to elucidate the course of eq 3.[8a]

Chemistry of SNS⁺: Expectations, Predictions, Comparisons, and Early Discoveries

Although the "double bond rule" states that $p\pi-p\pi$ bonds involving heavier main group elements are unstable with respect to catenation, formation of

(9) Ayres, B.; Banister, A. J.; Coates, P. D.; Hansford, M. I.; Rawson, J. M.; Rickard, C. E. F.; Hursthouse, M. B.; Malik, K. M. A.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* 1992, 3097.
(10) (a) Johnson, J. P.; Passmore, J.; White, P. S.; Banister, A. J.; Kendrick, A. G. *Acta Crystallogr.* 1987, C43, 1651. (b) Thewalt, Von U.; Berhalter, K.; Müller, P. *Acta Crystallogr.* 1982, B38, 1280.
(11) Silaghi-Dumitrescu, I.; Haiduc, I. *J. Mol. Struct.* 1984, 106, 217.
(12) Parsons, S.; Passmore, J. *Inorg. Chem.* 1992, 31, 526.
(13) Passmore, J.; Schriver, M. J. *Inorg. Chem.* 1988, 27, 2749.

Scheme 1.   Some Cycloaddition Reactions of SNSAsF₆[a]
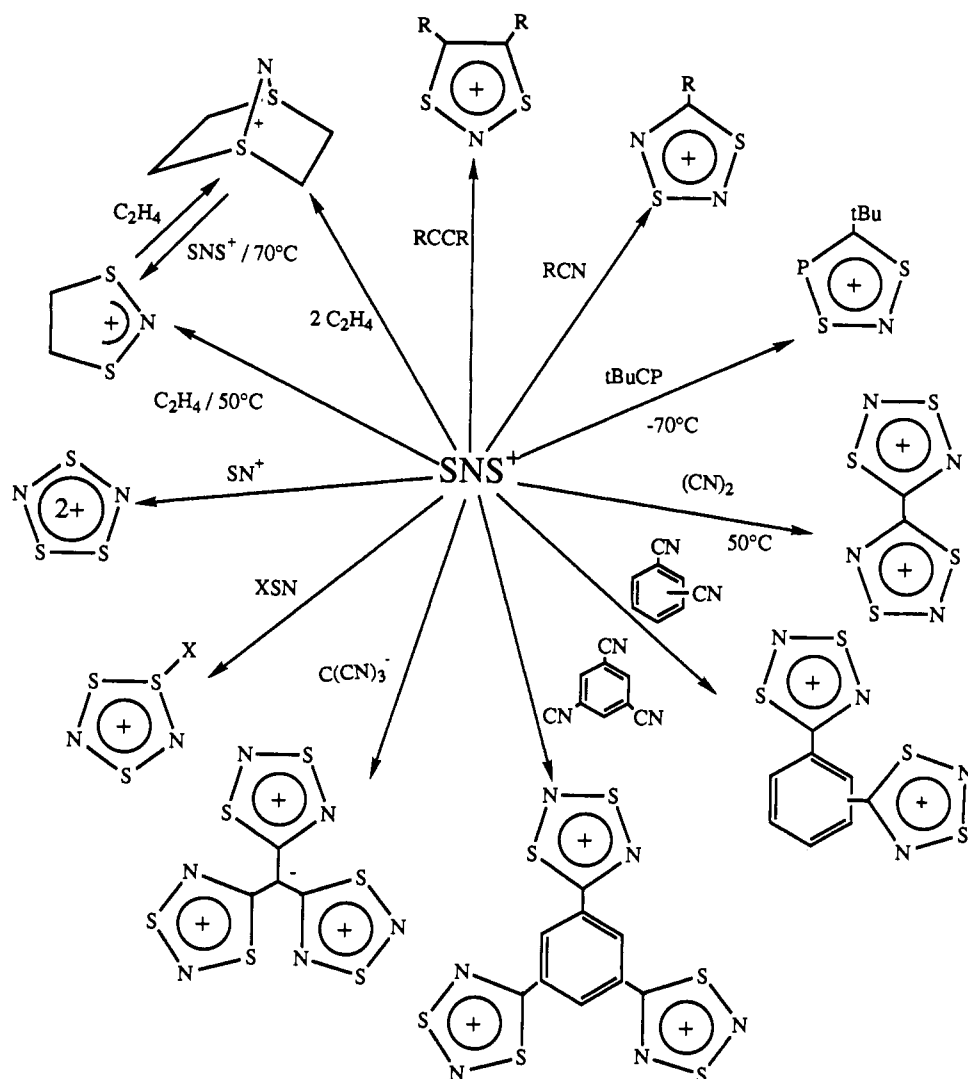
[a] All reactions were performed at room temperature in liquid sulfur dioxide unless otherwise indicated.

π-bonded structures can be promoted either in the presence of bulky ligands (e.g., RP=PR, R = mesityl) or a positive charge. Thus π-bonding is observed in $I_2^{•+}$, M_4^{2+} (M = S, Se, or Te), and the prismatic $S_2I_4^{2+}$, the most highly π-bonded main group species containing non-second row elements known to date.[7e] Therefore, positively charged sulfur often behaves like a second-period element, forming discrete species containing 3pπ–3pπ or 3pπ–2pπ bonds rather than exclusively σ-bonded frameworks.[7b,c] This feature is clearly reflected in the structures of SN⁺ and SNS⁺, which, unlike other sulfur–nitrogen compounds, bear a close structural resemblance to their oxygen analogs. SNS⁺ and ONO⁺ might therefore naively have been predicted to possess similar chemistries, but even at the most basic level there are fundamental differences in their reactivities. Reduction of ONO⁺, for example, yields the well-known and very stable ONO·, and analogously reduction of SNS⁺ might have been predicted to produce SNS·. While SNS· has been observed (in the presence of its dimer SNSSNS) in an inert gas matrix at 12 K,[14a] and there is one claim to have observed it in the cyclic voltammogram of SNSAsF₆ in acetonitrile

(14) (a) Hassanzadeh, P.; Andrews, L. *J. Am. Chem. Soc.* **1992**, *114*, 83. (b) Hanford, M. I. Ph.D. Thesis, University of Durham, 1989.
(15) MacLean, G. K. Ph.D. Thesis, University of New Brunswick, 1984.

(*E* = 0.72 V) and SO₂ (*E* = 0.76 V),[14b] it is very unstable. On a preparative scale, reduction of SNSAsF₆ with sodium dithionite (Na₂S₂O₄) in SO₂ yields the SNSNS·⁺ radical cation (Scheme 2),[15] which has no analog in oxygen–nitrogen chemistry, but which represents a commonly occurring structural fragment in sulfur–nitrogen chemistry.

Reactions with ONO⁺ produce bonds to the central nitrogen atom, and its most familiar use is as a nitrating agent in organic chemistry. By contrast, all reactions involving SNS⁺ known to date lead to the formation of bonds to the *terminal* sulfur atoms. Hence, whereas the reaction of ONO⁺ with F⁻ yields FNO₂, reaction of CsF with SNSAsF₆ in SO₂ gives the FSNSNS⁺ cation (together with S₄N₄ and S₃N₂O₂),[15] a derivative of the particularly stable SNSNS⁺ ring system described above. The reaction likely proceeds via SNSF, which has yet to be identified. Reaction of SNSAsF₆ with the pseudo-halide N₃⁻ was important as the first "chemical" synthesis of the conducting polymer (SN)ₓ,[16] which exhibits superconductivity at low temperatures.

$$xCsN_3 + xSNSAsF_6 \rightarrow xCsAsF_6 + (x/2)N_2 + (SN)_x \quad (11)$$

(SN)ₓ was previously obtained by the polymerization

Scheme 2.   Reactions of SNSAsF₆ Which Do Not Obviously Proceed via a Concerted Cycloaddition Mechanism
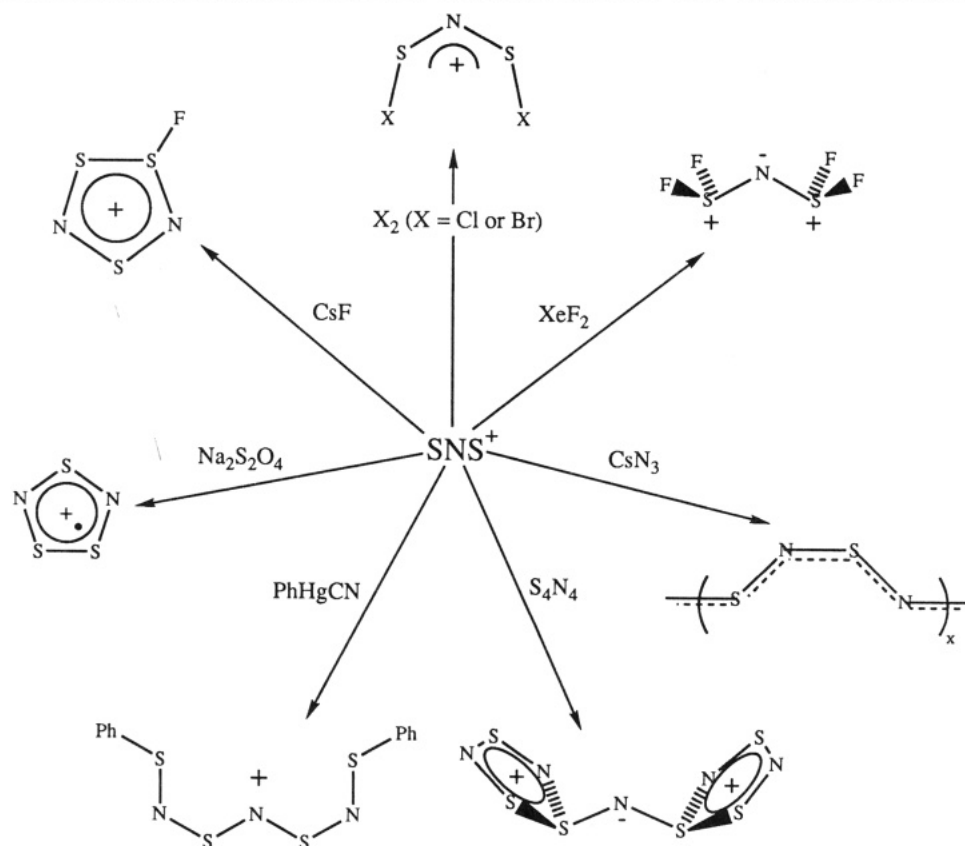
of S₂N₂, prepared by the pyrolysis of S₄N₄ over silver wool, which was technically difficult and extremely hazardous. Discovery of the "chemical" route to this polymer led to the development of other, still more convenient routes from S₃N₃Cl₃, S₃N₂Cl₂, S₃N₂Cl, and even S₂Cl₂![16] Subsequently Banister and Hauptmann obtained thin, golden, homogeneous conducting layers of (SN)ₓ by the electrolysis of solutions containing the S₅N₅⁺ cation.[17]

The differing chemistries of SNS⁺ and ONO⁺ are in part due to the differences between the strengths of the bonds formed and broken, the differing ionization potentials of S (1000 kJ mol⁻¹), O (1310 kJ mol⁻¹), and N (1400 kJ mol⁻¹) (thermodynamic effects), and frontier molecular orbital distributions (a kinetic effect). Hence, the weakness of oxygen–halogen bonds, the high strength of NO π bonds, and the high IP of oxygen mean that ONO⁺ does not react with oxidizing agents such as chlorine, bromine, and iodine. By contrast, oxidized derivatives of SNS⁺ (ClSNSCl⁺ [18] and Me₂-SNSMe₂⁺ [19]) were known prior to 1978, and SNSAsF₆ reacts with chlorine and bromine[20] (but not with iodine due to the weakness of S–I bonds)[7b] to form XSNSX⁺ cations (X = Cl or Br). SNSAsF₆ is completely fluorinated to SF₆, AsF₅, and N₂ by elemental fluorine, although with the milder fluorinating agent XeF₂ the F₂SNSF₂⁺ cation is given quantitatively (Scheme 2).[20] The structure of this cation is similar to that of Me₂-SNSMe₂⁺ [19] and the F₂P–N–PF₂ portion of P₃N₃F₆. This is also a feature of the S₆N₅⁺ cation, which is given in

50% yield by the reaction of S₄N₄ with SNSAsF₆ and which incorporates the ubiquitous ⌐SNSNS⁺ ring system (see Scheme 2).[21a]

The differing reactivities of SNS⁺ and ONO⁺ may further be ascribed to differing frontier molecular orbital distributions. Unoccupied antibonding molecular orbitals tend to concentrate on the electropositive centers in a molecule or ion, and the LUMO of ONO⁺ (1) therefore resides principally on the nitrogen atom, while that of SNS⁺ (2) resides predominantly on the terminal sulfur atoms (CNDO/2 calculations[21b]). Reactions with nucleophiles (e.g., reductions and reactions with halide ions and unsaturated bonds) therefore tend to occur preferentially at the atoms which contribute most to the LUMO, i.e., the central atom in ONO⁺ and the terminal atoms in SNS⁺.

Cycloaddition Chemistry of the SNS⁺ Cation

SNSAsF₆ dissolves in SO₂ and AsF₃ and very sparingly in CH₂Cl₂; an attempt by Greg MacLean at UNB to

(16) Kennett, F. A.; MacLean, G. K.; Passmore, J.; Rao, M. N. S. *J. Chem. Soc., Dalton Trans.* **1982**, 851.

(17) Banister, A. J.; Hauptman, Z. V.; Kendrick, A. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1016.

(18) Mews, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 691 and references therein.

(19) Griffin, A. M.; Sheldrick, G. M. *Acta Crystallogr.* **1975**, *B31*, 893.

(20) Brooks, W. V. F.; MacLean, G. K.; Passmore, J.; White, P. S.; Wong, C.-M. *J. Chem. Soc., Dalton Trans.* **1983**, 1961.

(21) (a) MacLean, G. K.; Passmore, J.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1984**, 211. (b) E.g., 6-31G* *ab initio* calculations give approximately equal coefficients to S and N in SNS⁺; see Figure 2. However, ²/₃ of the LUMO is located on S.

(22) MacLean, G. K.; Passmore, J.; Rao, M. N. S.; Schriver, M. J.; White, P. S.; Bethell, D.; Pilkington, R. S.; Sutcliffe, L. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1405.

dissolve it in acetonitrile gave crystals which were shown by X-ray crystallography to be MeCNSNSAsF$_6$,[22] formed by the cycloaddition reaction

MeCN + SNSAsF$_6$ ⟶

[12]
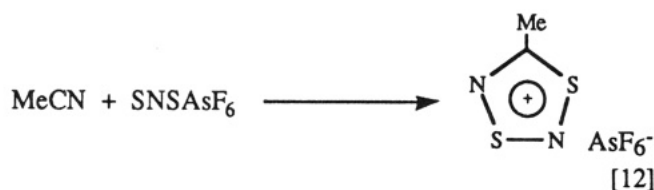
Thus, like so many other important discoveries, the cycloaddition chemistry of SNS$^+$ was stumbled upon inadvertently. We have subsequently shown that, quite unlike ONO$^+$ salts, SNSAsF$_6$ undergoes general, quantitative, symmetry-allowed cycloaddition reactions with a wide range of unsaturated molecules (Scheme 1). We believe that the combination of simplicity, predictability, and generality of these reactions, which is almost unique in sulfur–nitrogen chemistry, will establish SNS$^+$ as an important reagent in synthetic chemistry.

Reactions with Triple Bonds

Alkynes, nitriles,[6,9,23a] and thiazyl halides[23a,b] (NSF and NSCl) undergo general quantitative cycloadditions with SNSAsF$_6$ in SO$_2$ at room temperature to give 1,3,2-dithiazolium, 1,3,2,4-dithiadiazolium, and 5-halo-1,2,5-trithia-3,5-diazolium salts, respectively (Scheme 1) as analytically and spectroscopically (NMR and IR) pure materials.[6,9,23]

The first application of frontier molecular orbital (FMO) theory to the analysis of cycloaddition reactions involving sulfur–nitrogen compounds[24a] was Oakley and Fukui's treatment of the reaction of S$_4$N$_4$ with strained alkenes (e.g., norbornadiene), and this affords a simple explanation of the more general reactions between SNSAsF$_6$ and alkynes and nitriles. In common with 1,3-dipoles,[24b] the π_n HOMO (highest occupied molecular orbital) and π^* LUMO (lowest unoccupied molecular orbital) of SNS$^+$ are of the correct symmetry to interact with the π^* LUMOs of simple alkynes and nitriles (Figure 2). Although both HOMO–LUMO interactions in Figure 2 are symmetry allowed, in practice the interaction between the MOs closest in energy will dominate the cycloaddition (i.e., SNS$^+$ acts as a Lewis acid while the alkynes and nitriles act as bases). The high electronegativities of S and N and the presence of a positive charge make the frontier orbitals of SNS$^+$ of such low energy that the interaction between the HOMO(triple bond) and the LUMO-(SNS$^+$) was predicted to dominate all reactions of SNS$^+$ with alkynes and nitriles, whatever their substituents. This corresponds closely to "reverse electron demand" Diels–Alder cycloaddition reactions, but such exclusive behavior is extremely unusual. Factors, such as electron-donating substituents, which *increase* the energy of HOMO(triple bond) will obviously *decrease* the HOMO(triple bond)–LUMO(SNS$^+$) energy gap and thereby *increase* the rate of cycloaddition. From these very simple considerations we predicted that there
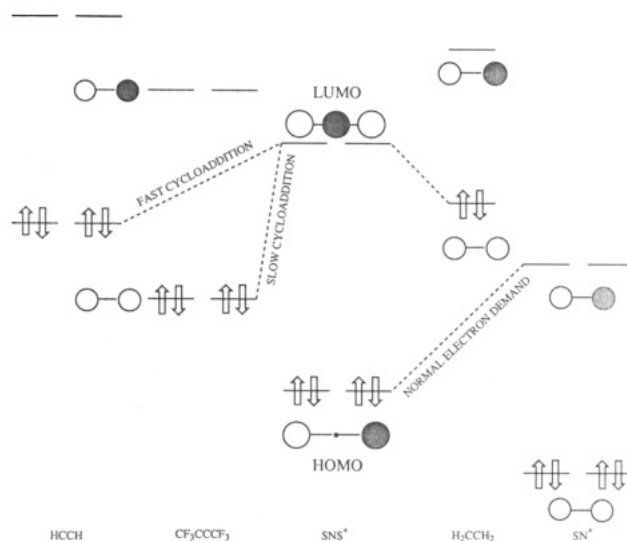
(23) (a) Passmore, J.; Sun, X.; Parsons, S. *Can. J. Chem.* **1992**, *70*, 2972. (b) Padma, D. K.; Mews, R. *Z. Naturforsch.* **1987**, *B42*, 699.
(24) (a) Liblong, S. W.; Oakley, R. T.; Cordes, A. W.; Noble, M. C. *Can. J. Chem.* **1983**, *61*, 2062. Yamabe, T.; Tanaka, K.; Tachibana, A.; Fukui, K.; Kato, H. *J. Phys. Chem.* **1979**, *83*, 767. (b) Padwa, A., Ed. *1,3-Dipolar Cycloaddition Chemistry*; John Wiley: New York, 1984.

Figure 2. The frontier molecular orbitals of SNS$^+$ compared with those of alkynes, alkenes, and SN$^+$.
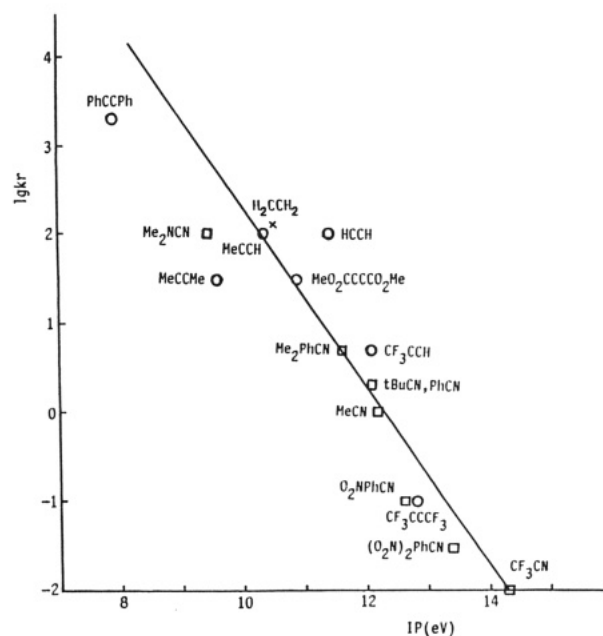

Figure 3. Plot of the logarithm relative rates of cycloaddition of some nitriles (□), alkynes (○), and ethene (×) against ionization potential (eV). (Rates are given relative to MeCN.)

should be a correlation between the rate of cycloaddition and the ionization potential of alkynes and nitriles. Accordingly the cycloadditions of SNS$^+$ with alkynes and nitriles are second order, and a plot of $\log_{10} k_{rel}$ against IP (Figure 3) is roughly linear, confirming the anticipated trend in rates. Deviations from ideal linearity can be ascribed to factors such as electrostatic effects, steric effects, in-plane MOs, or the inductive effect on the orbital coefficients in the HOMO. None of these are included in the simple frontier molecular orbital treatment, although they do appear in more rigorous (e.g., perturbational or *ab initio*) models.[24b]

Separate analysis of the nitrile and alkyne data can be used to probe the role of steric effects in these reactions. The correlation coefficient for the nitrile data alone, −0.97, shows that steric effects have little or no effect in determining the rates of cycloaddition of nitriles to SNS$^+$ (note that even tBuCN adds faster than MeCN, implying pure electronic control). Although the rates of alkyne cycloadditions follow the trend anticipated on the basis of their IPs, steric effects

appear to be significant, and the data no longer fall on a straight line. The differences between the alkyne and nitrile cycloadditions may be traced to nitriles being substituted on only one side of the triple bond, whereas alkynes are substituted on both sides, so that a nitrile can approach SNS⁺ with its substituent pointing away from the center of reaction, whereas there will always be a steric interaction with the substituent of an alkyne, whatever the direction of its approach.

These results clearly have predictive value both in determining the likely site of a reaction with multiply unsaturated molecules (see below) and in assessing the suitability of potential substrates of SNS⁺ cycloadditions. For example, the phosphaalkyne tBuC≡P is isolobal with nitriles, has a relatively low ionization potential (9.70 eV), and would therefore be expected to undergo a rapid, symmetry-allowed cycloaddition reaction with SNS⁺. Recent results in this laboratory have confirmed this prediction, and tBuCPSNS⁺, the first example of a 1,2,4,3-phosphadithiazolium cation, was given quantitatively in a very rapid reaction (in SO_2) at -70 °C, and characterized *in situ* by ¹H, ¹³C, ¹⁴N, ¹⁵N, and ³¹P NMR.[25]

Thermodynamic Limitations and the Reaction of SNS⁺ with SN⁺ to give the SNSNS²⁺ Cation

Although SNS⁺ is potentially useful in the synthesis of any XSNSY⁺ ring system (eq 1), thermodynamics can present one obstacle since orbital symmetry becomes irrelevant if a reaction is endothermic (e.g., with N_2). This principle was illustrated in our work on the SNSNS²⁺ cation,[26] which has long been of theoretical interest as an "aromatic" 6π ring system. However, although the frontier orbitals of SN⁺ and SNS⁺ are of suitable symmetry for a cycloaddition reaction yielding the SNSNS²⁺ cation, no reaction occurs between SNAsF₆ and SNSAsF₆ in solution. In fact, far from being a stable 6π aromatic, the SNSNS²⁺ cation dissociates quantitatively in solution and is only stable in the solid state in salts such as SNSNS(AsF₆)₂ and SNSNS(SbF₆)₂. High-level MO calculations show that SNSNS²⁺ is unstable (by 400 kJ mol⁻¹) with respect to symmetry-allowed dissociation into SN⁺ and SNS⁺ in the gas phase, although it does represent a shallow local potential energy minimum (activation barrier to dissociation: 45 kJ mol⁻¹; see below). In the solid state $S_3N_2(AsF_6)_2$ is 28 kJ mol⁻¹ more stable than SNSAsF₆ and SNAsF₆ because of its high lattice energy (1493 kJ mol⁻¹) compared to the combined lattice energies of the 1:1 salts (1065 kJ mol⁻¹). Replacement of AsF₆⁻ with a larger counteranion decreases the lattice energy and therefore the stability of the resulting salt, and although we were able to prepare the larger SNSNS-(SbF₆)₂, an attempt to obtain SNSNS(Sb₂F₁₁)₂ led only to a mixture of SNSSb₂F₁₁ and SNSb₂F₁₁. Simple
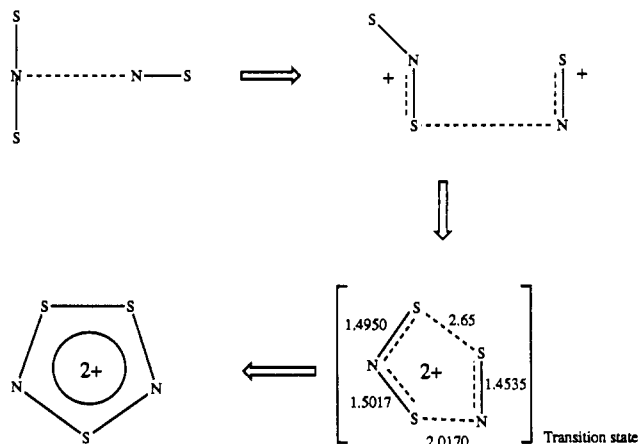
estimates of the solution thermochemistry suggest that SNSNS²⁺ is only marginally unstable in SO_2, while the well-known preference of Se for extended σ-bonded structures reduces the gas-phase dissociation energy for $Se_xS_{3-x}N_2{}^{2+}$ ($x = 1–3$), enabling these cations to be stable in solution.[27] It is therefore clear that the symmetry-allowed cycloaddition of SNS⁺ and SN⁺ will not occur without the energy gained on crystal lattice formation and constitutes the first example of a "*lattice-enforced*" cycloaddition reaction.

The mechanism of the reaction between SNS⁺ and SN⁺ has been shown[28] to be highly asynchronous, proceeding as shown in Scheme 3. It is interesting to note that whereas FMO theory predicts the reaction coordinate to be a S⋯S interaction which maximizes overlap of the orbitals shown in Figure 2, this pathway is at higher energy than that shown in Scheme 3. This is a consequence of the minimization of electrostatic repulsion between SNS⁺ and SN⁺. However, FMO theory correctly predicted that electron density flows from SNS⁺ to SN⁺ in this reaction, consistent with the dominance of the HOMO(SNS⁺)–LUMO(SN⁺) interaction described above. In accordance with the Hammond postulate, the transition state is rather late, and it looks like an expanded version of the final product. This can be compared to the reactions between nitriles and SNS⁺, which are exothermic and appear to proceed through an early transition state (see above); such reactions form the subject of current studies at UNB.

Reactions of SNS⁺ with Alkenes

The frontier molecular orbitals of alkenes are isolobal with those of alkynes and nitriles. Predictably, therefore, SNSAsF₆ undergoes a 1:1 cycloaddition with ethene to give H₂CSNSCH₂AsF₆ (eq 13).[29] However, SNS⁺ has two mutually perpendicular π manifolds, whereas ethene has only one, so that the formation of a purely σ bonded C_2H_4 moiety on cycloaddition of ethene and SNS⁺ can be viewed to a first order of

Scheme 3. Calculated (3-21G(*)) Reaction Path for the Cycloaddition of SN⁺ with SNS⁺ To Give the S₃N₂²⁺ Cation

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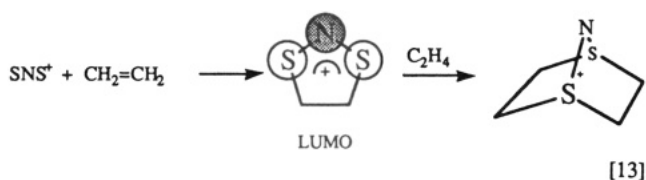
(28) Grein, F. *Can. J. Chem.* **1993**, *70*, 335.

(29) Burford, N.; Johnson, J. P.; Passmore, J.; Schriver, M. J.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1986**, 966.

approximation as leaving the second π system of SNS^+ unaffected, and a second cycloaddition occurs rapidly with ethene to give $S_2N(C_2H_4)_2{}^+$ in quantitative yield (eq 13).

[13]

Similar cycloadditions have been performed with *cis*- and *trans*-2-butene, 2-methylpropene, propene, and norbornene. The "mixed" cation $S_2N(C_2H_4)(MeCH-CHMe)^+$ has also been prepared by the reaction of $H_2\overline{CSNSCH_2}{}^+$ with *trans*-MeCH=CHMe. It is noteworthy that alkynes and nitriles only undergo *one* cycloaddition with SNS^+ due to the stabilizing effects of the π interaction between the now unsaturated RCCR or RCN and SNS fragments. Reaction with a second alkyne would require disruption of the fully delocalized ring π manifold.

The IP of ethene is 10.50 eV, and the rate of its reaction with SNS^+ compares well[30a] with that expected from the IP/rate correlation developed for alkynes and nitriles (Figure 2), reflecting the similarity of the electronic features of all these cycloadditions. Consistently the rate of the cycloaddition with *cis*-2-butene (IP = 9.12 eV) is faster than with ethene, and it is likely that the reactions of alkenes with SNS^+, like those of alkynes and especially nitriles, are dominated by electronic factors.[30a]

Developments in the Synthesis of Novel Materials Using SNS^+: The Stable 7π Radicals $R\overline{CNSNS}\cdot$ and $R\overline{CSNSCR}\cdot$ and Precursors to Synthetic Metals

"Organic" or nonmetal radicals which are stable as pure materials are rare; numerous examples exist in dilute solution, while others are postulated as extremely short-lived reaction intermediates. Few can be isolated as pure materials, and those that are known usually contain second-period elements (e.g., $NO\cdot$, $ONO\cdot$, $tBu_2\text{-}NO\cdot$, and $OO^{2\cdot}$). $R\overline{CNSNS}{}^+$ and $R\overline{CSNSCR}{}^+$ salts are unusual in that they can be reduced to stable 7π radical ring systems in dilute solutions, many of which can be isolated and possess unusual and intriguing properties.

The stabilities of derivatives of the $R\overline{CSNSCR}\cdot$ ring system parallel those of the corresponding nitroxides (R_2NO), so that if R = Me the radical is only stable in dilute solution, whereas if R = Ph it is stable in solutions up to a concentration of 0.5 M.[23a] Reduction of $CF_3\overline{CSNSCCF_3}AsF_6$ (eq 14) yields the radical $CF_3\overline{CSNSC}\text{-}CF_3\cdot$, a blue gas over a green paramagnetic liquid at room temperature that has no detectable tendency to dimerize either in the pure form or in solution, even though it is not sterically hindered from doing so.[31] It

is also indefinitely stable, provided it is kept in the dark, and can be heated to 200 °C for a short time with only minimal decomposition.
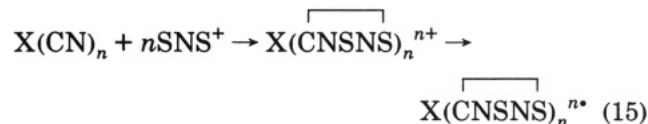
$$2CF_3\overline{CSNSCCF_3}AsF_6 + SbPh_3 + 2Me_4NCl \rightarrow$$
$$2CF_3\overline{CSNSCCF_3}\cdot + SbPh_3Cl_2 + 2Me_4NAsF_6 \quad (14)$$
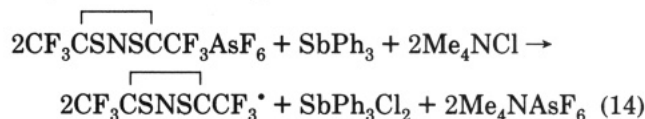
$R\overline{CNSNS}{}^+$ salt may also be reduced by similar methods to $R\overline{CNSNS}\cdot$ radicals in dilute solution. In some cases the products can be isolated, e.g., R = Me (at low temperatures in small amounts),[32] Ph, $p\text{-}O_2\text{-}NC_6H_4$ (as solids),[23a] and tBu (a paramagnetic liquid), but all rearrange at various rates to give more stable $R\overline{CNSSN}\cdot$ radicals. The net result is that adjacent sulfur and nitrogen atoms within the ring have switched positions! The reaction is a quantitative photochemically symmetry allowed concerted rearrangement and proceeds via a $\pi^*\text{-}\pi^*$ dimer[30b,32a,b] (see Figure 1c). $tBu\overline{CNSSN}\cdot$ is also a paramagnetic liquid at room temperature, while other derivatives become paramagnetic on melting.[31a,b,32b] All these radicals dimerize in the solid state via $\pi^*\text{-}\pi^*$ interactions, which[7c,33] we now know are also responsible for the long S–S interactions in $S_8{}^{2+}$ [7b,c] and $(S_3N_2{}^{\cdot+})_2$[33a] (see Figure 1). The reader will recall that the puzzling nature of these weak bonds initiated the work described in this Account.

Recent research has sought to exploit the stability and properties of these radicals in the synthesis of novel materials such as organic metals and magnets. For example, a polymer consisting of an unsaturated backbone with appending thiazyl radicals has been predicted to possess superior electrical conductivity to $(SN)_x$ (see above) and would potentially exhibit high-temperature superconductivity. More recent interest has developed around using dithiadiazolyl diradicals as building blocks for stacked organic metals.[33b] In this regard, stable organic multiradicals are clearly of interest, although they are even rarer than stable monoradicals. Successive cycloadditions of SNS^+ with a multifunctional alkyne or nitrile, followed by reduction, presents one systematic route to such compounds.

The possibility of achieving multiple cycloadditions of SNS^+ onto one substrate as a means to obtain the precursors to stable thiazyl multiradicals was realized simultaneously by Banister and us.[34] Schematically our strategy can be represented, for example, by eq 15,

$$X(CN)_n + nSNS^+ \rightarrow X(\overline{CNSNS})_n{}^{n+} \rightarrow$$
$$X(\overline{CNSNS})_n{}^{n\cdot} \quad (15)$$

where X may be a supporting group, e.g., a phenyl ring.

(30) (a) Schriver, M. J.; Passmore, J.; Sun, X. Manuscript in preparation. (b) Burford, N.; Passmore, J.; Sun, X. Manuscript in preparation.

(31) (a) Awere, E. G.; Burford, N.; Mailer, C.; Passmore, J.; Schriver, M. J.; White, P. S.; Banister, A. J.; Oberhammer, H.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* **1987**, 66. (b) Schriver, M. J. Ph.D. Thesis, University of New Brunswick, 1989.

(32) (a) Burford, N.; Passmore, J.; Schriver, M. J. *J. Chem. Soc., Chem. Commun.* **1986**, 140. (b) Brooks, W. V. F.; Burford, N.; Passmore, J.; Schriver, M. J.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* **1987**, 69 and references cited therein.

(33) (a) Banister, A. J.; Rawson, J. M. The Chemistry of Inorganic Ring Systems. In *Studies in Inorganic Chemistry*; Steudel, R., Ed.; Elsevier: Amsterdam, 1992; Vol. 14, p 323. (b) Cordes, A. W.; Haddon, R. C.; Hicks, R. G.; Oakley, R. T.; Palstra, T. T. M.; Schneemeyer, L. F.; Waszczak, J. V. *J. Am. Chem. Soc.* **1992**, *114*, 1729, 5000 and references cited therein. Banister, A. J.; Rawson, J. M. *Chem. Br.* **1992**, 148 and references cited therein.

(34) (a) Parsons, S.; Passmore, J.; Schriver, M. J.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1991**, 369. (b) Banister, A. J.; Rawson, J. M.; Clegg, W.; Birkby, S. L. *J. Chem. Soc., Dalton Trans.* **1991**, 1099.

Although eq 15 is shown as proceeding directly to the fully reduced neutral multiradical $X(\overline{CNSNS})_n{}^{n\bullet}$, partial reduction would lead to families of radical cations, $X(\overline{CNSNS})_n{}^{m+}$, which may undergo isomerization (Figure 1c) and be reoxidized or reduced further to give an array of multicyclic cations and multiradicals. The versatility of this strategy potentially allows systems to be tailor-made for any given application.

The simplicity of the cycloaddition chemistry of SNS$^+$ makes it an ideal starting material in strategically designed syntheses of this type, and o-, m-, and p-$(CN)_2C_6H_4$, $C_6H_3(CN)_3$, and $Hg(CN)_2$ undergo cycloaddition reactions with SNSAsF$_6$ to give the corresponding $(\overline{CNSNS})_2C_6H_4{}^{2+}$, $(\overline{CNSNS})_3C_6H_3{}^{3+}$,[34b,35a] and $Hg(\overline{CNSNS})_2{}^{2+}$ [35b] salts. We have shown that the thermodynamically *and* kinetically preferred product in the reaction of cyanogen $((C\equiv N)_2)$[36] with SNSAsF$_6$ is the dication $(\overline{CNSNS})_2{}^{2+}$, while Banister[37] has recently observed *three* successive cycloadditions of SNS$^+$ with KC(CN)$_3$. So far investigations on fully reduced multiradicals obtained by routes analogous to eq 15 have been performed on $(\overline{CNSNS})_2{}^{2\bullet}$ and o-, m-, and p-$C_6H_4(\overline{CNSNS})_2{}^{2\bullet}$. These multiradicals retain their high-spin state in solution, but exhibit much reduced paramagnetism in the solid state due to the formation of dimers or extended stacked structures. Similar results have been obtained by Oakley in isomeric $\overline{CNSSN}{}^\bullet$ containing multiradicals, in which the solid-state stacks are subject to a Peierls distortion, making them insulators or semiconductors rather than the organic metals that were initially hoped for.[33b] However, iodine salts of p-$C_6H_4(\overline{CNSSN})_2$[38a] and $H\overline{CNSSN}$[38b] have symmetric stacked structures and conduct. In related work we[39] have recently prepared the planar dicationic diradical $\overline{SSSNC}$-$\overline{CNSSS}{}^{2\bullet 2+}$ according to eq 16, which is the only nonmetal multiradical

$$2S_4(AsF_6)_2 + 2S_8(AsF_6)_2 + (CN)_2 \rightarrow$$

$$(\bullet\overline{SSSNC}\text{-}\overline{CNSSS}\bullet)(AsF_6)_2 \quad (16)$$
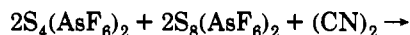
system other than dioxygen to retain its paramagnetism in the solid state ($m = 2.81$ m$_B$), intercationic dimerization being electrostatically hindered by the positive charges on the rings.

Conclusion

Although sulfur–nitrogen chemistry has a long history, it is only fairly recently that salts of SNS$^+$ have been prepared. SNS$^+$ is structurally similar to the isolobal ONO$^+$ and is one of the relatively few known stable isolable triatomic species. Its chemistry is very different from that of ONO$^+$, but is generally simple and quantitative in contrast to much S/N chemistry,[40] as well as being understandable in terms of FMO and thermodynamic considerations. The kinetics of the general quantitative concerted symmetry-allowed cycloaddition reactions with C$\equiv$C, C$=$C, and C$\equiv$N bonds are among the simplest of any known cycloadditions. These cycloadditions and multicycloadditions of SNS$^+$ are applicable to a very wide range of unsaturated centers and provide a general route to a potentially huge range of SNS$^+$-containing heterocyclic and multiheterocyclic compounds. Reduction of the known cycloaddition products has led to the synthesis of novel stable radicals that are of interest in themselves and that are precursors to synthetic metals. It can be anticipated that the reduction of other heterocyclic addition products will yield other stable radicals with unusual properties. Reaction with N$_3^-$ led to the first chemical synthesis of polymeric (SN)$_x$, and it is likely that other ionic reactions of SNS$^+$ will also lead to new discoveries. The electrophilic substitution reactions of ONO$^+$ with aromatics are very important in organic chemistry. Very recently we have shown that SNS$^+$ also undergoes an electrophilic substitution reaction with benzene,[41] thus opening up yet another area of SNS$^+$ chemistry. Banister and his co-workers have very recently found that reaction with PhHgCN gives, surprisingly, PhSNSNSNSPhAsF$_6$.[42] Thus only a beginning has been made in the exploration of the chemistry of the simple triatomic SNS$^+$, which we anticipate will be extensive and significant.

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(36) Parsons, S.; Passmore, J.; White, P. S. *J. Chem. Soc., Dalton Trans.* 1993, 1499.

(37) Banister, A. J.; Lavender, I.; Rawson, J. M.; Clegg, W. *J. Chem. Soc., Dalton Trans.* 1992, 859.

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(39) Boyle, P. D.; Parsons, S.; Passmore, J.; Wood, D. J. *J. Chem. Soc., Chem. Commun.* 1993, 199.

(40) For example the reaction of S$_4$N$_4$ and MeO$_2$CC$\equiv$CCO$_2$Me in the following: Morris, J. L.; Rees, C. W. *Chem. Soc. Rev.* 1986, *15*, 1 and references therein. For older examples, see: Heal, H. G. *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus*; Academic Press: London, 1980.

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(42) Lavender, I. Ph.D. Thesis, University of Durham, 1993.