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Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926081>

The Chemistry of Compounds Containing the -SNSO or -SNSS Chromophores

T. Chivers^a

^a Department of Chemistry, The University of Calgary, Alberta, Canada

To cite this Article Chivers, T.(1986) 'The Chemistry of Compounds Containing the -SNSO or -SNSS Chromophores', *Journal of Sulfur Chemistry*, 7: 2, 89 – 104

To link to this Article: DOI: 10.1080/17415998609410044

URL: <http://dx.doi.org/10.1080/17415998609410044>

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THE CHEMISTRY OF COMPOUNDS CONTAINING THE -SNSO OR -SNSS CHROMOPHORES

T. CHIVERS

(Department of Chemistry, The University of Calgary, Calgary, T2N 1N4,
Alberta, Canada)

(Received April 21, 1986)

The chemistry of compounds containing the -SNSO or -SNSS chromophores is compared in the context of synthesis, structure, bonding, spectroscopic properties and reactivity.

Key words: N-Sulfinylsulfenamides, N-thiosulfinylsulfenamides

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1. INTRODUCTION

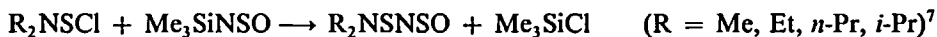
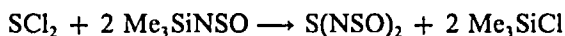
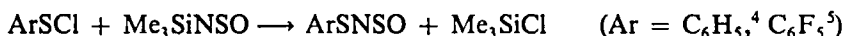
In this article the chemistry of derivatives of the hypothetical compounds HSNSO (sulfinylamino sulfides) and HSNSS (thiosulfinylamino sulfides) will be compared. The review will begin with a discussion of the methods available for the preparation of such compounds. Their molecular structures and spectroscopic properties will then be discussed in the context of molecular orbital calculations of the electronic structures of model species. Finally the reactions of RSNSO and RSNSS will be described. The literature is covered to the end of 1985.

Reviews on the closely related compounds RNSS (*N*-thiosulfinylamines)¹ and *N*-sulfinylamines, RNSO,² have been published in earlier volumes of this series.

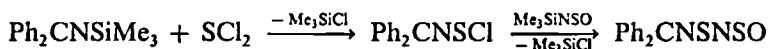
2.A. SYNTHESIS OF RSNSO DERIVATIVES

(i) *Me₃SiNSO and Sulfur-halogen Compounds*

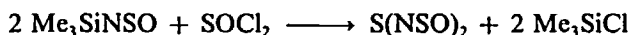
The availability of the reagent $\text{Me}_3\text{SiNSO}^3$ provides easy access to compounds of the type RSNSO via reactions with compounds containing sulfur-halogen bonds. This method provides an excellent synthesis of aryl derivatives^{4,5} and of S(NSO)_2 .⁶ It has also been used to prepare dialkylamino derivatives.⁷



The diphenylmethyleneamino derivative has been obtained by this route via Ph_2CNSCl prepared *in situ*.⁸



The initial products of the reactions of Me_3SiNSO with sulfur(IV) halides, e.g. dimethylaminosulfinyl chloride or thionyl chloride, undergo disproportionation to give sulfinylamino derivatives of sulfur(II).⁹

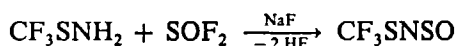


(ii) Reaction of SOCl₂ with RSN(SiMe₃)₂

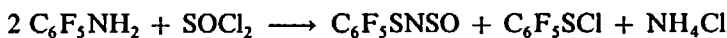
Compounds of the type RSN(SiMe₃)₂ are suitable reagents for the preparation of RSNSO via reaction with SOCl₂.^{4,5}

*(iii) Condensation of Sulfenamides with Thionyl Halides*

The trifluoromethyl derivative was originally obtained by hydrolysis of CF₃SNSF₂ in a glass vessel.¹⁰ The condensation of CF₃SNH₂ with SOF₂ provides a better preparation of this derivative.¹⁰



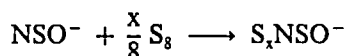
This synthetic approach has also been used for the preparation of the pentafluorophenyl derivative.¹¹



This derivative has also been obtained from C₆F₅SONH₂ or (C₆F₅S)₂NH and thionyl chloride in the presence of pyridine.¹¹

(iv) Reaction of NSO⁻ with Sulfur

The colourless anion NSO⁻ is obtained as an insoluble potassium salt on treatment of Me₃SiNSO with potassium *t*-butoxide in THF.¹² This anion can also be generated by the electrochemical reduction of Ph₂CNSNSO.¹³ Addition of elemental sulfur to a solution of electrochemically produced NSO⁻ or to a slurry of KNSO in acetonitrile produces an unstable red anion, S_xNSO⁻ (λ_{max} 496 nm) where x = 1 or 2.^{13,14}

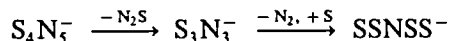
**2.B. SYNTHESIS OF RSNSS DERIVATIVES**

Although a number of organo derivatives of *N*-thiosulfinylamines, RNSS, are well characterized,¹ the thio analogue of the versatile reagent Me₃SiNSO is not known. Consequently, approaches to the synthesis of compounds containing the -SNSS chromophore differ from those used to prepare RSNSO. In fact, no general method is available for RSNSS and most of the examples given below are unique for a particular derivative.

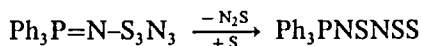
(i) Thermolysis of Cyclic S-N Compounds

The acyclic anion SSNSS⁻ can be prepared by the thermal decomposition of the bicyclic anion S₄N₅⁻ in acetonitrile at 90 °C.¹⁵⁻¹⁷ This reaction occurs via the intermediate formation of the six-membered ring, S₃N₃⁻. It is necessary to use large cations, e.g.

$(\text{Ph}_3\text{P})_2\text{N}^+$ (PPN^+)^{15,16} or Ph_4As^+ ,¹⁷ in order to stabilize the SSNSS^- ion in the solid state.



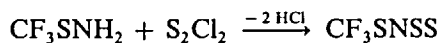
A related thermal transformation involves the conversion of the six-membered ring $\text{Ph}_3\text{P}=\text{N}-\text{S}_3\text{N}_3$ to the acyclic compound Ph_3PNSNSS in boiling acetonitrile.^{18,19}



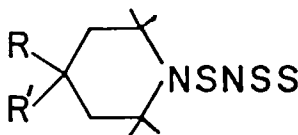
In contrast, the thermolysis of $\text{Ph}_3\text{As}=\text{N}-\text{S}_3\text{N}_3$ produces the four-membered ring S_2N_2 .¹⁹

(ii) *Condensation of Sulfenamides with S_2Cl_2*

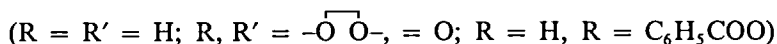
In the presence of quinoline or acridine, CF_3SNH_2 condenses with S_2Cl_2 to give CF_3SNSS .²⁰



The preparation of piperidino derivatives of type **1**²¹ from the corresponding piperidine, sulfur monochloride and aqueous ammonia probably occurs via the intermediate formation of a sulfenamide.²² These compounds can also be obtained in very low yields from bis(2,2,6,6-tetramethylpiperidino)disulfides under similar reaction conditions.

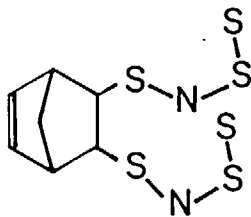


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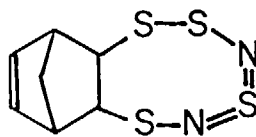


(iii) *Reaction of S_4N_2 with Norbornadiene*

The reaction of the six-membered ring 1,3- S_4N_2 with an excess of norbornadiene gives compound **2**, in which two SNSS groups are attached to a norbornenyl residue, as a minor product (<1%).²³ The major product is **3**, the result of the insertion of a $>\text{C}=\text{C}<$ bond of norbornadiene into an $\text{S}-\text{S}$ bond of S_4N_2 .²⁴



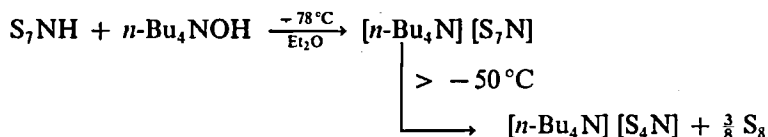
2



3

(iv) Deprotonation of Cyclic Sulfur Imides

The blue species formed when cyclic sulfur imides, e.g. S_7NH , are treated with a base has been identified as the acyclic S_4N^- anion.^{25,26} The first salt of this anion was isolated from the following reaction.



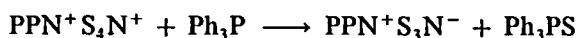
The Wittig reagent, $Ph_3P=CH_2$, is a suitable alternative for the deprotonation of S_7NH .¹⁴ The $SSNSS^-$ ion is also produced from S_7NH or $1,4-S_6(NH)_2$ upon electrochemical reduction.²⁷

(v) Other Routes to the $SSNSS^-$ Anion

The dark blue $SSNSS^-$ ion plays a central role as an intermediate in the preparation of cyclic sulfur imides from sodium azide and elemental sulfur in HMPA or disulfur dichloride and ammonia in polar solvents (see Section 5 (v)), but these reactions are not useful for the preparation of salts of this anion.^{28,29} The $SSNSS^-$ is also formed in solutions of sulfur in liquid ammonia,^{30,31} which have found use as a reagent in organic syntheses.³²

(vi) Preparation of the $SNSS^-$ Anion

Crystalline salts of the red-orange $SNSS^-$ anion can be obtained by treatment of the $SSNSS^-$ ion with triphenylphosphine followed by addition of diethyl ether.^{33,34} Large counterions, e.g. PPN^+ or Ph_4As^+ , are necessary for the preparation of stable salts.

**3. STRUCTURE AND BONDING***(i) RSNSO Derivatives*

The X-ray crystal structures of two derivatives of the type RSNSO have been determined and the bond lengths and bond angles are compared in Table I. The CNSNSO unit in $Ph_2CNSNSO$ ⁸ and both SNSO units in $S(NSO)_{235,36}$ adopt planar, *cis-trans* conformations. The S(1)-N(2) and S(2)-N(2) bond distances of ca. 1.65 and 1.53 Å and the bond angles of ca. 97° and 118° at S(1) and S(2) suggest that these compounds are best represented by the valence bond structures **4a-c**, which involve divalent sulfur in the formal oxidation states +2 and +4, respectively.

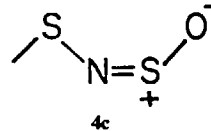
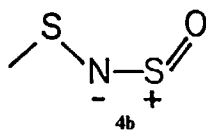
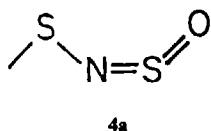


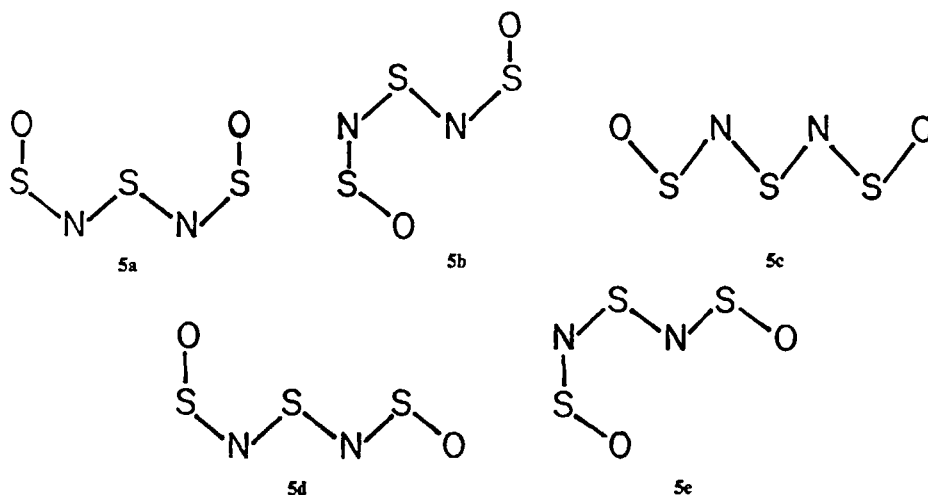
TABLE I
Bond Lengths (Å) and Angles (deg) in Ph_2CNSNSO and S(NSO)_2

Bond length/ Bond angle	Ph_2CNSNSO	S(NSO)_2^a	S(NSO)_2^b
N(1)-S(1)	1.680(3)	1.657(2)	1.647(3)
S(1)-N(2)	1.644(2)	1.657(2)	1.647(3)
N(2)-S(2)	1.529(2)	1.534(2)	1.535(3)
S(2)-O	1.453(3)	1.465(2)	1.446(4)
N(1)-S(1)-N(2)	96.9(1)	97.2(1)	97.3(2)
S(1)-N(2)-S(2)	122.7(2)	123.6(2)	124.3(2)
N(2)-S(2)-O	117.2(1)	117.5(1)	118.0(2)

^a Ref. 35, determined at -105°C .

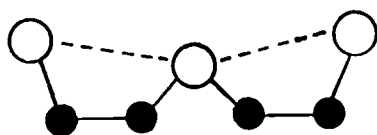
^b Ref. 36, determined at 31°C .

MNDO calculations of the heats of formation of various chain conformations of S(NSO)_2 show that structures **5a** and **5b**, which have a *cis,trans* configuration of the two SNSO units, are more stable than those involving one *cis,trans* and one *trans,trans* SNSO unit, **5d** and **5e**, by ca. 30 kJ mol^{-1} .³⁷ The structure **5c** with an all *trans* arrangement about the S-N bonds is the least stable of those that were considered. The designations *cis* and *trans* refer to the geometric arrangement of substituents at individual S-N bonds.

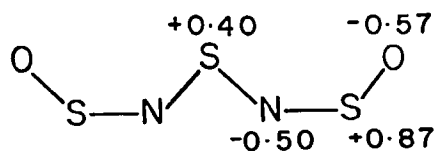


The stabilization of the *cis,trans* structure in S(NSO)_2 has been attributed to the in-phase relationship of the O and $\text{S } p_2$ atomic orbitals in the HOMO for this geometrical arrangement that results in a weakly bonding interaction, **6**.³⁷ In addition, the calculated

net atomic charges indicate there is a strong electrostatic attraction between the central sulfur atom and the oxygen atoms for the *cis,trans* structure, 7.³⁷

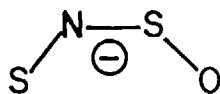


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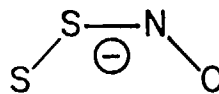


7

Although the SNSO⁻ ion, 8, has not yet been characterized (Section 2 A (iv)), the X-ray structure of an isomer of this ion, SSNO⁻, 9, has been reported recently.³⁸ It adopts a *cis* conformation with an S-S bond length of 1.99 Å. Salts of this red anion (λ_{max} 448 nm) can be prepared by the action of nitric oxide on an acetone solution of [PPN]₂S₁₂ or by the reaction of [PPN]NO₂ with sulfur in acetone.³⁹



8



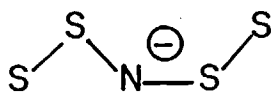
9

The reaction of the SSNO⁻ anion with triphenylphosphine produces SNO⁻ (monothionitrite).^{39,40} The latter anion is thought to be the active constituent of gunpowder.^{41,42}

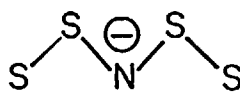
(ii) RSNSS Derivatives

The X-ray crystal structures of three covalent derivatives containing the SNSS unit and two salts of the SSNSS⁻ ion have been reported and the structural parameters are compared in Table II. The common features of these structures are essentially planar *cis,trans* XSNSS units and short (1.90–1.93 Å) terminal S-S bonds. There is no consistent pattern for the S-N bond lengths in the different derivatives.

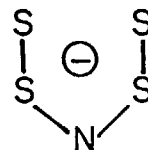
The relative energies of the *cis,trans*-, 10a, *trans,trans*-, 10b, and *cis,cis*-, 10c, conformations of the SSNSS⁻ ion have been estimated on the basis of *ab initio*¹⁶ and MNDO³⁷ MO calculations.



10a



10b



10c

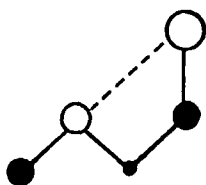
TABLE II
Bond Lengths (Å) and Bond Angles (deg) for X-SNSS Derivatives

Compound	d(S-S)	d(SS-N)	d(XS-N)	<NSS	<SNS	<XNS	Ref.
C ₇ H ₈ (SNSS) ₂ ^a	1.903	1.572	1.641	114.9	119.0	97.2	23
Ph ₄ As ⁺ S ₄ N ^{-b}	1.93	1.56	1.62	114.0	120.1	1211.5	17
PPN ⁺ S ₄ N ^{-b}	1.91	1.62	1.57	111.0	120.5	110.5	16
Ph ₃ PNSNSS	1.908	1.592	1.587	111.4	120.9	107.7	19
C ₁₁ H ₂₀ O ₂ NSNSS, 1	1.912	1.569	1.657	114.9	119.2	105.7	21

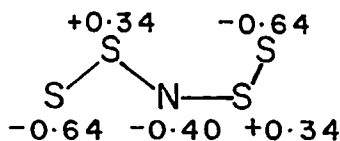
^a Mean values from two SNSS groups.

^b Mean values from two disorder models.

Both methods indicate the *cis,trans* structure to be more stable than the other two geometrical isomers. The two factors which explain the observed *cis,trans* structure of S(NSO)₂ also account for this geometrical arrangement in the SSNSS⁻ ion. In the HOMO of this anion there is a spatial interaction between the p_z orbitals of one of the terminal S atoms and one of the internal S atoms, **11**,³⁷ (d(S-S) ~ 3.15 Å),^{16,17} in the *cis,trans* conformation that cannot occur in the *trans,trans* isomer. Further, the calculated net atomic charges show that the internal sulfur atoms are positively charged while the terminal sulfur atoms carry a substantial negative charge so that there is also an electrostatic interaction between these sulfur atoms in the *cis,trans* conformation, **12**, (the charges shown in **12** were calculated by the MNDO method;³⁷ ab initio MO calculations reveal a similar trend¹⁶). These calculations also show that the S-S bonds in SSNSS⁻ are highly polar, a characteristic that probably contributes to the shortness of these bonds.



11



12

The structure of the SNSS⁻ anion has not been solved due to disorder problems.⁴³ However, *ab initio* MO calculations indicate that the statistical energy of the planar *cis* conformation is lower than that of the *trans* by at least 40 kJ mol⁻¹.³⁴

The acyclic ions SNSS⁻ and SSNSS⁻ can be regarded as electron-rich analogues of butadiene and a pentadienyl ligand, respectively. In these ions the π MOs are formed by overlap of p_z orbitals on sulfur and nitrogen. As indicated in Figures 1 and 2, the SNSS⁻ and SSNSS⁻ ions are 6 and 8 π-electron systems, respectively. In contrast to their

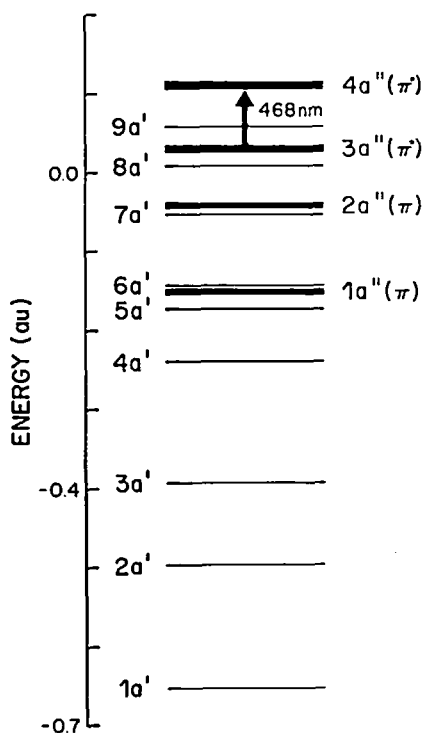


FIGURE 1. Orbital energy level diagram for *cis*-SSNS—showing the $\pi^*(3a'') \rightarrow \pi^*(4a'')$ transition (taken from ref. 34). The π orbitals are represented by thick lines. The HOMO is $9a'$ and the LUMO is $4a''$.

hydrocarbon analogues the π^* levels are partially occupied in these anions. As a result, the S–S and S–N π -bond orders are lower than the corresponding C–C π -bond orders in the hydrocarbon systems. A second consequence of the partially occupied π^* levels in SNSS^- and SSNS^- is the appearance of strong absorption bands in the visible spectra of these anions as discussed in the next section.

4. SPECTROSCOPIC STUDIES

(i) Electronic Spectra

Strong visible absorption bands appear at 470 nm for SNSS^- and at 582 nm for SSNS^- . They have been attributed to $\pi^* \rightarrow \pi^*$ transitions on the basis of *ab initio* HFS-SCF calculations (Figures 1 and 2).^{16,34} Other molecules of the type R-SNSS also exhibit intense visible absorption bands (Table III) and similar $\pi^* \rightarrow \pi^*$ transitions are likely to be responsible. When the substituent R is a π -donor ligand capable of conjugation with the SNS chromophore, e.g. S or Ph_3PN , a large bathochromic shift of this absorption band is observed. The molecule $\text{C}_7\text{H}_8(\text{SNSS})_2$, **2**, exhibits two visible absorp-

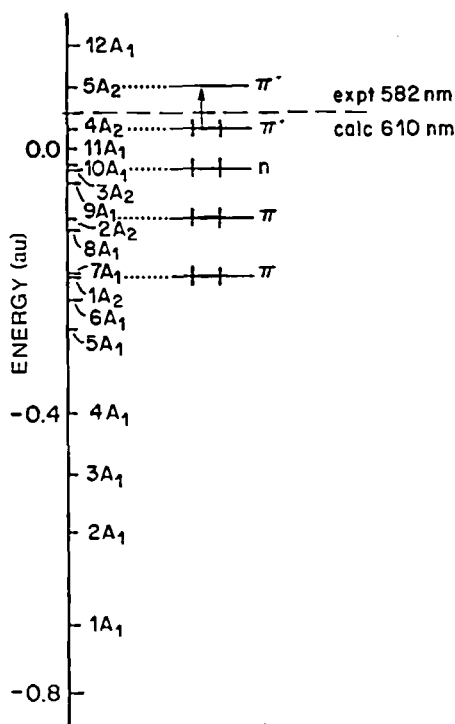


FIGURE 2. Orbital energy level diagram for *cis,trans*-SSNS- showing the $\pi^*(4a_2) \rightarrow \pi^*(5a_2)$ transition (data taken from ref. 16).

tions at 433 and 408 nm that have been assigned to the excitonically coupled $\pi^* \rightarrow \pi^*$ transitions of the two SNS units.²³

The corresponding visible absorption band for R-SNSO derivatives occurs at lower wavelengths (Table III). MNDO calculations for the model compounds HSNSO and HSNS indicate that the higher energy of the LUMO in HSNSO compared to that in HSNS is primarily responsible for the higher π^* (HOMO) $\rightarrow \pi^*$ (LUMO) transition energies for RSNSO.⁸

(ii) Vibrational Spectra

The infrared and Raman spectra of $S(NSO)_2$ have been assigned.^{35,36} Solution IR data indicate there is no conformational change of $S(NSO)_2$ upon dissolution. A strong band at ca. 1185cm^{-1} in the IR spectra of RSNSO derivatives has been attributed to $\nu_{as}(NSO)$.^{4-9,11}

The Raman spectra of the isotopically enriched SN^*SS^- and SSN^*SS^- ions (where $N^* = 30\% \text{ }^{15}\text{N}$) facilitate the assignment of vibrations involving the nitrogen atom.^{16,34} These occur at ca. $890 [\nu_{as}(SNS)]$ and $685\text{--}710\text{cm}^{-1} [\nu_s(SNS)]$. Strong Raman bands are observed in the region $570\text{--}590\text{cm}^{-1}$ for the S-S bond in R-SNS, consistent with the

TABLE III
 λ_{max} Values (nm) for RSNSO and RSNS Derivatives

Compound	λ_{max}	Ref.
CF ₃ SNSO	colourless	10
OSNSNSO	365	13
Ph ₂ CNSNSO	370	8
Me ₂ NSNSO	intense yellow	7, 9
MeSNSO	yellow	4
C ₆ F ₃ SNSO	yellow	11
PhSNSO	orange	5
CF ₃ SNSS	red	20
C ₇ H ₈ (SNSS) ₂	408, 433	23
SNSS ⁻	470	34
Ph ₃ PNSNSS	491	19
SSNSS ⁻	582	16

shortness of these bonds. For SSNSS⁻ two bands are observed at 570 and 592 cm⁻¹ attributed to the two inequivalent S-S bonds.¹⁶ For SNSS⁻ only one band is observed in the S-S stretching region, but the observation of this band rules out a branched structure for S₃N⁻ (cf. NO₃⁻). Strong bands attributed to $\nu(\text{S-S})$ also appear at 565–590 cm⁻¹ in the IR spectra of SNSS⁻ and SSNSS⁻, consistent with the calculated high polarity of these bonds (Section 3 (ii)).

The Raman spectra of SNSS⁻ and SSNSS⁻ also exhibit strong resonance enhancement.^{16,34} This characteristic has allowed the detection of small amounts of SSNSS⁻ in the presence of SNSS⁻ in the solid state³⁴ and the identification of SSNSS⁻ in dilute solutions of sulfur in liquid ammonia.³⁰

(iii) ¹⁵N NMR Spectra

The ¹⁵N chemical shifts of isotopically enriched SSNSS⁻, Ph₃PNSNSS and SNSS⁻ occur at 244.2, 472.0 and 617.6 ppm (ref. NH₃(l) at 25 °C), respectively.^{34,44} The R-SNSS derivatives do not conform to the δ/λ correlation found for simple chromophores, e.g. XNO.⁴⁵ The intense visible absorption bands observed for RSNS are not relevant to nitrogen shielding because they are magnetic dipole forbidden and/or the charge circulation is closer to sulfur than to nitrogen (using LUMOs based mainly on sulfur).

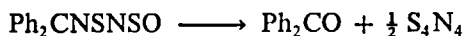
(iv) Photoelectron Spectra

The He(I) PE spectrum of S(NSO)₂ has been recorded and good agreement between the first five measured ionization potentials and the orbital energies calculated by the MNDO method was observed.^{37,46}

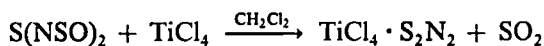
5. REACTIONS OF RNSO AND RSNSS DERIVATIVES

(i) Thermal Decomposition

The solid state thermal decomposition of Ph_2CNSNSO at 200°C occurs with the elimination of Ph_2CO and formation of S_4N_4 .⁸



The latter product is probably formed by the well known dimerization reaction of S_2N_2 ,⁴⁷ but attempts to trap this important intermediate were unsuccessful.⁸ The thermolysis of $\text{S}(\text{NSO})_2$ at $200\text{--}400^\circ\text{C}$ under ultrahigh vacuum also failed to produce S_2N_2 , but treatment of $\text{S}(\text{NSO})_2$ with TiCl_4 gives an adduct of this ligand in 95% yield.⁴⁸



N-Thiosulfinylaminothiopiperidines, **1**, exhibit good thermal stability. For example, no detectable decomposition was detected after 3 h at reflux in chloroform.²² By contrast the trifluoromethyl derivative CF_3SNSS decomposes at 20°C with the formation of sulfur and the corresponding sulfur diimide.²⁰



(ii) Cycloaddition reactions

The molecule CF_3SNSS undergoes 1,3-dipolar cycloaddition with 1,3-cyclopentadiene to give a mixture of the two isomers **13** and **14**.²⁰



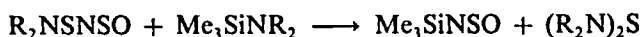
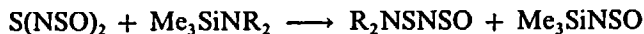
13



14

(iii) Reactions with Si-N or Si-S bonds

Treatment of $\text{S}(\text{NSO})_2$ with Si-N reagents produces R_2NSNSO , which reacts further with excess Me_3SiNR_2 , as indicated below.⁴⁹

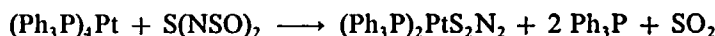


N-(Phenylthio)sulfinylamine readily undergoes metathesis with Si-S reagents.⁵



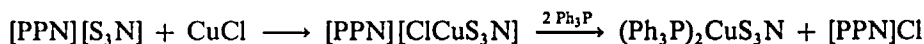
(iv) Reactions with metal complexes

The zerovalent metal complex $(\text{Ph}_3\text{P})_4\text{Pt}$ reacts with $\text{S}(\text{NSO})_2$ to give the five-membered cyclometallathiazene, $(\text{Ph}_3\text{P})_2\text{PtS}_2\text{N}_2$.⁵⁰



The reaction of $\text{S}(\text{NSO})_2$ with AgAsF_6 in SO_2 gives the polymeric complex $[\text{Ag}_4\{\text{S}(\text{NSO})_2\}_9][\text{AsF}_6]_4 \cdot \text{SO}_2$ in which there are two crystallographically independent silver atoms.⁵¹ One is octahedrally coordinated by the terminal oxygens of six $\text{S}(\text{NSO})_2$ ligands, while the other is unsymmetrically coordinated by the nitrogen atoms of three $\text{S}(\text{NSO})_2$ ligands. The complex $\text{Zn}[\text{S}(\text{NSO})_2]_2(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ is formed from the reaction of $[\text{Zn}(\text{SO}_2)_2](\text{AsF}_6)_2$ with $\text{S}(\text{NSO})_2$ in liquid SO_2 .⁵² Each zinc atom is octahedrally coordinated to four oxygen and two fluorine atoms. The $\text{S}(\text{NSO})_2$ ligands are in a *cis* arrangement and form bridges between two zinc atoms in a two-dimensional network. The *cis, trans-* geometry and localization of single and double S–N bonds in the free ligand is unchanged upon coordination in these two complexes.

The SNSS^- ion forms a number of complexes with transition metal ions, e.g. Co, Ni, Pd, Cu, Ag and Au, in which it behaves as a chelating bidentate ligand bonded to the metal via the terminal sulfur atoms.⁵³ In certain cases, e.g. Cu(I) or Ag(I),⁵⁴ these complexes can be prepared by metathetical reactions between a salt of the S_3N^- ion and the metal halide, but this approach is frequently thwarted by competing redox reactions.³⁴

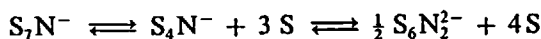


The same complexes are obtained when $[\text{PPN}][\text{S}_4\text{N}]$ is used instead of $[\text{PPN}][\text{S}_3\text{N}]$.⁵³

As indicated in Section 2 B (iv) the acyclic ions SSNSS^- and SNSS^- ions are produced upon deprotonation of S_7NH . It is not surprising, therefore, that complexes containing the five-membered MS_3N ring can be prepared by the reactions of S_7NH with metal halides in the presence of a base e.g. KOH ,⁵⁵ aq. ammonia,⁵⁵ Ph_4AsOH ,⁵⁶ or $n\text{-BuLi}$.⁵⁷ The complex $(\text{Ph}_3\text{PS})\text{CuCl}$ was isolated in low yield from the reaction of $(\text{Ph}_3\text{P})\text{CuCl}$ with S_7NH in methylene chloride (without addition of a base).⁵⁸ Presumably, dissociated Ph_3P serves as the deprotonating agent in this system.

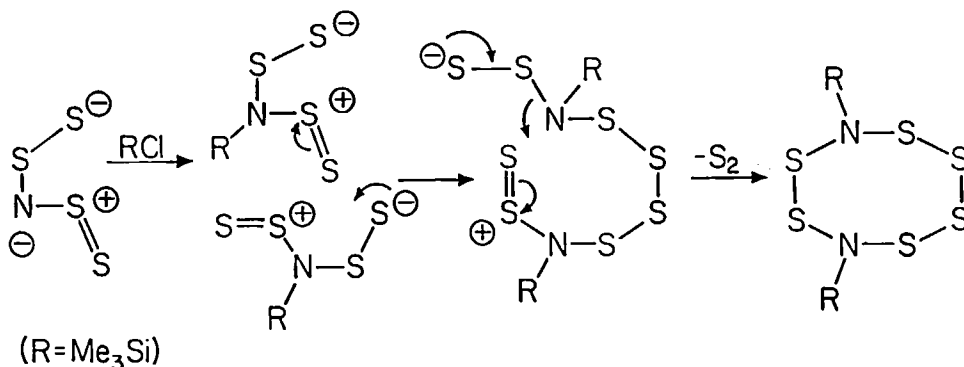
(v) Hydrolysis

The cyclic sulfur imides S_7NH and 1,3-, 1,4-, and 1,5- $\text{S}_6(\text{NH})_2$ are obtained by acid hydrolysis of the deep blue solutions formed from the treatment of S_2Cl_2 with ammonia in DMF ⁵⁹ or by the reaction of sodium azide with sulfur in HMPA .²⁹ The blue chromophore in these solutions is the SSNSS^- ion and it has therefore been suggested that this anion is involved in equilibria with cyclic S–N anions which are the precursors of the imides.²⁹



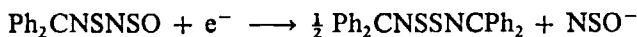
It seems likely that the SNSS^- ion should also be included in such equilibria since it has been shown by Raman spectroscopy that solutions of $\text{PPN}^+\text{S}_4\text{N}^-$ in liquid ammonia contain the S_3N^- ion.³⁰

The exclusive formation of 1,4-S₆N₂(SiMe₃)₂ from the reaction of S₇N⁻ (produced from S₇NH and *n*-butyllithium in THF) has been explained by invoking the intermediate formation of SSNSS⁻ in the following mechanism.⁶⁰



(vi) Reduction

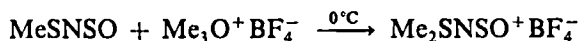
The electrochemical reduction of Ph₂CNSNSO at a mercury pool or Pt gauze electrode at -1.6 or -1.75 V (vs Ag/0.1 M AgClO₄-MeCN), respectively, occurs via the following one-electron process.¹³



The reduction of the SSNSS⁻ ion (λ_{max} 580 nm) on a mercury pool or Pt gauze electrode in acetonitrile-0.1 M Et₄N⁺ ClO₄⁻ at -1.8 V produced SNSS⁷ (λ_{max} 465 nm) via cleavage of an S-S bond. Further reduction of the S₃N⁻ ion gave rise to a new, unidentified S-N anion (λ_{max} 375 nm).²⁷

(vii) Alkylation

The alkylation of methylsulfinylamino sulfide with trimethyloxonium tetrafluoroborate has been reported.⁶¹



The product undergoes a cycloaddition reaction with dienes.

6. SUMMARY

Although a variety of organic derivatives containing the -SNSO chromophore have been characterized, studies of this class of compounds have been sporadic. These compounds exhibit quite high thermal stability independent of the nature of the organic group, but there have been no systematic investigations of their chemical behaviour. Fewer derivatives of the -SNSS chromophore are known and their thermal stability appears to be dependent on the substituent R. The reaction of reagents of the type RSN(SiMe₃)₂ (or RSNH₂) with S₂Cl₂ is potentially a general synthetic route to these

interesting compounds that could provide the basis for a detailed investigation of their physical and chemical properties. As well as cycloaddition reactions, the coordination chemistry of RSNSO would be of considerable interest in view of the versatile behaviour demonstrated by ligands of the type RNSO or RNSNR in complexes with transition metals.⁶²

7. ACKNOWLEDGEMENT

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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