The Energetics of Formation and X-Ray Crystal Structure of $\overline{SNSNS}(AsF_6)_2$, containing the Lattice-stabilized Aromatic 6π 1,3,4,2,5-Trithiadiazolium(2+) Cation formed by the Crystal-lattice-energy-driven, Symmetry-allowed Cycloaddition of SN^+ and SNS^+

Wendell V. F. Brooks,[b] T. Stanley Cameron,*[a] Friedrich Grein,*[b] Simon Parsons,[b] Jack Passmore*[b] and Melbourne J. Schriver[b]

[a] *Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3*
[b] *Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2*

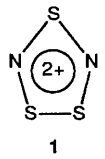
We report the preparation, vibrational spectra and X-ray crystal structure of $\overline{SNSNS}(AsF_6)_2$, containing the 6π 1,3,4,2,5-trithiadiazolium(2+) cation, which dissociates in solution to SN^+ and SNS^+, consistent with *ab initio* 6-31G* calculations (estimated gas-phase dissociation enthalpy: −400 kJ mol^{-1}); the $\overline{SNSNS}^{2+}$ ring represents a local energy minimum, and the cycloaddition of SN^+ and SNS^+ is driven in the solid state by the high lattice energy of the 1 : 2 salt.

The $\overline{SNSNS}^{2+}$ heterocycle, **1**, has long been of interest in sulphur–nitrogen chemistry as an example of a 6π 'electron-rich aromatic'.[1] No conclusive evidence for this cation has yet been presented, although paradoxically the 7π radical $\overline{SNSNS}^{+\cdot}$ is well known and indefinitely stable.[2,3] Roesky[4] and Mews[5] have prepared compounds which analysed as $\mathbf{1}(SbCl_6)_2$ and $\mathbf{1}(AsF_6)_2$, although direct structural evidence was not presented. We have recently prepared and characterized the series of cations $Se_xS_{3-x}N_2^{2+}$ (x = 1–3),[6] and shown that they are indefinitely stable in the solid state and in solution. We have also previously presented some preliminary results on the synthesis and stability of $\mathbf{1}(AsF_6)_2$.[7,8] We now describe the synthesis of crystalline $\mathbf{1}(AsF_6)_2$ by the lattice-energy-driven, symmetry-allowed cycloaddition of SNS^+ and SN^+, and its characterization by vibrational spectroscopy and X-ray crystallography.[7,8] Far from being a stable 6π species, **1** is only stable in the solid state, and quantitatively dissociates in SO_2 solution back to SN^+ and SNS^+. This is consistent with lattice energy and *ab initio* calculations, which show that although $\Delta H[S_3N_2^{2+}(g) \rightarrow SN^+(g) + SNS^+(g)]$ is −400 kJ mol^{-1}, in the solid state **1** is held in a shallow potential energy well by the high lattice energy of the 1 : 2 salt.

The ^{14}N NMR spectrum[7] (14.45 MHz, 20 °C) of a pale yellow solution obtained by condensing SO_2 (1.79 g) onto $SNAsF_6$ (0.267 g, 1.0 mmol) and $SNSAsF_6$ (0.263 g, 1.1 mmol) in a 10 mm NMR tube showed only resonances due to SNS^+ (δ −91, Δν 8 Hz) and SN^+ (δ 202, Δν 250 Hz).[7] Removal of the solvent (at −20 °C) gave a white solid, which was characterized *in situ* by its Raman spectrum, and its IR spectrum (Nujol mull).† Neither spectrum showed bands assignable to either SN^+ or SNS^+, and the Raman spectrum was composed entirely of bands assignable to $\mathbf{1}(AsF_6)_2$. The IR spectrum showed some peaks due to $F\overline{SNSNS}AsF_6$,[5,9] likely formed by F^- abstraction and loss of AsF_5 on grinding. Redissolving the white solid in SO_2 (2 g) regenerated SN^+ and SNS^+ quantitatively according to eqn. (1). Fluoride ion abstraction from $F\overline{SNSNS}AsF_6$[5,9] by AsF_5 and oxidation of $S_6N_4(AsF_6)_2$[2] using AsF_5–Br_2 (trace) (both in SO_2) also generated 1 : 1 solutions of SN^+ and SNS^+ (^{14}N NMR).

$$SNSAsF_6 + SNAsF_6 \underset{\text{Solid state}}{\overset{\text{Solution}}{\rightleftharpoons}} S_3N_2(AsF_6)_2 \qquad (1)$$

Crystals of $\mathbf{1}(AsF_6)_2$ were obtained by evaporation (over 3 weeks) of a clear yellow solution of $SNSAsF_6$ (0.479 g, 1.79



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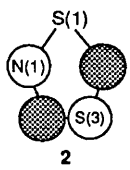

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† Raman spectrum (solid at 20 °C, with intensities relative to that of the most intense band (100)) (in cm^{-1}): 1060 [11%, ν_{as}(NS)], 972 [v. weak, ν_s (NS)/δ_s(ring)], 780 [100, ν_{as}(NS), δ_{as} (ring)], 688 [100, $\nu_1(AsF_6^-)$], 562 [93, $\nu_2(AsF_6^-)$], 490 [45, ν_s(SN)/δ_s (ring)], 395 [95, ν(SS)] and 372 [64, $\nu_5(AsF_6^-)$]. IR (Nujol mull, excluding peaks due to $S_3N_2FAsF_6$): 1051(m), 968m, 700vs, br. [$\nu_3(AsF_6^-)$], 668sh [ν_s(SN)/δ_s(ring)], 558ms, 483m, 438ms [δ_{as}(ring)] and 388vs, [$\nu_4(AsF_6^-)$].

Table 1 Calculated geometries and total energies for $S_3N_2^{2+}$, SNS^+ and SN^+; all calculations were performed at the 6-31G* level

Cation	Bond distances/Å, calc. [expt.[20]]		Bond angles/°, calc. [expt.[20]]		Total energy[a]
$S_3N_2^{2+}$[b]	S(1)–N(1),(2)	1.596 [1.591(10)]	S(1)[e]	98.84 [101.5(5)]	−1300.50403
	N(1),(2)–S(2),(3)	1.535 [1.532(11)]	N(1),(2)[e]	124.34 [122.6(6)]	
	S(2)–S(3)	2.092 [2.093(5)]	S(2),(3)[e]	96.24 [96.8(4)]	
SNS^+	S–N	1.474 [1.510[c]]	N[e]	180	−849.09024
SN^+	S–N	1.397 [1.42(1)[d]]			−451.56553

[a] Total energies in Hartree. [b] Numbering shown in Fig. 1. [c] Corrected for thermal effects. Uncorrected value: 1.480(3) Å. [d] Corrected for thermal effects. Uncorrected value: 1.361(6) Å; gas-phase value 1.44 Å.[21] [e] Central atom.

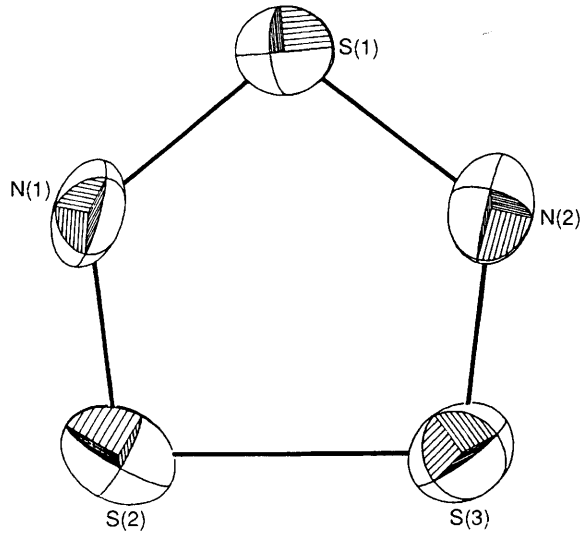

Fig. 1 The structure of the $S_3N_2^{2+}$ cation. Distances (Å): S(1)–N(1) 1.597(10), N(1)–S(2) 1.538(11), S(2)—S(3) 2.093(5), S(3)–N(2) 1.525(11), N(2)–S(1) 1.584(10). Ring angles (°) at: S(1) 101.1(5), N(1) 121.7(6), S(2) 97.3(4), S(3) 96.3(4), N(2) 123.5(6).

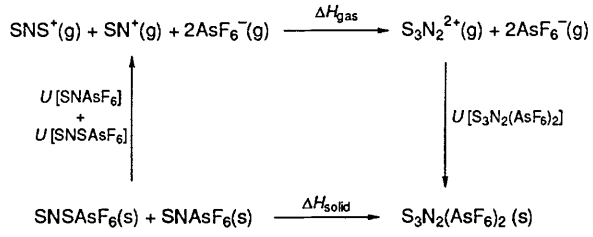

Fig. 2 Thermochemical cycle for the estimation of the stability of $\mathbf{1}(AsF_6)_2$ in the solid state. See text for definitions of symbols *etc.* The lattice energies U[SNSAsF$_6$] and U[$(S_3N_2(AsF_6)_2$] were calculated to be 509 and 1493 kJ mol^{-1} respectively, using the extended procedures described by Bartlett.[22] Since the crystal structure of $SNAsF_6$ is unknown its lattice energy was estimated at 556 kJ mol^{-1} using the linear correlation of lattice energy with molar volume, also due to Bartlett.[23] Use of 400 kJ mol^{-1} for the value of ΔH_{gas} gives ΔH_{solid} as −28 kJ mol^{-1}.

mmol) and $SNAsF_6$ (0.444 g, 1.89 mmol) in SO_2 (4.490 g) in a cold room at 0–5 °C. Several crystals suitable for X-ray crystallography were quickly picked under dry nitrogen at room temperature, and kept at −78 °C prior to data collection.‡

The unit cell of $\mathbf{1}(AsF_6)_2$ is isomorphous with those of $Se_xS_{3-x}N_2(AsF_6)_2$ (x = 1–3),[6] and consists of discrete, cyclic $SNSNS^{2+}$ cations and AsF_6^- anions. The structure of **1** is shown in Fig. 1, and like its selenium-containing analogues it is completely planar. S(2)–S(3) and N(1),(2)–S(2),(3) (see Fig. 1 for numbering) are both significantly (*i.e.* more than 3σ) longer§ in the 7π radical cation $S_3N_2^{+\cdot}$ owing to the antibonding interactions between these centres in its SOMO (**2**),[15] whereas N(1),(2)–S(1) are not significantly different.[2] The bond lengths in **1** are indicative of significant 2pπ(N)–3pπ(S) bonding in the SN portion of the ring, but very weak or no S–S 3pπ–3pπ bonding. Similar effects are present in the $Se_xS_{3-x}N_2^{n+}$ (x = 2, 3; n = 1, 2) ring systems.[6]

Banister's bond length–stretching frequency correlation[16] for NSN moieties predicts that IR and Raman bands will occur at 1015 [ν_{as}(NSN), *cf.* 1051] and 940 cm^{-1} [ν_s(NSN), *cf.* 968]. Normal coordinate analyses have been carried out on **1** and the related rings $Se_xS_{3-x}N_2^{2+}$ (x = 1–3), and a consistent set of force fields obtained for all four ring systems. These confirm the assignments implied by Banister's correlation, although all vibrations were found to be strongly coupled, as is normal in small rings. A detailed discussion of the vibrational spectra of **1** and the related selenium containing analogues will be given in a future publication.[17]

The instability of the **1** in solution [eqn (1)], while surprising in the context of its 6π electron count and the stabilities of $Se_xS_{3-x}N_2^{2+}$ (x = 0–2), is consistent with the results of geometry-optimized, *ab initio* 6-31G* calculations on $S_3N_2^{2+}$, SNS^+ and SN^+ (see Table 1). The optimized geometry of **1** is in excellent agreement with experiment, and the total energies imply that SNS^+(g) and SN^+(g) are together 400 kJ mol^{-1} more stable than $S_3N_2^{2+}$(g).

The stability of $\mathbf{1}(AsF_6)_2$ in the solid state can be understood in terms of the Born–Haber cycle shown in Fig. 2, by which

‡ *Crystal data*: M = 502.0174, monoclinic, space group $C2$, a = 12.558(2), b = 8.454(1), c = 10.583(3) Å, β = 92.51(2)°, U = 1122.5(2) Å^3, Z = 4, D_c = 2.9704 Mg m^{-3}, crystal size 0.15 × 0.22 × 0.28 mm, λ = 0.70926 Å. The data were reduced[10] to a standard scale; Lorentz-polarisation and absorption[11] corrections were applied. The positions of the As and S atoms were derived from an E map[12] and the positions of the remaining F and N atoms were determined from subsequent Fourier synthesis. The structure was refined, initially using large-block least-squares[13] and subsequently with full-matrix least-squares analyses.[14] R = 3.89%, R_w = 4.71% for 770 reflections [$I > 3\sigma(I)$, 897 total], and 163 parameters, with anisotropic thermal parameters for all atoms. Atomic coordinates, thermal parameters, and bond distances and angles have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

§ Corresponding average bond distances in $S_3N_2^{+\cdot}$ and $S_3N_2^{2+}$ (in square brackets): S(1)–N(1),(2) 1.560(7) [1.591(10)]; N(1),(2)–S(2),(3) 1.606(6) [1.532(11)]; S(2)–S(3) 2.147(3) [2.093(5)]. All distances in Å. Numbering is the same as in Fig. 1.

ΔH for eqn. (1) is estimated to be -28 kJ mol^{-1}. The exothermicity of this process is consistent with the observed stability of **1**$(AsF_6)_2$, and ascribable to the large lattice energy of the 1:2 salt (1493 kJ mol^{-1}) compared with the lattice energies of the two 1:1 salts ($SNAsF_6$: 556 kJ mol^{-1}, $SNSAsF_6$: 509 kJ mol^{-1}). The entropy change of the dissociation of **1**$(AsF_6)_2$(s) is estimated to be approximately zero by the method of Latimer,[18] and so the stability of **1** in the solid state is primarily an enthalpy effect.

We have previously shown that the SNS^+ cation undergoes quantitative, completely general, reverse-electron-demand cycloadditions with alkynes and nitriles.[9] Our calculations show that the frontier orbitals of SN^+ are isolobal with those of alkynes and nitriles, but much lower in energy, and the symmetry-allowed reaction of SNS^+ with SN^+ to give **1** is the first reported normal-electron-demand cycloaddition involving SNS^+. Consistent with our *ab initio* results, this cycloaddition does not occur in solution because **1** is *thermodynamically* unstable with respect to SN^+ and SNS^+. However, our calculations show that **1** represents a local potential energy minimum, with an activation barrier to dissociation of about 45 kJ mol^{-1} (3-21G*). In the solid state the high lattice energy of $S_3N_2(AsF_6)_2$ forces the reaction into the local $S_3N_2^{2+}$ minimum. To our knowledge this is the first example of a crystal-lattice-enforced cycloaddition reaction.

We thank Drs A. Kendrick and A. Apblett for their preliminary work on this system,[19] Mr E. G. Awere for valuable technical assistance, Professor N. Bartlett for a program to calculate the electrostatic terms of lattice energies, NATO for a collaborative grant with Dr A. J. Banister (University of Durham, UK), NSERC (Canada) for operating grants and the Canadian Commonwealth Scholarship and Fellowship Committee for a graduate fellowship (S. P.).

Received, 19th April 1991; Com. 1/01843D

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