5,5′-Bi(1,3,2,4-dithiadiazolylium)(2+) Bis[hexafluoroarsenate(V)]: a General Synthetic Strategy to Molecules and Radicals containing Thiazyl Rings†

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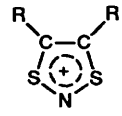
The salt [SNS][AsF_6] undergoes a quantitative multiple cycloaddition reaction with cyanogen to give the planar, centrosymmetric dication $(CNSNS)_2{}^{2+}$, which has been characterised by vibrational and ^{13}C NMR spectroscopy, chemical analysis and X-ray crystallography. While the reaction between cyanogen and SNS^+ must proceed *via* a 1:1 cycloadduct, $NCCNSNS^+$, this was not prepared or observed. The cycloaddition of SNS^+ to $NCCNSNS^+$ must therefore be kinetically preferred, contrary to arguments based on simple frontier molecular orbital (FMO) theory. By contrast, the reaction of [SNS][AsF_6] with [N≡CCNSNSCH][AsF_6] to give [HCSNSC–CNSNS][AsF_6]$_2$ was complete only after 10 weeks at 50 °C, in complete accord with FMO theory. These results are rationalised in terms of the influence of high-energy, in-plane molecular orbitals and the electrostatic interaction between SNS^+ and the slightly negatively charged nitrogen atom (*N*) in the C*N*SNS$^+$ ring, which facilitates the second cycloaddition. The salt [$(CNSNS)_2$][AsF_6]$_2$ potentially provides access to a new family of eight other bicyclic CNS dications, radical cations and diradicals, of which $^{\bullet}SNSNC–CNSNS^+$, $^+SNSNC–CNSSN^{\bullet}$ and $^+NSSNC–CNSNS^+$ are reported.

We have previously shown that SNS^+ undergoes completely general, quantitative, reverse-electron-demand cycloaddition reactions with monofunctional alkynes[1–4] and nitriles[1,4,5] to give 1,3,2-dithiazolylium **1** or 1,3,2,4-dithiadiazolylium **2** cations respectively. The neutral 7π radicals given on reduction of **1** and **2** possess surprising physical properties. For example, $CF_3CSNSCCF_3{}^{\bullet}$ is a blue gas over a green paramagnetic liquid at room temperature;[1,3] likewise $RCNSNS^{\bullet}$ (R = Bu^t) is also a paramagnetic liquid, although it undergoes an unprecedented rearrangement to a second paramagnetic liquid, the thermodynamically more stable $RCNSSN^{\bullet}$ isomer.[5]

In the course of an investigation into the kinetics of cycloaddition reactions of SNS^+ with alkynes and nitriles[4] we found that 2:1 cycloadditions occurred with cyanogen and cyanoacetylene to give $^+SNSNC–CNSNS^+$ $\mathbf{3}^{2+}$ and $HCSNSC–CNSNS^{2+}$. The capacity of SNS^+ to undergo multiple cycloadditions, simultaneously demonstrated by Banister[6a] in reactions with *o*-, *m*- and *p*-$(NC)_2C_6H_4$, and more recently with $KC(CN)_3$,[6b] greatly expands its already considerable potential in cycloaddition chemistry. Single and double reduction of $\mathbf{3}^{2+}$, followed by single and double isomerisation and subsequent reoxidation, leads to eight possible new products conceivably derivable from $\mathbf{3}^{2+}$ (Scheme 1). This provides rational access to a new class of $S_2N_2C–CN_2S_2$ bicyclics, as well as a large range of multicyclics, the systematic preparation and reduction of which potentially furnishes a powerful and general synthetic strategy in the production of novel materials (*e.g.*) synthetic metals or new magnetic materials).[6c] The results of this study demonstrate both the strengths and limitations of this synthetic strategy. We have successfully identified (Scheme 1) $\mathbf{3}^{\bullet+}$, $\mathbf{4}^{\bullet+}$ and $\mathbf{4}^{2+}$ in solution, but $\mathbf{3}^{\bullet+}$ rearranges rapidly to $\mathbf{4}^{\bullet+}$ and so is not isolable, while attempts to obtain $\mathbf{4}^{\bullet+}AsF_6{}^-$ and $\mathbf{4}^{2+}2AsF_6{}^-$ on a gram scale led to impure products or gave low yields. The double reduction of $\mathbf{3}^{2+}2AsF_6{}^-$ to the neutral diradical $\mathbf{3}^{2\bullet}$ will form the subject of a future publication. A preliminary communication of this work has been published.[7]



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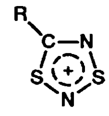

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Experimental

The apparatus, techniques and chemicals, unless specified, have been previously described.[9] The compounds $SbPh_3$ (Lancaster Synthesis), NBu_4Cl (Kodak) and AsF_5 (Ozark-Mahoning) were used as received. Cyanogen (Matheson) was degassed at −78 °C prior to use in order to remove CO_2 impurity. Bromine (Anachemia) was dried over P_4O_{10}, and SO_2 over CaH_2. The salts [SNS][AsF_6][10] and [NCCNSNS][AsF_6][4] were prepared according to literature procedures. All solids were manipulated under dry nitrogen in a Vacuum Atmospheres Dri-Lab. All apparatus was carefully dried prior to use.

Proton and ^{13}C NMR spectra were acquired on a Varian Associates XL-200 spectrometer, using previously described acquisition procedures[11] and externally referenced with $SiMe_4$ in SO_2 with the high-frequency direction positive. Samples were contained in thick-walled 10 mm precision NMR tubes (Wilmad) fitted with J. Young O-Ringette valves or sealed 5 mm NMR tubes (Wilmad). Infrared spectra were obtained as Nujol mulls between KBr (4000–350 cm^{-1}) or CsI (4000–200 cm^{-1}) plates on a Perkin Elmer 683 instrument. Raman spectra of samples contained in sealed melting-point tubes were obtained

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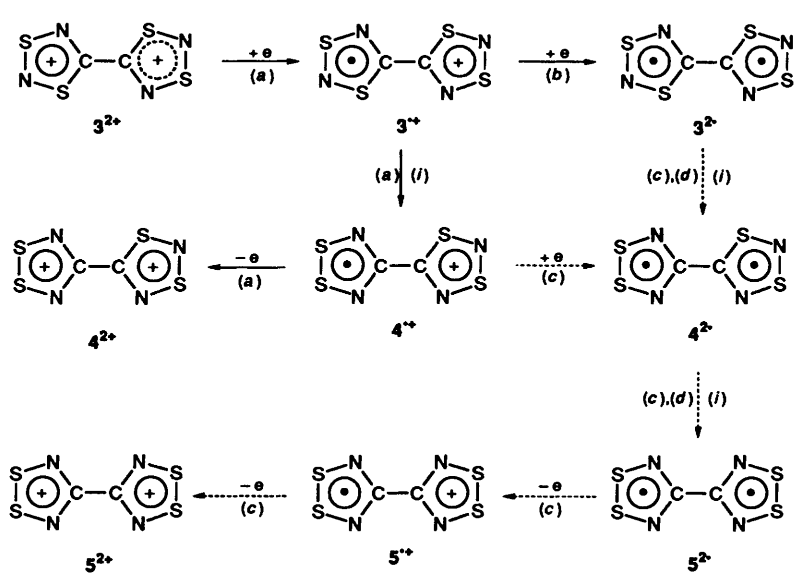
† *Supplementary data available* (No. SUP 56934, 13 pp.): vibrational, ESR and mass spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-S.I. units employed: eV ≈ 1.60×10^{-19} J, G = 10^{-4} T, au ≈ 4.36×10^{-18} J.



Scheme 1 (*a*) This work; (*b*) ref. 7 and future publication; (*c*) possible reaction, not yet attempted; (*d*) an analogous solid-state rearrangement has been described.[8] (*i*) Rearrangement

at room temperature on a Spex Ramalab instrument using a green-line laser (Ar^+, λ = 5145 Å) and a slit width of 4 cm^{-1}. Samples for mass spectrometry were contained in sealed glass capillaries under dry nitrogen, and introduced into the spectrometer by direct inlet. Spectra were obtained in electron-impact mode using 27 eV ionising voltage on a Kratos MS-50TC instrument. The ESR spectra were obtained on a locally modified Varian E-4 spectrometer. Owing to the absorption of microwave power by SO_2, samples dissolved in this solvent were contained in narrow-gauge (3 mm) sealed quartz tubes. Elemental analyses were carried out by Beller Mikroanalytisches Laboratorium, Göttingen.

Copies of the original IR, ESR and mass spectra have been deposited as SUP 56934, along with an extended listing of mass spectral peaks with assignments.

Preparation of $3^{2+}2AsF_6^-$ *and* $3^{2+}2Cl^-$.—In a preliminary experiment, SO_2 (3.01 g) and $(CN)_2$ (0.056 g, 1.08 mmol) were condensed onto $[SNS][AsF_6]$ (0.327 g, 1.23 mmol) in a 10 mm NMR tube. The ^{13}C NMR spectrum after 14 h at room temperature (r.t.) showed only one resonance at δ 96.7 [$(CN)_2$], but after heating to 50 °C for 10 d there was a single additional resonance at δ 187 (3^{2+}). Resonances assignable to any other species were never observed.

The salt $[SNS][AsF_6]$ (3.608 g, 13.5 mmol) was placed on a sintered glass frit incorporated into a condenser with a pressure-equalising side-arm joined to a Pyrex bulb (50 cm^3) and closed with a J. Young valve (see Fig. 1 in ref. 12). Sulfur dioxide (9.08 g) and cyanogen (0.53 g, 10.4 mmol) were successively condensed into the bulb, which was then heated to 50 °C in an oil-bath, causing the solution to reflux and wash the $[SNS][AsF_6]$ into the solution. The reaction mixture was initially yellow, but after 5 d the solution was colourless over a colourless, highly crystalline precipitate. The reaction volatiles [SO_2 and excess of $(CN)_2$, IR spectroscopy] were removed under dynamic vacuum, giving sparingly soluble, crystalline $3^{2+}2AsF_6^-$ (3.959 g) in 97% yield. The IR and Raman spectral data for 3^{2+}-$2AsF_6^-$ are included in Table 1, and original spectra have been deposited. NMR: δ_C 187 [Found (Calc.): C, 4.15 (4.10); As, 25.70 (25.55); F, 38.60 (38.90); N, 9.65 (9.55); S, 22.00 (21.90%)]. Crystals of $3^{2+}2AsF_6^-$ were loaded into rigorously dried glass capillaries and characterised by X-ray crystallography (see below). Mass spectrum of $3^{2+}2AsF_6^-$ ground with a little CsF as a fluoride-transfer agent to facilitate its volatilisation (m/z, I > 10%): 208 (27.8, $C_2S_4N_4^+$, M), 144 (19.3, $M - S_2$), 132 (11.2, AsF_3^+), 130 (37.7, $M - S_2N$), 113 (11.2, AsF_2^+), 78 (100, S_2N^+), 65 (10.3, NSF^+), 64 (28.8, S_2^+), 52 (11.5, $C_2N_2^+$), 48 (13.4, ?SO^+), 46 (72.2, SN^+), 44 (29.0, CS^+); a peak at 151 (2.5%) corresponding to AsF_4^+ was also observed.

Sulfur dioxide (4.668 g) was condensed onto a mixture of 3^{2+}-$2AsF_6^-$ (1.053 g, 1.80 mmol) and NBu_4Cl (1.099 g, 3.95 mmol) in a one-bulbed glass vessel fitted with a J. Young valve. The solution, which became dark orange over an orange solid within a few minutes of thawing, was stirred for 2 d at r.t. The volatiles were removed leaving a yellow solid (2.151 g), which was ground and extracted with SO_2 for 2.5 d to give an orange insoluble solid ($3^{2+}2Cl^-$, 0.370 g, 74% yield) and NBu_4AsF_6 (1.583 g) (IR spectroscopy). The salt $3^{2+}2Cl^-$ was characterised by its infrared (Table 1) and mass spectra (m/z, I > 10%): 208 (30.4, $C_2S_4N_4^+$, M), 130 (22.5, $M - S_2N$), 78 (100, S_2N^+) and 46 (32.6, SN^+) [Found (Calc.): C, 8.85 (8.60); Cl, 25.10 (25.40); N, 20.25 (20.05); S, 45.60 (45.95%)].

Reduction of $3^{2+}2AsF_6^-$ *followed* in situ *by ESR Spectroscopy*.—Sulfur dioxide (5.4 g) was condensed onto a mixture of $3^{2+}2AsF_6^-$ (10 mg, 0.17 mmol), $SbPh_3$ (2 mg, 0.006 mmol) and NMe_4Cl (excess), contained in a bulb connected *via* a sintered-glass frit and a J. Young valve to an ESR tube; the vessel was closed with a second valve. A light tan-coloured solution was given immediately on thawing, and a portion was poured into the ESR tube, frozen and sealed off. The ESR spectrum of this solution (radical concentration 10^{-3} mol dm^{-3}) at r.t. (taken after the sample had been thawed for a total of 10 min after the addition of SO_2) showed a 1:1:1 triplet [$3^{\cdot+}$, g = 2.0069, $a(^{14}N)$ = 11.0 G] superimposed on a weak pentet. The intensity of the triplet had decreased after 10 min, and after 12 h at r.t. the ESR spectrum consisted essentially entirely of the pentet [$4^{\cdot+}$, g = 2.0119, $a(^{14}N)$ = 4.9 G], with only a trace of $3^{\cdot+}$. In a second experiment a solution prepared from 3^{2+}-$2AsF_6^-$ (0.098 g, 0.17 mmol), NMe_4Cl (0.024 g, 0.22 mmol) and $SbPh_3$ (0.029 g, 0.08 mmol) in SO_2 (5.98 g) was poured into a ESR tube containing $SbPh_3$ (9 mg) and NMe_4Cl (10 mg). The ESR spectrum of the black solution showed $3^{\cdot+}$ and $4^{\cdot+}$ after 15 min at r.t. A black precipitate under a yellow solution formed during the following 4.5 h, and the ESR spectrum was considerably weaker, indicating only the presence of $4^{\cdot+}$. The ESR signal had essentially disappared after 50 h at r.t. The preparation and characterisation of 3 will form the subject of a forthcoming paper.

Attempted Preparation of $4^{\cdot+}AsF_6^-$ *and* $4^{2+}2AsF_6^-$ *on the Gram Scale*.—Sulfur dioxide (9.156 g) was condensed at

−196 °C onto a mixture of $\mathbf{3}^{2+}2\mathrm{AsF}_6^-$ (1.783 g, 3.04 mmol), SbPh_3 (0.527 g, 1.49 mmol) and $\mathrm{NBu}_4\mathrm{Cl}$ (0.828 g, 2.98 mmol) contained in one bulb of a two-bulb vessel incorporating a medium sintered-glass frit and closed with a J. Young valve. Some darkening of the reactants was observed even at −196 °C, and the reaction mixture became completely black with a fine precipitate during thawing and warming to room temperature. After stirring at r.t. for 4 d, with no change in appearance, a portion (1.725 g) of the SO_2 was removed and replaced by CFCl_3 (7.866 g), again giving a black solution over a black precipitate. The reaction mixture was filtered leaving a black insoluble residue, which was washed three times (using all the solvent). The solvent was removed overnight under dynamic vacuum, leaving a grey soluble solid (1.902 g, $\mathrm{SbPh}_3\mathrm{Cl}_2$ and $\mathrm{NBu}_4\mathrm{AsF}_6$, IR spectrum; calc. 1.879 g) and a black, sparingly soluble solid (0.936 g, calc. for pure $\mathbf{4}^{\bullet+}\mathrm{AsF}_6^-$ 1.207 g). The ESR spectrum of the black solid redissolved in SO_2 (5×10^{-4} mol dm^{-3}) was identical to the five-line pattern described above for $\mathbf{4}^{\bullet+}$, and at −60 °C showed a partially resolved pentet of triplets, $g = 2.0119$, $a(^{14}\mathrm{N}^{a}) = 4.578$, $a(^{14}\mathrm{N}^{b}) = 0.25$ G (see structure **III** in Discussion section) (simulated parameters, observed and simulated spectra have been deposited). However, elemental analyses (C, 8.70; As, 20.85; F, 25.8; N, 14.10; S, 30.60%) were consistent with a composition of approximately 85% $\mathbf{4}^{\bullet+}\mathrm{AsF}_6^-$, 10% $\mathbf{3}^{2\bullet}$ and 5% $\mathrm{NBu}_4\mathrm{AsF}_6$.

When SO_2 (3.458 g) and AsF_5 (0.490 g, 2.88 mmol) were condensed onto a sample of '$\mathbf{4}^{\bullet+}\mathrm{AsF}_6^-$' (0.356 g, 0.9 mmol) in a thick walled 10 mm NMR tube the ^{13}C NMR spectrum of the brown solution consisted of peaks at δ 190.0 and 169.8 ($\mathbf{4}^{2+}$), 187.2 ($\mathbf{3}^{2+}$), 58.8 (t, $\mathrm{CH}_2\mathrm{N}^+$, J = 140 Hz) and a complex group of resonances between δ 9 and 26 (NBu_4^+).[13] Details of the preparation and further characterisation of $\mathbf{4}^{2+}2\mathrm{AsF}_6^-$ have been deposited.

The IR spectral data for $\mathbf{4}^{\bullet+}\mathrm{AsF}_6^-$ and $\mathbf{4}^{2+}(2\mathrm{AsF}_6^-)_2$ are listed in Table 1.

Attempted Preparation of [NCCNSNS][AsF_6].—Sulfur dioxide (3.52 g) and $(\mathrm{CN})_2$ (1.30 g, 25 mmol) were condensed onto [SNS][AsF_6] (0.45 g, 1.7 mmol) in a Monel reaction vessel. The reaction mixture was heated to 80 °C for 1 week. The volatiles were removed leaving a dark solid (0.6 g). The IR spectrum mainly consisted of bands assignable to $\mathbf{3}^{2+}2\mathrm{AsF}_6^-$, although a weak band at 2271 cm^{-1} [ν(C≡N)[13]] suggested that $\mathrm{NCCNSNS}^+$ may have been present in trace quantities.

Reaction of [SNS][AsF_6] *with* [HCSNSCCN][AsF_6]: *Synthesis of* [HCSNSC–CNSNS][AsF_6]$_2$.—Sulfur dioxide (3.797 g) was condensed onto a mixture of [SNS][AsF_6] (0.427 g, 1.6 mmol) and [NCCSNSCH][AsF_6] (0.508 g, 1.6 mmol) in a 10 mm NMR tube (see above) giving an orange solution; the solution was heated to 45 °C, and the reaction monitored by ^{13}C NMR spectroscopy. After 10 weeks the ^{13}C NMR spectrum consisted of resonances at δ 187.7 (HCSNS*C*–CNSNS^{2+}), 172.8 (H*C*SNSC–CNSNS^{2+}), 168.5 (HCSNSC–*C*NSNS^{2+}), and the resonances due to [NCCSNSCH][AsF_6] (δ 175.1, 155.5 and 105.1)[4] had essentially disappeared. The solution was attached *via* a compression fitting to a one-bulb vessel; the solution was poured into the vessel and the volatiles removed to give an off-white solid [HCSNSC–CNSNS][AsF_6]$_2$ (0.725 g, 76% recovered yield). IR: 3080vs [ν(CH)], 1697m, 1328s, 1207s, 1165m (sh) [ν(CN)], 1143s, 986s, 968m [ν_{asym}(SN)], 894w (sh), 867ms [ν_{sym}(SN)], 846s, 824s, 789m (sh), 755 (sh), 700vs [$\nu_3(\mathrm{AsF}_6^-)$], 595w, 570s, 547m, 525m, 450s, 425m (sh), 390vs [$\nu_4(\mathrm{AsF}_6^-)$], 315vw, 295w and 263w cm^{-1} [Found (Calc.): C, 6.35 (6.15); H, 0.20 (0.15); As, 25.50 (25.60); F, 38.8 (38.95); N, 7.20 (7.20); S, 22.15 (21.90%)]; ^{1}H NMR: δ 11.6 (94%), together with a weak resonance at δ 11.1 ($\mathrm{NCCSNSCH}^+$, 6%).

The Crystal Structure of $\mathbf{3}^{2+}2\mathrm{AsF}_6^-$.—Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer, equipped with graphite-monochromated Mo-Kα radiation and controlled by the NRCCAD software package.[14] ω–2θ Scans were performed at 1.5° min^{-1}, and profile analysis was used to improve the background estimates. Three standard reflections, monitored every hour during data collection, showed no significant deviations from their mean intensities. The crystallographic data are summarised in Table 2.

The structure was solved by direct methods to determine the S and As positions. The C and N positions were obtained from a subsequent difference synthesis. The data were corrected for absorption using the routines of Walker and Stuart.[15] In the final cycles of least-squares refinement all the atoms were assigned anisotropic thermal parameters. The quantity minimised was $\Sigma w^{\frac{1}{2}}|\Delta F|$ where the statistical weights were obtained from counter statistics. Scattering factors were taken from ref. 16 and corrected for anomalous dispersion. All calculations were performed using the personal computer version of NRCVAX.[17] The final atomic coordinates are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Molecular-orbital Calculations.—Molecular-orbital calculations were performed on $\mathbf{3}^{2+}$, $(\mathrm{CN})_2$, HCCCN, $\mathrm{HCSNSCCN}^+$ and SNS^+ using the STO-3G basis set with experimental geometries.[7,18,19] Similar calculations were carried out for $^{+}$SNSNC–CSNSCH^{+}, in which the geometry of the CNSNS^+ ring was assumed to be the same as in $\mathbf{3}^{2+}$, and the C–C and C≡N bond lengths 1.47 and 1.20 Å respectively. Unrestricted Hartree–Fock/minimum neglect of differential overlap (UHF/MNDO) calculations were performed on $\mathbf{3}^{\bullet+}$ because *ab initio* methods failed to converge. The geometries of the CNSNS^+ and $\mathrm{CNSNS}^{\bullet}$ rings were assumed to be the same as in $\mathbf{3}^{2+}$ and $\mathrm{C}_6\mathrm{H}_4(\mathrm{CNSNS}^{\bullet})_2$-*p*[6a] respectively, and the planes of the two rings perpendicular to one another. An STO-3G calculation was also performed on $\mathbf{3}^{2+}$ in which the two CNSNS^+ rings were placed orthogonal to one another, but the ring geometries were assumed to be the same as in the crystal structure of $\mathbf{3}^{2+}$-$2\mathrm{AsF}_6^-$. All calculations were carried out using the GAUSSIAN 86 suite of programs.[20]

Discussion

Preparation and Characterisation of $\mathbf{3}^{2+}2\mathrm{AsF}_6^-$, $\mathbf{3}^{2+}2\mathrm{Cl}^-$ *and* [HCSNSC–CNSNS][AsF_6]$_2$.—The salt [SNS][AsF_6] is the most general reagent for the syntheses of 1,3,2-dithiazolylium and 1,3,2,4-dithiadiazolylium salts, but until recently only reactions with alkynes and nitriles containing one triply bonded site had been reported.[4] Cyanogen (N≡C–C≡N) reacts quantitatively [equation (1)] with [SNS][AsF_6] to give

$$2[\mathrm{SNS}][\mathrm{AsF}_6] + \mathrm{NC{-}CN} \longrightarrow [\mathrm{SNSNC{-}CNSNS}][\mathrm{AsF}_6]_2 \quad (1)$$

[SNSNC–CNSNS][AsF_6]$_2$ $\mathbf{3}^{2+}2\mathrm{AsF}_6^-$ as colourless crystals which were characterised by their satisfactory elemental analyses, vibrational, mass and ^{13}C NMR spectroscopy and X-ray crystallography. The salt $\mathbf{3}^{2+}2\mathrm{Cl}^-$ was prepared in 74% yield by the double displacement of $\mathbf{3}^{2+}2\mathrm{AsF}_6^-$ with $\mathrm{NBu}_4\mathrm{Cl}$, as an orange, insoluble, amorphous solid [equation (2)]. The

$$[\mathrm{SNSNC{-}CNSNS}][\mathrm{AsF}_6]_2 + 2\mathrm{NBu}_4\mathrm{Cl} \longrightarrow [\mathrm{SNSNC{-}CNSNS}]\mathrm{Cl}_2 + 2\mathrm{NBu}_4\mathrm{AsF}_6 \quad (2)$$

very soluble $\mathrm{NBu}_4\mathrm{AsF}_6$ was completely removed from the

Table 1 Vibrational spectral data for $3^{2+}2Cl^-$, $3^{2+}2AsF_6^-$, $4^+AsF_6^-$ and $4^{2+}2AsF_6^-$

$3^{2+}2Cl^-$		$3^{2+}2AsF_6^-$	$4^{2+}AsF_6^-$	$4^+AsF_6^-$	Assignment
IR	Raman	IR			ν(CN)
	1489vs		1490 (sh)		
	1466s (sh)				
	1425w				
1401m		1393m			
1360 (sh)			1360s	1336vw	
			1276m	1300m	
	1215m				
			1150w	1110m	
			1122ms	1094ms	
944s		979s	975m	950mw	ν_{asym}(SN)
	947m		934ms	904m	
	896m		881ms	821s	
874s		861s	863ms	790ms	ν_{sym}(SN)
781m		829m	828ms	770ms	
	790vs		777ms (sh)		
	768vw				
727s		751s			Ring vibrations
	737w				
	700mw	698vs	696vs	698vs	$\nu_3(AsF_6^-)$
	674 (sh)			681(sh)	
662ms	662vs	662mw	665 (sh)	667ms	$\nu_1(AsF_6^-)$
	588s	590m	594m	583mw	ν(CS)
576ms		578ms	577m	553m	
	563mw		564m		$\nu_2(AsF_6^-)$
530s		553ms	553m	509m	
402 (sh)		437s	445m	444m	
394s		406 (sh)	400 (sh)		
		391 (sh)	390 (sh)	395vs	$\nu_4(AsF_6^-)$
	365ms		371 (sh)	371 (sh)	$\nu_5(AsF_6^-)$
	346ms				
	289mw			287mw	
	260mw			268w	

product by extraction with SO_2 for 2 d, and $3^{2+}2Cl^-$ was characterised by its satisfactory elemental analyses and IR and mass spectra. The mass spectra of $3^{2+}2AsF_6^-$ and $3^{2+}2Cl^-$ both exhibited intense molecular ion peaks at *m*/*z* 208 ($C_2S_4N_4^+$).

The X-ray crystal structure of $3^{2+}2AsF_6^-$ shows that the midpoint of the C–C bond lies on an inversion centre. This is consistent with IR and Raman spectra (Table 1), which show few coincidences.* The ν(CN) band (1489–1425, IR; 1393 cm^{-1}, Raman) occurs between the commonly accepted single- and double-bond stretching regions (C–N 1020–1250, C=N 1470–1690 cm^{-1}), consistent with the CN bond order (1.7). The bands between 979 and 861 cm^{-1} were identified as the asymmetric and symmetric S–N stretches using Banister's S–N bond length–stretching frequency correlation.[21,†]

With the exception of the band at 590 cm^{-1}, bands present in the IR spectrum of $3^{2+}2AsF_6^-$ are also present in that of 3^{2+}-$2Cl^-$, with a similar intensity but lower frequency. This may reflect stronger contacts from the more basic Cl^- anion involving donation into unoccupied, largely antibonding, molecular orbitals of the cation. The similarity of these spectra implies that $3^{2+}2Cl^-$ is ionic, and its low solubility in SO_2 is consistent with this. While 1,3,2,4-dithiazolylium chlorides RCNSNSCl (R = Me or Ph) have covalent structures RCNS(Cl)NS,[22] the much higher lattice energy of a 1 : 2 ionic salt leads to the ionic form for $3^{2+}2Cl^-$.

The ^{13}C NMR spectrum of 3^{2+} shows one resonance at δ 187, which is typical for RCNSNS$^+$ derivatives (δ 144–223).[4] When the reaction of SNS^+ with $(CN)_2$ was followed by ^{13}C NMR spectroscopy over time no resonances other than those due to 3^{2+} or $(CN)_2$ were ever observed, and although our previously described[4] reactions of SNS^+ with cyanoacetylene and a wide variety of monofunctional alkynes and nitriles suggest that this reaction likely proceeds *via* a 1 : 1 cycloadduct NCCNSNS$^+$, this intermediate must be very short lived. Consistently, our attempt to prepare it by heating $[SNS][AsF_6]$ with a large excess of $(CN)_2$ in SO_2 for 1 week at 80 °C was unsuccessful, and produced mainly $3^{2+}2AsF_6^-$, with only minor amounts of the 1 : 1 cycloadduct. The ion NCCNSNS$^+$ should under these conditions have been favoured by both entropy and stoichiometry, but these results imply that 3^{2+} is the thermodynamically and kinetically favoured product in this system.

By contrast, HC≡C–C≡N reacts quantitatively with $[SNS]$-$[AsF_6]$ according to equation (3), and it was necessary to heat

$$[SNS][AsF_6] + HCCCN \longrightarrow [HCSNSCCN][AsF_6] \quad (3)$$

$[NCCSNSCH][AsF_6]$ with $[SNS][AsF_6]$ in SO_2 to 50 °C for 10 weeks in order to drive the second cycloaddition [equation (4)] to 94% completion. The salt $[HCSNSC–CNSNS][AsF_6]_2$

$$[HCSNSCCN][AsF_6] + [SNS][AsF_6] \longrightarrow [HCSNSC–CNSNS][AsF_6]_2 \quad (4)$$

has been characterised by ^{13}C NMR and IR spectroscopy and its satisfactory elemental analyses. The ^{13}C NMR spectrum exhibits three characteristic resonances at δ 187.7 (HCSNSC–

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* According to the mutual exclusion principle there should be no coincidences at all; those that are observed (at 700, 662 and 588 cm^{-1}) can be associated with the AsF_6^- anions, which do not lie on inversion centres.

† λ(S–N) = 0.1941*d*(S–N) − 20.66, where λ(S–N) is the S–N stretching wavelength in cm × 10^{-4} and *d*(S–N) is the S–N distance in pm.

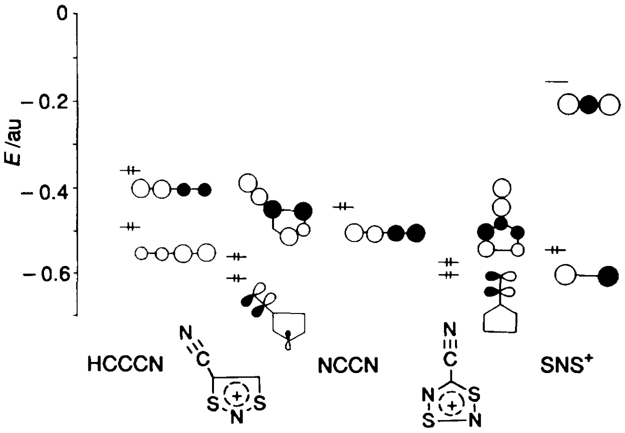

Fig. 1 Relative frontier molecular orbital energies for HCCCN, NCCSNSCH$^+$, NCCN, NCCNSNS$^+$ and SNS$^+$. All calculations were performed using experimental geometries (where available) at the restricted Hartree–Fock/STO-3G level

CNSNS), 172.8 (HCSNSC–CNSNS, relatively intense due to the nuclear Overhauser effect) and 168.5 (HCSNSC–CNSNS), while the ^{1}H NMR spectrum shows a typically deshielded resonance[4] at δ 11.6.

Kinetics of Cycloadditions of NCCN *and* HCCCN *with* SNS$^+$.—Cycloaddition reactions of SNS$^+$ with nitriles and alkynes follow the reverse-electron-demand regime in which the principal orbital interaction is between the lowest unoccupied (LUMO, SNS$^+$) and highest occupied molecular orbital (HOMO, C≡N or C≡C).[4,7] Consistently, there is a roughly linear correlation between the ionisation potential (i.p.) (CN or CC) and −log(cycloaddition rate constant). The chemistry of the HCCCN/SNS$^+$ system is typical: the i.p.s of the C≡C and C≡N bonds are 11.06 and 14.03 eV[23] respectively, and SNS$^+$ therefore undergoes a facile cycloaddition at the C≡C bond to give **1** (R = CN or H). The HOMOs of the 1 : 1 cycloadduct lie at much lower energy than those of HCCCN (see Fig. 1), and accordingly the cycloaddition of SNS$^+$ to the cyano group was only 94% complete after the reaction mixture was heated to 50 °C for 10 weeks.

Predictably, these effects are less acute in the reactions of [SNS][AsF$_6$] with dicyanobenzenes, in which the nitrile moieties are spatially well separated, leaving the energies of the orbitals located on the remote CN group of the analogous 1 : 1 cycloadduct essentially unaffected by the reaction with SNS$^+$. These reactions proceed to give the corresponding 5,5′-phenylenebis(1,3,2,4-dithiazolylium) dications over 18 h at room temperature.[6a]

The i.p. of (CN)$_2$ is 13.36 eV,[23] and a very slow reaction with SNS$^+$ was anticipated. In fact the cycloaddition does not proceed at room temperature, and it was necessary to heat the reaction mixture to 50 °C for 5 d to complete it. There is a strong kinetic preference in this system for 2 : 1 cycloadduct (**3**$^{2+}$), and we were unable to obtain the intermediate 1 : 1 cycloadduct, **2** (R = CN). This result is surprising in the context of the HCCCN/SNS$^+$ system, and the results of MO calculations (Fig. 1). Paradoxically, Banister *et al.*[6b] have recently shown that the reaction of K[C(CN)$_3$] with [SNS][AsF$_6$] proceeds in three distinct stages, according to equations (5)–(7). All three cycloadducts were isolated in yields ranging from 60 to 80%. The initial reaction between SNS$^+$ and C(CN)$_3^-$ proceeds rapidly (even at liquid-nitrogen temperatures), whereas the subsequent cycloadditions occur more slowly (reaction time 16 h at r.t.). Although this pattern of reactivity appears to be consistent with the simple frontier molecular orbital (FMO) model, detailed examination of orbital interactions indicated a substantially more complex mechanism (see below).

$$[\mathrm{SNS}][\mathrm{AsF_6}] + \mathrm{K[C(CN)_3]} \longrightarrow \mathrm{(NC)_2C{=}CNSNS} + \mathrm{KAsF_6} \tag{5}$$

$$[\mathrm{SNS}][\mathrm{AsF_6}] + \mathrm{(NC)_2CCNSNS} \longrightarrow \mathrm{(NC)C(CNSNS)_2} \tag{6}$$

$$[\mathrm{SNS}][\mathrm{AsF_6}] + \mathrm{(NC)C(CNSNS)_2} \longrightarrow \mathrm{C(CNSNS)_3} \tag{7}$$

Deviations from behaviour predicted by simple FMO theory may be ascribed to a variety of factors which it does not consider, *e.g.* in-plane orbital interactions, differences in atomic orbital coefficients and/or electrostatic or solvation effects.[24] As shown in Fig. 1, although the HOMO of NCCNSNS$^+$ is an a″ out-of-plane π MO, the closely proximal HOMO − 1 is an a′ in-plane π MO almost entirely located on the cyano group. The atomic orbital coefficients in this MO (C 0.59, N 0.61) are greater than those in the cyanogen HOMO (C 0.50, N 0.41), which would facilitate the second cycloaddition occurring *via* the in plane HOMO − 1. Molecular-orbital calculations (STO-3G) on 1,3,2,4-dithiadiazolylium rings indicate that the ring nitrogen atoms carry a small negative charge (of *ca.* 0.2–0.3, as calculated by Mulliken population analysis).[25] This is supported by the crystal structures of [MeCNSNS][AsF$_6$], **3**$^{2+}$-2AsF$_6^-$, and the related salts [MeCSNSCH][AsF$_6$], ^{2}C$_6$H$_4$-S$_2$NCl,[26] [NCCSNSCH][AsF$_6$][7] and CH$_2$(SCl)N(SCl)CH$_2$-AsF$_6$,[11] which never show anionic contacts to the ring nitrogen atoms, even though the rest of the heterocycle is extensively contacted. The in-plane approach of an SNS$^+$ ion would therefore be facilitated by a ring nitrogen atom to produce the observed planar, centrosymmetric dication.

By contrast, the cycloaddition of SNS$^+$ with (NC)$_2$C-(CNSNS) [equation (6)] is slow, and the 1 : 1 cycloadduct can be isolated. Once again it appears that an electrostatic interaction between SNS$^+$ and the CNSNS ring is important,* although in this case the MO involved in the cycloaddition with SNS$^+$ is the more remote HOMO − 5[6b] (*cf.* HOMO − 1 in NCCNSNS$^+$), consistent with the much reduced cycloaddition rate.

The related 2 : 1 cycloaddition of SNS$^+$ to NCCSNSCH$^+$ may be inhibited by the lack of the facilitating influence of a suitable ring nitrogen atom. The crystal structure of [NCCSNSCH][AsF$_6$] shows fluorine contacts to the ring carbon atom (NCCSNSCH), indicating that it carries a δ+ charge. Multiple cycloaddition reactions involving [SNS]-[AsF$_6$] therefore occur either spontaneously or under forcing conditions depending upon the nature of the system.

Crystal Structure of **3**$^{2+}$2AsF$_6^-$.—The unit cell of **3**$^{2+}$-2AsF$_6^-$ contains two independent, centrosymmetric **3**$^{2+}$ cations (Fig. 2) and two independent AsF$_6^-$ anions. Both cations are completely planar to within experimental error, and chemically equivalent bond distances and angles in the two cations (Table 4) do not differ significantly (*i.e.* by more than 3σ). Average cationic bond distances and angles are shown in Table 5, together with the corresponding parameters in [MeCNSNS]-[AsF$_6$],[2] which, with the exception of the S–C–N angle, are not

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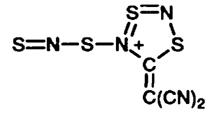
* Banister *et al.*[6b] has suggested that this interaction takes the form of a discrete, covalently bonded intermediate:



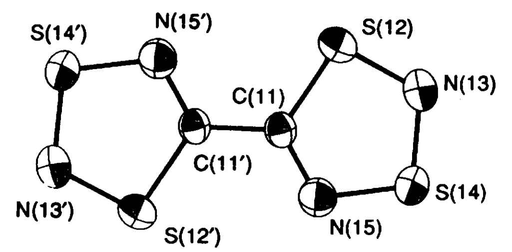


Fig. 2 The structure of 3^{2+}. The primed and unprimed atoms refer to symmetry-equivalent atoms related by a crystallographic inversion centre

Table 2 Crystallographic data for $3^{2+}2AsF_6^-$

Formula	$C_2As_2F_{12}N_4S_4$
M	586.11
System	Triclinic
Space group	$P\bar{1}$
Crystal dimensions/mm	0.56 × 0.40 × 0.33
a/Å	8.3729(11)
b/Å	9.4306(7)
c/Å	10.0240(11)
α/°	82.875(7)
β/°	67.743(10)
γ/°	89.425(9)
U/Å^3	726.29(14)
Z	2
D_c/g cm^{-3}	2.680
μ/mm^{-1}	5.28
F(000)	556
λ(Mo-Kα)/Å	0.710 73
No. of reflections	5071
Independent reflections	2538
Observed [$I > 2.5\sigma(I)$]	2057
R	0.048
R'	0.068
No. of parameters	218
Difference synthesis:	
highest peak/e Å^{-3}	0.800
deepest hole/e Å^{-3}	−0.630

Table 3 Atomic coordinates with estimated standard deviations (e.s.d.s) in the last digit

Atom	x	y	z
C(11)	0.424 6(9)	0.044 9(8)	0.520 7(8)
S(12)	0.300 2(3)	0.058 60(24)	0.69 901(22)
N(13)	0.166 9(9)	0.166 2(8)	0.666 7(8)
S(14)	0.210 3(3)	0.208 3(3)	0.496 30(24)
N(15)	0.379 1(9)	0.116 4(7)	0.424 0(7)
C(21)	0.922 4(10)	0.459 9(8)	0.010 5(8)
S(22)	0.741 0(3)	0.449 83(24)	0.168 18(23)
N(23)	0.630 5(10)	0.346 2(8)	0.119 7(8)
S(24)	0.728 8(3)	0.304 63(25)	−0.040 0(3)
N(25)	0.912 7(9)	0.388 3(7)	−0.090 4(7)
As(1)	0.291 45(11)	0.661 71(8)	0.424 12(9)
F(11)	0.218 9(10)	0.787 6(7)	0.536 5(7)
F(12)	0.468 2(9)	0.653 2(6)	0.471 2(9)
F(13)	0.118 9(7)	0.670 7(6)	0.375 1(7)
F(14)	0.191 5(10)	0.529 1(7)	0.559 8(7)
F(15)	0.373 4(8)	0.539 1(8)	0.308 4(8)
F(16)	0.391 9(7)	0.795 3(6)	0.287 6(6)
As(2)	0.185 17(11)	0.148 85(8)	0.112 94(9)
F(21)	0.172 1(8)	−0.006 9(5)	0.048 3(6)
F(22)	0.396 0(7)	0.126 7(7)	0.082 2(7)
F(23)	0.122 0(8)	0.059 5(6)	0.285 8(6)
F(24)	0.237 1(8)	0.239 5(6)	−0.059 5(5)
F(25)	0.194 1(9)	0.306 6(6)	0.175 2(7)
F(26)	−0.027 6(7)	0.173 7(5)	0.142 5(5)

Table 4 Bond distances (Å) and angles (°) in 3^{2+}

C(11)–C(11a')	1.467(14)	C(21)–C(21')	1.441(15)
C(11)–S(12)	1.715(7)	C(21)–S(22)	1.721(8)
C(11)–N(15)	1.285(10)	C(21)–N(25)	1.311(10)
S(12)–N(13)	1.597(8)	S(22)–N(23)	1.589(8)
N(13)–S(14)	1.604(7)	N(23)–S(24)	1.595(8)
S(14)–N(15)	1.622(7)	S(24)–N(25)	1.608(7)
S(12) ··· F(12)	3.242(6)	S(22) ··· F(14)	3.016(7)
S(12) ··· F(16)	2.990(6)	S(22) ··· F(15)	3.021(7)
S(12) ··· F(21)	3.228(6)	S(22) ··· F(24)	2.978(6)
S(12) ··· F(24)	3.014(6)	S(22) ··· F(26)	3.208(6)
S(12) ··· F(26)	3.004(6)	S(24) ··· F(13)	3.088(7)
S(14) ··· F(12)	3.146(6)	S(24) ··· F(15)	3.298(9)
S(14) ··· F(13)	2.858(6)	S(24) ··· F(16)	3.251(6)
S(14) ··· F(14)	3.158(7)	S(24) ··· F(21)	2.922(6)
S(14) ··· F(23)	2.984(6)	S(24) ··· F(22)	3.013(6)
S(14) ··· F(25)	3.290(7)		
C(11')–C(11)–S(12)	122.0(6)	C(21b)–C(21)–S(22)	122.7(6)
C(11')–C(11)–N(15)	121.1(7)	C(21b)–C(21)–N(25)	121.3(6)
S(12)–C(11)–N(15)	116.9(6)	S(22)–C(21)–N(25)	116.0(6)
C(21)–S(22)–N(23)	96.0(4)	C(11)–S(12)–N(13)	96.2(4)
S(22)–N(23)–S(24)	113.8(4)	S(12)–N(13)–S(14)	112.9(4)
N(23)–S(24)–N(25)	102.3(4)	N(13)–S(14)–N(15)	102.1(4)
C(21)–N(25)–S(24)	112.0(5)	C(11)–N(15)–S(14)	111.9(5)

Table 5 Average bond distances (Å), angles (°) and bond orders in 3^{2+}, and comparison with equivalent parameters in [MeCNSNS][AsF$_6$]

	3^{2+}		MeCNSNS$^+$
Equivalent bonds[a]	Bond lengths or angle[b]	Bond order[b]	Bond length or angle
C(1)–C(1')	1.454(15)	1.0	
C(1)–S(1)	1.718(8)	1.1	1.77(2)
S(2)–N(3)	1.593(8)	1.6	1.63(2)
N(3)–S(4)	1.600(8)	1.6	1.59(2)
S(4)–N(5)	1.615(7)	1.5	1.57(2)
N(5)–C(1)	1.298(10)	1.8	1.32(3)
Angle at:			
C(1)	116.5(6)		110.6(11)
S(2)	96.1(4)		98.4(9)
N(3)	113.4(4)		110.4(10)
S(4)	102.2(4)		104.6(9)
N(5)	112.0(6)		115.7(16)

[a] Atom numbering C(1)N(5)S(4)N(3)S(2). [b] See text and ref. 27.

significantly different. π Bonding*,[28] is delocalised over the CNSNS rings with π bond strengths in the order CN > SN > CS (Table 5), while the average C–C bond length in 3^{2+} [1.454(15) Å] when compared to the H_5C_6–C_6H_5 bond in biphenyl [1.493(3) Å],[29] and the 'standard' sp^2–sp^2 C–C bond length (1.46 Å),[27] implies no significant C–C π-bond character. These features are all reflected to a first order of approximation in the π-electronic structure of 3^{2+} shown in Fig. 3, obtained from STO-3G calculations, which also imply that the observed planar geometry of 3^{2+} is *ca.* 36 kJ mol^{-1} more stable than the alternative conformation with the CNSNS$^+$ rings orthogonal to one another. The electronic structure of 3^{2+} may be reasonably represented by resonance structures **I** and **II**. In this view each ring contains six π electrons (sulfur, carbon and nitrogen each contribute two, one and one electron to the π net), consistent with the molecular-orbital calculations (see Fig. 3).

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* For S–N bonds in which the nitrogen possesses a non-interacting lone pair the bond order (b) is related to S–N bond length [d(S–N) in Å] by $b = 0.429 + 6.850d(\text{S–N}) - 3.825d(\text{S–N})^2$ (ref. 2). For other bonds $D_b = D_1 - 0.71 (\log b)$ where D_1 is the sum of the covalent radii of the atoms making the bond {C, 0.73 [half the usual C(sp^2)–C(sp^2) bond length, see ref. 27); N, 0.75; S, 1.02 Å} and D_b is the length of a bond of order b.

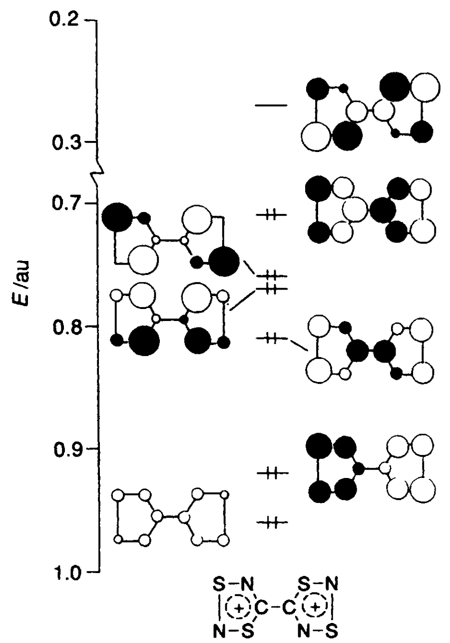
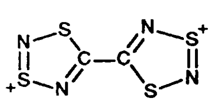
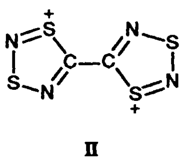


Fig. 3 The π-electronic structure of 3^{2+} calculated at the STO-3G level using the average experimental parameters from the crystal structure of $3^{2+}2AsF_6^-$ (see Table 5)



I



II

However, 3^{2+} and related ring systems are planar,[6] presumably at least in part because of electronic delocalisation over both rings (see Fig. 3). The average N–S–N and S–N–S bond angles [102.2(4) and 113.4(4)°] are in reasonable agreement with those predicted on the basis of the S–N bond lengths* (106 and 121°), showing that ring strain is not significant in this structure.[30]

Anionic contacts to the cations are shown in Fig. 4, with distances listed in Table 4. The contacts to the sulfur atoms are distributed around a 'hole' lying in the plane of the ring, corresponding to the location of the lone pair, and defining the primary co-ordination to be of planar, AEX_2 type where A is the central atom, E the lone pair, X the ligands in the primary co-ordination sphere, and Y the contacts in the second co-ordination sphere. Consistent with valence shell electron pair repulsion (VSEPR) theory,[31] secondary bonds either cap the faces (Y) or bridge the edges (Y′) of this triangle, giving overall geometries AEX_2Y_3 [S(12) and S(22)], AEX_2Y_3Y' [S(14)] and $AEX_2YY'_2$ [S(24)]. The carbon atoms may similarly be shown to have AX_3Y_2 [C(11)] and AX_3Y_3 [C(21)] co-ordination.

The contacts to S(12), S(14), S(22) and S(24) comprise 0.36, 0.32, 0.30 and 0.24 bond valence units (b.v.u.s) respectively,[32] while those to the carbon atoms are much weaker [totalling 0.05 and 0.07 b.v.u. to C(11) and C(21) respectively]. The data are consistent with the total charges calculated at the STO-3G level from Mulliken population analysis, which predicts substantial positive charges on the sulfur atoms (0.85), zero charge on the carbon atoms and small negative charges on the nitrogen atoms (−0.30).

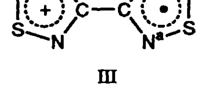
The As–F bond lengths in the anions vary from 1.687 to 1.727 Å, but their average is 1.700(5) Å, which is not significantly different from the 1.69 Å observed in $KAsF_6$.[33] There appears to be no correlation between the strengths of the contacts made to the cations and the As–F bond length.

Identification of $3^{\cdot+}AsF_6^-$, $4^{\cdot+}AsF_6^-$ *and* $4^{2+}AsF_6^-$.—The recently reported $C_6H_4(CNSNS)_2$-p^{2+} cation possesses two barely resolvable one- and two-electron reduction potentials, and only $C_6H_4(CNSNS^{\cdot})_2$-p could be obtained on reduction.[6] In contrast, the intermediate radical cation $3^{\cdot+}$ was obtained in dilute (10^{-3} mol dm^{-3}) solution from the reduction of 3^{2+}-$2AsF_6^-$ with NMe_4Cl and $SbPh_3$ [equation (8)] and identified

$$2\ 3^{2+}2AsF_6^- + 2\ NMe_4Cl + SbPh_3 \longrightarrow 2\ 3^{\cdot+}AsF_6^- + 2\ NMe_4AsF_6 + SbPh_3Cl_2 \quad (8)$$

by its ESR spectrum, which consists of a 1 : 1 : 1 triplet with $a(^{14}N) = 11.0$ G and $g = 2.0069$, typical for $RCNSNS^{\cdot}$ derivatives [ranges: $a(^{14}N) = 10.8$–11.2 G, $g = 2.0048$–2.0068].[34] Other hyperfine coupling in this spectrum may have been obscured by the rather broad linewidths and interference by a weak pentet due to $4^{\cdot+}$ (see below), and so a detailed description of the distribution of the unpaired spin is not possible from our data. However, coupling to N′ in $RCN'SN''S^{\cdot}$ radicals is always weak because the singly occupied molecular orbital (SOMO) resides principally on the SN″ portion of the ring (*e.g.* no hyperfine coupling is observed to N′ in CF_3-$CN'SN''S^{\cdot}$ at all[1]). The absence of significant coupling to the nitrogen atoms in the second CNSNS ring in $3^{\cdot+}$ implies that the positive charge and unpaired spin are localised on different rings. This arrangement is inconsistent with the planar C_{2h} framework of 3^{2+}, which demands that the charge distribution be symmetrical about the C_2 axis, and so the rings in $3^{\cdot+}$ must be staggered or freely rotating. Complete delocalisation over both rings can be ruled out as a pentet would be observed in the ESR spectrum. A UHF/MNDO calculation in which the planes of the rings were placed at 90° to one another reflected this result: the charges on the rings were 0.87 and 0.12, while the only coefficients in the SOMO > 0.1 were located on the second ring.

In common with other $RCNSNS^{\cdot}$ radicals in which R is electron withdrawing, $3^{\cdot+}$ rearranges rapidly at r.t. to $4^{\cdot+}$, also identified in dilute solution by its ESR spectrum, which consists of a partially resolved 1 : 2 : 3 : 2 : 1 pentet [$a(^{14}N^a) = 4.578$ G] of 1 : 1 : 1 triplets [$a(^{14}N^b) = 0.25$ G] with a $g = 2.0119$ (*cf.* $g = 2.0106$–2.0128 for similar derivatives,[34] see III). The pentet



III

splitting, due to coupling to the two equivalent nitrogen centres in the CNSSN ring, is slightly smaller than in other CNSSN derivatives (5.0–5.3 G[34]), presumably because of some limited delocalisation of the unpaired spin into the $CNSNS^+$ ring, as evidenced by the small triplet splitting. This implies that the ionisation potential of the $CNSNS^{\cdot}$ fragment is smaller than that of the $CNSSN^{\cdot}$ fragment, consistent with the half-wave reduction potentials of $RCNSNS^+$ and $RCNSSN^+$ derivatives, *e.g.* $MeCNSNS^+$ 0.16 V, $MeCNSSN^+$ 0.47 V.[35] Observation of coupling to the $CNSNS^+$ ring and the 1 : 2 : 3 : 2 : 1 pentet (from two *equivalent* nitrogen atoms in the CNSSN ring) may imply that free rotation occurs about the C–C bond.

An attempt was made to obtain $4^{\cdot+}AsF_6^-$ on a preparative scale by the reduction of $3^{2+}2AsF_6^-$ with $SbPh_3$ and NBu_4Cl;

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* In $-S^{II}-$ and $=S^{IV}=$ compounds the S–N bond length [d(S–N) in pm] is related to the N–S–N angle (in °) by $d(SN) = 213.00 - 0.4861$ (N–S–N). For cationic SNS moieties the angle at N is given by $d(S–N) = 187.03 - 0.2263$ (S–N–S).

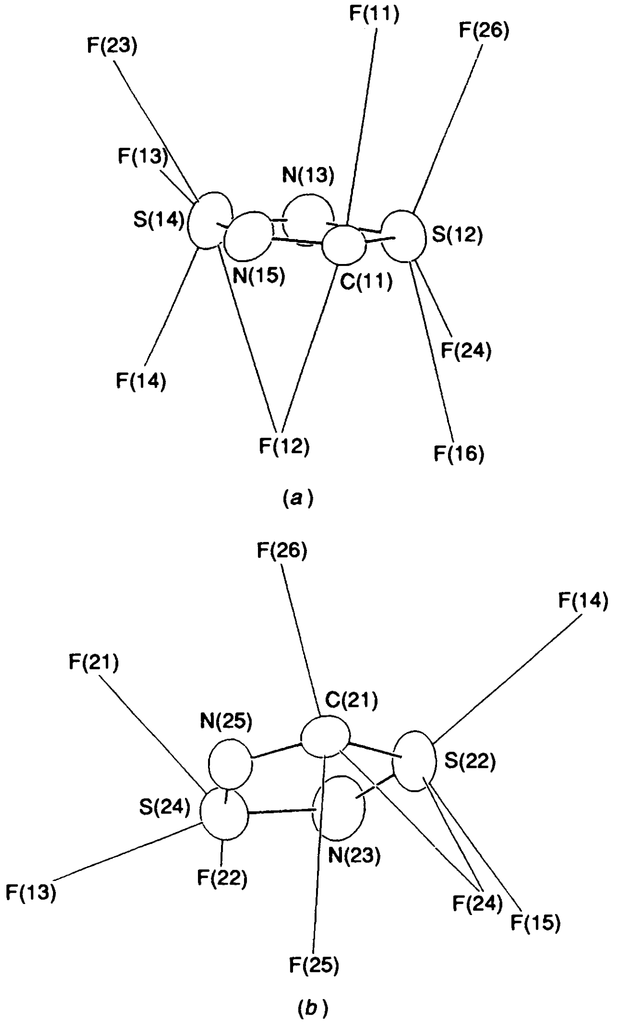

Fig. 4 Anionic contacts to the two crystallographically unique $\overline{\mathrm{CNSNS}}^+$ rings in $3^{2+}2\mathrm{AsF_6}^-$. Van der Waals radii: S 1.85, N 1.50, C 1.85, F 1.35 Å). Several other weak contacts also occur between 3.20 and 3.27 Å (see Table 4)

$\mathrm{NBu_4Cl}$ was used in preference to $\mathrm{NMe_4Cl}$ because the by-product, $\mathrm{NBu_4AsF_6}$ [see equation (8)], is much more soluble than $\mathrm{NMe_4AsF_6}$, and so more easily washed from the sparingly soluble $4^{\bullet+}\mathrm{AsF_6}^-$. The reduction proceeded rapidly, to produce a black solid identified as containing $4^{\bullet+}\mathrm{AsF_6}^-$ by its ESR and IR spectra. Chemical analyses showed that it contained significant amounts of impurities (5% $\mathrm{NBu_4AsF_6}$ and 10% **3**).

Oxidation of $4^{\bullet+}\mathrm{AsF_6}^-$ with $\mathrm{AsF_5}$ produced a black solution, shown by ^{13}C NMR spectroscopy to contain 4^{2+} (δ 190.0 and 169.8), 3^{2+} and $\mathrm{NBu_4AsF_6}$. Removal of the dark colouration by fractional recrystallisation proved very slow, and resulted in a low final yield (39%) of $4^{2+}2\mathrm{AsF_6}^-$ (details in SUP 56934). The mass spectrum showed a weak molecular ion peak at *m/z* 208 (4.3%), while absorptions in the IR spectrum occurred in similar positions to those in the IR and Raman spectra of $3^{2+}2\mathrm{AsF_6}^-$, consistent with the presence of a $\overline{\mathrm{CNSNS}}^+$ ring and the lower symmetry of the 4^{2+} cation.

Reduction of 4^{2+} would regenerate $4^{\bullet+}$ rather than its electronic isomer, $^+\overline{\mathrm{NSSNC}}\text{–}\overline{\mathrm{CNSNS}}^\bullet$, because the electron affinity of the $\overline{\mathrm{CNSSN}}^+$ ring is higher than that of the $\overline{\mathrm{CNSNS}}^+$ ring (see above). The fully symmetric disulfides **5** are only accessible *via* the fully reduced $3^{2\bullet}$ or $4^{2\bullet}$ as shown in Scheme 1. The neutral radical $5^{2\bullet}$ and the related $5^{\bullet+}$ and 5^{2+}, may also be obtained by multistep syntheses involving tris(trimethylsilyl)-amidine intermediates.[36]

Conclusion

We have shown previously that the kinetics[4] of the cycloaddition reactions of the SNS^+ cation with monofunctional alkynes and nitriles are amongst the simplest known, and constitute a text-book example of the importance of orbital interactions in cycloaddition reactions. In the reaction of SNS^+ with cyanogen to give 3^{2+}, we have applied the chemistry of SNS^+ to the synthesis of molecules containing more than one thiazyl ring, and thereby greatly enhance the synthetic potential of this cation. The facile self-assembly of multiple thiazyl ring systems, which was simultaneously demonstrated by Banister *et al.*[6a,b] is an important step towards the synthesis of new, thiazyl multiradical-containing materials, which may exhibit unusual electrical or magnetic properties. For example, polymerisation of one of the rings in $3^{\bullet+}$ or $4^{\bullet+}$ would yield a backbone polymer incorporating a potentially conducting CNSNS backbone attached to reversibly reducible rings.

By successive reduction, rearrangement of $\overline{\mathrm{CNSNS}}^\bullet$ to $\overline{\mathrm{CNSSN}}^\bullet$, and subsequent reoxidation of multiple $\overline{\mathrm{CNSNS}}^+$ ring systems, it is feasible to obtain whole families of bi- and poly-cyclic molecules, radicals, multiradicals and ions in simple, rational, quantitative steps. This study not only exemplifies this strategy for one simple system, providing access to a new class of CNS bicyclics, but also demonstrates some effective limitations. For example, $\mathrm{R}\overline{\mathrm{CNSNS}}^\bullet$ derivatives appear to be stable only with non-electron-withdrawing substituents, so that the system underwent rapid rearrangement where R = $\overline{\mathrm{CNSNS}}^+$ ($3^{\bullet+}$). Further complications may arise during rearrangement from side reactions (*e.g.* photolysis),[37] polymerisation of $\overline{\mathrm{CNSSN}}^\bullet$ rings, and from inhomogeneous conditions arising from the low solubilities of products or reactants. The last of these was found to be particularly troublesome on a preparative (or gram) scale.

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