The Kinetics of the Quantitative, Symmetry Allowed, Reverse Electron Demand Cycloadditions of the Pseudo-1,3-Dipole SNS^+ with Alkynes and Nitriles; the Preparation and X-Ray Crystal Structures of $NC\overline{CSNSC}HAsF_6$ and $\overline{SNSNC}–\overline{CNSNS}(AsF_6)_2$: The Precursor to a New Class of $S_2N_2C–CN_2S_2{}^{n+}$ (n = 0,1,2) Bicyclics

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The rates of cycloaddition reactions of $SNSAsF_6$ with alkynes and nitriles increase as the ionization potential (E_i) of the triple bond decreases, and accordingly reaction with HCCCN occurs preferentially at the CC bond; however, it reacts with NCCN quantitatively to give the dication $(\overline{CNSNS})_2{}^{2+}$, from which several members of a new family of $S_2N_2C–CN_2S_2{}^{n+}$ (n = 0,1,2) bicyclics have been prepared.

Despite significant recent progress,[1] much of the chemistry of sulphur nitrogen compounds is non-quantitative and poorly understood.[2] In contrast, we have shown that the SNS^+ (*cf.* ONO^+) cation (as the $AsF_6{}^-$ salt) undergoes quantitative, symmetry allowed cycloaddition reactions with alkynes[3,4] (CF_3CCCF_3, HCCH and MeCCH), nitriles[3,5] (RCN, R = Me, Bu^t, CF_3 and I), alkenes[6] (*E*-MeCHCHMe and H_2CCH_2) and SN^+[1d] [see eqn. (1)].

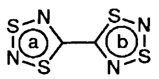
$$RC{\equiv}E + SNS^+ \longrightarrow R\overline{CSNSE}^+ \quad \begin{matrix} \mathbf{1}^+ : E = CR' \\ \mathbf{2}^+ : E = N \end{matrix} \qquad (1)$$

Quantitative cycloaddition reactions in fact occur[7] with a wide range of alkyne and nitrile derivatives in overall second-order reactions. The logarithm of the second-order rate constants is approximately proportional to $-E_i$ (ionisation potential) of the triple bond, showing that the cycloadditions follow the reverse electron demand regime.[8,9] SNS^+ undergoes a facile cycloaddition with the C≡C bond in HCCCN to give $\mathbf{3}^+$, consistent with the alkyne moiety having a lower E_i (11.60 eV) than the nitrile group (14.03 eV).[10] In contrast, dicyanogen (E_i 13.36 eV[10]) only gives the 1:2 cycloadduct $\mathbf{4}^{2+}(AsF_6)_2$. Reduction of $\mathbf{4}^{2+}$ provides systematic access to a new class of $S_2N_2C–CN_2S_2{}^{n+}$ (n = 0–2) bicyclics, some of which may be precursors to novel C–S–N synthetic metals.[11] The systematic, quantitative syntheses of multi-ring systems and their reduction products provides a powerful, general synthetic strategy to a wide range of materials with potentially novel properties, and greatly expands the already extensive cycloaddition chemistry of SNS^+.

The π-bonding in SNS^+ consists of two mutually perpendicular three centre–four electron manifolds, related to that in 1,3-dipoles, *e.g.* nitrile oxides and ozone.[8,9] A positive charge and the high electronegativities of S and N cause SNS^+ to possess a very low energy HOMO, and calculations (STO-3G) show that a reverse electron demand interaction between LUMO(SNS^+) and HOMO(triple bond) leads to the thermally allowed cycloadditions with alkynes and nitriles [eqn. (1)].

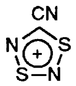
The reactions of CF_3CCCF_3 and RCN [R = Me, C_6H_5, *p*-$(O_2N)_2C_6H_4$ and 3,5-$(O_2N)_2C_6H_3$] with $SNSAsF_6$ were monitored by ^{19}F or ^1H NMR as a function of time, and were

$\mathbf{3}^+$

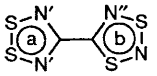


$\mathbf{4}^{2+}$ a = b = +

$\mathbf{4}^+$ a = • b = +



$\mathbf{5}^+$



$\mathbf{6}^{2+}$ a = b = +

$\mathbf{6}^+$ a = • b = +

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Table 1 Vertical ionization potentials and rates of cycloaddition to SNS^+ (relative to MeCN) for some alkynes and nitriles quoted to one significant figure (NMR integrations are accurate to ±5%)

1,3-Dipolarophile	k_{rel}[a]	E_i/eV	Ref.
CF_3CN	0.01	14.3	10,15
$3,5\text{-}(O_2N)_2C_6H_3CN$	0.03	13.4	16
CF_3CCCF_3	0.1	12.83	17
$p\text{-}O_2NC_6H_4CN$	0.1	12.63	16
MeCN	1	12.2	18
PhCN	2	12.09	16
Bu^tCN	2	12.11[b]	17,18
CF_3CCH	5	12.12	17
MeCCMe	30	9.59	19
MeO_2CCCCO_2Me	30	10.9	20
MeCCH	100	10.37	19
Me_2NCN	100	9.44[c]	21
HCCH	100	11.43	21,22

[a] Absolute second-order rate constants were also determined in some cases: (in $l\ mol^{-1}\ s^{-1}$) $(3.8 \pm 0.1) \times 10^{-5}$ [$3,5\text{-}(O_2N)_2C_6H_3CN$], $(1.97 \pm 0.08) \times 10^{-4}$ (CF_3CCCF_3), $(1.73 \pm 0.03) \times 10^{-4}$ [$p\text{-}(O_2N)C_6H_4CN$], $(1.49 \pm 0.01) \times 10^{-3}$ (MeCN) and $(2.6 \pm 0.3) \times 10^{-3}$ (C_6H_5CN). [b] This is the E_i of EtCN, that of Bu^tCN appears not to have been determined. [c] Ionization occurs principally from the amino lone pair. Ionization from the CN group occurs at 11.87 eV.

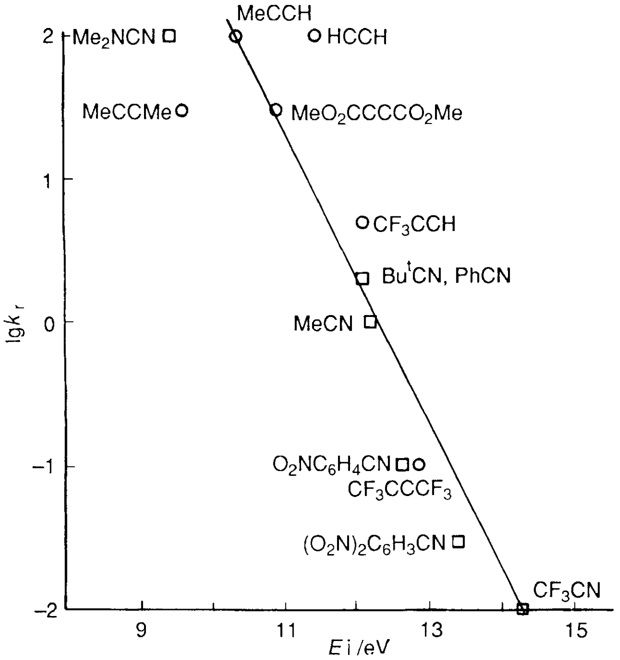

Fig. 1 Plot of the rates of cycloaddition of some nitriles (□) and alkynes (○) (relative to MeCN) against ionization potential (eV) (see also Table 1)

shown to be overall second-order (first-order in X and SNS^+), consistent with the proposed cycloaddition. Relative rate constants (k_{rel}) were also obtained[12] for a variety of pairs of nitriles and/or alkynes (Table 1). A plot (Fig. 1) of lgk_{rel} against Ei (triple bond) is almost linear (with a correlation coefficient of −0.91), the cycloaddition rates increasing as the LUMO(SNS^+) − HOMO(triple bond) energy gap decreases, confirming that the reactions are of the reverse electron demand type. There is minimal steric influence in the case of the nitrile cycloadditions, which produce a straighter line than the data as a whole (the correlation coefficient for the nitrile E_i values *vs.* lgk_{rel} is −0.97). This implies that the nitrile cycloadditions must be very asynchronous.

HCCCN (1.20 g, 19.0 mmol) reacted quantitatively with $SNSAsF_6$ (2.70 g, 10.1 mmol) in SO_2, to give colourless $HCSNSCCNAsF_6$ (**3**AsF_6) [3.19 g, 9.7 mmol, 96% yield based on eqn. (2)], which was recrystallised from SO_2 and characterised by its elemental analyses, IR, NMR (^{13}C δ 175, 154 and 105), and X-ray crystal structure‡ (Fig. 2).

$$HCCCN + SNSAsF_6 \rightarrow HCSNSCCNAsF_6\ (\mathbf{3}AsF_6) \quad (2)$$

Ionizations from the CC and CN triple bonds in HCCCN occur at 11.60 eV and 14.03 eV respectively,[10] and the cycloaddition of SNS^+ to the CC triple bond in HCCCN is therefore expected. STO-3G calculations show that the HOMOs of **3**$^+$ are considerably lower in energy than those in HCCCN, and a second cycloaddition of SNS^+ to the cyano group to give $(SNSNC\text{–}CSNSCH)(AsF_6)_2$ (IR, chemical analyses and NMR ^{13}C δ 169, 173 and 188) was only complete after ten weeks at 50 °C.

Reaction of dicyanogen (0.53 g, 10.4 mmol) with $SNSAsF_6$ (3.608 g, 13.5 mmol) at 50 °C for 5 days gave highly crystalline $(SNSNC\text{–}CNSNS)(AsF_6)_2$, **4**$(AsF_6)_2$ [eqn. (3)], 3.959 g, 97% yield, which was characterised by chemical analysis, IR and Raman spectroscopy, NMR (^{13}C δ 187), mass spectrometry and X-ray crystallography.§ Attempts to prepare the intermediate 1 : 1 cycloadduct (**5**AsF_6, $NCCNSNSAsF_6$) according to eqn. (4) only produced **4**$(AsF_6)_2$ with possible traces of **5**AsF_6 (IR).

$$2SNSAsF_6 + NCCN \rightarrow (CNSNS)_2(AsF_6)_2 \quad (3)$$

$$SNSAsF_6 + NCCN \rightarrow NCCNSNSAsF_6 \quad (4)$$

The E_i of dicyanogen is relatively high (13.36 eV[10]), and its slow reaction with SNS^+ is not unexpected. However, the apparent kinetic preference for the 2 : 1 cycloadduct **4**$^{2+}$ over the 1 : 1 cycloadduct **5**$^+$ was very surprising in the context of the reaction of SNS^+ with HCCCN (see above). MO calculations (STO-3G) on 1,3,2,4-dithiadiazolium cations place small (*ca.* 0.2 au) negative charges on the ring nitrogen atoms, and this is supported by the crystal structures of several related C–S–N cationic heterocycles,[3,14] which never show anionic contacts to these atoms. We propose that the approach of SNS^+ to **5**$^+$ is facilitated by an in plane electrostatic interaction with the nitrogen atom in the 4-position of the 1,3,2,4-dithiadiazolium ring. Consistently, the related 2 : 1 cycloaddition of SNS^+ and HCCCN may be inhibited by the lack of the facilitating influence of a suitable ring nitrogen atom.

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‡ *Crystal data* for **3**AsF_6: M = 318.90, monoclinic, space group $P2_1/c$, a = 7.9152(18), b = 19.305(5), c = 11.3437(13) Å, β = 100.446(19)°, U = 1704.4(6) Å^3, Z = 8, D_c = 2.48 g cm^{-3}, μ = 4.41 mm^{-1}, crystal size 0.28 × 0.25 × 0.25 mm. Data were collected at 100 K using Mo-$K\alpha$ radiation (λ = 0.71073 Å) with $2\theta_{max}$ = 50°. The structure was solved by direct methods and an empirical absorption correction applied using the DIFABS[13] routine. Two independent cations were observed, one of which was disordered by means of 180° rotation about the C(22)–N(24) axis, but only the structure of the ordered cation is discussed here. Hydrogen atoms were located in a slant plane difference synthesis. Final difference synthesis: deepest hole 0.97 e Å^{-3}, highest peak 1.10 e Å^{-3}. R = 0.044, R_w = 0.059 (0.064 and 0.060 including all reflections) for 2354 reflections with $I > 2.5\sigma(I)$ (2947 total) and 254 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ *Crystal data* for **4**$(AsF_6)_2$: M = 586.11, triclinic, space group $P\bar{1}$, a = 8.3729(11), b = 9.4306(7), c = 10.0240(11) Å, α = 82.875(7), β = 67.743(10), γ = 89.425(9)°, U = 726.29 Å^3, Z = 2, D_c = 2.680 g cm^{-3}, μ(Mo-Kα) = 5.28 mm^{-1}, crystal size 0.56 × 0.40 × 0.33 mm. Intensity data were collected at room temp. as described in footnote ‡. The structure was solved by direct methods. Final difference synthesis: deepest hole −0.630 e Å^{-3}, highest peak 0.800 e Å^{-3}. R = 0.048, R_w = 0.068 (0.064 and 0.071 including unobserved) for 2057 reflections $I > 2.5\sigma(I)$ (2538 total) and 218 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

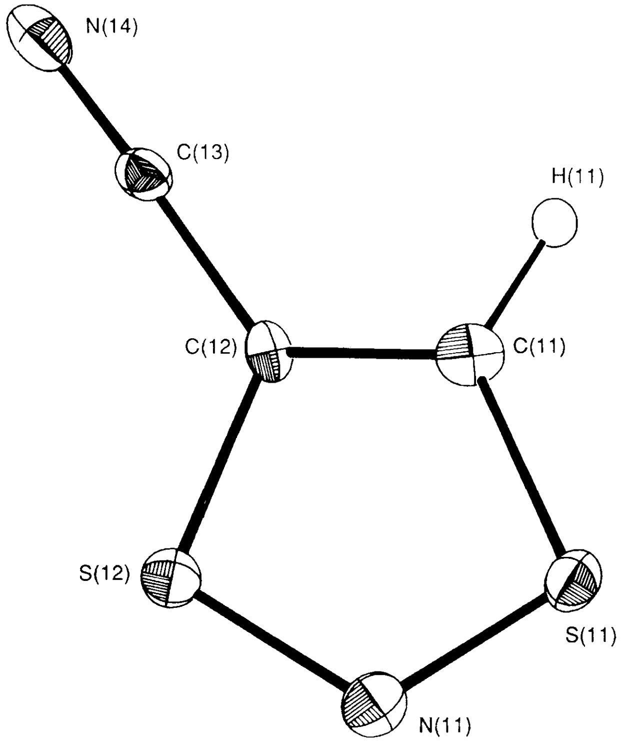

Fig. 2 Molecular structure of **3**$^+$. Bond distances (Å): C(11)–H(11) 1.09(1), C(11)–C(12) 1.356(13), C(12)–S(12) 1.712(9), S(12)–N(11) 1.585(8), N(11)–S(11) 1.617(9), S(11)–C(11), 1.689(9), C(12)–C(13) 1.44(1), C(13)–N(14) 1.15(1). Angles (°): H(11)–C(11)–S(11) 123.7(8), S(11)–C(11)–C(12) 112.9(8), S(12)–C(12)–C(13) 121.1(7), C(11)–C(12)–C(13) 124.0(9), S(11)–C(11)–H 123.7(8), C(11)–C(12)–S(12) 113.9(7), C(12)–S(12)–N(11) 98.7(4), S(12)–N(11)–S(11) 115.3(5), N(11)–S(11)–C(11) 99.3(5), S(12)–C(12)–C(13) 122.1(7), C(12)–C(13)–N(14) 177(1). **3**$^+$ is planar [max deviation N(14) 0.024(11) Å], and there are significant anion contacts to the ring sulphur atoms, and weaker contacts to C(11), C(13) and N(14). There are no contacts to N(11) or C(12).

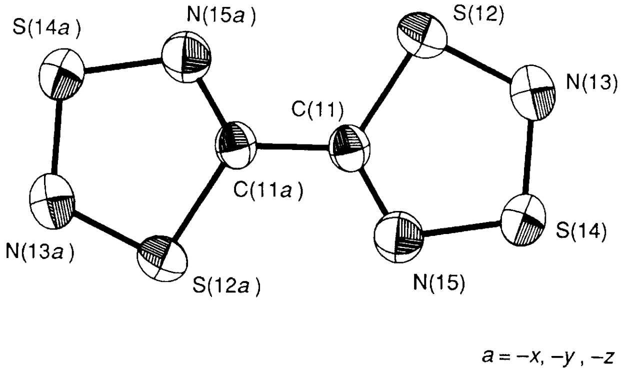

Fig. 3 Molecular structure of **4**$^{2+}$ in **4**$(AsF_6)_2$. Bond distances for cation 1 [corresponding values for cation 2]: C(11)–C(11)*a* 1.467(14) [1.441(15)], C(11)–S(12) 1.715(7) [1.721(8)], S(12)–N(13) 1.597(8) [1.589(8)], N(13)–S(14) 1.604(7) [1.595(8)], S(14)–N(15) 1.622(7) [1.608(7)], N(15)–C(11) 1.285(10) [1.311(10)]. Angles (°): C(11)*a*–C(11)–N(15) 121.1(7) [121.3(7)], S(12)–C(11)–N(15) 116.9(6) [116.0(6)], C(11)*a*–C(11)–S(12) 122.0(6) [122.7(6)] C(11)–S(12)–N(13) 96.2(4) [96.0(4)], S(12)–N(13)–S(14) 112.9(4) [113.8(4)], N(13)–S(14)–N(15) 102.1(4) [102.3(4)], S(15)–N(15)–C(11) 111.9(6) [112.0(5)]. **4**$^{2+}$ is centrosymmetric and planar (to within 0.01 Å).

Compound **4**$(AsF_6)_2$ was reduced by $SbPh_3/NBu_4Cl$ in SO_2 to the radical cation **4**$^+$ [ESR, $a(^{14}N) = 11.0$ G, $g = 2.0069$], which rapidly rearranged to **6**$^+$ [ESR, $a(^{14}N') = 4.578$ G, $a(^{14}N'') = 0.25$ G, $g = 2.0119$]. The latter was also prepared in 79% yield according to eqn. (5), and then reoxidised with AsF_5 to give **6**$(AsF_6)_2$ (39% purified yield, ^{13}C NMR δ 190.0, 169.8).

$$2\,\mathbf{4}(AsF_6)_2 + SbPh_3 + 2NBu_4Cl \rightarrow 2\,\mathbf{6}AsF_6 + SbPh_3Cl_2 + 2NBu_4AsF_6 \quad (5)$$

Two electron reduction of **4**$(AsF_6)_2$ gives a completely insoluble black solid of empirical formula CN_2S_2 (84% yield). The mass spectrum of this material shows a molecular ion peak at 208 (61.1%, $C_2N_4S_4^+$), and it is possible that this material consists of $\overline{\text{SNSNC}}\text{–}\overline{\text{CNSNS}}$ units incorporated into some form of extended structure (perhaps a stacked polymer).

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References

1 (*a*) K. T. Bestari, R. T. Boere and R. T. Oakley, *J. Am. Chem. Soc.*, 1989, **111**, 1579; (*b*) A. W. Cordes, J. D. Goddard, R. T. Oakley and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1989, **111**, 6147; (*c*) R. T. Oakley, *Prog. Inorg. Chem.*, 1988, **36**, 299; (*d*) J. Passmore and M. J. Schriver, *Inorg. Chem.*, 1988, **27**, 2749; T. S. Cameron, F. Grein, S. Parsons, J. Passmore and M. J. Schriver, manuscript in preparation.
2 H. G. Heal, *The Inorganic Chemistry of Sulphur, Nitrogen and Phosphorus*, Academic Press, London, 1980.
3 G. K. MacLean, J. Passmore, M. N. S. Rao, M. J. Schriver, P. S. White, D. Bethell, R. S. Pilkington and L. H. Sutcliffe, *J. Chem. Soc., Dalton Trans.*, 1985, 1405.
4 E. G. Awere, N. Burford, C. Mailer, J. Passmore, M. J. Schriver, P. S. White, A. J. Banister, H. Oberhammer and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 66.
5 N. Burford, J. Passmore and M. J. Schriver, *J. Chem. Soc., Chem. Commun.*, 1986, 140.
6 N. Burford, J. P. Johnson, J. Passmore, M. J. Schriver and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1986, 966.
7 S. Parsons, J. Passmore, M. J. Schriver, X. P. Sun, unpublished results; M. J. Schriver, Ph.D. Thesis, University of New Brunswick, Fredericton, Canada, 1989.
8 R. Huisgen in *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, John Wiley, 1984.
9 R. L. Kulzkowski in *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, John Wiley, 1984.
10 G. Bien, E. Heilbronner, V. Horning, E. Kloster-Jensen, J. P. Mailer and F. Thoomen, *Chem. Phys.*, 1979, **36**, 1.
11 M. -H. Whangbo, R. Hoffmann and R. B. Woodward, *Proc. R. Soc. London, Ser. A.*, 1979, **366**, 23.
12 D. G. Williamson and R. J. Cvetanovic, *J. Am. Chem. Soc.*, 1968, **90**, 3668.
13 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
14 (*a*) E. G. Awere, N. Burford, R. C. Haddon, S. Parsons, J. Passmore, J. V. Waszczak and P. S. White, *Inorg. Chem.*, 1990, **29**, 4821; (*b*) S. Parsons, J. Passmore, M. J. Schriver and P. S. White, *Can. J. Chem.*, 1990, **68**, 852.
15 H. Bock, D. Dammel and D. Lentz, *Inorg. Chem.*, 1984, **23**, 1535.
16 T. Juska, *Coll. Czech. Chem. Commun.*, 1985, **50**, 650.
17 W. R. Cullen, D. C. Frost and W. R. Leader, *J. Fluorine Chem.*, 1971/2, **1**, 227; P. Baybutt, M. F. Guest and I. H. Hillier, *Mol. Phys.*, 1973, **25**, 1025.
18 R. F. Lake and H. Thompson, *Proc. R. Soc. London, Ser. A.*, 1970, **317**, 187.
19 J. P. Delwiche, M.Th. Praet, G. Caprace, M. J. Hubin-Franskin, P. Natalis and J. E. Collins, *J. Electron Spectrosc. and Relat. Phenom.*, 1977, **12**, 395.
20 R. Sustmann and H. Trill, *Tetrahedron Lett.*, 1972, **42**, 4271.
21 H. Stafast and H. Bock, *Chem. Ber.*, 1974, **107**, 1882.
22 R. G. Cavell and D. A. Allison, *J. Chem. Phys.*, 1978, **69**, 159.