Reactions of $S_3N_2Cl_2$ and $(NSCl)_3$ with a new Silylcyanamide Reagent $(Me_3Si)_2N{\cdot}CN$: Synthesis and *X*-Ray Crystal Structure of $\overline{\mathrm{SNSNS}}$: N·CN† and Bicyclic $CClS_3N_5$‡

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The new reagent bis(trimethylsilyl)cyanamide reacts with $S_3N_2Cl_2$ and $(NSCl)_3$ to give $\overline{\mathrm{SNSNS}}{\cdot}NCN$ and $CClS_3N_5$ in good yields; the crystal structures of both products have been determined.

The sulphur–nitrogen–chlorine compounds $S_3N_2Cl_2$ and $(NSCl)_3$ are among the most convenient starting materials for preparing sulphur–nitrogen species; consequently efficient reagents for replacing chlorine by other functional groups are of special interest. We report a new silyl reagent, bis-(trimethylsilyl)cyanamide (**1**) which, in reactions with $S_3N_2Cl_2$ and $(NSCl)_3$, introduces two different types of NCN group, to give compounds (**2**) and (**3**). In the first case (**2**) the =N·CN group is introduced at one sulphur atom despite the different positions and bonding of the replaced chlorine atoms. In the second case (**3**) substitution by a bridging >N·CN group occurs, followed by an internal rearrangement.

The silyl reagent was prepared by dropwise addition of trimethylsilyl chloride (160 mmol) dissolved in dichloromethane (50 cm^3) to silver cyanamide (80 mmol) in dichloromethane (250 cm^3; 21 °C). Subsequent filtration, removal of the solvent, and distillation through a short column under reduced pressure (b.p. 75 °C at 35 Torr) gave a clear, colourless liquid $(Me_3Si)_2NCN$ (15.7 g, 80%, $n_D{}^{20}$ 1.4299, $D_4{}^{20}$ 0.827 ± 0.003 g cm^{-3}).

The related bis(silyl)cyanamide $(SiH_3)_2N{\cdot}CN$ has been prepared previously in low yield,[1] Unlike some other substituted cyanamides,[2] the reagent (**1**) does not rearrange thermally below the b.p. (100 °C at 760 Torr) to the corresponding tautomeric carbodiimide.

Compound (**2**) was prepared by dropwise addition of $(Me_3Si)_2NCN$ (13 mmol) in acetonitrile (20 cm^3) to a well stirred slurry of $S_3N_2Cl_2$ (13 mmol) in acetonitrile (80 cm^3) at −17 °C. Filtration at 21 °C after 36 h gave a dark red

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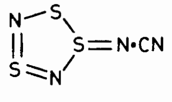
† 1-Cyanoimino-1,2,4,3,5-trithiadiazole.

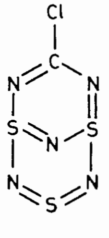
‡ 7-Chloro-$1\lambda^4$, $3\lambda^4$, δ^2, $5\lambda^4$-trithia-2,4,6,8,9-penta-azabicyclo[3.3.1]-nonane.

$(Me_3Si)_2NCN$

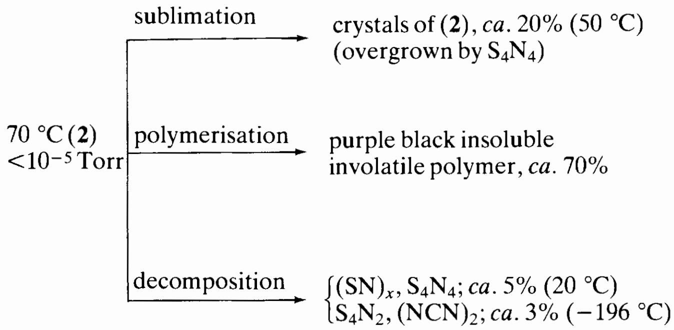
(1)



(2)



(3)



Scheme 1

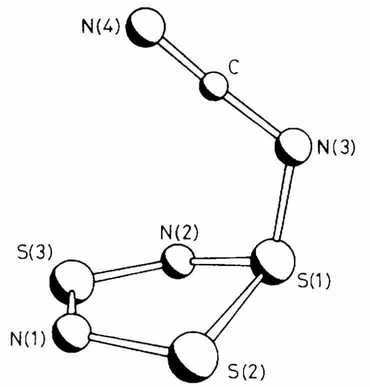


Figure 1. Perspective view of the S_3N_2=NCN molecule; key dimensions: S(1)–S(2) 2.207(2), S(1)–N(3) 1.580(4), N(3)–C 1.336(6), N(4)–C 1.141(6), S(1)–N(2) 1.654(3), S(3)–N(1) 1.546(4) Å; S(2)–S(1)–N(2) 93.5(1), N(2)–S(1)–N(3) 109.1(2), N(1)–N(3)–S(2) 109.8(2), S(1)–N(2)–S(3) 117.9(2), S(1)–N(3)–C 119.0(3), N(3)–C–N(4) 176.4(5)°.

polymeric solid (0.75 g), and removal of solvent from the filtrate gave a red-brown solid, S_3N_2NCN (1.31 g, 62%), m.p. 105 °C (decomp.) Several of the i.r. absorptions were typical of S_3N_2 derivatives.[3]

Vacuum thermolysis of (2) was rather complex (see Scheme 1): *ca.* 0.6 g of (2) was heated to 70 °C *in vacuo* (<10^{-5} Torr) for 24 h. The volatile products were separated *via* a train of sealable tube sections kept at constant temperatures (shown in the Scheme). All the light volatile materials were trapped at −196 °C. The sublimate consisted of well facetted transparent orange crystals of (2) (up to 1 mm across). Examination of many of these crystals revealed that they were overgrown by an oriented single-crystal layer of S_4N_4 decomposition product [{001}S_3N_2NCN//{001}S_4N_4].

The nature of the decomposition products (Scheme 1) and especially of the light volatile materials trapped at −196 °C [dicyanodiazene NC·N=N·CN and no $(CN)_2$], indicated that after initial thermal scission of (2) into [S_3N_2] and [NCN] (cyanonitrene), the former unknown species rearranged to give $(SN)_x$, S_4N_2 and S_4N_4, and the latter dimerised to give the red volatile solid $(NCN)_2$.[4]

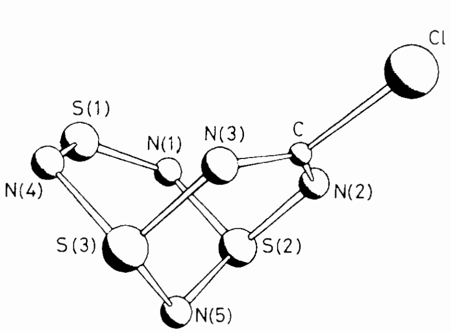


Figure 2. Perspective view of the $CClN_5S_3$ molecule; key dimensions: S(1)–N(1) 1.550(2), N(1)–S(2) 1.731(2), S(2)–N(2) 1.633(2), S(2)–N(5) 1.634(2), N(2)–C 1.320(2), C–Cl 1.751(2), C–N(3) 1.319(2), N(3)–S(3) 1.632(2) Å; N(2)–C–N(3) 135.2(3), C–N(3)–S(3) 117.9(1), N(3)–S(3)–N(5) 109.0(1), S(3)–N(5)–S(2) 113.6(1), N(5)–S(2)–N(2) 108.6(1), S(2)–N(2)–C 116.8(1), N(5)–S(3)–N(4) 105.9(1), S(2)–N(4)–S(1) 119.1(1), N(4)–S(1)–N(1) 120.4(1), S(1)–N(1)–S(2) 120.8(1), N(3)–S(3)–N(4) 102.3(1), N(1)–S(2)–N(2) 103.2(1)°.

At −10 °C fast polymerisation of crystalline S_3N_2=NCN occurred in contact with its saturated solution in dry liquid SO_2. Conversion into a purple-black polymer started spontaneously in a small volume, from which it spread radially throughout the layer of solid (*ca.* 0.5 g). We attribute the instability to the combination of a strained ring and the presence of (as yet unidentified) free radicals co-produced in the preparative reaction. It was found that the spontaneous polymerisation was completely inhibited in 'wet' liquid SO_2. Recrystallisation of (2) (0.52 g) from liquid SO_2 (13 cm^3) containing water (0.058 cm^3) gave air-stable orange prisms of pure (2) free of polymer and of S_4N_4 overgrowth; consequently a crystal structure determination§ became possible (Figure 1).

Bicyclic species based on the S_3N_3 ring [*i.e.* similar to (3)] have been prepared previously as cations with bridging RNC(O)NR (R = Me or Ph)[5,6] or $NSMe_2N$[7] groups or as neutral species with bridging –NXN– groups where X can be PF_2,[8] PR_2 (R = Me or Ph),[9] CR (R = Ph[10] or CF_3[11]), or CNR_2(R = Me, Ph, or Pr^i).[12]

Compound (3) was prepared by the slow addition of (1) (6 mmol) in acetonitrile (20 cm^3) to a vigorously stirred slurry of $(NSCl)_3$ (6 mmol) in acetonitrile (60 cm^3) at −17 °C. The mixture was stirred (36 h) and filtered at 21 °C to give a red

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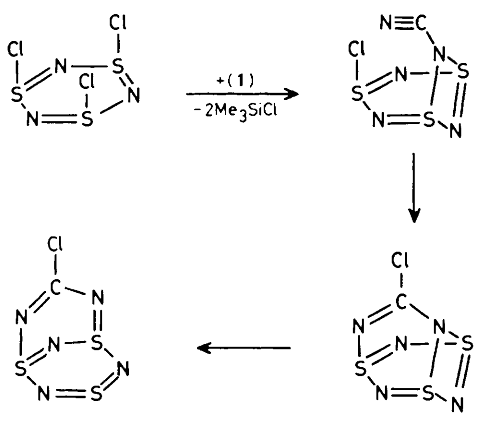
§ *Crystal data* for (2): CN_4S_3 M = 164.22, monoclinic, space group $P2_1/n$(No. 14), a = 5.4507(2), b = 8.751(1), c = 11.833(1) Å, β = 99.57(1)°, U = 556.57 Å^3, D_c = 1.960 g cm^{-3}, Z = 4, μ(Mo-K_α) = 1.17 mm^{-1}, F(000) = 328, T = 20 °C, 982 unique reflections, 715 'observed' with $F \geq 4\sigma(F)$, Mo-K_α radiation λ = 0.71073 Å, R = 0.0357, R_w = 0.0326, $w = 1/\sigma^2(F_0)$ for 73 refined parameters, $\Delta\rho_{fin}$ = +0.47/−0.28 e Å^{-3}.

Crystal data for (3): CN_5S_3Cl, M = 213.69, monoclinic, space group $P2_1/c$(No. 14), a = 4.722(5), b = 10.52(1), c = 14.05(1) Å, β = 103.4(1)°, U = 678.81 Å^3, D_c = 2.091 g cm^{-3}, Z = 4, μ(Mo-K_α) = 1.30mm^{-1}, F(000) = 424, T = 20 °C, 2156 unique reflections, 2156 'observed' with $F \geq \sigma(F)$, R = 0.0364, R_w = 0.059, w = 2.70 ($\sigma^2 F_0$ + 0.01F_0^2) for 92 refined parameters $\Delta\rho_{fin}$ = 0.73 −0.56 e Å^{-3}. Atomic co-ordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre [compound (3)] and the University of Bonn [compound (2)]. See Notice to Authors, Issue No. 1.



Scheme 1.

polymeric solid (0.06 g) and an orange-red filtrate which was pumped dry to give an orange-brown solid, S_3N_5CCl, (0.92 g, 70%) contaminated with a minute quantity of a dark polymeric material. Since spontaneous polymerisation was inhibited by treatment with SO_2Cl_2, the product was purified by dissolving in CH_2Cl_2 containing a little SO_2Cl_2, followed by precipitation with hexane and filtration to give yellow crystals, m.p. 95.4 °C (decomp.). Crystals suitable for *X*-ray analysis were obtained by high vacuum sublimation at 70 °C.

The molecular structure§ of (**3**) is shown in Figure 2. The main feature of structural interest is the large angle (135.2 °) at carbon, 5° or 8° greater (respectively) than in the analogous C_6H_5[10a] or $N(Pr^i)_2$ derivatives.[12b] The angular strain is presumably responsible for the rather long C–Cl distance [1.751(2) *cf.* 1.68(3) in $(NCCl)_3$[13]]. The other distances are normal for such compounds. A likely mechanism of formation involves a bimolecular reaction of $(NSCl)_3$ with (**1**) followed by intramolecular rearrangement, as shown in Scheme 2.

This work shows the value of $(Me_3Si)_2N{\cdot}CN$ for the synthesis of cyanoamino S/N compounds including precursors of C/S/N polymers.

We thank the S.E.R.C. for research grants to A. J. B. and Z. V. H. and to W. C.

Received, 21st April 1987; Com. 523

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