# Chemical Syntheses of Poly(sulphur nitride), $(SN)_x$

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Poly(sulphur nitride) is prepared in *ca.* 65% yield by the reaction of excess of $SiMe_3N_3$ with $S_3N_3Cl_3$, $S_3N_2Cl_2$, or $S_3N_2Cl$ at −15°C in acetonitrile solution. The polymer was also prepared by the reaction of $S_3N_3Cl_3$ and excess of $NaN_3$. The preparation of $(SN)_x$ from $S_3N_3Cl_3$ is dependent on solvent and reaction conditions. Reaction of $S_2Cl_2$ with $NaN_3$ in acetonitrile gave a powder containing $S_3N_2Cl$, $S_8$, NaCl, and unreacted $NaN_3$, which when treated with an excess of $SiMe_3N_3$ in acetonitrile yielded $(SN)_x$. The $(SN)_x$ polymer was also formed by the reaction of $CsN_3$ and $S_2NAsF_6$ in $SO_2$ at −20 °C. Better quality polymer was prepared from $S_3N_3Cl_3$, $S_3N_2Cl_2$, or $S_3N_2Cl$ with excess of $SiMe_3N_3$, after washing with various solvents. Analogous reactions of $Se_2Cl_2$ and $SeBr_4$ gave blue-black explosive solids.

POLY(sulphur nitride) is an anisotropic conducting polymer, made up of the non-metals sulphur and nitrogen, which becomes superconducting at low temperatures.[1-4] It has been intensively studied in recent years, and has been incorporated into various potentially useful devices,[5-7] such as Schottky barrier based solar cells. It is still prepared[8] by the same route, although with modifications, reported by Burt[9] in 1910. In a recent review it was stated,[1] ' there have been no innovations in the preparation of $(SN)_x$ since 1910,' and in another,[3] ' that if polymers analogous to $(SN)_x$ are to be prepared, new synthetic routes will have to be found.'

The current synthesis[8] of $(SN)_x$ consists of cracking $S_4N_4$ vapours at low pressure, usually over heated silver wool, to yield colourless crystals of $S_2N_2$, which polymerise to $(SN)_x$ over time, under controlled conditions. The explosive $S_4N_4$ has been replaced[10] by $S_4N_3Cl$ but the method is similar in other respects, *i.e.* use of high vacuum technology, careful control of conditions, and small amounts of material. Films of $(SN)_x$ have been prepared by the pyrolysis of $[S_5N_5][FeCl_4]$[11a] and in Burt's original paper[9] he reports that Davies observed formation of a blue substance $[(SN)_x?]$ on heating $S_4N_4{\cdot}SbCl_5$ *in vacuo*. Very recently, heating $Ph_3As{=}NS_3N_3$ has been shown[11b] to give $S_2N_2$ and hence $(SN)_x$. Poly(sulphur nitride) seems[12] to have been formed by the cyclohexene reduction of $S_3N_3Cl_3$, although the reductions of $S_3N_3Cl_3$ in the literature[13,14] report $S_4N_4$ as the product. Various sulphur–nitrogen chlorides have been reduced[13,14] by metals, leading to $S_4N_4$ and in some cases $S_4N_2$. We report here the direct chemical syntheses in solution of poly(sulphur nitride) by the reaction of $S_3N_3Cl_3$, $S_3N_2Cl_2$, $S_3N_2Cl$, and $S_2Cl_2$ with $NaN_3$ and/or $SiMe_3N_3$; the reaction of $S_2NAsF_6$ with $CsN_3$; and the attempted synthesis of $(SeN)_x$. A preliminary account of the preparation of $(SN)_x$ by reaction of $S_3N_3Cl_3$ with azides has been reported.[15]

## EXPERIMENTAL

The starting materials $S_3N_3Cl_3$, $S_3N_2Cl_2$, and $S_3N_2Cl$,[16] $Se_2Cl_2$, $SeBr_4$,[17] and $S_4N_3Cl$[18] were prepared by known methods. Disulphur dichloride, $NaN_3$ (B.D.H.), $CsN_3$ (Eastman), $SiMe_3N_3$ (Petrarch), and 88% formic acid (Anachemia) were used without purification. Acetonitrile (B.D.H. Analytical reagent grade) was refluxed and distilled over $P_4O_{10}$, and other solvents purified by conventional means. The $SO_2$ (Matheson) in addition to drying over $CaH_2$ (Fisher) was stored over dried 3A molecular sieves (B.D.H.). The $S_2NAsF_6$ was prepared according to ref. 19. Chemicals were manipulated under a dry nitrogen or argon atmosphere, and moisture-sensitive materials and $(SN)_x$ were handled in a Vacuum Atmospheres Corp. Dri-Lab fitted with a Dri-Train (HE-493).

Infrared (Nujol mulls, KBr plates) and mass spectra were obtained as previously described.[20] *X*-Ray powder diffraction data were obtained using a Debye-Scherrer powder camera ($d$ = 114.8 mm), 0.5-mm glass capillaries, and nickel-filtered Cu-$K_\alpha$ radiation (40 kV, 20 mA) with the exposure time ranging from 1 to 5 d. Elemental analyses were obtained from: (*a*) Canadian Microanalytical Service, Vancouver, B.C., Canada; (*b*) Mr. Bob Coult, University of Durham, Durham, England; and (*c*) A. Bernhardt, Analytische Laboratorien, 5270 Elbach, Germany.

Reactions were carried out in a two-necked round-bottomed flask fitted with a pressure-equalised dropping funnel, whose top was connected to two drying towers containing molecular sieve (type 3A) and concentrated sulphuric acid. In the case of reactions with sulphur–nitrogen chlorides, a solution of $SiMe_3N_3$ in MeCN was added dropwise (1—2 h) at −15 °C to a stirring solution (in case of $S_3N_3Cl_3$) or suspension of $S_3N_2Cl_2$, $S_3N_2Cl$, or $S_4N_3Cl$ in acetonitrile. Immediate reactions (quick colour changes and evolution of nitrogen) were observed with $S_3N_3Cl_3$ and $S_3N_2Cl_2$. An intense green solution was initially produced, which then underwent a series of colour changes, finally giving blue-black powdered $(SN)_x$. In reactions using $S_3N_2Cl$ and $S_4N_3Cl$ nitrogen was slowly evolved and initial dark green solutions were not observed. After evolution of nitrogen was complete, the mixtures were stirred at room temperature (r.t.).

Some typical reactions are given below, and in Table 1.

*Reactions.*—(1) $S_3N_3Cl_3$ *with* $NaN_3$ *at* −10 °C. A solution of $S_3N_3Cl_3$ (1.1 g, 4.5 mmol) in MeCN (50 cm$^3$) was added (2 h) to a stirred slurry of $NaN_3$ (1.4 g, 21.5 mmol) in MeCN (20 cm$^3$) at −10 °C. An immediate reaction occurred with a series of colour changes, orange-yellow, red-brown, brown, brown-black, and after 0.5 h blue-black. On stirring at r.t. for 3 h the mixture was filtered giving a blue-black powder (1.48 g) and an orange-red filtrate which contained 0.2 g of solid, mainly $S_4N_4$ (as shown by i.r.).

The blue-black solid was washed with $CCl_4$ (8 × 10 cm$^3$), quickly (10 min) with water (5 × 10 cm$^3$), and finally with $CS_2$ (2 × 10 cm$^3$), giving a deep blue-black solid (0.28 g).

TABLE 1

Reactions of azides with sulphur–nitrogen chlorides [a]

| Reactant A | | | Reactant B | | | Reaction solvent (cm$^3$) | | Reaction temp./ °C | Reaction time [b]/ h | Product analysis [c] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | g | mmol | | g | mmol | | | | | g | Precipitate [d] compound | Yield (%) | g | Filtrate compound | Yield (%) |
| $S_3N_3Cl_3$ | 1.18 * | 4.8 | $NaN_3$ | 2.0 | 30.8 | MeCN | 60 | 20 | 3 | 2.1 | Mixture [e] | | 0.075<br>0.50 | $Na^+S_4N_5^-$<br>Mixture ($S_4N_4$) | |
| $S_3N_3Cl_3$ | 0.8 [f] | 3.3 | $NaN_3$ | 1.0 | 15.4 | MeCN | 25 | 20 | 7 | 1.48 | Mixture ($S_3N_2Cl$)<br>NaCl, $S_8$ | | 0.11 | $S_2N_2CMeCl$ | 15 |
| $S_3N_3Cl_3$ [g] | 1.1 * | 4.5 | $NaN_3$ | 1.4 | 21.5 | MeCN | 70 | −10<br>12 | 1<br>2 | 1.48 | Mixture<br>$(SN)_x$ 0.28 g<br>$S_4N_4$ 0.04 g | 45<br>6 | 0.05<br>0.15 | $S_4N_4$<br>Mixture ($S_4N_4$) | 8 |
| $S_3N_3Cl_3$ | 1.05 * | 4.3 | $SiMe_3N_3$ | 3.45 | 30.0 | MeCN | 60 | 20<br>40 | 22<br>2 | 0.5 | Mixture<br>$S_4N_4$ 0.4 g<br>$(SN)_x$ 0.1 g | 67<br>16 | 0.02<br>0.15 | $S_4N_4$<br>Mixture ($S_4N_4$) | 3 |
| $S_3N_3Cl_3$ | 1.65 | 6.8 | $SiMe_3N_3$ | 3.0 † | 26.1 | MeCN | 55 | −15<br>20 | 1<br>2 | 0.8 | Mixture<br>$(SN)_x$ 0.5 g<br>$S_4N_4$ 0.15 g<br>$S_4N_3Cl$ 0.15 g | 53<br>20 | 0.03<br>0.20 | $S_4N_4$<br>Mixture ($S_4N_4$) | 4 |
| $S_3N_3Cl_3$ | 1.0 | 4.1 | $SiMe_3N_3$ | 2.3 † | 20.0 | thf | 45 | −15<br>15 | 1<br>2 | 0.04 | Mixture ($S_4N_3Cl$) | | 0.01<br>0.74 | $S_4N_4$<br>Mixture ($S_4N_4$) | 2 |
| $S_3N_3Cl_3$ | 0.5 | 2.0 | $SiMe_3N_3$ | 1.15 † | 10.0 | MeCN | 20 | −10 | 0.5 | 0.10 | Mixture [h]<br>$S_4N_4$<br>$S_4N_4Cl$ | | 0.10 | Mixture ($S_4N_4$) | |
| $S_3N_3Cl_3$ | 1.4 | 5.7 | $SiMe_3N_3$ | 3.45 † | 30.00 | $CH_2Cl_2$ | 55 | −12<br>20 | 1<br>48 | 0.32 | $S_3N_2Cl$ | 35 | 0.2 | Mixture ($S_4N_4$) | |
| $S_3N_3Cl_3$ [g] | 1.93 | 7.9 [i] | $SiMe_3N_3$ | 5.75 † | 50.0 | MeCN | 75 | −15<br>20 | 1<br>24 | 0.86 | Mixture<br>$(SN)_x$ 0.8 g<br>$S_4N_4$ 0.06 g | 72<br>5 | 0.05<br>0.42 | $S_4N_4$<br>Mixture ($S_4N_4$) | 4 |
| $S_3N_2Cl$ [g] | 1.9 | 11.9 | $SiMe_3N_3$ | 5.75 † | 50.0 | MeCN | 80 | −15<br>20 | 1<br>16 | 1.12 | Mixture [j]<br>$(SN)_x$ 0.75 g | 46 | 0.4 | Mixture ($S_4N_4$) | |
| $S_3N_2Cl_2$ [g] | 1.8 | 9.2 | $SiMe_3N_3$ | 3.45 † | 30.00 | MeCN | 55 | −10<br>20 | 1<br>48 | 0.9 | Mixture [j]<br>$(SN)_x$ 0.8 g | 63 | 0.2 | Mixture ($S_4N_4$) | |
| $S_3N_2Cl_2$ | 0.5 | 2.6 | $SiMe_3N_3$ | 1.4 † | 12.2 | thf | 60 | −15<br>20 | 1<br>18 | | | | 0.25 | Mixture ($S_4N_4$) | |
| $S_4N_3Cl$ [g] | 1.6 | 7.8 | $SiMe_3N_3$ | 3.7 † | 32.2 | MeCN | 50 | −15<br>20 | 1<br>16 | 1.04 | $S_4N_4$ | 72 | 0.56 | Mixture ($S_4N_4$) | |
| $S_3N_3Cl_3$ | 0.5 [k] | 2.05 | $SiMe_3N_3$ | 3.45 † | 30.0 | MeCN | 30 | −15<br>20 | 1<br>48 | 0.08<br>0.12 | $(SN)_x$<br>$S_4N_4$ | | 0.10 | Mixture ($S_4N_4$) | |
| $S_3N_3Cl_3$ | 0.37 * | 1.51 | $SiMe_3N_3$ | 2.53 | 22.0 | MeCN | 50 | −15<br>20 | 1<br>48 | 0.05 | Impure [l] $(SN)_x$ | | 0.25 | Impure $S_4N_4$ | |

[a] In general, a solution of reactant A (or B) was added slowly dropwise over a period of *ca.* 2 h to a stirring solution or suspension of B (or A) in the specified solvent at the given temperature. [b] In all the low-temperature reactions, the time taken to attain room temperature (2—3 h) is not included in the stated reaction time. [c] The identified S–N component in the mixture is given in parentheses. [d] Weights of polymers are given prior to washing with formic acid. The weight decrease on removal of $NH_4Cl$ is small (*ca.* 5—6%). [e] The i.r. spectrum did not show any peaks in the S–N region. [f] Powdered $NaN_3$ was added in small aliquots over *ca.* $\frac{1}{2}$ h to a solution of $S_3N_3Cl_3$ in acetonitrile. [g] This reaction has been described in detail in the Experimental section. [h] The i.r. spectrum of the blackish powdery solid in addition to peaks attributable to $S_4N_4$ and $S_4N_3Cl$ gave a broad peak at 880 cm$^{-1}$. [i] Carried out under a dry argon atmosphere (instead of dry $N_2$). [j] The mixture also contains $S_4N_4$. [k] Carried out using distilled high-performance liquid chromatography grade acetonitrile (Baker) which was refluxed and distilled over $P_4O_{10}$ and $CaH_2$ and stored over dried moleular sieves. [l] Probably $S_3N_2Cl$ and $S_4N_4$ (very small amounts) in the impurities (i.r. spectrum).

* In this reaction, reactant A was added to reactant B. † In this reaction, reactant B was added to reactant A.

(2) $S_3N_3Cl_3$ *with* $SiMe_3N_3$ *at* −15 °C. A solution of $SiMe_3N_3$ (5.75 g, 50.0 mmol) in MeCN (15 $cm^3$) was added (2 h) to a stirred solution of $S_3N_3Cl_3$ (1.93 g, 7.9 mmol) in MeCN (60 $cm^3$) at −15 °C. The mixture initially became dark green, then yellow, orange-yellow, red-brown, and finally black. After complete addition, the mixture was stirred at r.t. for 24 h, and filtered, giving a fine blue-black powder (0.86 g) and a red-brown filtrate which contained mostly $S_4N_4$ (0.47 g).

(3) $S_3N_2Cl$ *with* $SiMe_3N_3$ *at* −15 °C. A solution of $SiMe_3N_3$ (5.75 g, 50.0 mmol) in MeCN (20 $cm^3$) was added (3 h) at −15 °C to a stirred slurry of powdered $S_3N_2Cl$ (1.9 g, 11.9 mmol) in MeCN (60 $cm^3$). Nitrogen evolution was slow and the colour changed from orange-yellow to red-brown. After complete addition the mixture was black. The mixture was stirred for 16 h at r.t. and filtration yielded a black powder (1.12 g) and a deep red filtrate (containing mostly $S_4N_4$).

An i.r. spectrum and an *X*-ray powder diffraction photograph showed some unreacted $S_3N_2Cl$ in the black solid. The sample was finely ground, treated with $SiMe_3N_3$ (3.45 g) in MeCN (50 $cm^3$) at r.t. for 4 d, and the mixture then filtered giving a blue-black powder and a red filtrate (containing $S_4N_4$). The black powder was washed with $CCl_4$ (10 × 10 $cm^3$), $CS_2$ (5 × 10 $cm^3$), and dried ($10^{-3}$ Torr)* for 24 h giving $(SN)_x$ (0.75 g) only.

(4) $S_3N_2Cl_2$ *with* $SiMe_3N_3$ *at* −10 °C. A solution of $SiMe_3N_3$ (3.45 g, 30.0 mmol) in MeCN (15 cm) was added (1.5 h) to a stirred slurry of powdered $S_3N_2Cl_2$ (1.8 g, 9.2 mmol) in MeCN (40 $cm^3$) at −10 °C. The mixture became green, green-yellow, orange-red, and red-brown, and finally blue-black. It was stirred for 2 d at r.t. and filtered giving a blue-black solid (0.9 g) and a red-brown filtrate (containing 0.2 g solid which was largely $S_4N_4$). The blue-black solid was washed with $CS_2$ (10 × 10 $cm^3$) and dried in a vacuum to give $(SN)_x$ (0.8 g).

(5) $S_4N_3Cl$ *with* $SiMe_3N_3$ *at* −15 °C. A solution of $SiMe_3N_3$ (3.7 g, 32.2 mmol) in MeCN (10 $cm^3$) was added (2 h) to a stirred slurry of powdered $S_4N_3Cl$ (1.6 g, 7.8 mmol) at −15 °C in MeCN (40 $cm^3$). Reaction was slow and by the end of the addition the acetonitrile solution had turned pale orange-yellow. The mixture was stirred for 16 h at r.t. and filtered giving a slightly green-yellow powdery solid and a dark reddish brown filtrate.

Both the solid (1.04 g) and filtrate contained (0.56 g) $S_4N_4$ as the major product (i.r.).

(6) $S_2Cl_2$ *with a large excess of* $SiMe_3N_3$ *in* MeCN. A solution of $S_2Cl_2$ (1.65 g, 12.2 mmol) in MeCN (10 $cm^3$) was added (1 h) to a vigorously stirred solution of $SiMe_3N_3$ (11.5 g, 100 mmol) in MeCN (30 $cm^3$) at −12 °C. Within 10 min the mixture became blue-black and by the end of the addition a blue-black powder was clearly visible. The mixture was stirred for 1 h and filtered giving a blue-black solid and a pale red-brown solution.

The blue-black solid (1.32 g) was slightly sticky after attempted drying and contained peaks in the i.r. spectrum, attributable to $S_3N_2Cl$, $S_4N_3Cl$, $S_4N_4$, and $(SN)_x$ in addition to a small peak at 760 $cm^{-1}$. About 0.6 g of the solid could be extracted with $CS_2$ (10 × 10 $cm^3$). The residual blue-black solid gave a poorly resolved i.r. spectrum.

The solid (50 mg) obtained by removal of solvent from the filtrate contained $S_4N_4$ and $\mathrm{Me}\overline{\mathrm{CNSSN}}{}^{+}\mathrm{Cl}^{-}$ [21] (i.r.).

(7) $S_2Cl_2$ *with* $NaN_3$ *in acetonitrile*. A solution of $S_2Cl_2$ (3.3 g, 24.4 mmol) in MeCN (10 $cm^3$) was added (1 h) to a stirred slurry of $NaN_3$ (3.25 g, 50 mmol) in MeCN (50 $cm^3$) at 0 °C. The mixture immediately became orange-yellow, red-brown, dark brown, and finally purple with $N_2$ evolution. The mixture was stirred at r.t. for 1 h and filtered giving a purple powder (A) (4.7 g) and a pale red-brown solution.

The solid was washed with $CS_2$ (10 × 10 $cm^3$) giving a residual solid mixture of $S_3N_2Cl$, NaCl, and $NaN_3$ (3.9 g). Its mass spectrum was consistent with that of an authentic sample of $S_3N_2Cl$ and contained no detectable $S_8$. Its *X*-ray powder photographs contained strong and weak lines due to NaCl and $NaN_3$ respectively and other lines consistent with $S_3N_2Cl$.

Removal of solvent from the original filtrate gave a solid (0.29 g) containing $\mathrm{Me}\overline{\mathrm{CNSSN}}{}^{+}\mathrm{Cl}^{-}$ and a small amount of $S_4N_3Cl$ (i.r.).

*Reaction of the purple solid with* $SiMe_3N_3$ *in* MeCN. A ground sample of the purple solid (A) (1.2 g) was reacted with excess of $SiMe_3N_3$ (1.4 g) in acetonitrile at r.t. for 24 h and was worked up as in reaction (3) to give a blue-black powder. This was washed three times with $CCl_4$, *etc.* as described below in section (10) and dried for 8 h giving $(SN)_x$ (0.25 g). Other similar reactions gave a yield of *ca.* 30% $(SN)_x$.

TABLE 2

Preparations of $(SN)_x$ from $S_2NAsF_6$ and $CsN_3$

| $S_2NAsF_6$ g, mmol | $CsN_3$ g, mmol | $SO_2$/ g | Temperature/ °C | $(SN)_x$/ g |
|---|---|---|---|---|
| 0.45, 1.68 | 0.30, 1.73 | 19.89 | 20 | 0.02 |
| 0.65, 2.43 | 0.42, 2.41 | 23.29 | −20 | 0.12 |
| 0.99, 3.72 | 0.68, 3.87 | 34.57 | −20 | 0.19 |

(8) $S_3N_2Cl$ *with water*. Powdered $S_3N_2Cl$ (0.6 g) was washed with water (3 × 10 $cm^3$; 10 min), MeCN (5 × 15 $cm^3$; 75 min), and dried at $10^{-3}$ Torr for 2 h. The solid became black (0.44 g) and contained considerable amounts of $S_3N_2Cl$ (i.r.). It was re-treated twice in a similar manner giving a blue-black solid (50 mg) containing $(SN)_x$ and $S_4N_4$ (i.r.).

(9) $S_2NAsF_6$ *and* $CsN_3$ *in sulphur dioxide solution*. In a typical reaction $S_2NAsF_6$ (0.48 g, 1.81 mmol) and $CsN_3$ (0.31 g, 1.80 mmol) were placed in two separate bulbs of a reaction vessel that incorporated a Teflon-stemmed glass J. Young valve. The arms connecting the bulbs to the horizontal glass tubing were 135° to one another.

Sulphur dioxide (31.42 g, 490.4 mmol) was condensed in approximately equal amounts onto both solids.† At −20 °C the $CsN_3$ solution was poured onto the $S_2NAsF_6$ solution. Immediately a dark blue precipitate formed in the now dark red solution. After 15 min the reaction was allowed to warm to r.t. and the $SO_2$ and $N_2$ (0.06 g, 2.02 mmol) along with a small amount of an unidentified dark red liquid were removed on pumping. The crude product was thoroughly ground and purified as described below (10). The solubles (0.63 g) contained $CsAsF_6$ and $S_4N_4$ (i.r.). The dark blue insoluble material (0.14 g) was identified as $(SN)_x$ (i.r.). An unidentified impurity was also present, with very weak bands at 1 170, 965, and 451 $cm^{-1}$. An *X*-ray powder photograph contained lines attributable to $(SN)_x$ and some lines possibly attributable to traces of $S_4N_4$. Table 2 gives a summary of similar reactions.

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* Throughout this paper: 1 Torr = (101 325)/760 Pa.

† **CAUTION:** The $CsN_3$ must be frozen down to −196 °C before any $SO_2$ is introduced into the vessel as it will ignite in the presence of $SO_2$ vapours at room temperature.

(10) *Purity and purification of* $(SN)_x$ *samples.* Analysis of samples of $(SN)_x$ prepared from $S_3N_3Cl_3$, $S_3N_2Cl_2$, $S_3N_2Cl$, and $SiMe_3N_3$ were similar to those for (*a*) in Table 3. Results for a sample prepared from $S_3N_3Cl_3$ and $NaN_3$, treated with water, were not as good (Table 3). Samples prepared from compounds containing sulphur and chlorine contained small amounts of $S_4N_4$, $S_8$, $NH_4Cl$, and sulphur–nitrogen chlorides (*e.g.* $S_3N_2Cl$) as indicated by *X*-ray powder photography, i.r., and mass spectroscopy. The sulphur–nitrogen chloride impurities were removed by treating the finely powdered mixture with an excess of $SiMe_3N_3$ in MeCN for 2—3 d with stirring at r.t.; $S_4N_4$ and $S_8$, by washing with $CCl_4$ and $CS_2$ repeatedly; and $NH_4Cl$ (and other ionic salts) by washing with formic acid (7 × 10 cm$^3$) over a sintered-glass frit, each time with shaking (5 min per wash). This treatment was followed by washing with MeCN (5 × 10 cm$^3$, 1 h), $CS_2$ (5 × 10 cm$^3$, 2 h), and drying ($10^{-3}$ Torr, 8—10 h). A typical sample (0.75 g) lost weight (to 0.65 g) and contained no $NH_4Cl$ (*X*-ray powder photograph, i.r.). Elemental analyses are given in Table 3(*c*) and (*d*). Samples prepared from $S_2Cl_2$ with $NaN_3$ and $SiMe_3N_3$, and $S_2NAsF_6$ with $CsN_3$, both followed by washing as above were markedly less pure (Found: N, 21.5; S, 63.5, and N, 17.3; S, 69.5%, respectively).

TABLE 3

Analytical data [a] for $(SN)_x$ samples

| Source of sample | Analysis (%) S | N | Cl | C | H | Total |
|---|---|---|---|---|---|---|
| (*a*) $S_3N_3Cl_3$ + $SiMe_3N_3$ [b] | 68.0 | 25.0 | 4.2 | 1.1 | 0.35 | 98.6 |
| (*b*) $S_3N_3Cl_3$ + $NaN_3$ [b] + water treatment | 60.9 | 26.3 | 1.4 | | | 88.6 |
| (*c*) $S_3N_2Cl_2$ + $SiMe_3N_3$ + washed with formic acid for 15 min | 68.0 | 26.8 | 2.8 | 0.7 | | 98.3 |
| (*d*) $S_3N_3Cl_3$ [c] + $SiMe_3N_3$ + washed with formic acid for 30 min | 69.5 | 29.7 | | 1.0 | 0.0 | 101.2 [d] |
| Theoretical | 69.6 | 30.4 | | | | 100 |

[a] All analyses were at least duplicate, the second determination very clearly in agreement with that quoted. [b] No purification. [c] Material carefully recrystallised from $CCl_4$. [d] Si 0.15%.

*Characterisation of* $(SN)_x$ *samples.* Materials obtained from preparations (2)—(4) and (7) and purified as above produced powders that gave essentially identical *X*-ray powder photographs and were consistent with those obtained from the monoclinic [8] ($P2_1/c$) form of $(SN)_x$ and are compared in Table 4. Long exposure times were needed to obtain photographs, indicative of the low crystallinity of the solids.

TABLE 4

*X*-Ray powder diffraction data for $(SN)_x$ ($d_{hkl}$ values in Å)

| Mikulski *et al.*[8,a] | Present work [b] |
|---|---|
| | 4.53w? |
| 3.93s | |
| | 3.77s [c] |
| 3.59s | |
| 3.26vs | |
| | 3.26vs |
| 2.94s | |
| | 2.88s [c] |
| 2.81s | |
| 2.30w–m | 2.31w |
| 2.22w–m | 2.20w |
| 2.12w | 2.125vw |
| 2.04w | |

[a] These results have been confirmed by Banister and Hauptman,[22] and are in agreement with those given by M. Goehring and D. Voigt, *Z. Anorg. Allg. Chem.*, 1956, **285**, 181. [b] Uncorrected for film shrinkage as no back reflections resolved. All lines rather diffuse. [c] Probably two unresolved lines.

I.r. spectra of samples obtained from preparations (1)—(5) and (7) were essentially identical and in agreement with other reported i.r. spectra of $(SN)_x$ (see Table 5). The most satisfactory spectra were obtained for materials from preparations (2)—(4). Mass spectra of powdered $(SN)_x$ [preparations (2)—(4)] were also consistent with reported spectra (Table 6). Peaks attributable to $S_8$ and $S_4N_4$ are more pronounced in our spectra indicating that they are present as impurities in the sample, or are given on heating and/or evacuation of the sample.

On compression in a 1-in diameter pressing die to a pressure of 4.2 GPa, the powder formed a mechanically strong electrically conducting disc with the colour of a new copper coin. The disc tarnished on standing and, in general, our material appears to be more reactive and prone to decomposition than $(SN)_x$ prepared by conventional means.[22] The blue-black $(SN)_x$ powder gave golden flakes when ground by an agate pestle and mortar. These flakes had smooth surfaces as shown by scanning electron micrographs (magnification × 3 000) and samples did not have to be coated with gold prior to examination (*i.e.* the surfaces were conducting). The flakes also appeared dark under high current (at 30 kV). The conductivity of the hand-compacted powder, as measured by the von Hippel method [23] of determining dielectric properties at microwave frequencies, was 0.94 $\Omega^{-1}$ m$^{-1}$ (at 11.56 GHz). The powder was sublimed under high vacuum to give blue transparent $(SN)_x$ films which aquired an intense bronze colour on thickening.[22]

(11) *Attempts to prepare selenium–nitrogen compounds.* (*a*) *Reaction of* $Se_2Cl_2$ *with* $SiMe_3N_3$ *in* MeCN. Liquid diselenium dichloride (2.75 g, 12.0 mmol) was added (1 h) to a stirring solution of $SiMe_3N_3$ (2.85 g, 2.47 mmol) in MeCN (25 cm$^3$) at r.t. Colour changes (red-brown, black-red) occurred with brisk evolution of nitrogen accompanying an exothermic reaction. On addition of the last few drops of $Se_2Cl_2$ the mixture became brown-black. The mixture was stirred (6 h) and filtered giving a purple-black powder (2.2 g) and a deep orange filtrate. I.r. spectrum of the dried black solid (Nujol mull): 830s, 820w (sh), 790vw, 765vw, 730w (br), 590m, 575m, 560s, and 510w (br) cm$^{-1}$. **CAUTION:** The compound seemed to be fairly stable in air but exploded at *ca.* 100 °C in the mass spectrometer. The black solid was insoluble in $CS_2$, and on digestion in nitric acid a faint precipitate was given on addition of $AgNO_3$.

(*b*) *Reaction of* $Se_2Cl_2$ *with* $SiMe_3N_3$ *in* $CH_2Cl_2$. Liquid diselenium dichloride (2.75 g, 12.0 mmol) was added (1 h) to a stirred solution of $SiMe_3N_3$ in $CH_2Cl_2$ (25 cm$^3$) (2.85 g, 24.7 mmol) at r.t. Evolution of nitrogen was slow with colour changes, clear orange, yellow-red, red-brown, and finally a small amount of a black powder was formed. The reaction did not appear to be exothermic. The reaction mixture was refluxed for 5 h, stirred overnight at r.t., and

TABLE 5

Infrared spectral data (cm$^{-1}$) of powdered $(SN)_x$ and $(SN)_x$ samples obtained by earlier workers

| Macklin *et al.* [a,b] | Iqbal and Downs [c,d] | [e] | Powdered $(SN)_x$ [f] |
|---|---|---|---|
| 1 001 | 995s | 1 004m | 1 015m |
| 918vw (br) | | | |
| 812 | | | 765—850vw (vbr) |
| 768 | | | |
| 689 | 695s | 696s | 695s |
| 662 (sh) | | | |
| 629 | | 630w | 625w |
| 590 (sh) | | | |
| 560 (sh) | | | |
| 500 | | 509w | 505w |

[a] J. W. Macklin, G. B. Street, and W. D. Gill, *J. Chem. Phys.*, 1979, **70**, 2425. [b] Spectra of an $(SN)_x$ thin film deposited on a CsI window. [c] Spectra of $(SN)_x$ film deposited on a KBr window. [d] Z. Iqbal and D. S. Downs, *Chem. Phys.*, 1979, **44**, 137. [e] Main peaks of the i.r. of $(SN)_x$ in a Nujol–CsCl mull between CsI plates.[22] [f] Nujol mull using KBr plates, this work.

TABLE 6

Mass spectra of powdered $(SN)_x$

| *m/e* | Ion [a] | Powdered $(SN)_x$ 70 eV, 120 °C | Powdered $(SN)_x$ 25 eV, 120 °C | $(SN)_x$, Smith *et al.* [c] 25 eV, 140 °C | $(SN)_x$, Smith and Street [d] 25 eV, 95 °C |
|---|---|---|---|---|---|
| 46 | $NS^+$ | 100 [b] | 100 | 100 | 100 |
| 64 | $S_2^+$ | 16 | 17 | 4.3 | 3.5 |
| 78 | $S_2N^+$ | 37 | 28 | 19 | 14 |
| 92 | $S_2N_2^+$ | 36 | 33 | 60 | 43 |
| 96 | $S_3^+$ | 2.5 | 3 | | |
| 110 | $S_3N^+$ | 8 | 7 | 0.6 | 0.7 |
| 124 | $S_3N_2^+$ | 5 | 5 | 3.0 | 2.7 |
| 128 | $S_4^+$ | 2 | 3 | | |
| 138 | $S_3N_3^+$ | 48 | 36 | 63 | 51 |
| 156 | $S_4N_2^+$ | 10 | 8.5 | 0.2 | 1 |
| 160 | $S_5^+$ | 3 | 3 | | |
| 184 | $S_4N_4^+$ | 9.5 | 4.5 | 0.2 | 0.8 |
| 192 | $S_6^+$ | 2 | 2 | | |
| 224 | $S_7^+$ | 1 | 1 | | |
| 256 | $S_8^+$ | 1 | 2 | | |

[a] $N^{14}$, $S^{32}$ peaks only reported. [b] Percentage intensity. [c] R. D. Smith, J. R. Wyatt, J. J. DeCorpo, F. E. Saalfeld, M. J. Morgan, and A. G. MacDiarmid, *J. Am. Chem. Soc.*, 1977, **99**, 1726. [d] R. D. Smith and G. B. Street, *Inorg. Chem.*, 1978, **17**, 938.

filtered to obtain a black powder (>1 g) and a pale red-brown filtrate.

The black solid was washed with $CH_2Cl_2$ (2 × 10 cm$^3$) and dried ($10^{-3}$ Torr) for 9 h at r.t. **CAUTION:** The material exploded violently when touched with a nickel spatula.

(*c*) *Reaction of* $SeBr_4$ *with* $SiMe_3N_3$ *in* MeCN. A solution of $SeBr_4$ (1.6 g, 4.0 mmol) in MeCN (50 cm$^3$) was added (2 h) to a stirred solution of $SiMe_3N_3$ (2.30 g, 20.0 mmol) in MeCN (20 cm$^3$) at −5 °C. Reaction was immediate, and a pink colour was observed which intensified with continued addition. At r.t. the mixture became clear dark red-brown, $N_2$ was given off, and a black precipitate was formed. The mixture was stirred at r.t. for 24 h and filtered giving a small amount of black powder and a pale yellow solution. The black powder gave an i.r. spectrum with peaks at 815s, 790w, 572s, and 545m cm$^{-1}$. The Nujol mull of the compound had the same blue-black colour of $(SN)_x$. Exposure of the sample on KBr plates to air for several minutes did not change the spectrum. **CAUTION:** The black solid exploded violently within 1 min at 0 °C.

## RESULTS AND DISCUSSION

*The Preparation of* $(SN)_x$ *from* $S_3N_3Cl_3$, $S_3N_2Cl_2$, *and* $S_3N_2Cl$.—Poly(sulphur nitride) is formed in up to 70% yield according to equation (i) by the slow addition of an excess of $SiMe_3N_3$ in MeCN to a vigorously stirred solution of $S_3N_3Cl_3$ in MeCN at −15 °C (see Table 1 for examples of this and other reactions). Tetrasulphur tetranitride is a minor product (*ca.* 20% yield) but is the major product when the mode of addition is reversed, or the temperature is raised. The polymer is also formed in about 50% yield by the addition of a solution of $S_3N_3Cl_3$ to an excess of a slurry of $NaN_3$ in MeCN at −15 °C. At room temperature a similar reaction gave mainly $S_4N_4$ and a small quantity of the known $Na^+S_4N_5^-$ presumably by reaction of $NaN_3$ and $S_4N_4$.[24] Addition of $NaN_3$ to $S_3N_3Cl_3$ solution gave a solid mixture containing $S_3N_2Cl$ and $\mathrm{Me\overline{CNSSN}^+Cl^-}$.[21]

$$S_3N_3Cl_3 + 3SiMe_3N_3 \longrightarrow \frac{9}{2}N_2 + 3SiMe_3Cl + \frac{3}{x}(SN)_x \quad \text{(i)}$$

The colour of the $SiMe_3N_3$ and $S_3N_3Cl_3$ mixtures became green and red-brown during reaction and it was surmised that $S_3N_2Cl$ (green) and $S_3N_2Cl_2$ (red-brown) might be reaction intermediates. The compound $S_3N_2Cl$ was observed as a product of the reaction of $SiMe_3N_3$ and $S_3N_3Cl_3$ in $CH_2Cl_2$ solvent. Therefore an excess of $SiMe_3N_3$ was added to slurries of $S_3N_2Cl_2$ and $S_3N_2Cl$ in MeCN at −15 °C yielding poly(sulphur nitride) in 60 and 75% yield respectively according to equations (ii) and (iii), with $S_4N_4$ as the minor product. A mixture containing $S_3N_2Cl$ also yielded polymer according to equation (iii) at 25 °C. An analogous reaction with $S_4N_3Cl$ gave $S_4N_4$ in high yield.

$$S_3N_2Cl_2 + 2SiMe_3N_3 \longrightarrow \frac{3}{x}(SN)_x + \frac{5}{2}N_2 + 2SiMe_3Cl \quad \text{(ii)}$$

$$S_3N_2Cl + SiMe_3N_3 \longrightarrow \frac{3}{x}(SN)_x + N_2 + SiMe_3Cl \quad \text{(iii)}$$

The nature of the solvent was critical for $(SN)_x$ synthesis and the polymer was only formed in acetonitrile. Reactions of $S_3N_3Cl_3$ and $SiMe_3N_3$ under analogous conditions in tetrahydrofuran (thf) and $CH_2Cl_2$

gave $S_4N_4 + S_4N_3Cl$, and $S_3N_2Cl + S_4N_4$ respectively, with no sign of $(SN)_x$ in either reaction (Table 1). When very pure acetonitrile was used the yield of $S_4N_4$ increased. It is possible that an impurity in the acetonitrile (*e.g.* water) may play a role in polymer formation as has been suggested for the solution synthesis of $(SNI_x)_n$.[25]

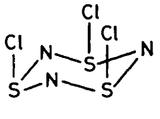
The compounds $S_3N_3Cl_3$, $S_3N_2Cl_2$, and $S_3N_2Cl$ may react in stepwise fashion with $SiMe_3N_3$, according to equations (iv)—(vii). Both $S_3N_3Cl_3$ (I)[26] and $S_3N_2Cl_2$ (II)[27] have been reported to react with reducing agents to give $S_3N_2Cl$[28,29] [which may have the structure (III)[30,31]] and therefore reaction (v) may be relatively fast.

$$S_3N_3Cl_3 + SiMe_3N_3 \longrightarrow S_3N_2Cl_2 + 2N_2 + SiMe_3Cl \quad \text{(iv)}$$

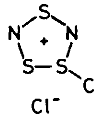
$$S_3N_2Cl_2 + SiMe_3N_3 \longrightarrow S_3N_2Cl + SiMe_3Cl + \frac{3}{2}N_2 \quad \text{(v)}$$

$$S_3N_2Cl + SiMe_3N_3 \longrightarrow \text{'}S_3N_2N_3\text{'} + SiMe_3Cl \quad \text{(vi)}$$

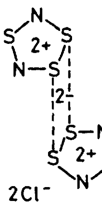
$$\begin{tikzcd} \text{'}S_3N_2N_3\text{'} \arrow[r] \arrow[rr, bend right, "\text{or}"'] & \text{'}S_3N_3\text{'} + N_2 \arrow[r] & \frac{3}{x}(SN)_x + N_2 \quad \text{(vii)} \end{tikzcd}$$



(I)



(II)



(III)

Clearly, the pathway suggested above is only tentative (N.B. ref. 12, page 10).

Previous applications of azides in the synthesis of sulphur-nitrogen compounds include the synthesis of salts of $S_3N_3^-$ and $S_4N_5^-$.[32]

Blue-black conducting poly(sulphur nitride) prepared according to equations (i)—(iii) and treated with various solvents gave similar i.r., mass spectra, and *X*-ray powder diffraction patterns (Tables 4—6). The purest polymer sample we prepared, as judged by elemental analyses [Table 3(*d*)], was obtained from $S_3N_3Cl_3$ that had been carefully recrystallised from $CCl_4$, and excess of $SiMe_3N_3$, followed by purification with various solvents and prolonged washing with formic acid. The purity of this sample may be due to high purity of the starting material, or the extended treatment with formic acid, or both. The polymer prepared by these routes was more reactive (air, moisture) and less thermally stable than conventionally prepared $(SN)_x$, perhaps due to our polymer having a shorter chain length. The fibrous nature of $(SN)_x$,[1-4] the greater reactivity of our material, and the fact that it is prepared in solution and washed with various solvents may account for its purity being less than 100%.

In an attempt to prepare $(SN)_x$ from readily available starting materials, $S_2Cl_2$ was treated with a large excess of $SiMe_3N_3$ in acetonitrile solution at $-12$ °C yielding a mixture containing the blue-black polymer $(SN)_x$ as well as $S_3N_2Cl$, $S_4N_3Cl$, $S_4N_4$, and $Me\overline{CNSSN}^{+}Cl^{-}$[21] in the filtrate. It has been reported[33] that $LiN_3$ and $S_2Cl_2$ in $C_6H_6$, $CCl_4$, or $CH_2Cl_2$ gave $S_4N_3Cl$ at r.t. and $S_4N_3Cl$ and $S_4N_4$ at 0 °C. We were unable to duplicate this result, and find it surprising in view of the low solubility of $S_4N_3Cl$ in non-polar solvents.[16] Fehér and Junkes[34] have reported that $S_xCl_2$ ($x = 2, 3,$ *etc.*) react with $LiN_3$ in polar solvents giving $S_7NH$ and small quantities of the three isomers of $S_6(NH)_2$, suggesting hydrolysis of the products and/or some reaction with the unspecified solvent. One other reference (35) is wrongly quoted in ref. 36 which, however, describes the preparation of $S_4N_4$ by the reaction of $S_4N_3Cl$ with $Al(N_3)_3$ in tetrahydrofuran. We have found that a solid mixture of $S_3N_2Cl$, NaCl, and $NaN_3$ is obtained on addition of $S_2Cl_2$ to a slurry of $NaN_3$ in MeCN at 0 °C. It has been shown above that $S_3N_2Cl$ can be converted into $(SN)_x$ by reaction with $SiMe_3N_3$. The mixture containing $S_3N_2Cl$ was therefore treated with an excess of $SiMe_3N_3$ in acetonitrile, and on purification gave a somewhat impure $(SN)_x$ in *ca.* 30% yield. The purity of this material was not high (elemental analyses), although it gave *X*-ray powder photographs and i.r. spectra that were very similar to those obtained from $S_3N_3Cl_3$, $S_3N_2Cl_2$, and $S_3N_2Cl$ and excess of $SiMe_3N_3$ and could also be ground into golden flakes. Interestingly, the polymer was also formed on fast washing of the $S_3N_2Cl$–$NaN_3$–NaCl mixture with water, and in small amounts by the reaction of $S_3N_2Cl$ and water. The former material gave good i.r. spectra and *X*-ray powder diffraction photographs for $(SN)_x$ on purification.

The preparation of $(SN)_x$ by these routes is no more difficult than the traditional $S_4N_4$ synthesis.[37]

Recently, a synthesis of $S_2NAsF_6$ in good yield has been described.[19] It reacts in $SO_2$ solution with $CsN_3$ to give impure $(SN)_x$ and $S_4N_4$ according to equation (viii). The yield of $(SN)_x$ is dependent upon reaction conditions, lower temperature and dilute solutions favouring $(SN)_x$ rather than $S_4N_4$ (see Table 2). In the reaction described in full, a recovered yield of 86% impure $(SN)_x$ was obtained. The reaction may proceed *via* an open-chain form of $S_2N_2$ which may polymerise to $(SN)_x$.

$$S_2NAsF_6 + CsN_3 \longrightarrow \frac{2}{x}(SN)_x + N_2 + CsAsF_6 \quad \text{(viii)}$$

With a view to exploiting the generality of the synthetic routes described above, preliminary reactions of $Se_2Cl_2$ and $SeBr_4$ with $SiMe_3N_3$ were carried out in the hope of preparing analogous selenium–nitrogen compounds, including $(SeN)_x$ hitherto unprepared except for $Se_4N_4$.[38,39] Blue-black explosive solids were obtained, the i.r. spectra of which were not inconsistent with the formation of selenium–nitrogen compounds, if not $(SeN)_x$. The explosive nature of the products led us to abandon this line of inquiry. Selenium tetrachloride and $SiMe_3N_3$

in $CH_2Cl_2$ have been reported[40] to give $Se_2Cl_2$ and selenium subchlorides.

We are very much indebted to Drs. Z. V. Hauptman and A. J. Banister (Durham University) for i.r. spectra and *X*-ray powder diffraction photographs of their $(SN)_x$ and our material, for various examinations of our $(SN)_x$ [*e.g.* sublimation of $(SN)_x$, compression into a disc], and for encouragement and helpful suggestions and discussions. We also thank Mr. R. Coult (Durham University) for analyses, Mr. G. N. Bance for scanning electron micrographs of $(SN)_x$, Dr. J. Tranquilla for the conductivity results (both of U.N.B.), and N.S.E.R.C. and N.A.T.O. (travel grant, to J. P.) for financial assistance.

*Notes added in proof.* (*i*) The preparation of $(SN)_x$ according to equation (i), in a closed system under anhydrous conditions, using very pure $S_3N_3Cl_3$, led to a crude product containing much smaller amounts of impurities (*e.g.* free from $S_8$ and $NH_4Cl$) than that described in section (2) of the Experimental section. Impurities (*e.g.* $S_4N_4$) were removed by continuously washing the mixture with liquid $SO_2$ in a refluxing system. On sublimation stable golden conducting eggs were obtained (A. J. Banister, Z. V. Hauptman, and J. Passmore, unpublished work). (*ii*) $(SN)_x$ has been shown to be formed by the slow decomposition of $S_4N_2$ (R. W. H. Small, A. J. Banister, and Z. V. Hauptman, *J. Chem. Soc., Dalton Trans.*, 1981, 2188).

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