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Synthesis and Structure of Metallic Polymeric Sulfur Nitride, (SN)$_x$, and Its Precursor, Disulfur Dinitride, S_2N_2

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Abstract: The synthesis of analytically pure single crystals, suitable for solid state studies, of the covalent, polymeric, metallic conductor, polymeric sulfur nitride, (SN)$_x$ (polythiazyl), is described. The (SN)$_x$ crystals were obtained by slowly growing crystals of S_2N_2 at 0° from the vapor phase during 48 hr followed by room temperature solid state polymerization over a period of 60 hr. Polymerization was completed by heating at 75° for 2 hr. The initially colorless tabular monoclinic crystals of S_2N_2 turned at first dark blue-black and became paramagnetic ($g = 2.005$) and then finally changed to lustrous golden, diamagnetic crystals which were pseudomorphs of, and had the same space group ($P2_{1/C}$) as, the S_2N_2 crystals from which they were derived. The (SN)$_x$ crystals are composed of an ordered array of parallel (SN)$_x$ fibers which consist of an almost planar chain of alternating sulfur and nitrogen atoms. The cell constants are $a = 4.153$ (6) Å, $b = 4.439$ (5) Å, $c = 7.637$ (12) Å and $\beta = 109.7$ (1)° with $\rho_c = 2.30$ g/cm^3 for four SN units per unit cell. The refined structure ($R = 0.11$) shows nearly equal S-N bond lengths, 1.593 (5) and 1.628 (7) Å. The S-N-S angle is 119.9 (4) and the N-S-N angle is 1.2 (2)°. Crystals of (SN)$_x$ show little reactivity toward oxygen or water at room temperature. In order to attempt to understand the solid state polymerization of S_2N_2 to (SN)$_x$, a single-crystal X-ray structural study of S_2N_2 was performed at −130°. Disulfur dinitride, S_2N_2, has the cell constants ($R = 0.03$) $a = 4.485$ (2) Å, $b = 3.767$ (1) Å, $c = 8.452$ (3) Å, and $\beta = 106.43$ (4)° with $\rho_c = 2.23$ g/cm^3 with two S_2N_2 molecules per unit cell. The molecule is square planar with essentially equal S-N bond lengths (1.657 (1) and 1.651 (1) Å). The S-N-S angle is 90.4 (1)° and the N-S-N angle is 89.6 (1)°. The mode of polymerization of S_2N_2, the nature of the bonding in (SN)$_x$, and a possible source of the metallic conduction band are discussed.

The study of organic metals and inorganic conductors whose electronic properties are quasi-one-dimensional has become a subject of broad interest.[2] Solids such as the organic charge transfer salts NMP-TCNQ[3] (*N*-methylphenazinium-7,7,8,8-tetracyanoquinodimethan), TTF-TCNQ[3] (tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethan), and the mixed valence platinum salt $K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O$[4] are experimental systems that exhibit a rich variety of many-body instabilities associated with their quasi-one-dimensionality.

The phenomena and concepts discovered and developed in the organic metals can be carried over directly to other potentially conducting solids such as polymers. Using specific chemical methods, whole new classes of materials might be anticipated that exhibit exciting electronic or magnetic properties.[2]

Of fundamental importance to attaining the metallic state is the presence of unpaired electrons in the primary molecular units.[2,5] In the case of the polymeric solid, polythiazyl, (SN)$_x$, commonly known as polymeric sulfur nitride, a single polymer chain can be considered schematically as a collection of covalently bonded monomeric NS free radicals each of which is the sulfur analog of NO. The NS molecule, like NO, contains an unpaired electron in the lowest occupied π^*-antibonding molecular level. In principle ina polymer of this type this π^* level may form the basis of the metallic conduction band.

Recently, (SN)$_x$ has been proposed as another example of a quasi-one-dimensional metal.[6] Labes et al.[6] prepared (SN)$_x$ *directly from the vapor phase* by passing S_4N_4 vapor over silver wool at 200° and allowed the resulting vapor to impinge upon a cold finger at 8°. Shiny bronze-colored crystalline bundles of (SN)$_x$ fibers formed directly on the cold finger during 4 hr. The resulting (SN)$_x$ material contained impurities ranging from 1.3 to 5.5%. Measurements of the dc electrical conductivity gave room temperature values ranging from (0.01 to 1.7) × 10^3 (Ω cm)$^{-1}$ and a negative temperature coefficient suggestive of metallic behavior. For comparison, the room temperature conductivity of a metal such as mercury is 10.4 × 10^3 (Ω cm)$^{-1}$.[7] How-

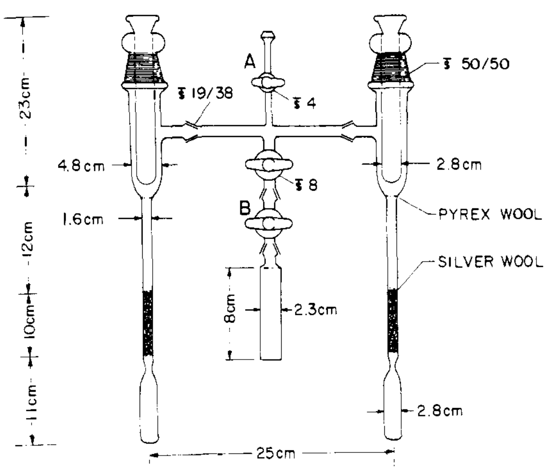


Figure 1. Apparatus for synthesis of $(SN)_x$ crystals.

ever, there are numerous examples directly demonstrating that the intrinsic electronic properties of anisotropic solids are extremely sensitive to impurities and defects. Therefore, a principal concern with $(SN)_x$ is that although the material was prepared as early as 1910 by Burt,[8] and studied occasionally over the years notably by Goehring[9] and by Labes,[10] no suitable method of preparation has been found to date which provides good yields and analytically pure crystalline material suitable for solid state studies.

In earlier communications[11] we have reported briefly on the synthesis of analytically pure crystalline $(SN)_x$, its structure, and visible optical reflectance. In this study, we present in detail a convenient method for reproducibly preparing in high yield crystalline $(SN)_x$ in analytically pure form by the solid state polymerization of S_2N_2. In addition, we report the results of the first single-crystal X-ray study of the molecular chain structure of $(SN)_x$ and of its precursor, S_2N_2.

Experimental Section

Apparatus. The apparatus shown in Figure 1 was constructed from Pyrex glass and was attached to a standard vacuum system equipped with a mechanical oil pump and mercury vapor diffusion pump. A detachable trap cooled in liquid nitrogen was inserted between the apparatus and the vacuum system so that any volatile condensible material escaping from the rctors during the experiment could be collected and weighed. Pressure in the system was monitored by means of a Hastings Vacuum Gauge Model VT-5B detector in conjunction with a DV-5M tube. EPR spectra were recorded with a Varian Model V4502 X-band spectrometer and gas-phase mass spectra were measured by means of a Hitachi Perkin-Elmer RMV-6 mass spectrometer. Infrared spectra were measured by means of a Perkin-Elmer Model 521 grating spectrophotometer.

Reagents. Sulfur nitride, S_4N_4, was prepared from S_2Cl_2 and ammonia,[12] purified by recrystallization from $CHCl_3$, and pumped for several hours on the vacuum system and then sublimed in vacuo before use. The compound was checked by its infrared spectrum[13] (KBr pellet) and by its melting point (found, 185.5-186°; lit. 178-187°).[14] Silver wool (Fisher Scientific Company) was used as obtained. The temperature of the silver wool was measured by chromel-alumel thermocouples.

Method. In a typical experiment, 0.60 g of S_4N_4 was placed in each of the two reactors shown in Figure 1. Two grams of silver wool were then teased out and placed in each reactor to fill a length of approximately 10 cm. Care was taken to ensure even packing of the wool. Three thermocouples were attached by means of electrical tape to the outside glass surface of the tube at the bottom, middle, and upper portions of the silver wool zone. These were then wrapped with a layer of aluminum foil and two layers of heating tape. Small tufts of Pyrex wool were placed below the cold fingers, as shown in Figure 1, to prevent S_2N_2 or $(SN)_x$ flakes from falling off the cold finger back onto the hot silver wool.

The apparatus was then attached to the vacuum system via the detachable trap and evacuated to $<10^{-4}$ Torr with all stopcocks open to the pump. The heating tapes were turned on so that a temperature of 220° was recorded by the middle thermocouple. The upper and lower thermocouples did not differ by more than ±10° from this temperature. The temperature of the oil baths was then raised to 85 ± 2° with the surface of the oil almost touching the lower portion of the heating tape. The S_4N_4 vapor was pumped through the heated silver wool for approximately 1 hr. The cold fingers were then filled with liquid nitrogen. The material which first collected on the cold fingers was white, but after several hours it usually took on a tan tint possibly depending on minor variations such as the closeness of packing of the silver wool and its temperature, etc.

After the S_2N_2 had collected on the cold fingers for 9 hr, an ice bath was placed around the rectangular trap constructed from square Pyrex glass tubing, and liquid nitrogen was evaporated from the cold fingers with a stream of air. If desired, it is possible to arrange conditions (e.g., using 1 g of silver wool and 0.60 g of S_4N_4 in each reactor, bath temperature 75-80°, silver wool zone temperature ca. 250°, reactor time ca. 12 hr) so that no S_4N_4 remains in the bottom of the apparatus or deposits above the silver wool.

Acetone was then added to each cold finger. By the time the temperature of the acetone had risen to approximately −10° as measured by a low temperature thermometer, the tan color of the deposit on the cold fingers should have faded. It has been suggested[15a] that this color may be due to a form of NS radical[16] or short-chain species which polymerizes on warming. During this warming process a small amount of an unidentified volatile material is liberated. If collected in a trap immersed in liquid nitrogen between the apparatus and the pump, it condenses to give a solid which is orange-tan in color at room temperature. Before continuing with the synthesis, it is desirable to check that all this unidentified material has been removed from the cold finger. This may be done by pumping a small amount of material from the cold finger on to a fresh glass surface in the trap. This solid, upon warming to room temperature, should now consist of colorless S_2N_2, which leaves only a characteristic thin blue film of $(SN)_x$ upon evaporation. At this stage in the synthesis stopcock A was closed and the acetone was removed by a syringe, and the cold fingers were permitted to warm to room temperature. By the time room temperature was reached, the cold fingers were covered with a pale grayish blue deposit composed of white S_2N_2 mixed with a small quantity of blue $(SN)_x$ which began to form as soon as the temperature rose from liquid nitrogen to room temperature. If a red color persists at room temperature it may be due to S_4N_2[9,15] impurity and the experiment should be discontinued since this material appears to interfere with the polymerization of S_2N_2 and will contaminate the $(SN)_x$. If the synthesis is carried out according to the method described none of this impurity should, however, be produced. It has been suggested[15a,17] that S_4N_4 vapor may partly decompose in the silver wool under certain conditions, viz.,

$$S_4N_4 \rightarrow 4S + 2N_2 \qquad (1)$$

and that the sulfur combines with S_2N_2 to give S_4N_2.

$$2S + S_2N_2 \rightarrow S_4N_2 \qquad (2)$$

After 48 hr, during which time ice was replenished as required, stopcock B was closed, the ice bath was removed, and the exterior of the rectangular trap was immediately dried to prevent temperature variations on the surface of the trap due to evaporation of water. Such variations might cause unpolymerized S_2N_2 to sublime from one portion of the trap to another and hence cause imperfections in the crystals. After an additional 60 hr at room temperature during which time any unpolymerized S_2N_2 on the cold fingers was pumped into the detachable trap, the rectangular trap was removed and weighed. The rectangular trap was then pumped for 2 hr at room temperature and reweighed. It was then heated from room temperature to 75° in an oil bath with constant pumping during 1 hr and weighed again. Finally it was heated to 75° for 2 hr with constant pumping and reweighed. At this stage no white deposit of S_2N_2 condensed on the cold glass surface of the rectangular trap after cotton soaked in liquid nitrogen was held to a wall for approximately 1 min while the bottom of the trap was at 75°.

]

Table I. Typical Elemental Analyses of $(SN)_x$ from Different Preparations

	Preparation	% N	% S	% C	% H	% O
Calcd.:		30.41	69.59			
Found	(1)[a–c]	30.56	69.29	0.00	0.00	0.00[d]
	(2)[a,b]	30.43	69.63	0[d]	0[d]	0[d]
	(3)[a,e]	30.20	70.18	–	–	–
	(4)[e]	30.37	69.16	0[f]	0[f]	
	(5)[e]	30.61	69.79	0.00	0.00	–
	(6)[e]	30.56	69.51	0.00	0.00	–
	(7)[c,e]	30.25	70.05	0.00	0.00	–
	(8)[c,e,g]	30.33	69.28	0.00	0.00	–

[a] Analyses from an earlier preparation using a modification of the gas-phase deposition method described by Labes et al.[6] [b] Performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921. [c] Emission spectrographic analyses showed no measurable metal impurities (<5 ppm). [d] Reported as "none or trace". [e] Performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. 11377. [f] Reported as "not detectable". [g] Analyses for a sample of $(SN)_x$ prepared by polymerizing S_2N_2 at room temperature over a period of 6 weeks.

During the initial stages of the heating process, a very thin film of orange-yellow solid (possibly S_4N_4) usually sublimed from the heated portion of the rectangular trap onto the upper cooler walls. This then was pumped away during the remainder of the heating process.

In a typical experiment all the S_4N_4 (1.20 g) was consumed. The per cent by weight of S_4N_4 which appeared in the following forms was as follows: crystalline $(SN)_x$, 57.8; blue $(SN)_x$ flakes on the cold finger, 8.0; material which appeared to consist mainly of S_2N_2 in the detachable cold trap, 0.2; weight loss (presumably S_2N_2) on pumping the rectangular trap at (a) room temperature for 2 hr, 5.3; (b) room temperature to 75° during 1 hr, 2.0; and (c) 75° for 2 hr, 0.2. From the weight gain in the silver wool (0.185 g) it can be calculated that 0.266 g of S_4N_4 (22.2%) was consumed in converting the silver to Ag_2S. A total of 95.7% of the S_4N_4 consumed was accounted for in the above figures.

The resulting lustrous, golden $(SN)_x$ crystals are analytically pure as shown by the elemental analyses given in Table I. When 50-mg samples of $(SN)_x$ were ground with 0.2 ml of $CHCl_3$ no S_4N_4 was extracted.

The infrared spectrum of $(SN)_x$ was measured using a thin film sublimed[11a] onto a sodium chloride window. Principal absorption maxima in the 600–1200 cm^{-1} region were 620–625 (w), 670 (vs), 720–840 (m, broad), and 995 (s) cm^{-1}.

Preliminary chemical studies were carried out on the $(SN)_x$ crystals when they were exposed in the vacuum system to dry oxygen, moist oxygen, degassed distilled water, and when heated *in vacuo*. If they did not change in appearance and if no significant weight change was observed, it was assumed that no reaction occurred.

Results and Discussion

A. Synthesis of $(SN)_x$. The method used in the present study for the synthesis of single crystals of $(SN)_x$ involves first the production of pure S_2N_2; subsequently, single crystals of colorless S_2N_2 are then grown under reproducible experimental conditions. When crystals of appropriate size have been obtained they are permitted to polymerize spontaneously in the solid state at room temperature whereupon they convert to brilliant, highly lustrous golden crystals of $(SN)_x$ which are pseudomorphs of and have the same space group as the S_2N_2 crystals from which they are derived.

It should be stressed that S_2N_2, which is a slightly volatile colorless solid, has been reported to be extremely explosive and sensitive to slight mechanical shock;[9,10,17] however, neither we nor Patton[15] have ever experienced any explosions involving S_2N_2. Whether this is fortuitous or whether it is due to the fact that our material is completely free of organic solvent, as suggested by Patton, is not known. *It is recommended that the synthesis be handled with extreme care and that not more than 1–2 g of S_2N_2 be produced at one time.*

The vapor of S_4N_4 in two separate but identical reactors is passed ver heated silver wool and the resulting S_2N_2 vapor collects on the surface of a cold finger containing liquid nitrogen. The actual catalyst for the conversion is apparently Ag_2S formed at first by the reaction of silver with the S_4N_4 vapor,[15] viz.,

$$8Ag + S_4N_4 \rightarrow 4Ag_2S + 2N_2 \qquad (3)$$

$$S_4N_4(\text{vapor}) \xrightarrow{Ag_2S} 2S_2N_2(\text{vapor}) \qquad (4)$$

After 9 hr the liquid nitrogen cold traps are brought to room temperature, and the S_2N_2 is permitted to sublime slowly from them during a period of 48 hr into the rectangular trap held at 0°. This sublimation step assists in separating the S_2N_2 from any less volatile impurity and also permits the slow growth of good S_2N_2 crystals. The mass spectrum of the vapor of the subliming S_2N_2 shows no fragments higher than m/e 92$[(S_2N_2)^+]$ and contains no fragments inconsistent with those expected for S_2N_2.

A rectangular trap is used for growing the S_2N_2 crystals since it is believed that fewer distortions will be introduced in the S_2N_2 crystals if their (flat) faces grow on a flat rather than on a rounded glass surface.

The crystals of S_2N_2 which first deposit are completely colorless and transparent but soon become silvery and blue-black in color. It is apparent from the above that as the sublimation of S_2N_2 into the rectangular trap at 0° is continued fresh S_2N_2 will be constantly in the process of deposition on the blue-black S_2N_2 crystals.

After standing for 60 hr at room temperature, the golden $(SN)_x$ crystals will have formed, most of which will have fallen to the bottom of the trap. At this stage the $(SN)_x$ crystals will normally contain some unlymerized S_2N_2 which is removed by pumping the rectangular trap at room temperature for 2 hr, then for 1 hr as the temperature is raised from room temperature to 75°, and then finally for 2 hr at 75°. Heating promotes complete polymerization of the S_2N_2. In a typical experiment 0.694 g of golden crystals of $(SN)_x$ was obtained from 1.20 g of S_4N_4. If polymerization is permitted to proceed for 6 wees at room temperature, all the S_2N_2 undergoes polymerization and none is recovered during the above pumping and heating operation.

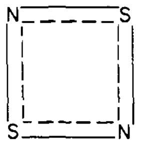
It is interesting to note that polymerization of the S_2N_2 appears to commence at the surface of the crystals. Thus lustrous, bronze, incompletely polymerized crystals can be isolated which visually are identical with $(SN)_x$ and yet give X-ray intensity data and unit cell dimensions identical with pure S_2N_2 crystals from which they are derived.

The criteria used for judging the purity of the $(SN)_x$ are that the crystals should be diamagnetic, show no vapor pressure of S_2N_2 above them at room temperature by mass spectrographic studies, do not have the characteristic iodine-like odor of S_2N_2, and are analytically pure as shown by some typical analyses given in Table I. They are free of S_4N_4[18] and S_2N_2[9a] as evidenced by their X-ray powder diffraction pattern (Table II) and by extraction with chloroform.

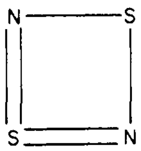
It should be stressed that the method described is most versatile and may be used to synthesize larger or smaller quantities of $(SN)_x$ crystals depending on the length of time S_2N_2 is deposited on the cold fingers in the reactors and on the length of time the S_2N_2 crystals are permitted to grow in the rectangular trap. A typical experiment normally yields several well-faceted single crystals of $(SN)_x$ ranging in size from 0.5 to 1.5 mm; these represent approximately 10% of the total mass. The remainder consists of less perfect crystals and also polycrystalline agglomerates. Crystals up to 3-4 mm in length have been obtained by this method.

The results of a single-crystal X-ray structural study of S_2N_2[19] at −130° provide insight into the ultimate formation of $(SN)_x$. Solid S_2N_2 crystallizes with a monoclinic unit cell ($P2_{1/c}$) with cell constants ($R = 0.03$) $a = 4.485$ (2) Å, $b = 3.767$ (1) Å, $c = 8.452$ (3) Å, and $\beta = 106.43$ (3)°. The S_2N_2 molecular units are flat and square planar (angles S-N-S = 90.42 (6)° and N-S-N = 89.58 (6)°) with essentially equal S-N bond lengths (1.657 (1) and 1.651 (1) Å). The $(SN)_x$ crystals obtained by the remarkable solid state polymerization of S_2N_2 at room temperature are tabular monoclinic pseudomorphs of the original S_2N_2 crystals from which they are derived. Since the density of $(SN)_x$ ($\rho_c = 2.30$ g/cm^3) is greater than that of S_2N_2 ($\rho_c = 2.23$ g/cm^3), the crystals decrease in volume and hence pull away from the glass wall and fall to the bottom of the rectangular trap as noted above. As polymerization proceeds the colorless diamagnetic S_2N_2 crystals turn intense blue-black and become paramagnetic giving a weak free radical signal at $g = 2.005$. As the blue-black color fades, the crystals become a metallic golden color and the free radical signal gradually decreases to zero.

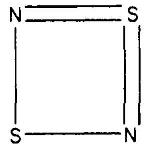
It appears that the planar S_2N_2[20] molecule spontaneously opens to form a radical species which can then link up or attack another S_2N_2 molecule in the solid crystal to give the dark blue-black paramagnetic partly polymerized S_2N_2 and finally $(SN)_x$. The square planar S_2N_2 can be formally represented as



a resonance hybrid of



and



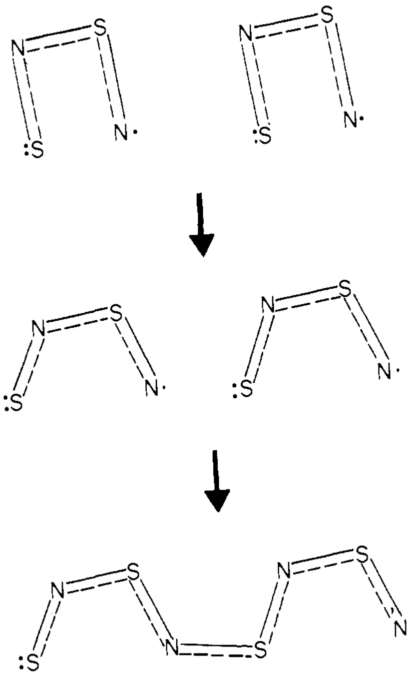
suggesting a bond order of approximately 1.5 for all of the equivalent S-N bonds. The S-N single bond length is expected to be approximately 1.74 Å[21] and that for the S-N double bond is approximately 1.54 Å.[21] Their average, 1.64 Å, expected for a bond order of ca. 1.5 is remarkably close to that found experimentally (1.654 Å).[19] Solid state polymerization of the S_2N_2 can be depicted diagrammatically as shown in Scheme I. According to this scheme, polymerization would be expected to be a relatively facile rearrangement involving principally a widening of the bond angles.

Table II. X-Ray Powder Diffraction Data for $(SN)_x$[a]

This study[b]		Goehring, et al.[c]
d spacings (A)	2θ, deg [Cu Kα]	2θ, deg [Cu Kα]
3.93	22.6 (s)	23.7 (s)
3.59	24.7 (s)	27.2 (vs)
3.26	27.3 (vs)	28.0[e] (vs)
2.94	30.3 (s)	31.1 (s)
2.81	31.8 (s)	38.9 (w)
2.30	39.1[d] (w−m)	39.1 (w)
2.22	40.6 (w−m)	40.8 (m)
2.12	42.6 (w)	42.6 (w)
2.04	44.3 (w)	44.3 (w)

[a] Abbreviations: s = strong; m = medium; w = weak; v = very. [b] Less prominent bands were observed but not tabulated. [c] Reference 9a. [d] Broad (may be two lines). [e] This band was absent in all samples examined in the present study. It is assumed to be due to an impurity.

Scheme I



B. Properties of $(SN)_x$. The $(SN)_x$ crystals consist of an ordered array of $(SN)_x$ fibers, each of which is a single crystal of $(SN)_x$, stacked parallel to one another. Scanning electron micrographs of an $(SN)_x$ crystal are shown in Figure 2. The face of the crystal depicted in Figure 2a is fairly smooth. The faces of less perfect crystals are often strongly striated causing light to be scattered at certain incident angles so that they appear almost black; at other incident angles, the crystal face appears a brilliant lustrous golden color. In Figure 2b an electron micrograph of a face, an edge, and an end of an $(SN)_x$ crystal is shown, and in Figure 2c the end is shown at a higher magnification. The ends of an $(SN)_x$ crystal always appear black due to both extensive scattering from the fiber ends and because there is no component of the incident radiation which is parallel to the $(SN)_x$ fibers on such a surface.

As pointed out previously, the optical[11a,22,23] and electronic properties[6,24,25] of a crystal of $(SN)_x$ are highly anisotropic with metallic behavior observed in the direction parallel to the $(SN)_x$ fiber axis. The $(SN)_x$ single crystals obtained by this method show dc conductivities as high as 2.5×10^3 $(\Omega\ \text{cm})^{-1}$ at room temperature. The conductivity increases approximately 225 times on lowering the temperature to 10 K.[24] Optical studies on single crystals and fully oriented epitaxial films indicate significant anisotropy.[23] However, in contrast to the quasi-one-dimensional organic metals, the optical properties in the transverse direction also have features characteristic of a (poor) metal. This is consistent with the fact that heat capacity studies[25] imply that $(SN)_x$ remains metallic at low temperatures and with the observation of superconductivity in $(SN)_x$ at 0.26 K.[25]

The $(SN)_x$ crystals are soft and malleable when compressed in a direction perpendicular to the fibers and may be flattened into thin golden sheets. Although $(SN)_x$ has shown no evidence of being explosive under normal conditions, small explosions have occurred on occasions when compressed. Good crystals of $(SN)_x$ may also be cleaved

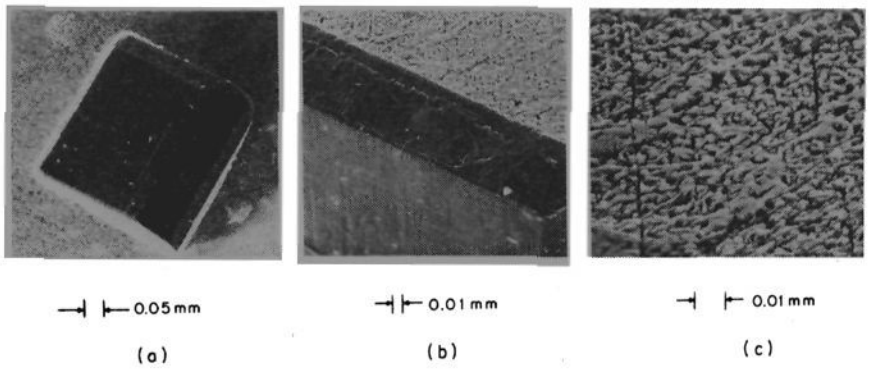


Figure 2. Scanning electron micrographs of a crystal of $(SN)_x$: (a) a face; (b) the face, the upper right hand edge and the end (not visible in (a)); (c) the end shown in (b) showing clearly the $(SN)_x$ fiber ends.

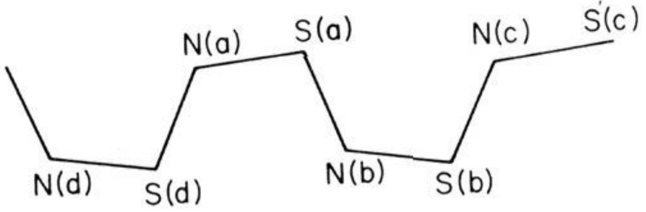


Figure 3. Diagrammatic representation of a single $(SN)_x$ chain from single-crystal X-ray diffraction studies.

Table III. Intramolecular Distances (Å) and Bond Angles (deg) in a $(SN)_x$ Chain Distance[a]

Atoms	X-Ray[b]	Electron diffraction[c]
S(a)–N(a)	1.593 (5)	1.58
S(a)–N(b)	1.628 (7)	1.72
S(a)–N(c)	2.864 (5)	2.91
S(a)–S(b)	2.789 (2)	2.76
N(a)–N(b)	2.576 (7)	2.72
N(a)–S(a)–N(b)	106.2 (2)	111.5
S(a)–N(b)–S(b)	119.9 (4)	113.5
S(b)–S(a)–S(d)	105.5 (1)	106.8
N(b)–N(a)–N(d)	119.0 (5)	–

[a] The refined X-ray structure shows clearly the existence of defects. For details see ref 11b. [b] This study. [c] Reference 26.

lengthwise readily. Long, fibrous strands of $(SN)_x$ may be mechanically stripped from crystal. These are strong and can be bent easily and twisted.

When $(SN)_x$ is heated it decomposes very rapidly at temperatures above ~208°. When held in an evacuated vessel completely immersed in an oil bath at 140–150°, it slowly decomposes to sulfur, nitrogen, and possibly other as et unidentified substances. Polymeric sulfur nitride can be sublimed in vacuo at 140–150° to yield lustrous, epitaxial $(SN)_x$ films having the same crystal structure as the $(SN)_x$ from which they were sublimed.[22,23]

Preliminary experiments indicate that at room temperature $(SN)_x$ crystals are not affected by exposure for 6 days to either 1 atm of dry oxygen or 1 atm of moist oxygen. When crystals are immersed in degassed distilled water in vacuo for 6 days, a very small amount of white solid is formed. Exposure of $(SN)_x$ to the atmosphere for 2 weeks at room temperature produced no change in the X-ray diffraction pattern, although exposure to air for significantly longer periods appeared to result in some decomposition.

C. Structure of a Single $(SN)_x$ Chain. Of central importance is the actual molecular structure of a single $(SN)_x$ chain. X-Ray results[11b,19] show that $(SN)_x$ crystallizes in a monoclinic system $P2_{1/C}$ with unit cell constants $a = 4.153$ (6) Å, $b = 4.439$ (5) Å, $c = 7.637$ (12) Å; $\beta = 109.7$ (1)° and $\rho_c = 2.30$ g/cm³, with four SN groups per unit cell. The structure was solved by the Patterson method. The refinement ($R = 0.11$)[11b] led to intrachain distances and bond angles shown in Figure 3 and Table III.

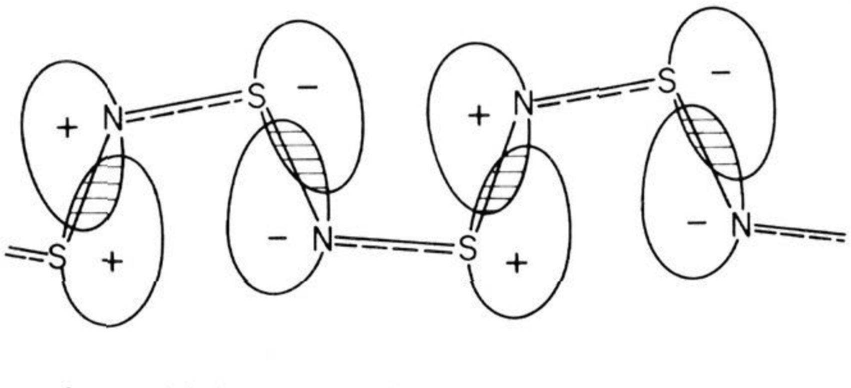
The general molecular chain structure (Figure 3) is qualitatively similar to the alternating SN structure of the earlier electron diffraction studies ($R = 0.35$).[26,27] Both studies show that a suggested zig-zag chain structure[6]

is incorrect.

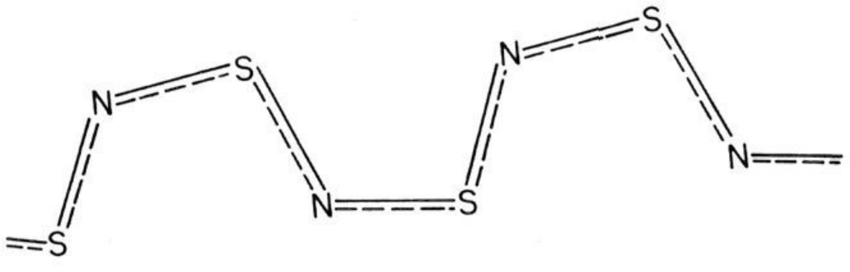
The first striking feature in the X-ray structure is the near equivalence of the SN bond lengths: S(a)–N(a) = 1.593 (5) and S(a)–N(b) = 1.628 (7) Å. At this level of refinement, the small bond length difference is barely significant ($3\sigma_{\text{diff}} = 0.03$). This feature is in marked contrast to the strong bond alternation, S(a)–N(a) = 1.58 ± 0.082 and S(a)–N(b) = 1.72 ± 0.082 Å given in the electron diffraction studies. Intrestingly, the average of the observed X-ray bond lengths is 1.61 Å which is intermediate between that expected for a single and double S–N bond.[21] It appears, also, that there may be significant secondary bonding interaction along the molecular chain, particularly between the nonbonded sulfur and nitrogen atoms S(a) and N(c). Their separation, 2.864 (5) Å, is significantly less than the sum of the van der Waals radii of sulfur and nitrogen 3.35 Å.[28] Similarly the separation of the sulfur atoms S(a) and S(b) (2.789 (2) Å) is less than the sum of the van der Waals radii of two sulfur atoms (3.70 Å).

The bond angles are the second important structural feature of the chains. The angles N–S–N = 106.2 (2)° and S–N–S = 119.9 (4)° should be compared to the electron diffraction results[26,27] of 111.5 and 113.5°, respectively. As a comparison the N–S–N bond angle (106.2°) is similar to that (105.5°) in S_4N_4, whereas the S–N–S angle (119.9°) is greater than the nitrogen bond angle (113.5°) in S_4N_4.[21]

The near equivalence of the intramolecular S–N bond lengths found in the present study and the presence of secondary bonding interactions between next nearest neighbors suggest complete electron delocalization into a conduction band llong the $(SN)_x$ chain. Considering a single $(SN)_x$ chain as a collection of monomeric SN diatomic units, one can identify the source of conduction electrons as the single unpaired electron in the π^* antibonding level of SN whose molecular orbital level scheme is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4 3\pi^1$.[29] In a chain, extensive rehybridization of the SN molecular states is expected. If $(SN)_x$ is regarded as being derived from the $N\equiv S$ monomer, then interaction of the lone electron in the $\pi_{p_z}{}^*$ orbitals (drawn as lying above and below the plane of the paper) could occur as indicated diagrammatically below



to give multiple bonding between the remaining nitrogen and sulfur atoms



Alternatively, a d or d_π hybrid orbital of appropriate symmetry on a sulfur atom could overlap simultaneously with the p_z orbitals of the sp_xp_y hybridized nitrogen atoms in two adjacent SN units to provide the multiple bond character. Either interaction results in delocalization of the SN unpaired electrons into a half-filled "super" molecular orbital. In the polymer structure, this half-filled orbital would correspond to a half-filled metallic conduction band. It must be emphasized that this description serves only as a schematic representation. For example, the presence of crystallographic symmetry elements, such as glide planes and screw axes, as well as effects of interchain coupling can play a major role in the actual energy band structure. Further description of the band structure must await detailed calculations now in progress.

Current solid-state studies underway in our laboratories are addressing the central question of the actual dimensionality of the electronic properties of $(SN)_x$. Although the chain-like structure suggests a high anisotropy in the electronic properties, detailed studies show that substantial coupling takes place between the $(SN)_x$ chains. In fact, the results indicate $(SN)_x$ should not be considered as strictly one dimensional but rather should be approached from the point of view of an anisotropic solid with a two- or, possibly, three-dimensional electronic band structure.[24]

In contrast to the well-known electrically insulating carbon based polymers, such as polyacetylene,[30] $(SN)_x$ is a metal. Ovchinnikov[31] has proposed that the insulating energy gap in the polyenes arises primarily from the electron-electron coulomb repulsion which tends to localize one electron per carbon atom. The extra freedom associated with a single unpaired electron per diatomic SN unit reduces the effective interaction making the metallic state accessible. The additional features of larger polarizability (S-N vs. C) and increased interchain coupling result in metallic $(SN)_x$.

This study shows that $(SN)_x$ can be prepared in analytically pure form, in a well-defined structure. It can be sublimed to form oriented epitaxial films on a variety of polymer substrates. This polymer system may well prove to be a forerunner of an entirely new class of materials: *polymeric metals*.

Acknowledgment. This research was supported in part by the National Science Foundation through the Laboratory for the Research on the Structure of Matter and Grants No. GH-39303 and No. GP-41766X and by the Advanced Research Projects Agency through Grant No. DAHC 15-72-C-0174.

The authors wish to thank Dr. A. A. Bright and Mr. M. J. Cohen for discussions throughout all phases of this work. The technical assistance of Mr. R. White on the electron microscopy studies is gratefully acknowledged. Many discussions on the X-ray results with Drs. J. M. Troup and B. A. Frenz of the Molecular Structure Corporation have been most helpful.

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