Heterocyclic compounds of S-N

The chemistry of Sulphur-Nitrogen compounds has several general features which are of great interest and importance, namely, stability of Sulphur-nitrogen bonds, tendency to make five and six membered rings, ring contraction, polymerization, and negative ion formation. Several heterocyclic compounds of S-N have been prepared in last century. Some of the important compounds are as following,

✓ Tetrasulphur tetranitride (S_4N_4)

Tetrasulfur tetranitride is an inorganic compound with the formula S_4N_4.This gold-poppy coloured solid is the most important binary sulfur nitride, which are compounds that contain only the elements sulfur and nitrogen. It is a precursor to many S-N compounds and has attracted wide interest for its unusual structure and bonding.

Preparation

1. **By the reaction of SCl_2 and NH_3**

$$6SCl_2 + 16NH_3 \longrightarrow S_4N_4 + 2S + 14\ NH_4Cl$$

S_4N_4 was first prepared by M. Gregory by the reaction of disulfur dichloride with ammonia.

$$6S_2Cl_2 + 16NH_3 \xrightarrow{CCl_4} S_4N_4 + 8S + 12NH_4Cl$$

2. **Reaction of Sulphur with anhydrous liquid ammonia**

$$10S + 4NH_3 \longrightarrow S_4N_4 + 6H_2S$$

Physical properties

- Solid
- M.P. = 178^{o}C
- Thermochromic; It changes color with temperature
  - ❖ At liquid ammonia temperature = Colorless
  - ❖ At room temperature = Orange-yellow
  - ❖ At 100^{0}C = Red
- Crystals are reasonably stable to attack by air, but explosively sensitive to shock and friction.

Chemical properties

Reduction

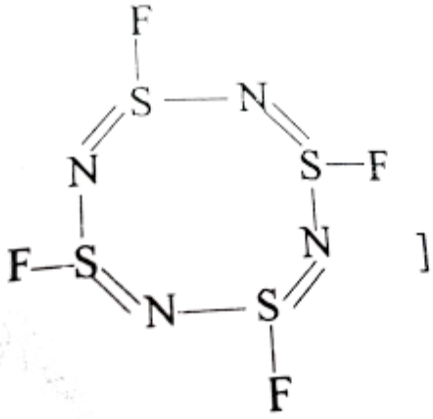
$S_4N_4 \xrightarrow{SnCl_2} S_4N_4H_4$

Oxidation

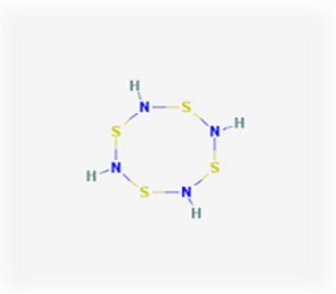
$3S_4N_4 + 6Cl_2 \longrightarrow 4N_3S_3Cl_3$

Fluorination

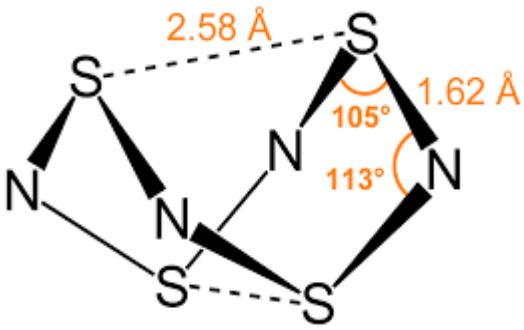
$S_4N_4 + 2F_2 \longrightarrow S_4N_4F_4$



Hydrogenation



Structure



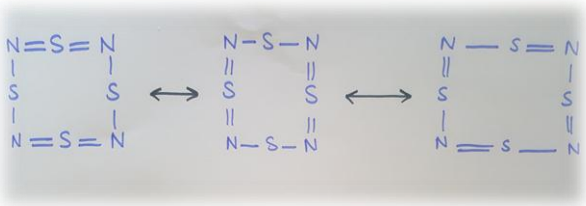
Cradle shaped structure

Average S-N bond length = 1.62 Å

S-N bond = partial double bond character

S…S distance = 2.58Å (weak bonding)

All bond lengths are equal so there is delocalization.



✓ Disulfur dinitride (S_2N_2)

Disulfur dinitride is the chemical compound S_2N_2 with a cyclic square planar structure.

Preparation

Passing gaseous S_4N_4 over silver metal wool at **250–300 °C** at low pressure (1mm Hg) yields cyclic S_2N_2. The silver reacts with the sulfur produced by the thermal decomposition of the S_4N_4 to form Ag_2S, and the resulting Ag_2S catalyzes the conversion of the remaining S_4N_4 into the four-membered ring S_2N_2.

$$S_4N_4 + 8\ Ag \rightarrow 4\ Ag_2S + 2\ N_2$$

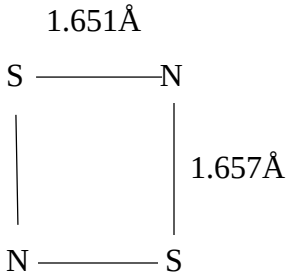
$$S_4N_4 \rightarrow 2S_2N_2$$

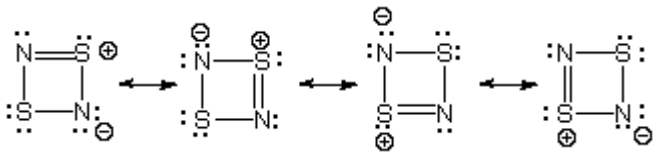
Physical properties

- Colorless
- Crystalline
- Soluble in diethyl ether
- Sublimes readily
- Molar mass = 92.144g/mol

Structure

The S_2N_2 molecule is virtually square and planar. The S-N bond lengths are 165.1Å and 165.7Å and the bond angles are very close to 90°.





Delocalization of pi electrons

Polythiazyle $(SN)_x$

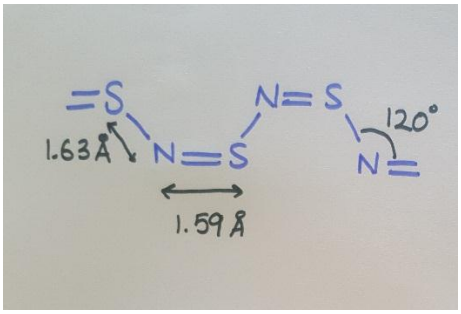
The compound was first reported as early as **1910** by **F.P. Burt,** who obtained it by heating tetrasulfur tetranitride in vacuum over silver wool.

Properties

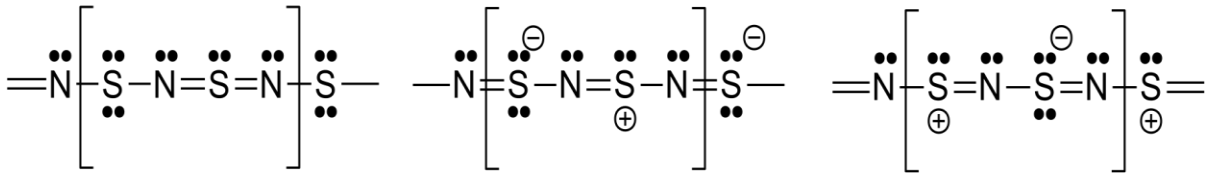
Polythiazyl is a **metallic-golden** and **shiny**, crystalline but fibrous material. The polymer is mostly inert to oxygen and water, but decomposes in air to a grey powder. At temperatures above 240 °C explosive decomposition can occur. The compound also explodes on impact. It is **highly conductive** at room temperature due to delocalization of pi electrons.

Structure

The material is a polymer. The S and N atoms on adjacent chains align. Several **structures** resonance can be written.



Zig zag structure



Resonating structures

The structure of the crystalline compound was resolved by **X-ray diffraction.** This showed alternating SN bond lengths of **159Å** and **163Å** and SNS bond angles of 120 °C and NSN bond angles of 106 °C.

Uses

Due to its electrical conductivity, polythiazyl is used in **LEDs, transistors,** battery cathodes, and **solar cells**.