S–N–F Compounds

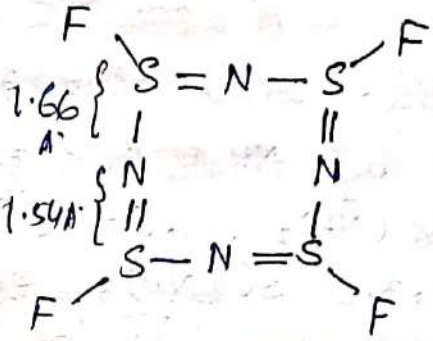
1. Tetrathiazyl Tetrafluoride, $(NSF)_4$

It is prepared by fluorination of S_4N_4

$$S_4N_4 + 4\,AgF_2 \longrightarrow N_4S_4F_4 + 4\,AgF$$

It is water sensitive white solid. It dissociates at 200–250°C to NSF which polymerises to the trimer $(NSF)_3$

Structure -



The ^{19}F n.m.r spectrum of $(NSF)_4$ gives a single resonance peak thereby indicating that all of the fluorine atoms are equivalent The molecule has a puckered ring structure with two alternating S–N distances of 1.66 and 1.54 Å in the ring. This indicates that the presence of fluorine substituents appears to distroy the delocalization of the electrons in the ring because the bond lengths in the ring alternate in length. Further the presence of fluorine substituents lead to a contraction of the Sulfur d orbitals and consquently thereby a better overlap. As the S electrons are more strongly held, it means that these are less available for delocalization

(2) Trithiazyl Trifluoride $(NSF)_3$

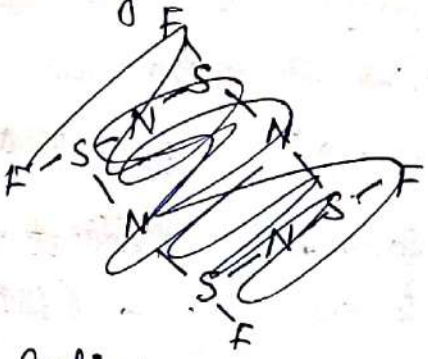
① It is prepared by fluorinating $(NSCl)_3$

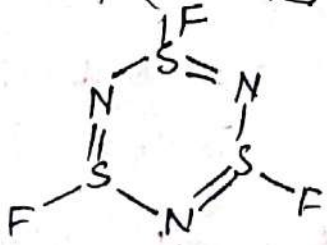
$$(NSCl)_3 \xrightarrow{AgF_2 \text{ in } CCl_4} (NSF)_3$$

② It is also prepared by heating $(NSF)_4$ at 200–250°C which dissociates to NSF followed by polymerization to $(NSF)_3$

Structure: The structure of $(NSF)_3$ is unknown although its n.m.r

Spectrum reveals that all the fluorine atoms are equivalent. However, it is likely to resemble that of $(NSCl)_3$

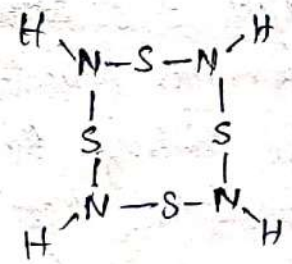


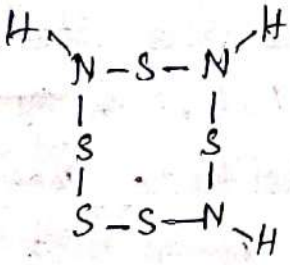


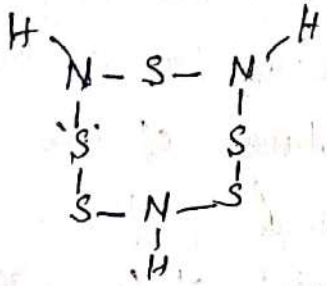
Imides of Sulfur

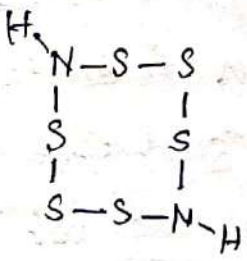
There is a no. of imides which may be regarded as derived from S_8 by replacing S by NH for e.g. S_7NH, 1,3- $S_6(NH)_2$, 1,4 – $S_6(NH)_2$, 1,5 – $S_6(NH)_2$. 1,3,5- $S_5(NH)_3$, 1,3,6 $S_5(NH)_3$ etc –

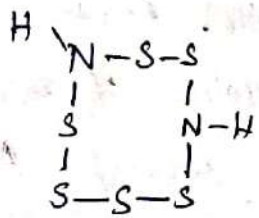
It is interesting to note that all possible $S_x(NH)_{8-x}$ isomers are known with exception of N–N bonded structures. The latter may be unstable due to weak N–N bond.

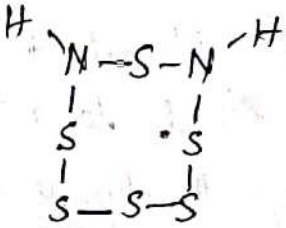


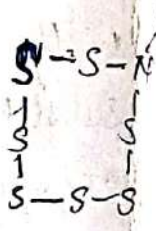












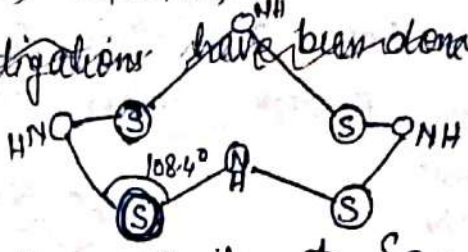
S_7NH

M.P. – 113°, It is a minor product in the preparation of S_4N_4 by ammonolysis of SCl_2. However it is formed in better yield in the ammonolysis of S_2Cl_2 in DMF. The latter prep^n also gives the products 1,3 – $S_6(NH)_2$, 1,4 – $S_6(NH)_2$, 1,5 – $S_6(NH)_2$, 1,3,5 – $S_5(NH)_3$ 1,3,6 – $S_5(NH)_3$ etc. These products have been separated by chromatography and fractional crystallization.

$S_4(NH)_4$ is prepared by reducing S_4N_4 with $SnCl_2$ in ethanol

$$S_4N_4 \xrightarrow{SnCl_2} S_4N_4H_4$$

Among these most of the investigations have been done for $S_4N_4H_4$ & S_4NH_4



Structure -

The structure of $S_4N_4H_4$ is very similar to S_8, the NSN angle being 108.4° and the SSS angle in S_8 is 107.8°. The N-S bond lengths are all the same 1.67 A°, although they are longer than those of S_4N_4 yet they are shorter than is required for a single bond.

Thiotrithiazyl Cation $S_4N_3^+$

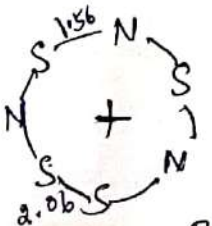
It is an interesting species because it forms several stable salts For eg. $[S_4N_3]^+Cl^-$ is obtained by boiling S_4N_4 with S_2Cl_2 in CCl_4 solution.

$$3\,S_4N_4 + 2\,S_2Cl_2 \longrightarrow 4\,[S_4N_3]^+Cl^-$$

Nitric acid converts the chloride into nitrate

$$[S_4N_3]^+Cl^- + HNO_3 \longrightarrow [S_4N_3]^+NO_3^- + HCl$$

Structure - x-ray structural study on nitrate showed that the highly stable $S_4N_3^+$ ion forms a planar 7-membered ring The absorption and n.m.r spectra imply the presence of a well defined delocalized aromatic π-system in this ring. The S-N bond lengths are nearly 1.56 A°. This is less than the value for a single bond, this also indicates some delocalization The S-S bond length (2.06 A°) is close to that for a single bo



Structure of $S_4N_3^+$ cati

Silicone Polymers

Silicones are organo-silicon polymers containing ···O-Si-O··· linkages. These may be linear silicones, cyclic silicones and cross linked silicones.

Preparation

These are prepared by the hydrolysis of alkyl or aryl ~~derivatives~~ derivatives of $SiCl_4$ like $RSiCl_3$, R_2SiCl_2 and R_3SiCl and polymerization of alkyl or aryl hydroxy derivatives obtained by hydrolysis. The method consists of the following steps —

(i) To prepare alkyl or aryl derivatives of $SiCl_4$ by the following methods.

(a) $$2\,CH_3Cl + Si \xrightarrow[300^\circ C]{Cu} \underbrace{(CH_3)SiCl_3 + (CH_3)_2SiCl_2 + (CH_3)_3SiCl}_{\text{Mixture of methyl chlorosilanes}} + \text{other compds}$$

The yield of $(CH_3)_2SiCl_2$ (b.pt. = 69.6°C) is over 50%. Careful fractionation is used to separate $(CH_3)_2SiCl_2$ from $(CH_3)SiCl_3$ (b.pt. = 66.9°C) and $(CH_3)_3SiCl$ (b.pt. = 87.7°C).

if $$CH_3Cl + 2HCl + Si \xrightarrow[300^\circ C]{Cu} (CH_3)SiCl_3 + H_2$$

(b) $$RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$$
(Grignard reagent)

$$2\,RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$$ (alkylchloro silanes)

$$3\,RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$$

(c) $$C_6H_6 + HSiCl_3 \xrightarrow[\text{Catalyst } BF_3, BCl_3 \text{ or } AlCl_3]{\Delta\ 230-300^\circ C} (C_6H_5)SiCl_3 + H_2$$

(ii) To prepare alkyl or aryl ~~d~~ hydroxy derivatives of ~~$SiCl_4$~~ chlorosilanes (called silanols or silandiols). These silanols are obtained by the hydrolysis of $RSiCl_3$, ~~and~~ R_2SiCl_2 and R_3SiCl

$$RSiCl_3 + 3HOH \xrightarrow{\text{hydrolysis}} RSi(OH)_3 + 3HCl$$

$$R_2SiCl_2 + 2HOH \longrightarrow R_2Si(OH)_2 + 2HCl$$

$$R_3SiCl + HOH \longrightarrow R_3Si(OH) + HCl$$

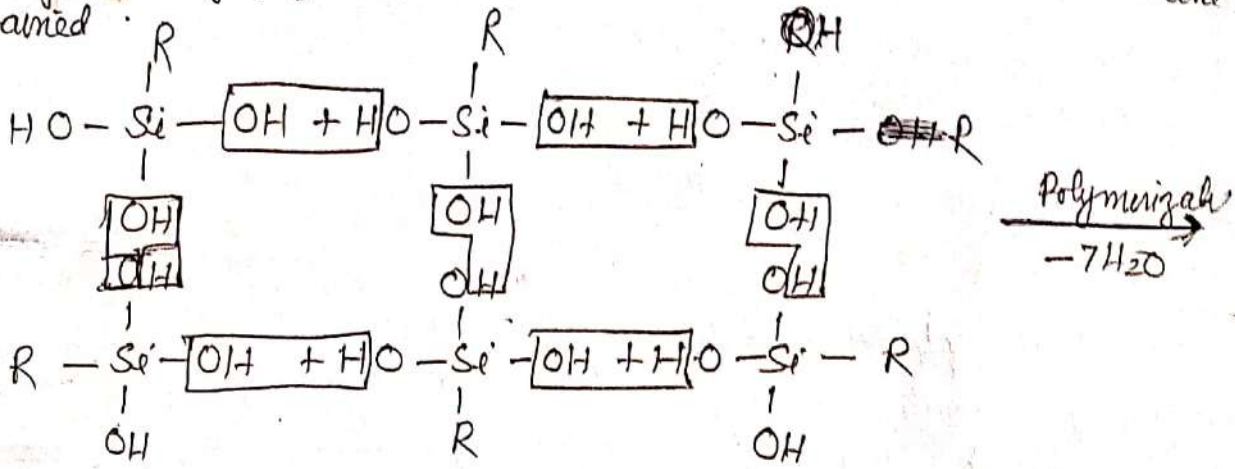
Chlorosilanes → Silanols

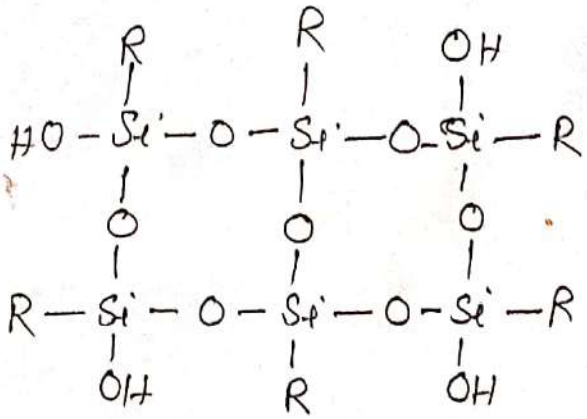
General equation for the hydrolysis reaction can be written as

Chlorosilanes + Water $\xrightarrow{\text{hydrolysis}}$ Silanols + HCl

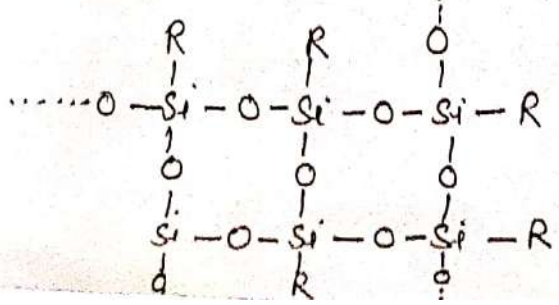
(iii) Polymerisation process involving removal of some H_2O molecules and formation of different types of silicones. The type of silicone obtained depends on the nature of alkyl or aryl hydroxy derivative and the way in which the hydroxy derivative undergoes polymerisation. For example -

(a) When many molecules of alkyl trihydroxy silane, $RSi(OH)_3$ undergoes polymerization, a cross-linked two dimensional silicone is obtained.





Since an active OH gp is present at each end of the chain, polymerization continues on both ends and hence the length of the chain increases. The increase in the length of the chain produces cross linked silicone as shown below



Two dimensional cross linked silicone