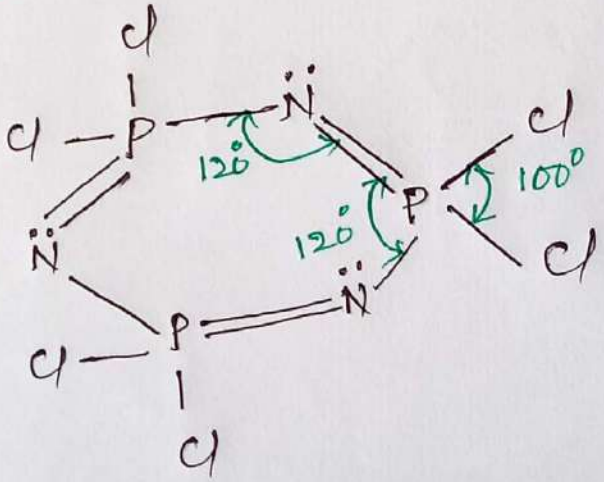
DTS

* Structure of $(NPCl_2)_3$ molecule:-

X-ray analysis has shown that $(NPCl_2)_3$ molecule has a planar six membered ring structure in which each N-atom is sp^2 hybridised and each P-atom is sp^3 hybridised. The lone pair of electrons on each N-atom resides in one of the three sp^2 hybrid orbitals. It is this lone pair of electrons which makes $(NPCl_2)_3$ molecule to show basic properties. The resonance str is also similar to C_6H_6 molecule.

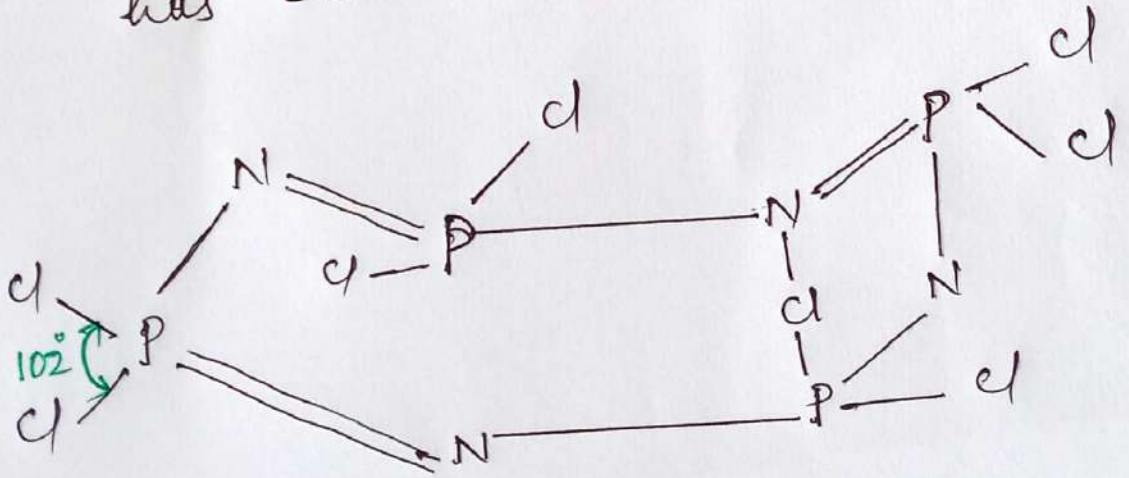


Unlike benzene which involves extensive $(p\pi - p\pi)$ bonding, $(N_3P_3Cl_6)$ molecule involves $(d\pi - p\pi)$ bonding. The extent of $(d\pi - p\pi)$ bonding appears

to be quite appreciable as the N-P distance (≈ 1.6 A°) is considerably shorter than the N-P single bond distance (1.75 - 1.80 A°). Whether there is complete delocalisation of π-electron charge cloud on all the ring atoms as in C_6H_6 molecule or there are intensely-localised islands of the electron cloud within the PNP-segments.

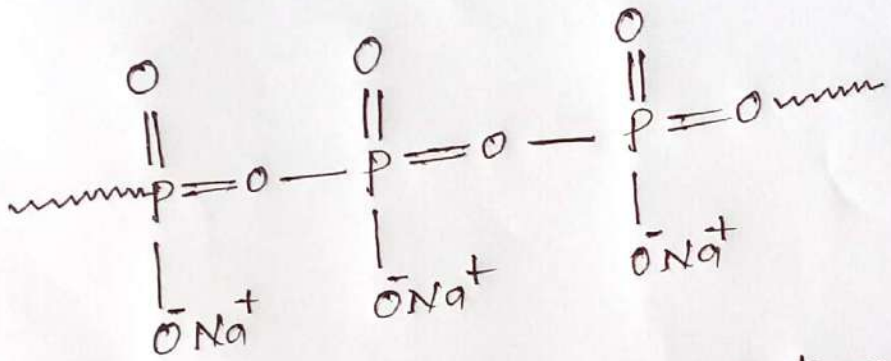
* Structure of $(NPCl_2)_4$ molecule :-

The structure of $(NPCl_2)_4$ molecule has a "tube-like puckered structure" that has been shown in Fig.



* Vitreous polyphosphates : phosphate glasses

In these polymers, the -ve charges present on the polyphosphate anions are balanced by the +ve charges present on the cations like Na^+, K^+ etc., as shown in Fig



The polyphosphate anions present these polymers have long straight chains, but one P-atom out of 1000 P-atoms forms a cross-linked b/w the chains. These cross-linked chains disappear with 12 hrs when the polymer is dissolved in water or in neutral aqueous Salt solutions.

* Crystalline polymetaphosphates :-

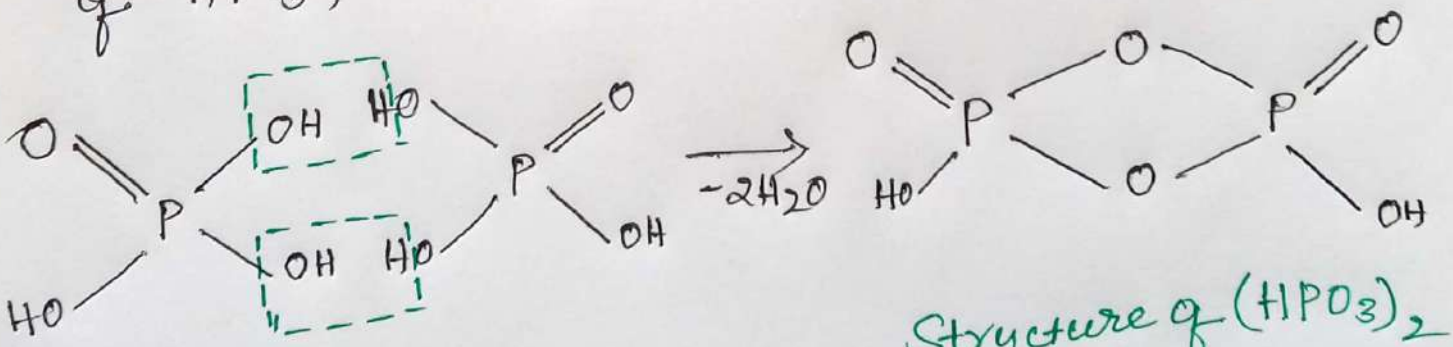
Structure of HPO_3, $(HPO_3)_2$, $(HPO_3)_4$

polymetaphosphates are the salts of polymetaphosphoric acids. These acids are represented by the general formula $H_nP_nO_{3n}$ or $(HPO_3)_n$. They are obtained by elimination of n moles of H_2O from n moles of H_3PO_4. Thus:

$$n\,H_3PO_4 \xrightarrow{-n\,H_2O} H_nP_nO_{3n}$$

* Preparation :-

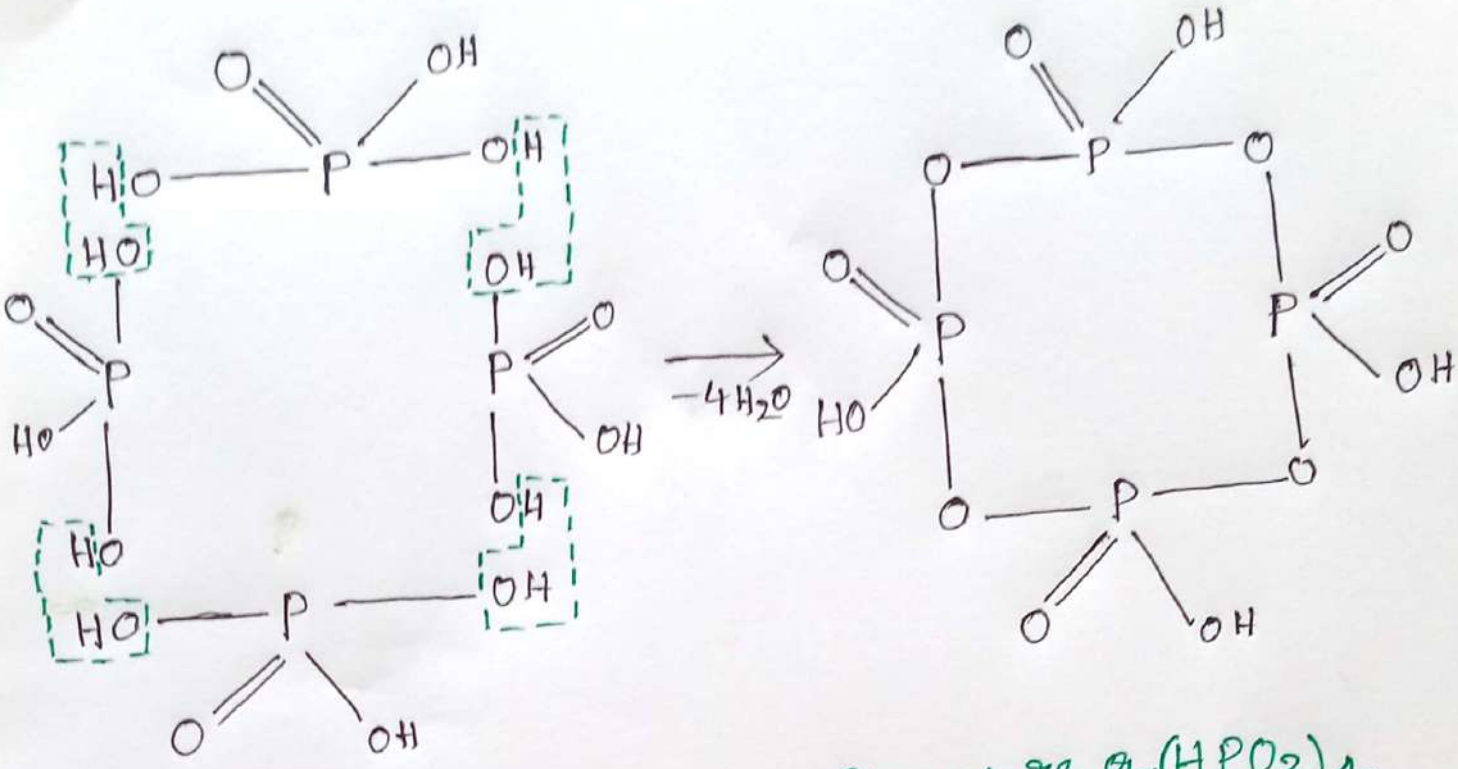
polymetaphosphoric acids and polymetaphosphates have cyclic str. The structures of HPO_3, $(HPO_3)_2$ (dimer) and $(HPO_3)_4$ tetramer



Two moles of H_3PO_4

Structure of $(HPO_3)_2$ [dimer]

Dimetaphosphoric acid

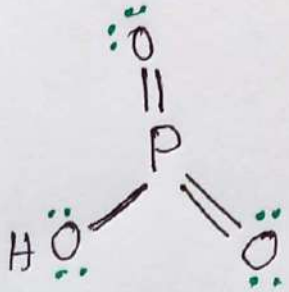


Four moles of H_3PO_4.

Structure of $(HPO_3)_4$
[tetramer]

Tetrametaphosphoric acid.

* Structure of HPO_3 :-



Metaphosphoric acid

*. polyorthophosphoric acid :-

OR

This is also called polyphosphoric acids. These acids can be represented by general formula $H_{n+2}P_nO_{3n+1}$.

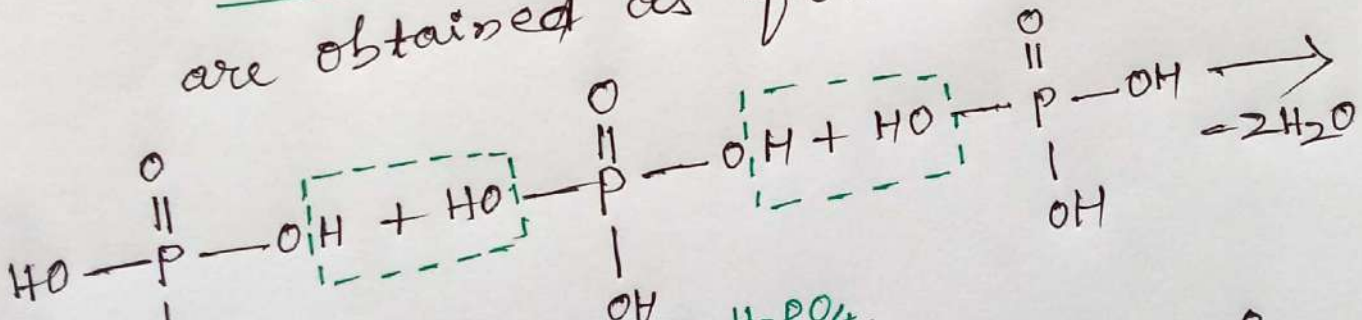
Ex :- $H_4P_2O_7$ Di(or pyro) phosphoric acid

$H_5P_3O_{10}$ Triphosphoric acid

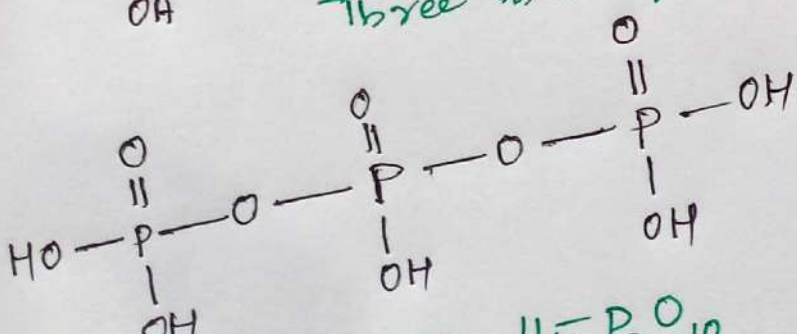
$H_6P_4O_{13}$ Tetraphosphoric acid

⟹ preparation :-

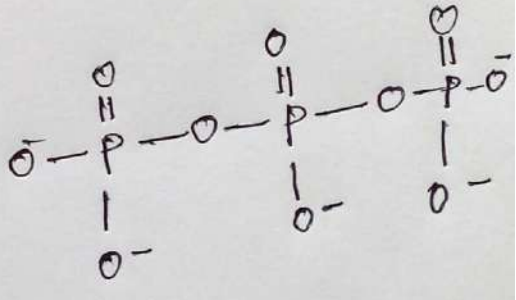
Triphosphoric acid $[H_5P_3O_{10}]$ and the anions are obtained as follows.



Three moles of H_3PO_4.



Structure of $H_5P_3O_{10}$,



Str of $P_3O_{10}^{5-}$

[NOTE:- Elimination of H^+ from $H_5P_3O_{10}$]

linking of three PO_4 tetrahedrons through three O-atoms, to get the str of $P_3O_{10}^{5-}$ ion

The str of polyphosphate molecules and ions each P-atom in each str is sp^3 hybridised.

* Borophosphate glasses:—

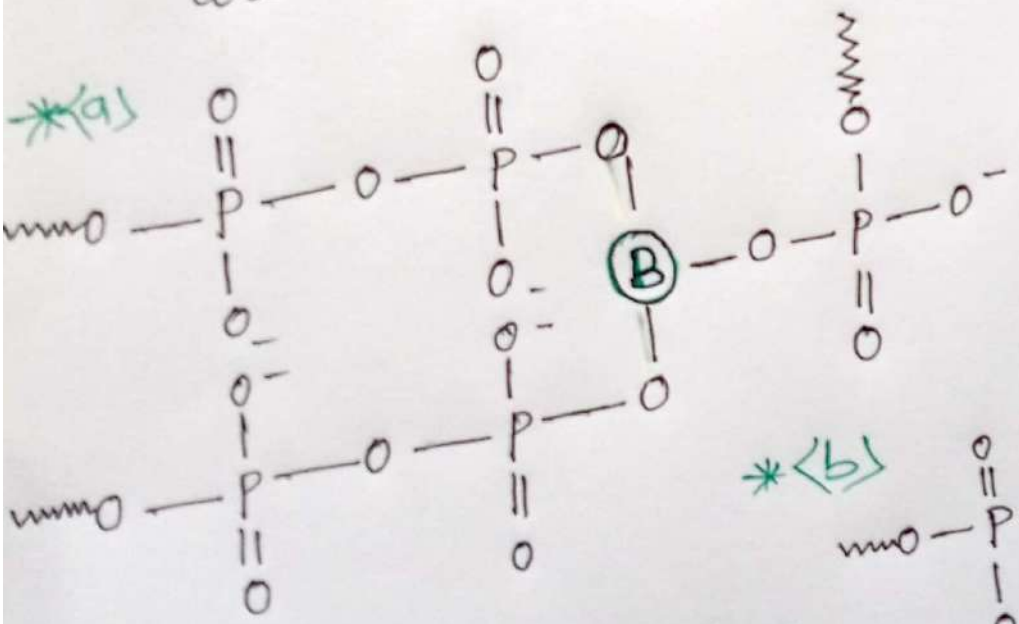
These are obtained by heating H_3PO_4, B_2O_3 and alkali metal carbonates or oxide at 700°. The Borophosphate glasses are the following three types:

i). Those which contain excess of alkali over P_2O_5. In this variety all the B-atoms are present as trigonal BO_3 groups.

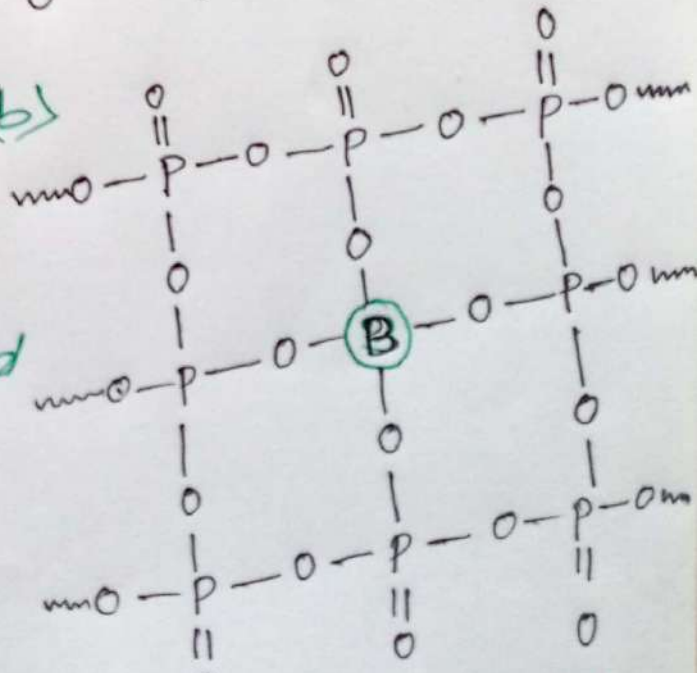
ii) Those which contain excess of P_2O_5 over alkali. These borophosphate glasses are called acidic borophosphosphate glasses. If there is less than 10 mole percent of B_2O_3 all B-atoms are four co-ordinated.

iii) Those which contain P_2O_5 and alkali in equivalent proportions. The no of 4 co-ordinated B-atoms decreases steadily with the increase in the content of B_2O_3 and becomes almost zero at 47 mole percent of B_2O_3.

Structures of borophosphate glasses having three- and four-coordinated B-atoms are shown below.



a) Borophosphate glass having 3-coordinated B-atom



b) Borophosphate glasses having 4 co-ordinated B-atom

* Polymeric compounds of Sulpher:

1) Nitrides of Sulpher:-

Sulpher has lower electronegetivity than nitrogen, compounds of Sulpher with nitrogen are known as nitrides of Sulpher. Sulpher forms many nitrides which are polymeric compounds. These are covalent compounds and have industrial and technical importance.

a) Tetrasulpher tetranitride $[S_4N_4]$ or $(SN)_4$

preparation:-

i) When Sulpher monochloride, S_2Cl_2 reacts with NH_3 either in soln in an inert solvent or it is heated over solid NH_4Cl, hence reaction takes place to form S_4N_4.

$$6\,S_2Cl_2 + 16\,NH_3 \xrightarrow{CCl_4} \underset{\text{Tetra sulpher tetranitride}}{S_4N_4} + S_8 + 12\,NH_4Cl$$

* properties :-

i) It is an orange - yellow crystalline solid

ii) It is diamagnetic

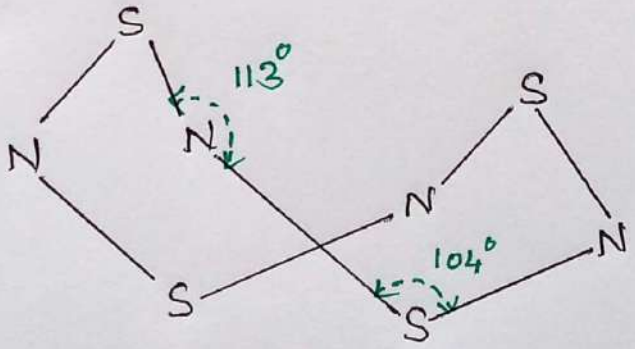
iii) It is insoluble in H_2O and soluble in many organic solvent

iv) Action of a boiling alkali :-

S_4N_4 undergoes hydrolysis readily by a boiling alkali. In this reaction all nitrogen of S_4N_4 is converted into $\ddot{N}H_3$

$$2S_4N_4 + 6OH^- + 9H_2O \longrightarrow \underset{\text{Trithionate}}{2S_3O_6^{2-}} + \underset{\text{Thiosulphate}}{S_2O_3^{2-}} + 8\ddot{N}H_3$$

* Structure of S_4N_4 :-



Eight-membered Cradle ring (cyclic) structure of S_4N_4 molecule.

Electron diffraction and X-ray measurements have shown that S_4N_4 molecule has an "eight-

membered cradle ring (cyclic) structure in which all the N-S bond lengths are equal to 1.62 Å. NSN bond angle = 104° and SNS bond angle = 113°

* Preparation of Disulpher dinitride [S_2N_2] :-

When S_4N_4 is heated to about 575K in a high vaccum or on Silver wood. Heat reaction takes place to form disulpher dinitride.

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

$$S_4N_4 \longrightarrow 2S_2N_2$$

* Preparation of pentasulpher dinitride [S_5N_2] :-

When S_4N_4 is heated in solution. S_5N_2 is obtained. It is some what less stable than S_4N_4 and is a deep red oil which freezes to a grey solid at 284K.

Thiazyl halides:-

Thiazyl halides can be represented by the general formula, $(NS)_n X_n$ or $(NSX)_n$
[X = F, Cl, Br n = 3, 4. etc]

Ex:- Trithiazyl trifluoride $(NSF)_3$.
Tetrathiazyl tetrafluoride $(NSF)_4$.
Trithiazyl trichloride $(NSCl)_3$.

1 Trithiazyl trifluoride $(NSF)_3$:-

* preparation:-

It is prepared i) by fluorinating the $(NSCl)_3$ with AgF_2 in CCl_4

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

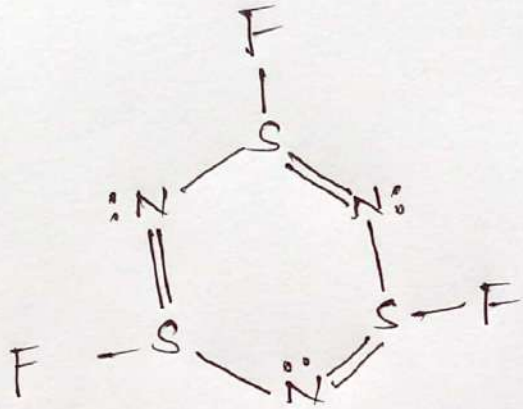
Trithiazyl trifluoride

ii) by heating trithiazyl tetrafluoride, $(NSF)_4$ at 200 - 250°c with dissociates into NSF, followed by polymerisation.

$(NSF)_4 \xrightarrow[200-250^\circ C]{\text{Dissociation}} 4\,NSF$; $3\,NSF \xrightleftharpoons{\text{polymerisation}} (NSF)_3$

Trithiazyltri fluoride.

* Structure:-



The structure of $(NSF)_3$ molecule is not known with certainly. However NMR spectrum of this molecule indicates that all F-atoms are equi Valent. $(NSF)_3$ molecule has a six-membered ring str which is almost planar with all the F-atoms on one side of the ring in axial position. All N–S distance are equal to 1.60 Å.

* Tetrathiazyl-tetrafluoride: — $(NSF)_4$:-

* preparation :-

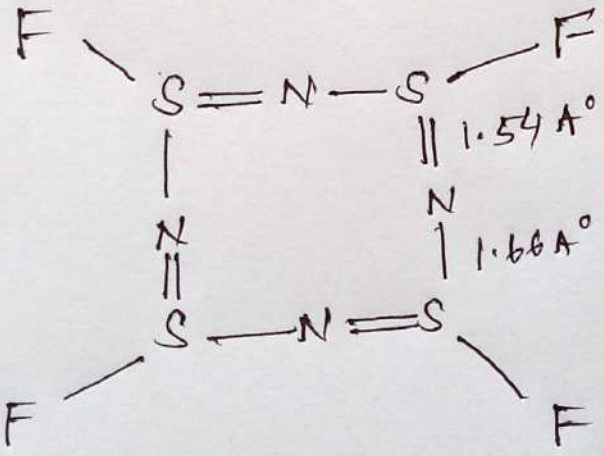
It is prepared by fluorinating S_4N_4 with AgF_2.

$$S_4N_4 + 4AgF_2 \longrightarrow (NSF)_4 + 4AgF$$

It dissociates at 200-250°C into NSF, which polymerises to trimer, $(NSF)_3$.

$$(NSF)_4 \xrightarrow[200-250^\circ C]{\text{Dissociates}} 4NSF; \quad 3NSF \longrightarrow (NSF)_3$$

* Structure :-



Eight-membered puckered ring str of $(NSF)_4$ molecule.

The ^{19}F NMR spectrum of tetramer, $(NSF)_4$ gives a single resonance peak which indicates that all the F-atoms are equivalent. $(NSF)_4$ molecule has "8-membered puckered ring" str., with alternating S-N distance of 1.66 A° and 1.59 A°.

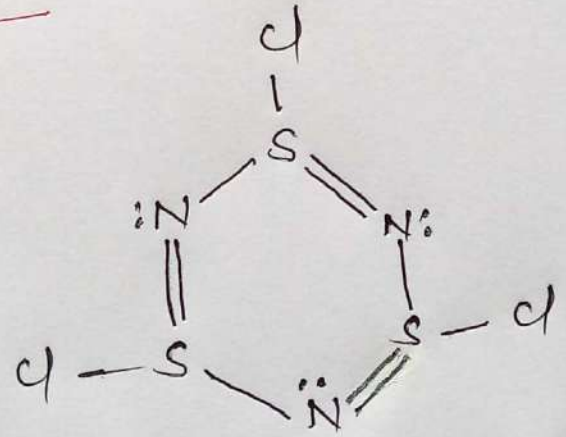
* Trithiazyl trichloride; $(NSCl)_3$:-

* preparation :-

It is prepared by oxidising tetrasulpher tetranitride (S_4N_4) by Cl_2.

$$3S_4N_4 + 6Cl_2 \longrightarrow 4(NSCl)_3$$

* Structure :-



$(NSCl)_3$ molecule has the same str as $(NSF)_2$ molecule.