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## \* Imides of Sulphur:-

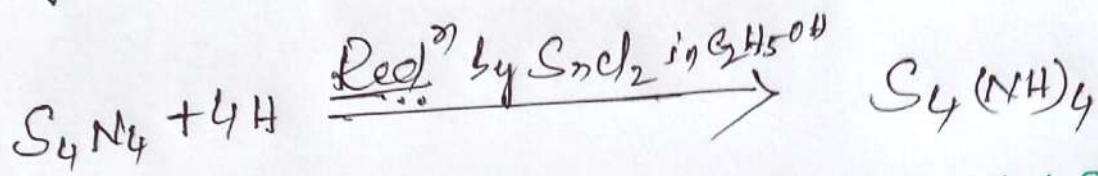
These compound may be regarded as having been obtained by replacing one or more S-atoms in  $S_8$  by imide group (NH). These compounds can be represented by the general formula,  $S_n(NH)_{8-n}$ . The compounds having two or more NH groups exist as isomers.

Ex:-  $S_7(NH)$ ,  $1,3-S_6(NH)_2$ ;  $1,4-S_6(NH)_2$ ;  $1,5-S_6(NH)_2$ ;  $1,3,5-S_5(NH)_3$ ;  $1,3,6-S_5(NH)_3$ ;  $S_4(NH)_4$  etc. The numbering system is based on  $S_8$  ring.

\* Preparation:- Tetra sulphur tetraimide  
When  $S_2Cl_2$  reacts with  $NH_3$  in dimethyl formide,  $S_7(NH)$ ,  $1,3-S_6(NH)_2$ ,  $1,4-S_6(NH)_2$ ,  $1,3,5-S_5(NH)_3$ ,  $1,3,6-S_5(NH)_3$  etc., are obtained. These products are separated from each other by Chromatography and/or fractional crystallisation.

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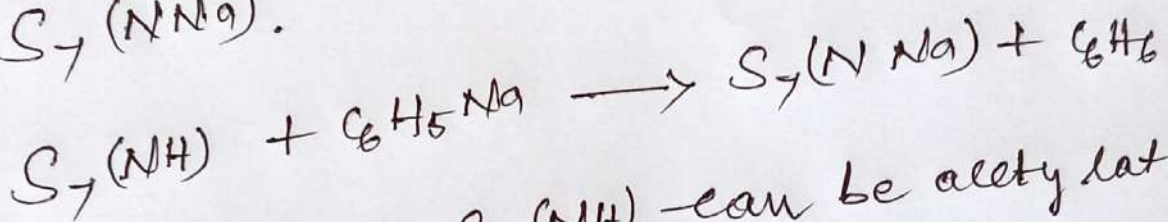
Tetra sulphur tetraimide,  $S_4(NH)_4$  is prepared by reducing  $S_4N_4$  with  $S_4N_4$  with  $SnCl_2$  in  $C_2H_5OH$



Tetra sulphur tetraimide

\* properties of  $S_7(NH)$  :-

i) The reaction of  $S_7(NH)$  with  $C_6H_5Na$  gives  $S_7(NNa)$ .



ii) N-H bonds in  $S_7(NH)$  can be acetylated and benzoylated.

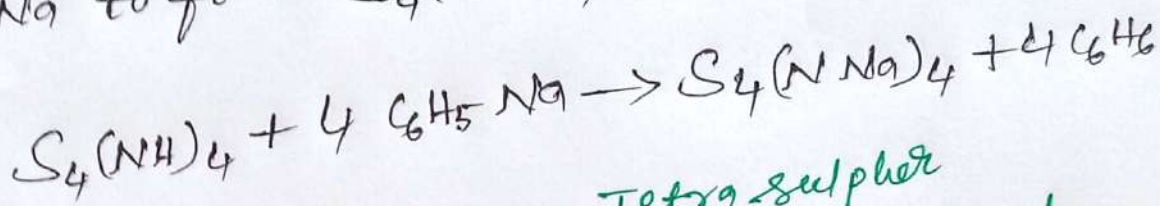
iii) The reaction of  $S_7(NH)$  with the salts of  $Hg(II)$  and  $Hg(I)$  in non-aqueous solvents gives  $Hg(NS_7)_2$  and  $Hg_2(NS_7)_2$  respectively.

\* properties of  $S_4(NH)_4$  :-

i) It is colourless compound and reacts with

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$C_6H_5Na$  to form  $S_4(NNa)_4$ .



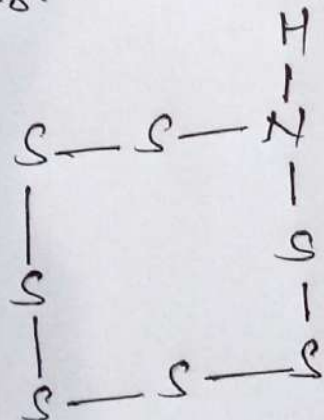
Tetra sulphur  
tetra sodium imide.

ii) N-H bonds in  $S_4(NH)_4$  molecule can be acetylated and benzoylated.

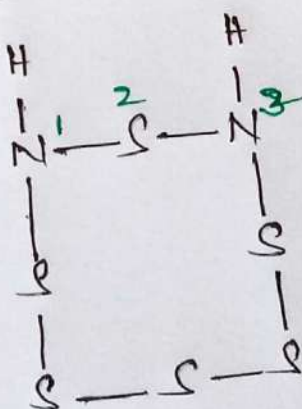
iii) Air oxidation of  $S_4(NH)_4$  at  $100^\circ C$  gives tetrameric thionyl imide  $(OS)_4(NH)_4$  or  $(OSNH)_4$

### \* Structure of imides of sulphur:

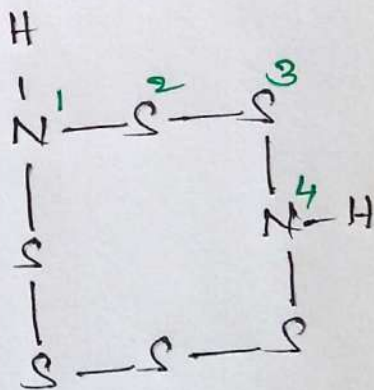
None of the imides has N-N bonds. the structure of some imides as follows.



$S_7(NH)$

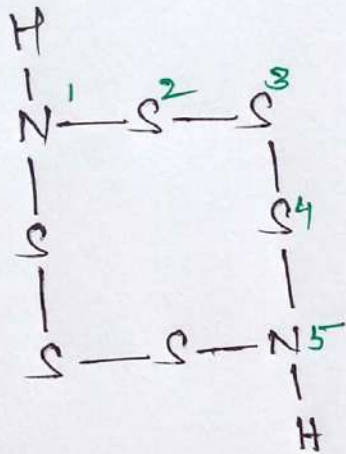


1,3- $S_6(NH)_2$

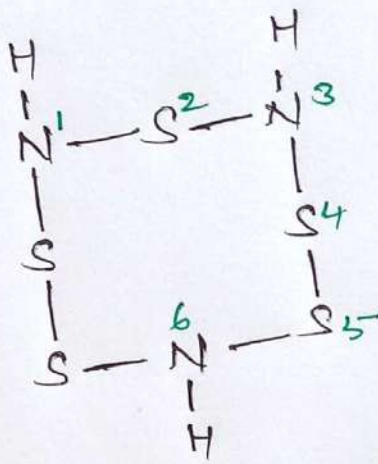


1,4- $S_6(NH)_2$

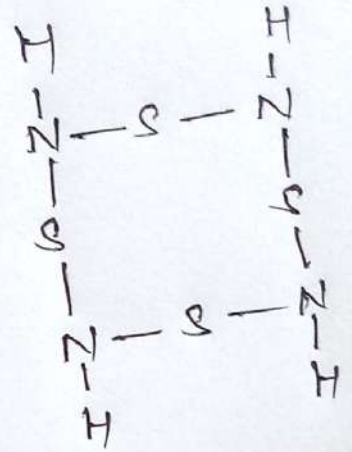
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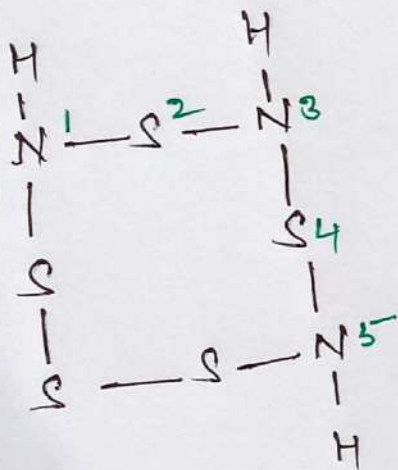
1,5-S<sub>6</sub>(NH)<sub>2</sub>



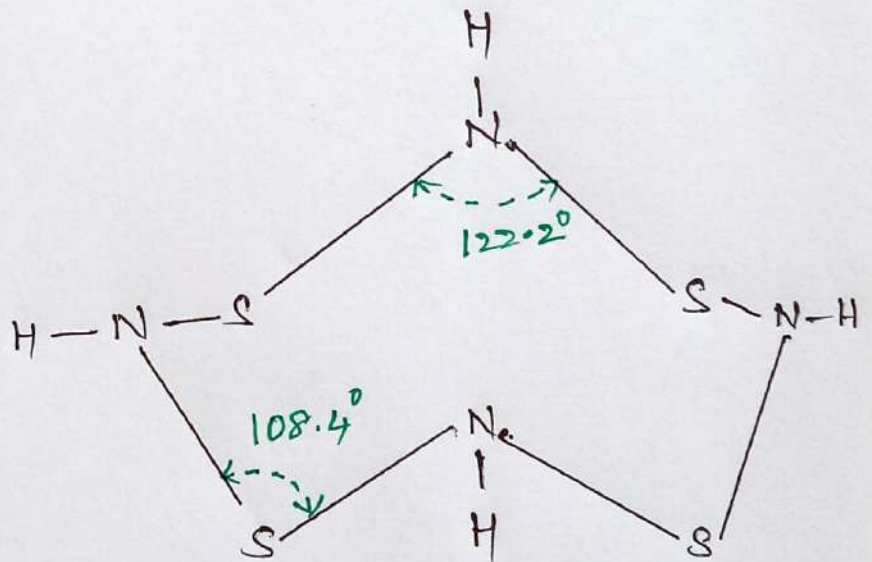
1,3,6-S<sub>5</sub>(NH)<sub>3</sub>



S<sub>4</sub>(NH)<sub>4</sub>



1,3,5-S<sub>5</sub>(NH)<sub>3</sub>



Structure of S<sub>4</sub>(NH)<sub>4</sub>

Structure shown in fig. It has one N-H bond. S<sub>6</sub>(NH)<sub>2</sub> has three isomers namely 1,3; 1,4 and 1,5 while S<sub>5</sub>(NH)<sub>3</sub> exists in two isomeric forms which are 1,3,5 and 1,3,6. The str of

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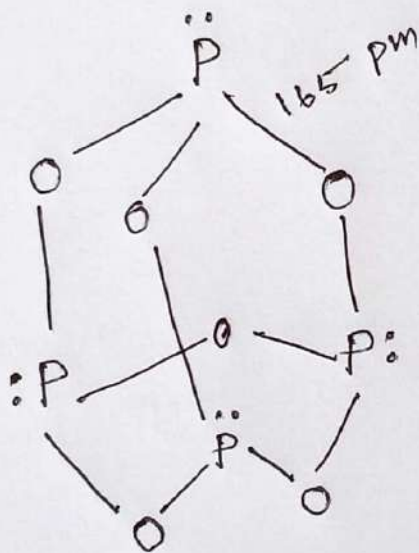
each isomer of  $S_6(NH)_2$  and  $S_5(NH)_3$  has been shown in fig. The str of  $S_4(NH)_4$  is the same as that of  $S_8$ . NSN and SNS bond angles are  $108.4^\circ$  and  $122.2^\circ$ . NOTE that SSS bond angle in  $S_8$  is  $107.8^\circ$ . All N-S bond lengths in  $S_4(NH)_4$  are the same ( $= 1.67 \text{ \AA}$ ).  $S_4(NH)_4$  cannot be reduced to hydrazine. This shows no two N-atoms are directly linked to each other in  $S_4(NH)_4$  molecule i.e.  $S_4(NH)_4$  does not have any N-H bonds.  $S_4(NH)_4$  molecule does not have any isomer and hence represented by a single structure.

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## \* CAGES :-

Cage structures range from clathrate compounds on the one hand to metal-metal clusters.

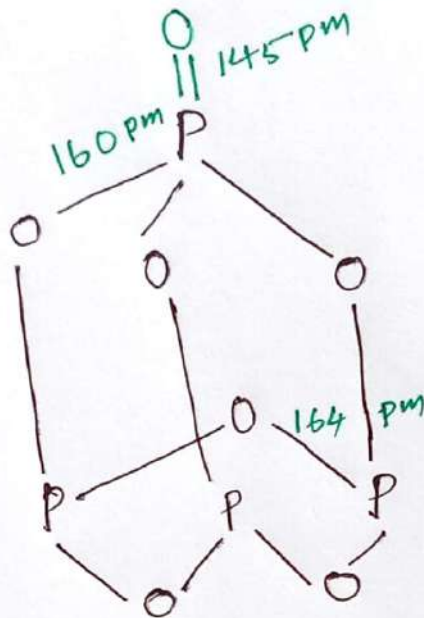
### ⇒ Structure of $P_4O_6$ :-



- \*  $P_4O_6$  is four lone pairs of electrons
- \*  $P_4O_6$  is also  $P_2O_3$  form
- \*  $P_4O_6$  is Tetrahedral symmetry

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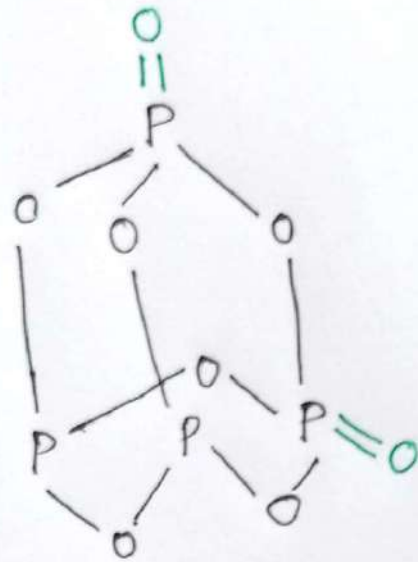
2) Structure of  $P_4O_7$  :-



- \* The  $P_4O_7$  molecule reacts to form both phosphoric acid and phosphorous acid
- \*  $P_4O_7$  is crystalline block phosphorous has a corrugated layer str

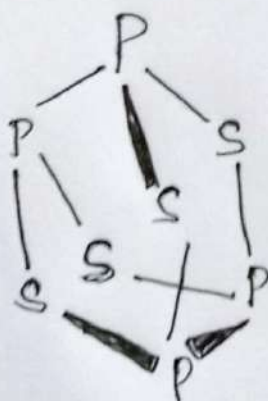
NOTE :- molecular structures of some phosphorus and sulphide distance in "picometer" (pm)

3) Structure of  $P_4O_8$  :-

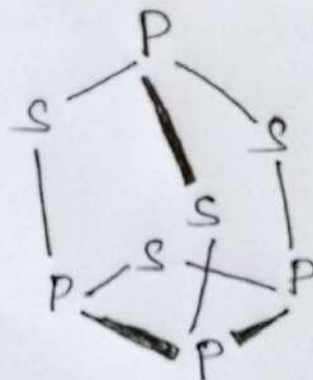


4) Structure of  $P_4S_4$  :-

$P_4S_4$  exists two isomers :- i)  $\alpha$ - $P_4S_4$  ii)  $\beta$ - $P_4S_4$



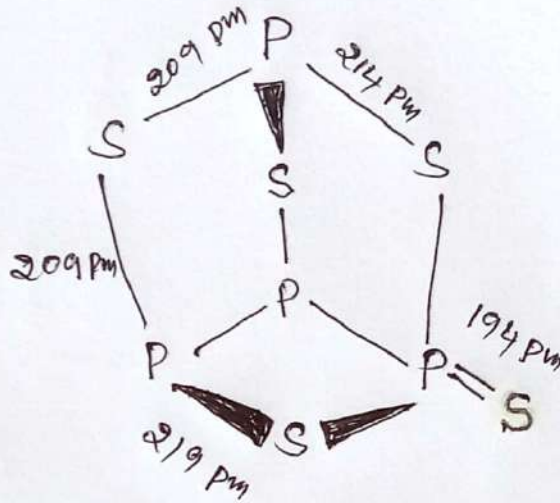
Str of  $\alpha$ - $P_4S_4$



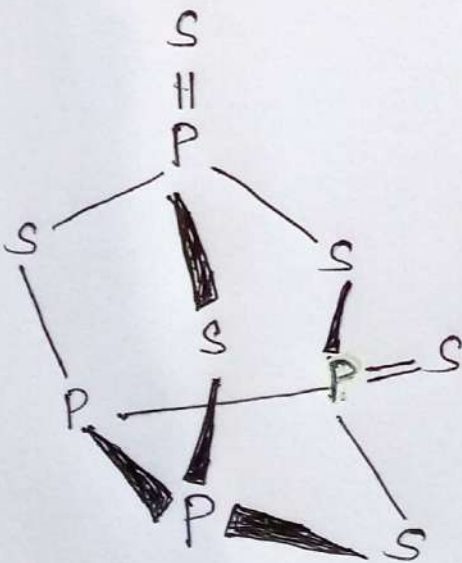
Str of  $\beta$ - $P_4S_4$

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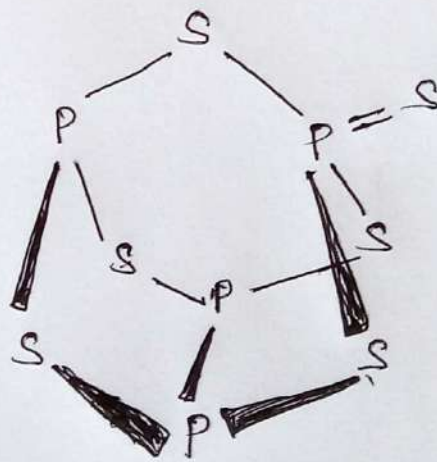
5) Structure of  $P_4S_5$  :-



6) Structure of  $P_4S_6$  :-  $P_4S_6$  exhibits three forms of str such as  $\alpha$ - $P_4S_6$ ,  $\beta$ - $P_4S_6$  and  $\gamma$ - $P_4S_6$

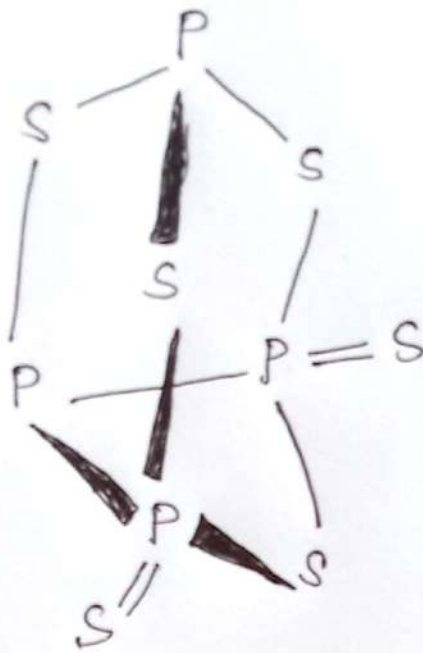


$\alpha$ - $P_4S_6$



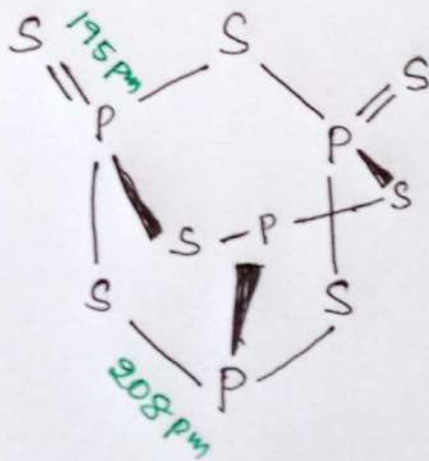
$\beta$ - $P_4S_6$

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$\sqrt{-} P_4S_6$

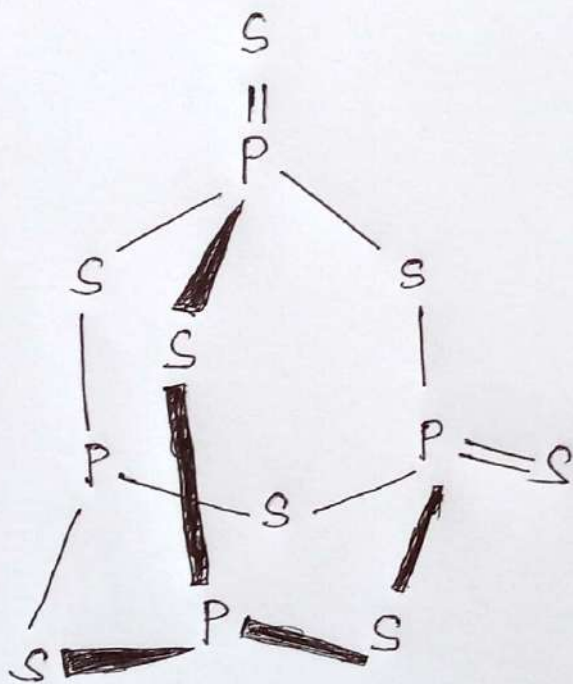
7) Structure of  $P_4S_7$  :-



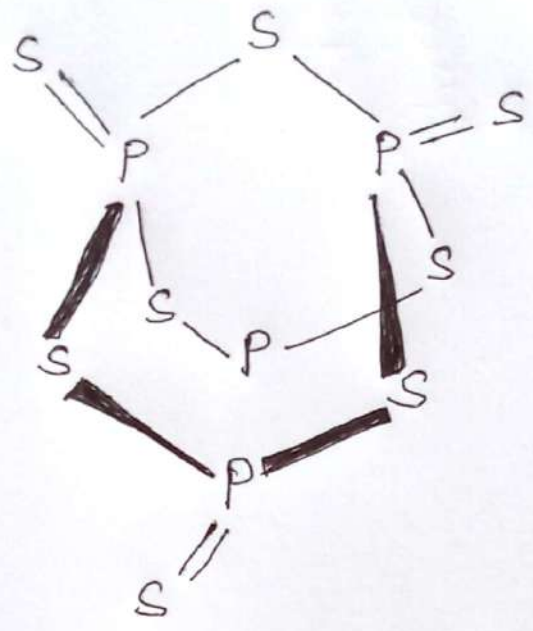
\* 8) Structure of  $P_4S_8$  Tetraphosphorous octa sulphide:-

The ~~str~~ of  $P_4S_8$  exhibits three structures such as  $\alpha$ - $P_4S_8$ ,  $\beta$ - $P_4S_8$  and  $\gamma$ - $P_4S_8$

i)  $\alpha$ - $P_4S_8$ :-



ii)  $\beta$ - $P_4S_8$  :-



iii)  $\alpha$ - $P_4S_8$  :-

