

Figure 2.1: The various type of (A)- polyphosphates and, (B)- polyphosphazenes.

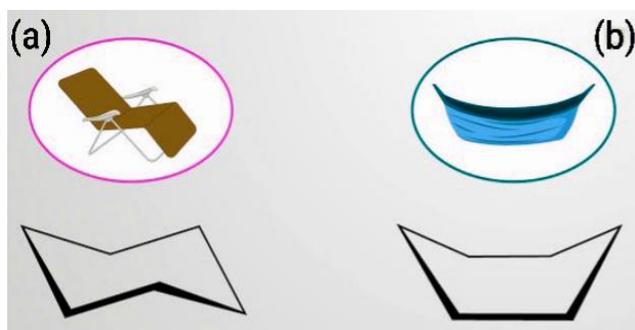


Figure 2.2: The possible imaginary (a)- chair and, (b)- boat shape for poly-(phosphates and phosphazenes).

The polyphosphates and polyphosphazenes have the linear, branched or cross-linked and cyclic ring structures (figure 2.1). These are may be cyclic -trimer, -tetramer or other higher polymers type. These can have possible stereochemistry with chair and boat conformation, as in figure 2.2, (source: from internet), which are well described earlier in our previous paper¹⁴. There is an ample evidence

that the trimeta-phosphate (P_3O_9)³⁻ ion rings have chair conformation with C_{3V} point-group¹⁵ in crystalline solid state and in solution consistent with D_{3h} molecular symmetry, where as the tetra- metaphosphate (P_4O_{12})⁴⁻ ion rings are puckered with boat (I) and chair (II), but conformations vary from compound to compound (figure 3a and b). The vibrational spectroscopic data of (P_3O_9)³⁻ ion having the P-O bond length of 0.1615 nm (endocyclic) and 0.1484 nm (exocyclic) even the larger one is about 0.01 nm shorter than would be anticipated for ion a single bond supporting the presence of pi- ($p\pi-d\pi$) bonding in all P-O bonds. Where the crystal structure of the chair form of $(NH_4)_4P_4O_{12}$ which gives equal ring (0.1607 nm) and terminal (0.1479 nm) P-O bonds with C_{2h} molecular symmetry. The structure of hexametaphosphate (P_6O_{18})⁶⁻ ion also shows equivalence in the two kinds of P-O bond, both in close agreement with these observed for the tri- and tetra- homologues of phosphates.

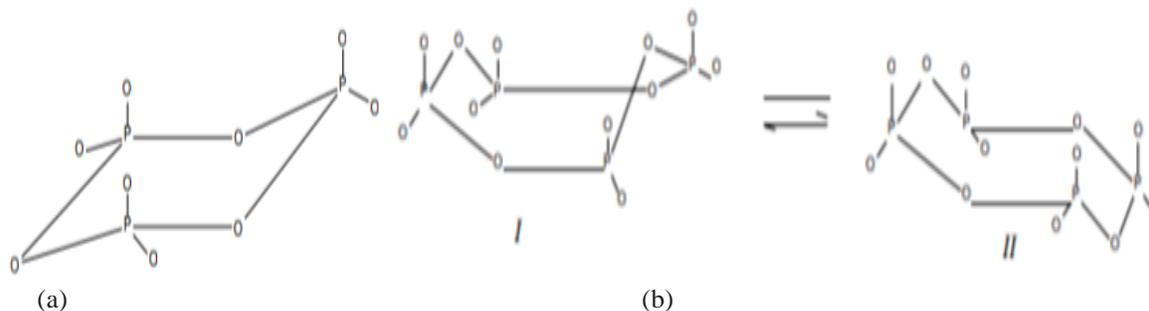


Figure 3: (a)- Chair form of trimetaphosphate, and (b)- boat (I)-chair (II) conformation in $(P_4O_{12})^{4-}$ ion.

Indeed, the extensive interest in the phosphazenes, the hydrolysis of trimeric chloride to the acid, takes place slowly with a tautomeric change as shown for the derivatives of alcohol and amines. The chelated trimer spiroposphazenes such as 1,1-dichloro-*trans*-3,5-*bis*(*p*-tolyl)-3,5-diphenyl cyclotriphosphazene have optical isomers¹⁶. However, some cyclophosphazene derivatives and aryl-halogenophosphazenes

also have geometrical (*cis-trans*) isomerism¹⁷. Consequently, the alkoxy- and aryloxyphosphazenes show tautomerism and the aziridinyphosphazene's derivatives, with partial replacement not only give-rise to positional but also *cis-trans* isomerism¹⁴. The molecular geometry of P-N polymers has been assigned by Raman, IR and X-Ray analysis resembles that of the $(NPF_2)_x$, where $x = 3$ or 4; are planar

with boat-chair conformation (figure 4a and b), but larger rings are not planar. For other $(\text{NPX}_2)_n$ compounds the six rings are planar with D_{3h} symmetry, but larger rings are generally non-planar and NPN angles of $\sim 120^\circ$ and PNP angles of $\sim 132^\circ$. The P-N bond distances which are generally equal in these ring systems, lie in the range 1.55-1.61 Å; there considerable attention to P-N stretching is at an appreciable higher frequency (1220 cm^{-1}) than that expected for a P-N single (about 750 cm^{-1}) bond of as 1.75-1.80 Å and paid to the nature of P-N π bonding¹⁴. Although, these rings are conformationally flexible and π -bonding is

only one of many factors that influence the conformation, but the matter is still subject to controversy. The main question concerns the extent of delocalization all around the rings show a kind of aromatic character or whether these are more localized 'islands' within the NPN segments. Although, there may be considerable differences between the essentially planar rings and those that are puckered. The problem is a complicated one owing to the large number of orbitals potentially involved and to the general lack of ring planarity which means that rigorous assignment of σ and π character to individual orbitals is impossible respectively¹⁷.

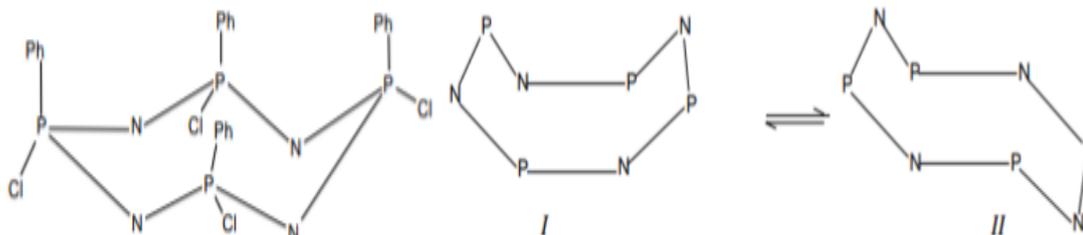


Figure 4: (a)- Tetramer, *cis*-(NPClPh)₄, and (b)- boat (I)-chair (II) conformation in tetramer (NPCl₂)₄, (skeletal form for tetrameric phosphonitrilic chloride).

4. Conclusions

In conclusion, we have reported the studies on about P-O and P-N bond containing phosphorus compounds. Where the various conformational data and chemical analyses confirm that, the polymeric P-O and P-N bonded compounds such as poly-(phosphates and phosphazenes) have been shown the stereo- and geometrical isomerism with chair-boat conformation as well as molecular symmetry (mostly C_{3v} , C_{2h} and D_{3h}), in their structure as well.

References

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