

NOTE**Isomerism, Conformation and Molecular Symmetry in Phosphorus Compounds**

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The phospha-V-ates and phospha-V-azenes have shown to the stereo- and geometrical isomerism, chair-boat conformation and C_{3v} , C_{2h} and D_{3h} molecular symmetry in their novel structure, which are structurally characterized by X-ray analyses, IR, Raman, ^{31}P NMR and vibrational spectra.

Key Words: Phosphorus polymers, Phosphates, Phosphazenes.

There is ample evidence that the trimeta-phosphate (P_3O_9)³⁻ ion rings have chair conformation with C_{3v} point-group¹ in crystalline solid state and in solution consistent with D_{3h} molecular symmetry², where as the tetrametaphosphate (P_4O_{12})⁴⁻ ion rings are puckered but conformations vary from compound to compound³.

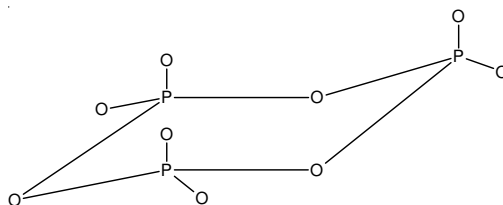


Fig. 1a. Chair form of trimetaphosphate

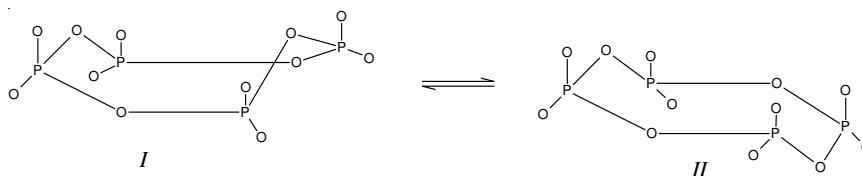


Fig. 1b. Boat(I)-chair(II) conformation in (P_4O_{12})⁴⁻ ion

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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 alcohol⁴ and amines⁵. The chelated trimer spiroposphazenes such as 1,1-dichloro-*trans*-3,5-bis(*p*-tolyl)-3,5-diphenyl cyclotriphosphazene have optical isomers⁶.

However, some cyclophosphazene⁷ derivatives and aryl-halogenophosphazenes also have geometrical (*cis-trans*) isomerism⁸⁻¹⁰.

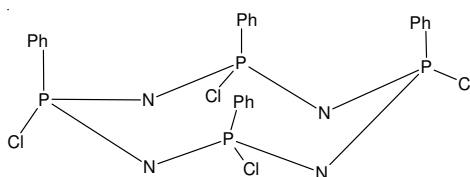


Fig. 2. Tetramer, *cis*-(NPClPh)₄.

For tetrameric phosphonitrilic chloride¹¹.

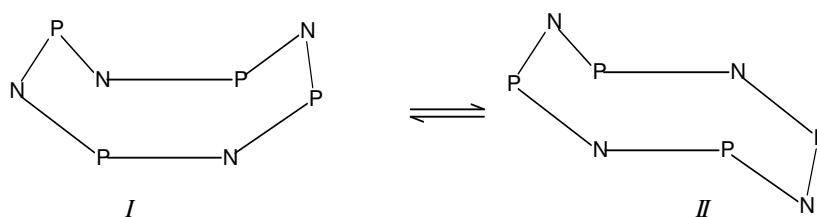


Fig. 3. Boat(I)-chair(II)-conformation in tetramer (NPCl₂)₄, (skeletal form)

Consequently, the alkoxy- and aryloxyphosphazenes show tautomerism^{12,13} and the aziridinyphosphazene's derivatives¹⁴ with partial replacement not only give rise to positional but also *cis-trans* isomerism¹.

The vibrational spectroscopic data of (P₃O₉)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 π-(pπ-dπ) bonding in all P-O bonds¹⁵. Where the crystal structure of the chair form of (NH₄)P₄O₁₂ which gives equal ring (0.1607 nm) and terminal (0.1479 nm) P-O bonds with C_{2h} molecular symmetry¹⁶. The structure of hexametaphosphate (P₆O₁₈)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.

The molecular geometry of P-N polymers has been assigned by Raman, IR and X-Ray analyses¹⁷, resembles that of the (NPF₂)_x, where x = 3 or 4; are planar, but larger rings are not planar. For other (NPX₂)_n compounds the six rings are planar with D_{3h} symmetry, but larger rings are generally non-planar and NPN angles of ~120° and PNP angles of ~132 °C. 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 stretching¹⁸ is at an appreciable higher frequency (1220 cm⁻¹) than that expected for a P-N single-(about 750 cm⁻¹) bond of *ca.* 1.75-1.80 Å and paid to the nature of P-N π bonding. 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, kind of aromatic character, or whether these are more localized 'islands' within the NPN segments. Of course 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.

Conclusion

The chemical analyses and spectroscopic data confirm that, the polymer of phosphorus such as phosphates and phosphazenes have shown the isomerism (stereo- and geometrical), chair-boat conformation and molecular symmetry (mostly C_{3v}, C_{2h} and D_{3h}), in this structure.

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