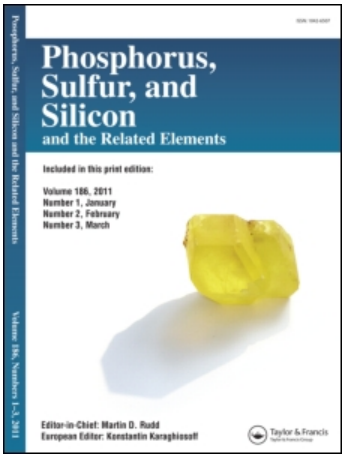

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STRUCTURAL CHEMISTRY OF NON - CYCLIC PHOSPHAZENES

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Abstract The crystal structures of some open-chained trichlorophosphazenes, the $NPCl_3$ groups attached to carbon, were determined at low temperature (90K, 100K), and the structures were compared in order to show the conformational variability of these compounds. This investigation comprises the structures of the cations in $[Cl\text{-}C(NPCl_3)_2]PCl_6$ and in $[CH_3\text{-}C(NPCl_3)_2]SbCl_6$, and the molecular structures of 2,2,4-trichloro-6-trichlorophosphazeno-1,3,5,2λ^5-triazaphosphorine, $C_2Cl_6N_4P_2$, and of a triclinic and a monoclinic modification of 2,4,6-tris(trichlorophosphazeno)-1,3,5-triazine, $C_3Cl_9N_6P_3$.

INTRODUCTION

From a synthetic and structural viewpoint phosphazene polymers constitute the broadest and most versatile of the known inorganic macromolecular systems. Since for polymers only limited structural data can be obtained it is reasonable to take small molecules as model compounds and to get precise data from single-crystal X-ray structural analyses of them. Most structural data of phosphazenes are known from the cyclic compounds which are not good model compounds for the polymers because of their ring constraints.

Concerning the important chlorophosphazenes, crystal structures of some non-cyclic compounds are described in the literature: $[Cl_3PNPCl_3]^+X^-$, $X^- = PCl_6^-$ [1], $X^- = MoCl_6^-$, $MoOCl_4^-$ [2], $[C(NPCl_3)_3]SbCl_6$ [3], $[C(NPX_3)_3]SbBr_6$, $X = Br_{0.78}Cl_{0.22}$ [4], $(Cl_3C)_2C(Cl)NPCl_3$ [5], $(F_3C)_3CNPCl_3$ at 153K and at 208K [6], $Cl_2P(O)NPCl_3$ at 223K, $Cl_2P(O)NPCl_2NPCl_3$ and $[Cl_3P(NPCl_2)_3Cl]PCl_6$ [7]; $[ClP(NPCl_3)_3]^+X^-$, $X^- = Cl^-$, PCl_6^- at 100K [8], $Cl_2P(O)NPCl_3$ at 100K [9], $[P(NPCl_3)_4]ICl_2 \cdot 2[(CCl_4)_x(CHCl_3)_{1-x}]$, x=0.67(2) at 105K and at 293K [10], $SO_2(NPCl_3)_2$ at 100K [11].

In this work the molecular structures of some open-chained trichlorophosphazenes, the $NPCl_3$ group attached to carbon were compared in order to show the conformational variability of these compounds.

STRUCTURE OF THE $[X\text{-}C(NPCl_3)_2]^+$ CATIONS

Chlorobis(trichlorophosphazeno)carbenium hexachlorophosphate, $[Cl\text{-}C(NPCl_3)_2]PCl_6$, may be obtained by reaction of cyanamide with PCl_5 [12]. There are two formula units in the asymmetric unit of the monoclinic cell. Both the cations show cis-trans conformations with respect to their Cl-C-N-P torsion angles instead of the most symmetric ($C2_v$-mm2) cis-cis conformation. A trans-trans conformation is not possible by sterical hindrance of the two $NPCl_3$ groups.

The related compound bis(trichlorophosphazeno)methyl-carbenium hexachloro-antimonate, $[CH_3\text{-}C(NPCl_3)_2]SbCl_6$, can be synthesized by reaction of ethanamidine with PCl_5 [13]. Once again there are two formula units in the asymmetric unit of the triclinic cell, and both the cations show cis-trans conformations with respect to their C_{Me}-C-N-P torsion angles as predicted for this compound [13]. The comparison of the four independent cations in the two compounds shows the agreement in the conformation (see Fig. 1). Solely the arrangement of the PCl_3 groups is different in the two compounds.

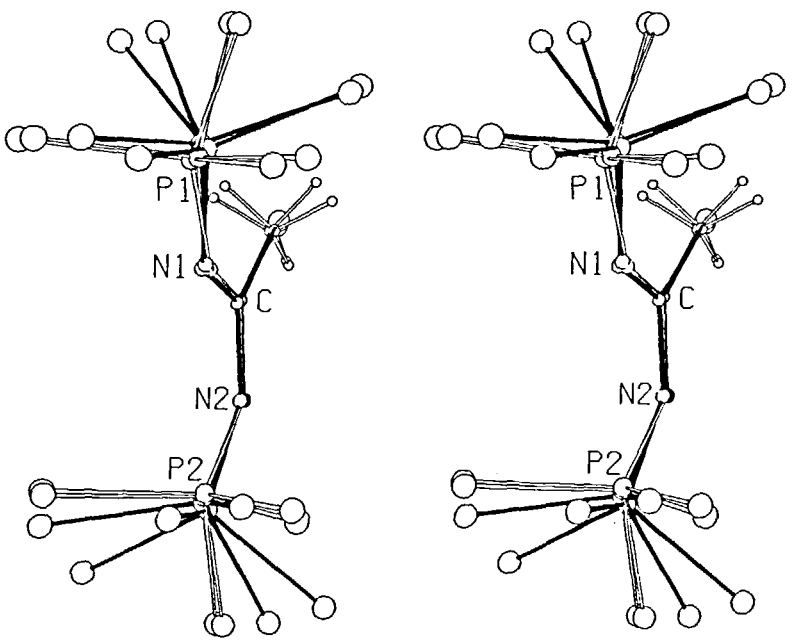

FIGURE 1 Stereographic projection of a fit of the cations in $[Cl\text{-}C(NPCl_3)_2]PCl_6$ (full lines) and in $[CH_3\text{-}C(NPCl_3)_2]SbCl_6$ (open lines).

STRUCTURE OF $C_2Cl_6N_4P_2$

The reaction product of dicyanodiamide with PCl_5 in a ratio of 1:2 is 2,2,4-trichloro-6-trichlorophosphazeno-1,3,5,2λ^5-triazaphosphorine and not 2,4,6-trichloro-2-trichlorophosphazeno-1,3,5,2λ^5-triazaphosphorine as given in the literature [12]. This is confirmed by an X-ray structure analysis at 90 K. A least-squares fit between the atomic positions of the ring atoms and the adjacent atoms of the two independent molecules of the asymmetric unit demonstrates the low variability in conformation of the compound (see Fig. 2).

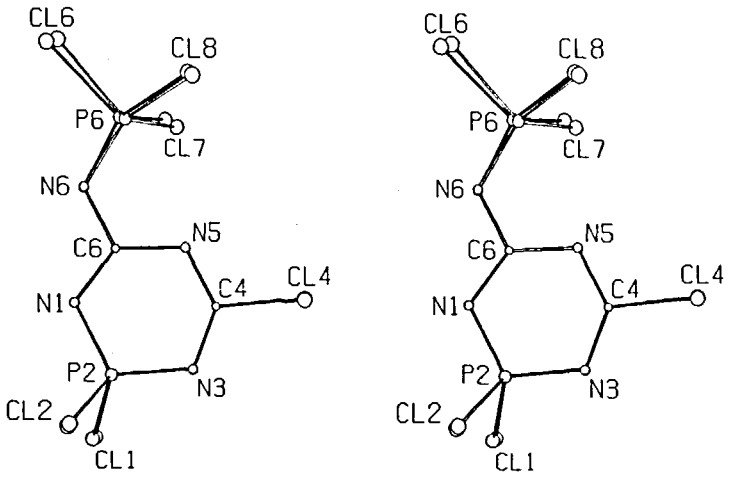

FIGURE 2 Stereographic projection of a fit of the two independent molecules in the asymmetric unit of $C_2Cl_6N_4P_2$.

STRUCTURE OF $C_3Cl_9N_6P_3$

By reaction of melamine with PCl_5 a triclinic and a monoclinic modification of 2,4,6-tris(trichlorophosphazeno)-1,3,5-triazine with totally different cell constants may be obtained. They both contain solvent molecules and PCl_6^- anions and make difficulties in the refinements (R = 10.5%, 10.8%) due to disorder in the included solvent molecules. But since the $C_3Cl_9N_6P_3$ molecules scarcely suffer from disorder, and since there are two molecules in the asymmetric units of both modifications, the average of the very similar conformations of the four independent molecules (see Fig. 3) may be taken as the most stable conformation of the molecule. This conformation showing approximately C_s symmetry is characterized by the longest possible all-trans chains.

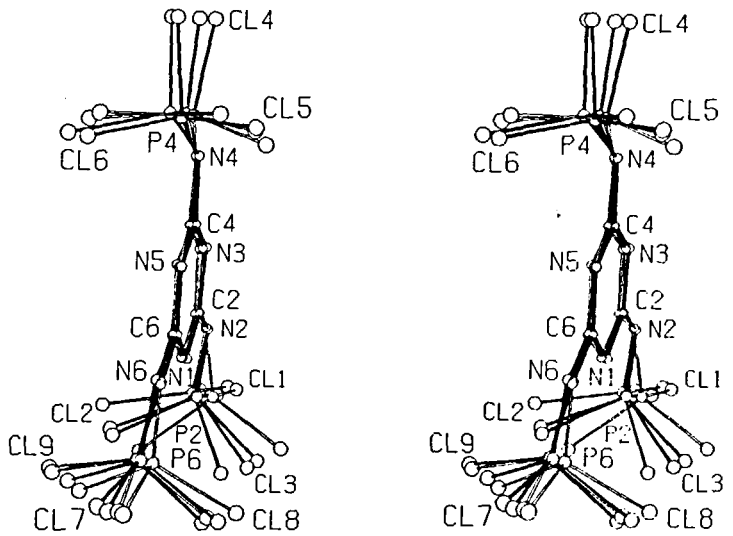

FIGURE 3 Stereographic projection of a fit of the four independent molecules in the triclinic (full lines) and monoclinic (open lines) modifications of $C_3Cl_9N_6P_3$.

The author thanks Prof. Kratky for the use of the diffractometer and Prof. Schmidpeter for the crystals of $[CH_3\text{-}C(NPCl_3)_2]SbCl_6$.

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