X-RAY CRYSTALLOGRAPHIC INVESTIGATIONS OF CYCLOTRIPHOSPHAZENES

A Thesis
Submitted for the Degree of
DOCTOR OF PHILOSOPHY
IN
PHYSICS

By
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DECLARATION

I hereby declare that the entire work embodied in this thesis is the result of the investigations carried out by me in the X-ray laboratory of the Department of Physics, S.V. University, Tirupati, under the guidance of Dr. L. Ramamurthy, and that it has not been submitted for the award of any degree, diploma or associateship.

In keeping with the general practice in reporting of scientific observations, due acknowledgements has been made wherever the work is based on the finding of other investigations.

M. Krishnaih

(M. KRISHNAIAH)

Tirupati

February, 1905
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PREFACE

The thesis entitled "X-ray crystallographic investigations of cyclotriphosphazenes" consists of five chapters and an appendix. This thesis embodies a detailed single crystal structure analysis of three cyclotriphosphazenes (Chapters 3, 4 and 5) and a quinoline derivative (Appendix).

Chapter 1 presents an introduction to the theoretical background and experimental techniques of crystal structure determination by X-ray diffraction methods. It describes briefly the diffraction by single crystals, intensity data collection, corrections for various geometrical and physical factors, the methods of structure solution with emphasis on the computer programmes which the author has used for the crystal structure determination and the refinement procedures.

Phosphazenes are a class of inorganic compounds containing alternate phosphorus and nitrogen atoms with two substituents on each phosphorus atom. The cyclo- and polyphosphazenes are probably the best known and most extensively studied P-N derivatives. The cyclophosphazenes are thermally stable and resistant to chemical attack. The phosphazenes were among the first heterocatom systems to be suspected of exhibiting aromatic-type delocalization behaviour. The bonding in these compounds is still a matter of debate and cyclophosphazenes have aroused considerable interest as they might serve as models for understanding the nature of
bonding in other inorganic ring systems.

Apart from the fundamental interest, cyclophosphazenes and phosphazene based polymers show considerable promise for a variety of applications. For example cyclophosphazene derivatives have been found to be valuable as flame retardants, pesticides and chemosterilant insecticides. The potential use of (aziridine) and platinum complexes cyclophosphazenes as antitumour agents has received much attention in the past few years.

Structural investigations of cyclophosphazene derivatives have become increasingly important in connection with the effect of substituents on the conformation of cyclophosphazene ring and the nature of bonds in the ring as well as those involving the exocyclic substituents.

A detailed analysis of the basicity values obtained for cyclophosphazenes having triphenylphosphazanyl groups as substituents (Shaw and co-workers, 1964-1969) revealed that these values fall into two groups which were called type I and type II. The basicity data suggest that protonation can take place either at the ring nitrogen atom (type I) or at the exocyclic nitrogen atom (type II). In type I conformation, the N-P bond of the NPh₃ group would be more or less parallel to the local N-P-N segment, whereas in type II conformation it is approximately perpendicular to the local ring N-P-N segment. X-ray crystallography would be an
important technique to substantiate these postulates.

In Chapter 2, the salient structural features that have emerged from the earlier X-ray crystallographic studies of cyclophosphazenes are discussed.

The first structure investigated by the candidate is that of 2,2,4,4-tetrachloro-6,6(2', 2' 2' triphenylphosphazeny) cyclophosphazatriene, \( \text{N}_3\text{P}_3\text{Cl}_4\text{(NPPh}_3\text{)}_2 \) (Chapter 3) I.

\[
\text{Ph} \quad \text{P} \quad \text{Ph} \\
\text{Ph} \quad \text{P} \quad \text{N} \quad \text{P} \quad \text{Ph} \\
\text{Ph} \quad \text{N} \quad \text{P} \\
\text{P} \quad \text{N} \quad \text{P}
\]

This is the first example of a structure containing geminal \( \text{NPPh}_3 \) groups and therefore their conformation is of considerable interest. The compound crystallises in the triclinic space group \( \text{P} \text{I} \) with \( a = 10.723(1) \), \( b = 11.567(2) \), \( c = 17.454(6) \) Å, \( \alpha = 102.5(2) \), \( \beta = 87.1(2) \) and \( \gamma = 114.6(1)^\circ \) and \( Z = 2 \). The structure was solved by direct methods and refined to an \( R \)-index of 0.036. Both \( \text{NPPh}_3 \) groups exhibit type II conformation. The conformation of phosphazene ring is a distorted chair. Results are compared with other triphenylphosphazenyI derivatives of cyclophosphazenes whose structures have been solved.

X-ray crystallographic results for a large number of the trimeric phosphazenes and their halogeno, amino, phenyl
and phenoxy-substituents have been reported in the literature, but sulphur substituted cyclophosphazenes have not been studied so far. In the present study, the crystal and molecular structures of two cyclotriphosphazenes with phenyl-thio groups as substituents have been determined for the first time. The molecule studied is 2,2,4,4-tetrachloro 6,6-bis(phenylthio)cyclotriphosphazatriene, \( N_3P_3Cl_4(SPh)_2 \) (II)

\[
\begin{align*}
\text{N} & \quad \text{P} \\
\text{Cl} & \quad \text{P} \\
\text{PhS} & \quad \text{P} \\
\text{Cl} & \quad \text{P} \\
\end{align*}
\]

The results obtained for this system are discussed in Chapter 4. The crystals belong to orthorhombic system, space group \( P_{ccn} \), with \( a = 6.963(7) \), \( b = 13.492(3) \) and \( c = 21.443(5) \, \text{Å} \) and \( Z = 4 \). The structure was solved by direct methods and refined to an \( R \)-index of 0.047. The molecule is found to lie on a 2-fold axis of symmetry. The conformation of the phosphazene ring is approximately planar with tendency towards chair conformation.

Chapter 5 discussed the crystal structure of Hexakis (phenylthio)cyclotriphosphazatriene \( N_3P_3(SPh)_6 \) (III)

\[
\begin{align*}
\text{PhS} & \quad \text{P} \\
\text{N} & \quad \text{P} \\
\text{PhS} & \quad \text{P} \\
\text{PhS} & \quad \text{P} \\
\end{align*}
\]

The compound crystallizes in orthorhombic space group \( P2_12_12 \) with \( a = 19.392(2) \), \( b = 7.559(2) \) and \( c = 12.685(2) \, \text{Å} \) with
Z = 2. The structure was solved by the direct methods using visually measured intensities and subsequently refined using diffractometer data to an R-index of 0.029. The molecule, as in the first case, lies on crystallographic two fold axis. The conformation of the phosphazene ring is planar and the results are discussed in comparison with those for the oxygen analogue \( \mathrm{N}_3\mathrm{P}_3(\mathrm{OPh})_6 \), whose structure has been earlier determined.

In the appendix, the results of the crystal structure analysis of 2-phenyl-3-methyl-4-hydroxyloporphynoquinoline \( \mathrm{C}_{16}\mathrm{H}_{23}\mathrm{NO}_4 \) are presented. The determination of this structure was undertaken to find out the conformational features of the piperidine ring. The crystals are orthorhombic, space group \( \text{Pbca} \) with \( a = 43.036(2), b = 12.344(3) \) and \( c = 10.451(3) \) Å and \( Z = 16 \). The structure was solved using direct methods and refined to an R-index of 0.009. The conformation of the piperidine ring of two molecules in the asymmetric unit differ. The hydrogen atom bonded to N is equatorial in one molecule whereas it is at axial position in the second molecule. The crystal structure is stabilized by O–H...N type of hydrogen bond.
List of the papers published and presented at various conferences:


5. The crystal and molecular structure of 2-phenyl-3-methyl-4-hydroxylperhydroquinoline, $C_{16}H_{23}NO$. M. KRISHNAIAH, L. Ramamurthy and K. Venkatesan. (1981). Paper presented at the XII National Crystallographic Conference held at Hyderabad. (INDIA),