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NITRILOHEXAPHOSPHONITRILIC CHLORIDE

by

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ABSTRACT

The isolation of nitrilohexaphosphonitrilic chloride is reported in this work, and its structure shown to be a tricyclic condensed ring. The physical and chemical properties of this molecule are unlike the monocyclic phosphonitrilic chlorides. The reasons for this are not fully understood, but are thought to involve the weakness of the central P-N bond; the crystal structure and mass spectrum of the molecule show that this central bond is long and weak. Substitution reactions, common in the monocyclic chlorides, bring about either a partial or total break-down of the tricyclic P_6N_7 skeleton. In the case of electron-withdrawing substituents (e.g. -F,OMe), complete loss of the phospho-nitrilic skeleton is achieved, and, in the case of electron-donating groups (-NMe$_2$), substitution onto the ring brings about cleavage of one of the internal P-N bonds. The molecule that is formed during the dimethylamination of $P_6N_7Cl_9$ is unique in phosphonitrilic chemistry and its suggested structure visually emphasizes the weakness of the central P-N bond in $P_6N_7Cl_9$.

A series of molecular orbital calculations on the $P_6N_7Cl_9$ molecule were carried out in this study, and it is suggested that the observed structural trends in the molecule can be attributed to the properties of the phosphorus $3d_{yz}$ orbital on the bridgehead atoms.

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To Mum and Dad

CHAPTER 1

INTRODUCTION

Inorganic ring systems, of the general type $(AB)_n$, have been prepared between many elements of the first two rows of the Periodic Table. However, polycyclic ring systems are much rarer. These poly-cyclic compounds are usually unstable and are formed in small yields as decomposition products of reactions involving monocyclic systems. In most instances where the isolation of a polycyclic condensed ring species has been reported, no discussion of the chemistry of these compounds has been given.

Condensed ring species in inorganic chemistry are of interest not only because of their novelty, but because their chemistry may be very different from that of ordinary cyclic systems, the properties of bridgehead atoms often being quite unusual in comparison to that of non-bridgehead atoms.

In siloxane chemistry, linear, cyclic and crosslinked species are all known. In borazine chemistry, the pyrolysis of cyclotriborazine at 380°C gives hydrogen and a mixture of condensed species,[1] one of which is believed to have the structure shown in Fig. 1.1a. B-trichlorocyclotriborazine reacts with methylmagnesium bromide to give the expected B-trimethyl derivative, $(MeB-NH)_3$. The other product, which is not expected, is again a naphthalene analogue[2] (see Fig. 1.1b).

Condensed ring silazanes have been prepared, and the compound shown in Fig. 1.1c has been isolated as a minor product during the reaction of cyclohexamethyltrisilazane with potassium hydroxide at ~180°C.[3] The ammonolysis of methyldichlorosilane yields, as a minor product, the compound illustrated in Fig. 1.1d.[4] In carbon-nitrogen ring systems, the pyrolysis of melamine $(NH_2-C=N)_3$ at 350°C yields a compound whose structure is suggested to be a condensed ring[5] (Fig. 1.1e).

Thus, within any heterocyclic ring system $(AB)_n$, there exist, at most, only a few condensed ring species, and very little is known of the physical and chemical properties of these species in comparison to their monocyclic congeners.

The family of compounds known as the cyclic phosphonitriles contain the same basic repeating unit $+PX_2=N+$. The classical reaction used in the preparation of cyclic phosphonitriles is that between phosphorus pentachloride and ammonium chloride, and was first carried out by Stokes in 1897:-[6]

$$PC\ell_5 + NH_4C\ell \longrightarrow \frac{1}{n}(NPC\ell_2)_n + 4HC\ell \qquad \ldots\ldots\ldots 1.1$$
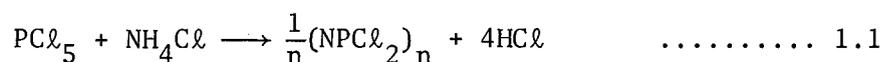
Unlike all other inorganic ring systems, and all organic annulenes, ring sizes corresponding to n = 3,4,5 ... are formed in this reaction. This fundamental property of these compounds, namely the ease of preparation of different ring sizes, illustrates the unique nature of the bonding in these compounds. The original theories[7,8] on the
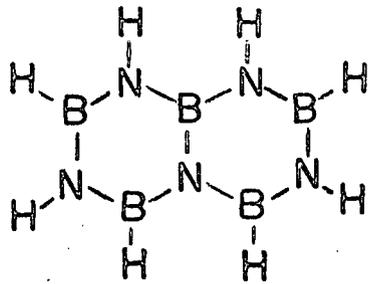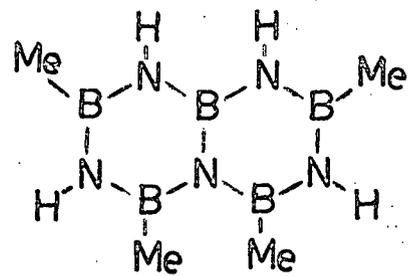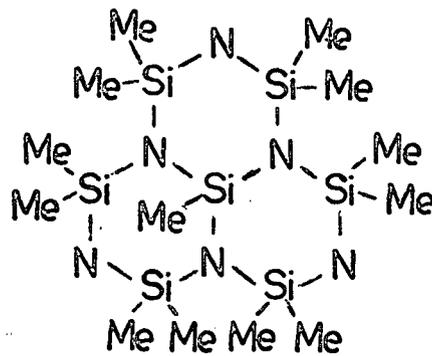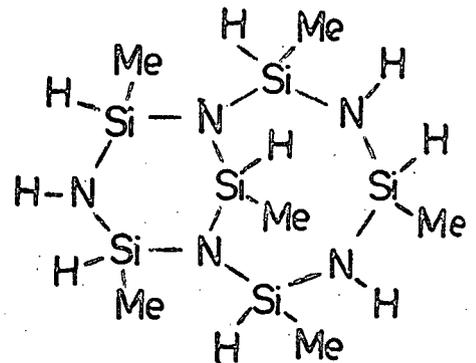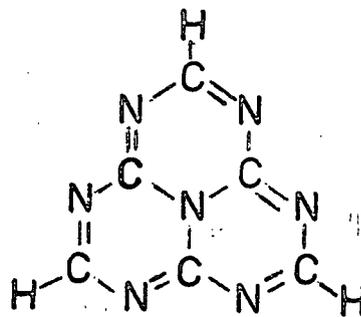
Fig. 1.1. Suggested structures of some inorganic molecules that are believed to be condensed ring compounds.

bonding in phosphonitriles invoked the use of d-orbitals to explain this unique type of bonding, the difference in symmetry properties of d- and p-orbitals being used to account for the general stability of all ring sizes.

The chemistry of the phosphonitriles has been studied extensively and ligand replacement reactions are numerous. However, up to the present time, all experimental and theoretical studies have been restricted to monocyclic derivatives. In the course of the work carried out by Stokes, a compound was isolated with the molecular formula $P_6N_7Cl_9$. This compound was made as a minor product in the reaction between phosphorus pentachloride and ammonium chloride (equation 1.1). This reaction, as carried out by Stokes, was done in sealed glass tubes at a temperature of 200°C. More recent workers have done this experiment in refluxing solvents at temperatures less than 140°C, and the compound $P_6N_7Cl_9$ has never been isolated during these reactions. The chemistry of this compound has, up until now, never been studied. Its structure, both molecular and electronic, has not been known.

In 1955, Krause apparently obtained the compound $P_6N_7Cl_9$ by the thermal depolymerization of a phosphonitrilic chloride high polymer.[9] However, few details were given by him on the characterization of this compound and no studies were made of its chemistry. At this time, the structure that was suggested for this molecule was a tricyclic con-densed ring (Fig. 1.2) but no evidence was given in support of this

structure.

Studies on the mass spectra of the phosphonitrilic chlorides[10] have shown evidence of the existence of ions, the parent molecules of which are thought to have condensed ring structures. One of these structures corresponds to that proposed for $P_6N_7Cl_9$ (Fig. 1.2). The proposed structures of the other condensed ring molecules are given in Fig. 1.3.

Thus, at the beginning of this work, there was only a small amount of scattered information on condensed ring phosphonitrilic chemistry. Because of the lack of information in this field, the purpose of this present work has been to study the chemistry of condensed ring phosphonitrilic chlorides. During this work, the isolation of $P_6N_7Cl_9$ has been carried out and the compound is now fully characterized. Vibrational, mass and ^{31}P n.m.r. spectra confirmed the condensed ring structure of the molecule, the proper name of which is 3,7,11,nitrilo-nonachlorocyclohexaphosphonitrile. The name assigned to the compound by Stokes was nitrilohexaphosphonitrilic chloride, and this nomenclature will be used throughout this work. Even though the compound was prepared in only very small quantities, the chemical properties of the molecule were studied and several ligand substitution reactions were attempted, in order that the chemistry of $P_6N_7Cl_9$ might be related to that of the ordinary cyclic phosphonitrilic chlorides $(PNCl_2)_x$.

Ligand substitution reactions with the ordinary phosphonitrilic chlorides are common. Fluorination of the chlorides with potassium
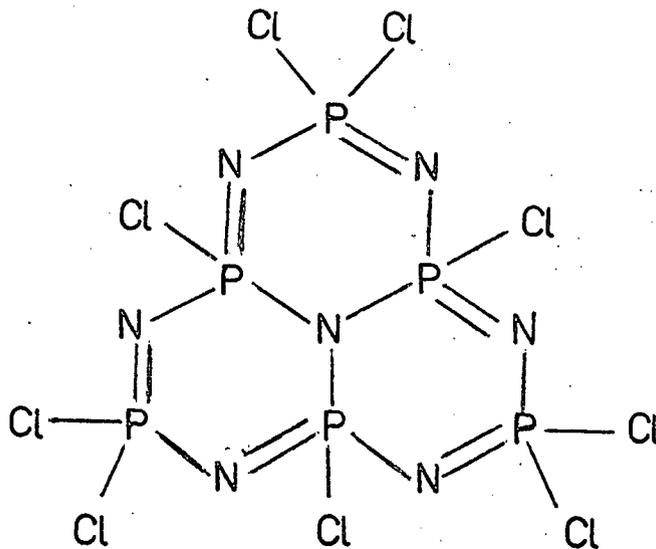
Fig. 1.2. Tricyclic condensed ring structure proposed[9] for nitrilo-
hexaphosphonitrilic chloride.

a).
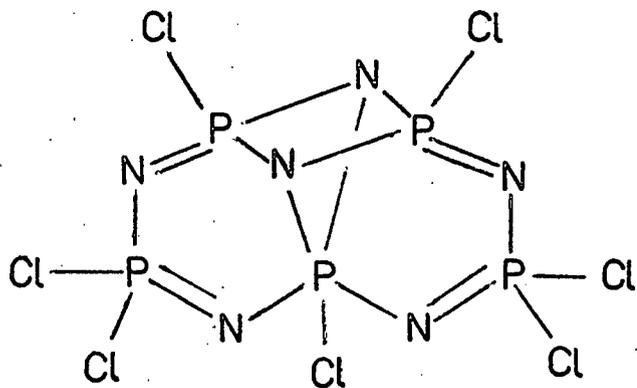
b).
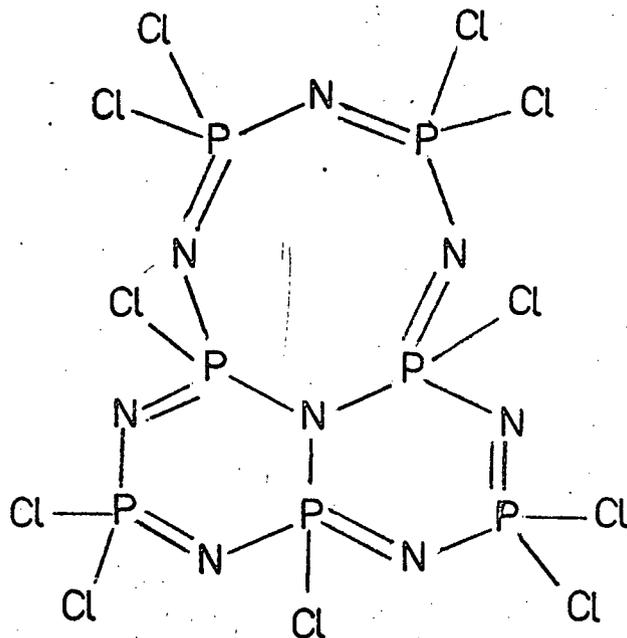
Fig. 1.3. Possible structures of parent molecules corresponding to
ions identified in mass spectra.

fluorosulphite produces the phosphonitrilic fluorides $(PNF_2)_n$[11];
amination of both the chlorides and the fluorides yields partially[12]
and fully[13,14] aminated phosphonitriles. Aryl[15] and alkyl[16]
derivatives can be prepared by reacting a phosphonitrilic fluoride
with the appropriate Grignard reagent.

The preparation of phosphonitrilic derivatives with different
substitution patterns has also received attention. For example,
substitution of a chlorine ligand in $(PNCl_2)_n$ by a fluorine atom
increases the electrophilicity of the phosphorus atom at which the
substitution has occurred. Further substitution is therefore favoured,
and in the case of fluorination, this substitution is always geminal.
On the other hand, amination of the phosphonitrilic ring deactivates
the ring to further substitution, especially at the substituted
phosphorus atom. Further substitution is therefore found to take
place in a non-geminal fashion.[12]

Unlike that of the ordinary cyclic chlorides, the chemistry of
nitrilohexaphosphonitrilic chloride is limited. The introduction of
the central nitrogen into the P_6N_6 ring system has a drastic effect
on the properties of the molecule. The fragmentation pattern and
crystal structure of the compound indicate that the internal PN bond
is weak. Various substitution reactions were attempted on the
condensed ring chloride. When ring activating groups are used (-F,
-OMe), the tricyclic ring structure of the PN skeleton is destroyed.
Reaction with deactivating groups ($-NMe_2$) is less destructive, and

only partial ring cleavage occurs, leading to the isolation of a compound in which the tricyclic PN skeleton has been lost, but in which some crosslinking of the ring is still apparent.

The differences between the condensed ring chloride and the ordinary cyclic phosphonitrilic chlorides are therefore quite marked. The latter are stable to substitution, whereas the former is not. The physical and chemical properties of $P_6N_7Cl_9$ suggest that the reason for this lies in the weakness of the internal PN bond, which appears to be weaker than an exocyclic PCl bond.

Simple Hückel molecular orbital calculations have been carried out on an idealized condensed ring framework, using the out-of-plane d-orbitals on phosphorus and the out-of-plane p_z orbital on nitrogen to form π molecular orbitals. In so far as lone pair delocalization of the central nitrogen takes place only through the out-of-plane π-system, any effect which this delocalization has on the in-plane π-system will only be secondary. Since it is thought that it is the in-plane π-system which controls the chemical reactivity of phosphonitriles, the effect of the central nitrogen on the properties of the molecule should only be minimal. The fact that this is not the case, and that the results of base strength measurements and trends in bond-lengths are the reverse of those predicted by the M.O. calculations on the out-of-plane π-system, indicates that more detailed calculations, as well as more experimental information are necessary, before a complete understanding of this system is accomplished.

In the following chapters, the points outlined above will be fully discussed. In chapter 2 a full account is given of the various methods, both successful and unsuccessful, that were used in the preparation of the condensed ring chloride.

CHAPTER 2

PREPARATION OF NITRILOHEXAPHOSPHONITRILIC CHLORIDE

The original isolation of $P_6N_7Cl_9$ by Stokes was achieved during a high temperature reaction. In the present work, several directed syntheses from $N_6P_6Cl_{12}$ have been attempted without success, and at present the only route to this compound seems to be via high temperature rearrangements.

For the purposes of this thesis, the discussion of the types of preparation can be divided into two parts, the first involving attempted direct condensation reactions, and the second involving high temperature rearrangements.

I. Condensation Reactions

Throughout the course of this work, many comparisons were made between nitrilohexaphosphonitrilic chloride and the open ring hexa-phosphonitrilic chloride. Because of this analogy, a series of experiments was carried out on the $(PNCl_2)_6$ molecule in attempt to add an extra nitrogen atom to the PN skeleton. Lithium nitride has been used to make tertiary amines,[17] and was used here in an attempt to condense the P_6N_6 ring with the elimination of lithium chloride. The use of amino- derivatives of the group IV metals as aminating agents has been reported in the literature,[18,19] and dimethylamino-

trimethylsilane and -stannane have been used effectively to prepare

monofunctional dimethylamino-derivatives of phosphonitrilic fluorides.[20]

In view of the strength of the M-Cℓ bond (M = Sn,Si), when compared

to the M-N bond, it was hoped that the reaction of $(Me_3M)_3N$ with hexa-

phosphonitrilic chloride might produce the condensed ring, following

the reaction path suggested in equation 2.1.

$$(R_3M)_3N + (PNCℓ_2)_6 \longrightarrow P_6N_7Cℓ_9 + 3R_3MCℓ \qquad \ldots\ldots\ldots\ldots (2.1)$$
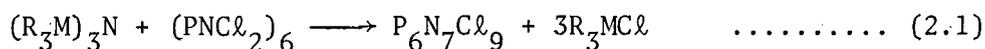
None of these reactions produced any $P_6N_7Cℓ_9$, nor was there any

indication that this type of direct preparation would do so. There is

an obvious steric strain involved in forming the molecule by this type

of reaction, and it is now thought that preparations of this type are

unfeasible.

II. <u>High Temperature Rearrangements</u>

The two previous reports of the isolation of $P_6N_7Cℓ_9$ have involved

the use of high temperatures. As has already been stated, the prepara-

tion of $(PNCℓ_2)_n$ in refluxing solvents does not produce any condensed

rings. The mechanism of the reaction between phosphorus pentachloride

and ammonium chloride has been studied by Becke-Goehring and

coworkers.[21,22] Essentially, the mechanism involves the formation of

linear cations of the type $[Cℓ_3P=N-PCℓ_3]^+$. These cations either

lengthen by further reaction or cyclize into the neutral phosphonitrilic

chlorides. If condensed ring species were formed in this reaction, at some stage an ion of the form $[=Cl_2P-N\begin{smallmatrix}PCl_2=\\PCl_2\equiv\end{smallmatrix}]^+$ would have to be present. That this is not the case implies that the $[\equiv P=N-P\equiv]^+$ linkage is stronger than the $[\equiv P-N\begin{smallmatrix}P\equiv\\P\equiv\end{smallmatrix}]^+$ moiety.

Although ring rearrangements of the phosphonitrilic chlorides have not been observed at low temperatures, transannular processes are noticeable in the reactions of, especially, the larger ring size phosphonitriles. The fluorination of hexameric chloride with potassium fluorosulphite always yields a small amount (~5% of all fluorinated products) of tetrameric fluoride. Also, the mass spectra of phosphonitrilic chlorides[10] show that transannular processes are very important in the fragmentation pattern of hexameric, heptameric, and octameric chlorides. For example, 40.6% of all fragments in the mass spectrum of $(PNCl_2)_6$ contain the $(PN)_3$ nucleus. A rearrangement by some sort of transannular process is therefore indicated.

$$\cdots\cdots\cdots (2.2)$$
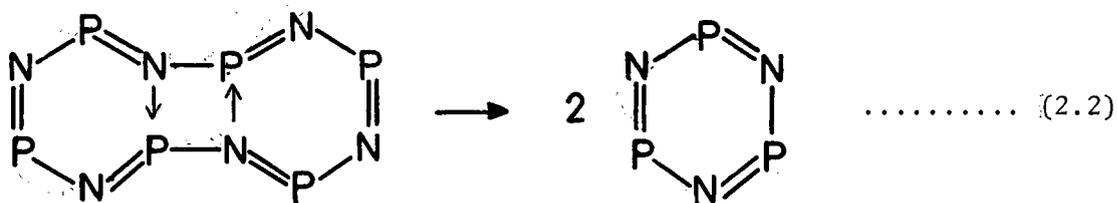
Pyrolysis of any phosphonitrilic chloride at a temperature >300°C for several hours produces a polymer, the structure of which can be rationalized in terms of a crosslinked matrix[23] with a molecular weight of the order of 60,000. The formation of the polymer proceeds in two steps. The first step is the formation of an apparently

uncrosslinked long chain polymer which then crosslinks to form the polymeric inorganic rubber.

As a result of the high temperature experiments carried out on the monocyclic chlorides and described below, the following conclusions were drawn. Depolymerization of phosphonitrilic chloride high polymer in vacuo invariably produces $(PNCl_2)_{3 \text{ and } 4}$ and sometimes, but not always, a trace of $P_6N_7Cl_9$. No other products are obtained, no matter which phosphonitrilic chloride is used to produce the high polymer. For instance, $P_6N_7Cl_9$ is even recovered from the depolymerization of polymer which has been prepared from trimeric and tetrameric chlorides. When the crosslinked high polymer is extracted into benzene, no condensed ring chloride is found in the benzene. These observations suggest that the $P_6N_7Cl_9$ is a product of the depolymerization process, rather than being formed as a side product of the polymerization step.

An X-ray diffraction study of the high polymer has shown that it consists of a long chain helix.[24] Thus the formation of nitrilohexa-phosphonitrilic chloride from the high polymer may be viewed in the following way.

.... (2.3)
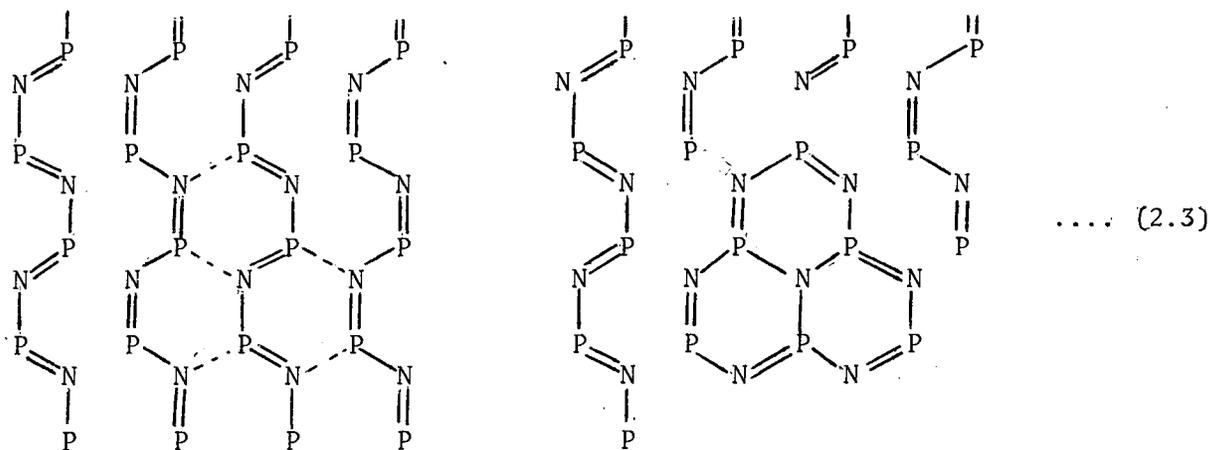
The results of a recent study by Todd et. al.[25] support this conclusion. They found that the slow, controlled polymerization of $(PNCl_2)_3$ at 250°C produces a pale yellow polymer which, upon extraction with light petroleum, yields some $(PNCl_2)_{4,5}$ and 6 as well as the crosslinked high polymer. The mechanism of the formation of these different ring sizes is thought to involve a polymerization-depolymerization equilibrium process of the linear polymer.

In the vapour phase, phosphonitrilic chlorides are remarkably stable. After passing the vapour of $(PNCl_2)_4$ through a silica furnace at 600°C, the condensate remained unchanged and no rearrangements occurred. A pyrolysis in the liquid phase was carried out by passing a liquid mixture of homologues $(PNCl_2)_n$, mean n ~5, through a vertical silica furnace at dull red heat (~600°C). Inside the furnace the liquid $(PNCl_2)_n$ rapidly polymerized. Depolymerization quickly followed, and the products of depolymerization were forced out of the furnace under a slight positive pressure of nitrogen. Although this sort of experiment did produce a trace of $P_6N_7Cl_9$, further investigations along this line were not pursued, since considerable breakdown of the polymer occurred in the furnace, with the formation of phosphorus pentachloride and elemental phosphorus.

The most reliable way of producing the condensed ring was found to be through the polymerization of the cyclic chlorides at 300°C to give the crosslinked high polymer. The subsequent distillation of polymer yielded, as a final fraction, a very small quantity of

$P_6N_7Cl_9$. The rate of polymerization was never reproducible, as trace amounts of impurities catalysed the reaction, e.g. water increased the rate of polymerization and the presence of air decreased it. The ring size of the starting chloride also affected the rate of polymerization. $(PNCl_2)_3$ takes up to 8 hours to polymerize at 300°C whereas $(PNCl_2)_6$ takes only half an hour.

It is not known if adaptations of these processes will improve the yield of the condensed ring compound. In general, from a polymerization involving 200 grams of phosphonitrilic chloride, only 0.2-0.5 gm of $P_6N_7Cl_9$ could be recovered. The high temperature chemistry of phosphonitrilic compounds has not received direct attention, and consequently, new compounds, similar to $P_6N_7Cl_9$, such as the $P_5N_6Cl_7$ and $P_7N_8Cl_{11}$ found by mass spectrometry may remain to be discovered.

EXPERIMENTAL

(a) <u>Thermal Decomposition of Phosphonitrilic High Polymer</u>

Several hundred grams of phosphonitrilic chloride oil $(PNCl_2)_n$ were added to a large round-bottomed flask which was fitted with a still-head, a short air condenser, and a receiver flask. Keeping the reaction vessel at room pressure, the oil was heated in a sand bath to a bath temperature of about 300°C. Trimeric phosphonitrilic chloride boils at 257°, but at a bath temperature of 300°C and even higher, distillation of this compound was almost negligible. After

heating the oil at this temperature for several hours, the oil slowly darkened and finally polymerized into a dark, rubbery polymer. The length of time required for polymerization was a function of the purity and composition of the oil. Filtration of a solution of the oil in petrol ether (30-60°) through silica gel or Clearsorb columns removed all polar impurities and produced a colourless liquid on evaporation of the solvent. This oil was more difficult to polymerize since the presence of polar impurities reduced the polymerization time.

The actual process of polymerization, once started, is quite rapid. The change from a dark, but mobile, liquid to a rubbery polymer, takes less than a minute. The presence of some polymer appears, therefore, to catalyse further polymerization. Depolymerization of this rubbery material was achieved by heating the polymer in vacuo. Depolymerization was best at a pressure of <0.1 torr and at a bath temperature of 300°C. The use of higher temperatures and higher pressures reduced the yield of the depolymerization products, which were trimeric and tetrameric phosphonitrilic chlorides and a trace of $P_6N_7Cl_9$. Even under high vacuum, complete depolymerization took about 48 hours. The final fraction, which was the condensed ring compound, usually solidified in the condenser arm, and was isolated by washing the condenser with petrol ether (30°-60°C) to remove the monocyclic chlorides) and then with benzene, in which $P_6N_7Cl_9$ is soluble. The receiver flask was also washed in the same way, i.e. firstly with petrol ether, and then with benzene.

The residue left in the distillation flask was a light flaky black ash, the composition of which is unknown. In a typical depolymerization reaction 200 grams of $(PNCl_2)_4$ were polymerized and the polymer cracked to yield 170 grams of a mixture of tetrameric and trimeric chlorides (in a ratio of ~2:1) and 0.30 grams of the condensed ring chloride. The yield of $P_6N_7Cl_9$ was variable, and in some reactions no condensed ring was recovered. The compound was identified by its melting point, 235°C (literature value[6] 237.2°C), and by analysis (calculated for $P_6N_7Cl_9$; P, 30.84; N, 16.29; Cl, 52.87; found N, 16.19; Cl, 52.81). The mass spectrum (which will be discussed in chapter III) of the compound completed the characterization of the compound.

The next three experiments were, like the first, all pyrolysis reactions carried out on phosphonitrilic chlorides, and although they did produce a little $P_6N_7Cl_9$, were not as reliable nor as efficient as the first process.

(b) This experiment involved the use of a vertical silica glass column (see Fig. 2.1a) with a constriction at the lower end to support a packing of hengar granules. The upper end of the column was so designed that phosphonitrilic oil could be introduced to the column under a slight positive pressure of nitrogen. The lower end of the column was heated to dull red heat (~600°C) with an electric furnace and phosphonitrilic chloride oil was added dropwise at the top of the column. Immediate polymerization of the oil occurred, and a depoly-
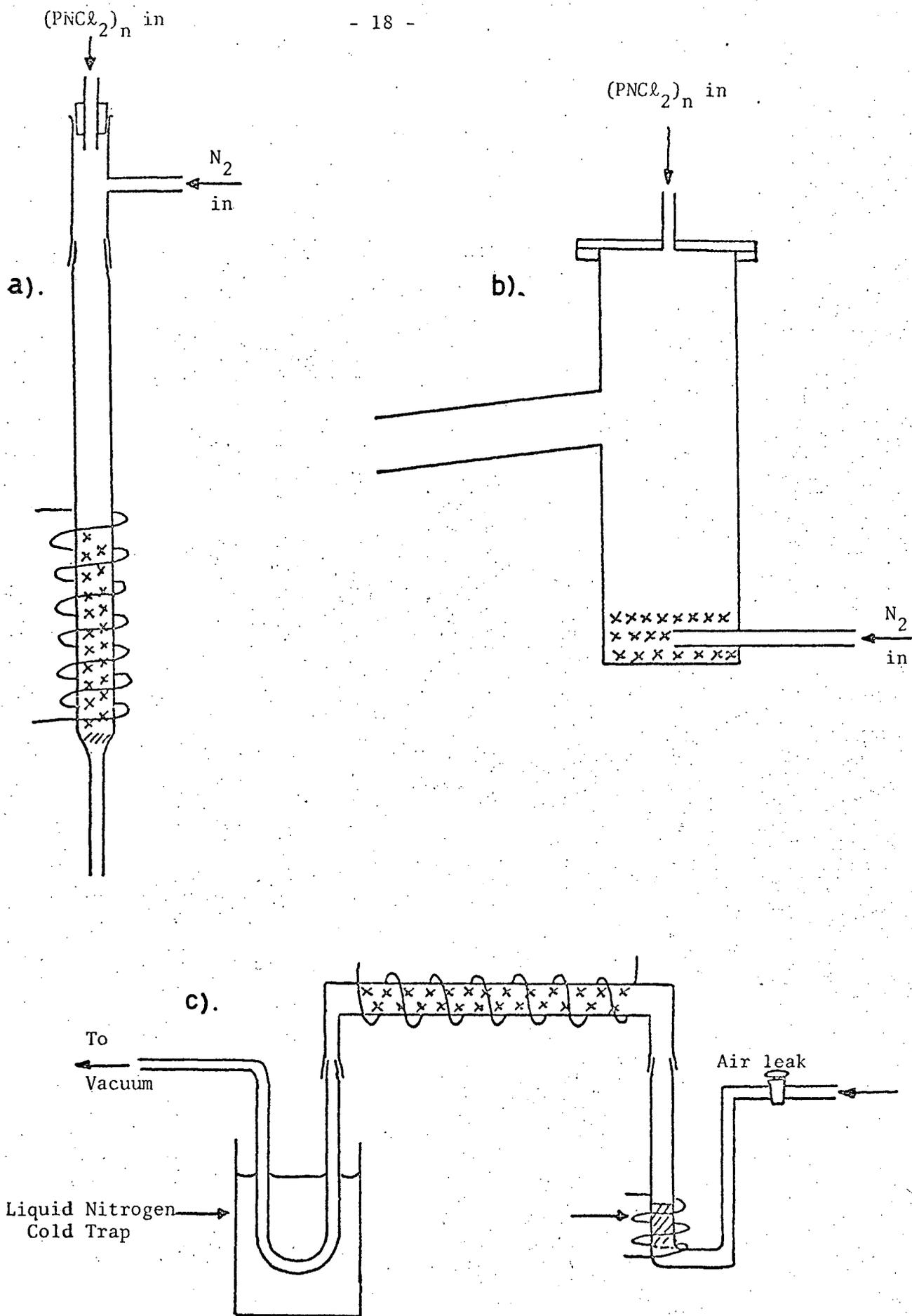
Fig. 2.1. Diagrams of furnaces used in the preparation of Nitrilo-
hexaphosphonitrilic Chloride.

merization-polymerization process ensued. Any volatile products passed out of the bottom of the heated zone, where they were collected as liquids. At the furnace temperature used, breakdown of the $(PNCl_2)_n$ unit was apparent, as in this type of experiment, phosphorus pentachloride was emitted from the column and red phosphorus solidified in the receiver flask. If lower temperatures were used to stop this breakdown, depolymerization of the high polymer could not be achieved and the column would quickly become blocked with polymer. In a typical experiment of this type, 100 grams of $(PNCl_2)_5$ were pyrolysed to give 55 grams of $(PNCl_2)_n$ (n = 3,4 and 5) and 0.10 grams of $P_6N_7Cl_9$. Separation and isolation of the condensed ring compound was done using the techniques described in experiment (a).

(c) This experiment was designed as a modification of experiment (b) and involved the use of the copper furnace illustrated in Fig. 2.1b. The bottom of the furnace was heated to dull red heat with a bunsen burner. Phosphonitrilic chloride oil was dropped onto the hot hengar granules on the bottom of the furnace. Polymerization, depolymerization and vaporization of the oil then occurred and any volatile products were collected through a short air condenser. No $P_6N_7Cl_9$ was recovered from this type of pyrolysis, and indeed much of the phosphonitrilic oil was decomposed, with less than 50% of the starting material being recovered.

(d) A pyrolysis reaction was attempted in the gas phase, to see if ring rearrangement occurs in the vapour. Using the apparatus shown in Fig. 2.1c, tetrameric chloride was distilled through a horizontal silica glass furnace packed with hengar granules, and heated to ~600°C. The products of the reaction were collected in a dry ice/ acetone trap. It was found that the tetrameric chloride had distilled unchanged through the apparatus, and no cyclic rearrangements had taken place in the gas phase.

(e) <u>Reaction of Lithium Nitride with Hexaphosphonitrilic Chloride</u>

A solution of $(PNCl_2)_6$ (8.8 g., 12.6 mmol.) in 50 ml. of tetrahydrofuran was added, over 10-15 minutes, to a stirred slurry of lithium nitride (0.44 g., 12.6 mmol.) in 50 ml. of tetrahydrofuran. The mixture was then gently heated under reflux for 2-1/2 hours, after which time the solution was filtered under nitrogen, and most of the tetrahydrofuran distilled off. 100 ml. of benzene were added and immediate precipitation (of LiCl) followed. The solution was allowed to settle and some of the clear solution drawn off and allowed to evaporate. The product left on evaporation was identified by its infra-red spectrum as being $(PNCl_2)_6$. The gummy white precipitate could not be characterized, but a strong O-H stretching band in its infra-red spectrum suggests that hydrolysis of the phospho- nitrilic ring had occurred. No $P_6N_7Cl_9$ was recovered.

(f) <u>Reaction of Tris(trimethylstannyl)amine with Hexaphosphonitrilic</u>
<u>Chloride</u>

A solution of $(Me_3Sn)_3N$ (3.0 g., 5.9 mmol.) in 30 ml. of benzene
was added over a period of 20 minutes to a stirred solution of the
phosphonitrilic chloride (4.1 g., 5.9 mmol.) in 50 ml. of benzene.
The reaction mixture was kept under an atmosphere of nitrogen and
allowed to boil gently under reflux overnight. On distillation of
the solvent, there remained a gum, half of which was then heated to
250°C at a pressure of 0.5 torr. This heating of the gum produced a
white lumpy solid, which had the characteristic smell of trimethyl
tin chloride, but which was insoluble in petrol ether, chloroform,
benzene, dilute mineral acid and dilute alkali. The mass spectrum
of the pyrolysed material showed a pattern characteristic of
$(PNC\ell_2)_6$. To that half of the gum which was not pyrolysed, a little
petrol ether was added. This produced an amorphous white precipitate
which was insoluble in hot alkali, nitric acid, chloroform and benzene.
The infra-red spectrum was characteristic of a phosphonitrilic com-
pound, with a broad peak at 1340 cm^{-1}, as well as others at 955 cm^{-1}
(med, broad), 790 cm^{-1} (w), 755 cm^{-1} (med), 601 cm^{-1} (st), 525 cm^{-1}
(med) and 470 cm^{-1} (w). However, it was not the condensed ring
compound, and no evidence of the formation of $P_6N_7C\ell_9$ was detected
at any stage in the reaction.

(g) <u>Reaction of Tris(trimethylsilyl)amine with Hexaphosphonitrilic</u>
<u>Chloride</u>

A solution of $(Me_3Si)_3N$ (1.4 g., 6.0 mmol.) in 25 ml. of benzene

was added over a period of 10 minutes to a solution of hexaphospho-
nitrilic chloride (4.1 g., 5.9 mmol.) in 50 ml· of benzene and the
mixture stirred and heated under reflux in an atmosphere of dry
nitrogen. After 24 hours, the benzene was distilled and the neat
liquid heated to 200°C at a pressure of 0.5 torr. for one hour. On
cooling, the residual liquid was identified as unreacted $(PNCl_2)_6$.

With the isolation of nitrilohexaphosphonitrilic chloride
achieved, the compound was subjected to a thorough spectroscopic
analysis. The results of the various physical measurements made on
the molecule are discussed in the following chapter.

Although no $P_6N_7Cl_9$ was isolated from the above-mentioned direct
syntheses, enough of it was isolated from the pyrolytic reactions to
allow a thorough spectroscopic analysis to be made of the molecule.
The results of the various physical measurements made on the molecule
are discussed in the following chapter.

CHAPTER 3

PROPERTIES OF NITRILOHEXAPHOSPHONITRILIC CHLORIDE

Although, up to now, no structural information has been available

on the $P_6N_7Cl_9$ molecule, a tricyclic structure has been proposed,

mainly from simple valence considerations. That this was indeed the

correct structure was confirmed by ^{31}P n.m.r. spectrometry. In this

present chapter, details are given of the results obtained from the

n.m.r., mass, ultraviolet, and vibrational spectroscopic investigations

carried out on the molecule.

I. ^{31}P n.m.r. Spectrum

Because of the low solubility of $P_6N_7Cl_9$ in all common solvents,

the ^{31}P n.m.r. spectrum proved very difficult to obtain. Saturated

solutions in hot benzene and xylene failed to produce a signal.

Finally, a 40% solution of the compound in molten naphthalene (at

150°C) produced a weak but definite spectrum, consisting of two peaks

of equal intensity. The peaks did exhibit fine structure but the

signals were too weak to allow any resolution of this fine structure

to be made. The ^{31}P chemical shifts of these two peaks are given in

Table 3:1 together with those of the monocyclic phosphonitrilic

chlorides. The ^{31}P n.m.r. pattern of two signals of equal intensity

is quite definitive and can only be interpreted in terms of a molecule

Compound	$(PNCl_2)_3$	$(PNCl_2)_4$	$(PNCl_2)_5$	$(PNCl_2)_6$	$P_6N_7Cl_9$
δ_P p.p.m. relative to 85% H_3PO_4	-20.0	+7.0	+17.0	+16.0	-20.2,+3.5

TABLE 3:1. ^{31}P n.m.r. chemical shifts for the phosphonitrilic chlorides $(PNCl_2)_{3-6}$ and for $P_6N_7Cl_9$. Values for $(PNCl_2)_{3-6}$ are from reference 26.

having two sets of three equivalent phosphorus atoms. The tricyclic condensed ring structure is unique in this regard, with one signal corresponding to the bridgehead ($\equiv$P-Cl) phosphorus atoms (see Fig. 1:2), and the other corresponding to the non-bridgehead ($\equiv$PCl$_2$ type) phosphorus atoms. The interpretation of phosphorus chemical shifts is difficult, as angular as well as electronic factors can contribute to the shift. However, the environment of the $\equiv$PCl$_2$ phosphorus atoms in the tricyclic condensed ring structure is very similar to that of the phosphorus atoms in $(PNCl_2)_3$, and the phosphorus chemical shifts are expected to be similar. Thus the resonance at δ = -20.2 p.p.m. is assigned to the $\equiv$PCl$_2$ type phosphorus atoms of the condensed ring. The signal at δ = +3.5 p.p.m. is therefore assigned to the bridge-head phosphorus atoms. On a simple first order basis, lone pair

delocalization from the central nitrogen atom would be expected to increase the chemical shift of the bridgehead phosphorus atoms with respect to the $\equiv PCl_2$ type, and this idea is in complete agreement with the above assignment.

The tricyclic condensed ring structure shown in Fig. 1.2 was thus established for $P_6N_7Cl_9$, and the subsequent X-ray crystal structure analysis (discussed in chapter 5) confirmed this assignment.

II. <u>Mass Spectrum</u>

The fragmentation pattern of this compound is of interest for several reasons. Not only does the mass spectrum serve as an excellent analytical tool for the characterization of the compound, but interesting comparisons may be made between the fragmentation pattern of this compound and those of the ordinary cyclic chlorides,[10] comparisons which may be related to the chemistry of the two types of compound.

As in the mass spectra of the ordinary cyclic chlorides, $(PNCl_2)_n$, fragments with an even number of electrons are more stable, and therefore more abundant, than fragments with an odd number of electrons. The fragments can be divided into three classes. Those with the formula $(P_xN_{x+1}Cl_y)^{n+}$ have stable singly charged ions for even numbers of chlorine atoms. For doubly charged ions in this series, the abundances of fragments are greatest for those with an odd number of chlorine atoms. The second type of fragment that is seen is of the

form $(P_xN_xCl_y)^{n+}$, which corresponds to a fragment with a cyclic structure. For these fragments abundances alternate with variation in y so that for singly-charged species, ions with an odd number of chlorine atoms predominate whilst for doubly charged species, those with an even number of chlorines predominate. The third type of fragment has the general formula $(P_xN_{x-1}Cl_y)^{n+}$ and these fragments are thought to be linear. This type of ion is known in preparative chemistry, the $(P_3N_2Cl_8)^+$ ion being an intermediate in the preparation of phosphonitrilic chlorides. These linear fragments, as would be expected, have abundance characteristics which are the reverse of those observed for the cyclic ions. Namely, for singly charged species, ions with an even number of chlorine atoms predominate, whilst for doubly charged species, those with an odd number of chlorine atoms are more abundant.

Thus, the important point of the above argument is that there is general correspondence between the chemical stability of an ion and its abundance in a mass spectrometer.

Fragments of the type $(P_xN_{x+1}Cl_y)^{n+}$ are thought to have condensed ring structures, with the central nitrogen atom, bound to three distinct phosphorus atoms, being maintained in the structure of the ion. The abundance ratio of ions with odd and even numbers of electrons is consistent with these fragments being completely cyclic. Within this series of ions, fragments with formulae corresponding to three values of x (= 6,5 and 4) are found. Frag-

-ments based on the P_6N_7 and the P_5N_6 nuclei have already been identified in mass spectra, but the ions based on the P_4N_5 nucleus have not been seen before. These ions are believed to be based on a tetrameric ring system (see Fig. 3.1), with an extra nitrogen atom bound to three separate phosphorus atoms. In the mass spectra of the
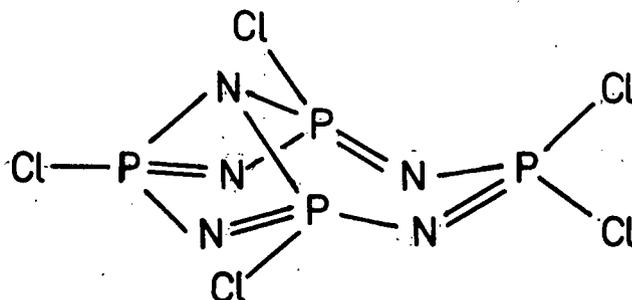
Fig. 3.1. Possible structure of parent molecule of ions based on the P_4N_5 nucleus.

phosphonitrilic fluorides,[27] the series $(P_nN_{n+2}F_{2n-6})^+$ (n = 4-12) has been seen. The smallest ion in this series, $P_4N_6F_2^+$, may be related to the $P_4N_5Cl_y^{n+}$ ions, except that in the former, there would be two nitrogen atoms triply bound to the tetrameric ring system, one being above the plane of the ring, and the other being below it.

The abundance of ions based on the P_4N_5 and P_5N_6 nuclei is much less than that of ions based on the parent P_6N_7 nucleus, which cleaves preferentially into cyclic fragments based on the P_3N_3 and P_4N_4 ring. Table 3.2 shows the fragmentation pattern of $P_6N_7Cl_9$, and for comparison, the fragmentation pattern of $(PNCl_2)_6$[10]. In this Table,

$P_6N_7C\ell_9$
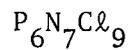
FRAGMENT	P	PN	P_2	P_2N	P_3N_2	P_3N_3	P_4N_3	P_4N_4	P_4N_5	P_5N_5	P_5N_6	P_6N_6	P_6N_7	TOTAL
Condensed Ring									1.3		4.2		17.8	23.3
Cyclic		2.4				19.4		9.6		1.1		0		32.5
Linear	14.8		1.2	18.2	7.4		2.3							43.9

$P_6N_6C\ell_{12}$
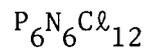
FRAGMENT	P	PN	P_2N	P_3N_2	P_3N_3	P_4N_3	P_4N_4	P_5N_4	P_5N_5	P_6N_6	TOTAL
Cyclic		0.4			40.6		10.3		15.1	12.0	78.4
Linear	6.2		9.0	3.8		2.3		0.1			21.4

TABLE 3.2. The fragmentation pattern of $P_6N_7C\ell_9$ and $P_6N_6C\ell_{12}$ into condensed, cyclic and linear species. The number given is the total percentage of ions of the type shown, irrespective of chlorine content or charge. For convenience, chlorides of phosphorus are included with the linear series, and the PN series with the cyclic compounds.

all ions, singly or doubly charged, belonging to a particular parent nucleus P_xN_y are grouped together.

Several conclusions can be made by comparing the two patterns. The $(P_xN_{x+1}Cl_y)^{n+}$ series only accounts for 23.3% of the total fragments, a high proportion of the fragments being small linear ions. This indicates a general instability of the condensed ring skeleton with respect to the cyclic and, more especially, linear species. $(PNCl_2)_6$ breaks down into mainly P_3N_3 fragments, which shows the importance of a transannular effect in cleaving the P_6N_6 nucleus into two P_3N_3 units. In the cyclic fragments formed from the breakdown of $P_6N_7Cl_9$, P_3N_3 units again predominate. The high proportion of P_4N_4 units does not find an obvious explanation.

The actual mechanisms involved in the breakdown of the phosphonitrilic chlorides are not understood. Nonetheless, some deductions can be made from the fragmentation pattern of the condensed ring. Within the series of cyclic fragments, the most abundant fragments are $(P_4N_4Cl_7)^+$ and $(P_3N_3Cl_5)^+$ (see Table 3.3). Any mechanism which is postulated for the formation of these ions must involve the cleavage of the internal PN bond and the loss of the bridgehead ($\equiv PCl$) phosphorus atoms. If $\equiv PCl_2$ type phosphorus atoms were lost, the resultant ions would have too few chlorine atoms.

In the formation of the $(P_4N_4Cl_7)^+$ ion, two PCl type phosphorus atoms must be lost. Of the three nitrogen atoms which must be lost from $P_6N_7Cl_9$ in order to form the $(P_4N_4Cl_7)^+$ fragment, one must be

PARENT RING		FRAGMENT FORMULA					CHARGE ON ION
P_5N_5	$P_5N_5Cl_7$	$P_5N_5Cl_6$	$P_5N_5Cl_5$				
	2.8	0	1.5				+
	0	0.7	0				++
P_4N_4	$P_4N_4Cl_7$	$P_4N_4Cl_6$	$P_4N_4Cl_5$	$P_4N_4Cl_4$	$P_4N_4Cl_3$		
	23.5	1.0	9.7	0	3.7		+
	0	2.2	0	2.0	0		++
P_3N_3	$P_3N_3Cl_6$	$P_3N_3Cl_5$	$P_3N_3Cl_4$	$P_3N_3Cl_3$	$P_3N_3Cl_2$	P_3N_3Cl	
	0	39.0	2.4	37.5	0	4.2	+
	0	0	1.7	0	0	0	++

TABLE 3.3. Relative abundances of all ions in the various cyclic series in the fragmentation pattern of $P_6N_7Cl_9$. The numbers given are not percentages and represent only the intensities of peaks relative to each other.

the central nitrogen atom. It is believed that the loss of this

nitrogen atom is achieved in a process which involves the cleavage

of the cyclic structure of the condensed ring nucleus to give a

linear species which can then either recyclize into the smaller P_4N_4

and P_3N_3 units, or form a series of linear fragments. The high

proportion of linear fragments from $P_6N_7Cl_9$ (43.9%), in comparison to

$(PNCl_2)_6$ (21.4%) supports this hypothesis.

In so far as the fragmentation pattern of $P_6N_7Cl_9$ is a guide to

its chemical properties, several interesting comparisons can be made.

Loss of the condensed ring nucleus is favoured in the mass spectrum,

with the formation of a large proportion of linear fragments (much

more so than in the monocyclic chlorides) and small cyclic fragments.

The central nitrogen atom, and the bridgehead phosphorus atoms, seem

to be lost in these processes. These results indicate a greater chemical

instability for $P_6N_7Cl_9$ in comparison to the monocyclic chlorides, and,

as the results of chapter 4 will show, the chemistry of the condensed

ring compound is limited by the instability of the P_6N_7 nucleus.

III. Ultra-violet Spectra

The monocyclic phosphonitrilic chlorides do not show any U.V. absorp-

tions above 2100 Å, where $\pi \rightarrow \pi^*$ transitions are normally expected. Below

2100 Å, $n \rightarrow \pi^*$ transitions on the chlorine ligands do occur, but these

transitions have not received any special attention. The U.V. spectrum

of $P_6N_7Cl_9$ was recorded in cyclohexane and acetonitrile solutions, and

no spectrum was observed above 2100 Å. The appearance of an absorption

below 2100 Å was noticed, indicating that the type of U.V. transitions

in $P_6N_7Cl_9$ are similar to those observed in the monocyclic chlorides,

and that the addition of the central nitrogen does not produce any

easily observable $\pi \rightarrow \pi^*$ transitions.

IV. Vibrational Spectra

Several detailed studies have been made on the vibrational assign-

ments of the trimeric[28-32] and tetrameric[28,29,33] phosphonitrilic

chlorides but only tentative assignments have been made for the penta-

meric[27] and hexameric chlorides. The infra-red (mull and solution)

and Raman (powder) spectra of $P_6N_7Cl_9$ were recorded. These spectra

are given in Table 3.4. The vibrational spectra of $(PNCl_2)_6$, detailed

in Table 3.5, act as an interesting comparison.

Whilst complete vibrational assignments are nearly settled for

$N_3P_3Cl_6$, for the larger ring sizes, assignments by different authors

vary considerably. For any molecule, vibrational assignments can be

given which fit the observed frequencies, but the reasons behind the

assignments are difficult to justify completely. Justifiable assign-

ments can really only be given when the spectra of a large number of

derivatives of a particular compound have been studied, and polariza-

tion measurements are available.

In the case of $P_6N_7Cl_9$, no substituted derivatives have been made.

Only a powder Raman spectrum has been obtained, so that no polarization

RAMAN SOLID cm^{-1}	INFRA-RED NUJOL MULL cm^{-1}	INFRA-RED SOLUTION cm^{-1}	ASSIGNMENT
149 (3.5)			
169 (7.0)			
288 (0.4)	280 w		
332 (7.0)	330 w		$\delta(PCl_2)$ in-phase
411 (0.6)	402 v.w		
442 (4.0)	435 m	430 w	$\nu_{sym}(PCl_2)$ in-phase
507 (0.8)	503 v.w		
	525 w		
	548 sh		
557 (1.0)	564 st	562 m	$\nu(P-Cl)$ in-phase
	592 v.st	603 m	$\nu_{sym}(P-Cl_2)$ out-of -phase
661 (1.5)	660 st	662	
807 (1.5)	804 m	805 w	A_1 ring vib'n (see text)
	870 st	858 sh	
		880 m	
	903 v.w		
	1188 sh		
	~1280 v.st	1279 st	degen ring vib'ns
	~1320 sh		

TABLE 3.4. Vibrational spectra of nitrilohexaphosphonitrilic chloride. For the Raman spectrum, the figures in parenthesis indicate the relative intensities of peaks with respect to each other.

RAMAN SOLID cm^{-1}	INFRA-RED NUJOL MULL cm^{-1}	INFRA-RED SOLUTION cm^{-1}	ASSIGNMENT
128 (1.5)			
154 (1.0)			
167 (0.8)			
198 (0.4)			
275 (1.5)			$\delta(PC\ell_2)$ in-phase
	343 w		
	430 m		
451 (10.0)			$\nu_{sym}(PC\ell_2)$ in-phase
	463 st	465 w	$\nu_{sym}(PC\ell_2)$ 1st degen.
	518 m	518 w	
578 (1.0)	584 sh	~580 sh	
	602 st	602 st	$\nu_{sym}(PC\ell_2)$ out-of-phase
	748 st	748 m	
	830 m	853 m	
	1432 v.st	1427 st	degen. ring vib'n

TABLE 3.5. Vibrational spectra of hexaphosphonitrilic chloride.
For the Raman spectrum, the figures in parenthesis
indicate the relative intensities of peaks with
respect to each other.

measurements are available. The low solubility of the compound in all solvents has made the detection of a Raman spectrum in solution unfeasible. Attempts to take Raman spectra of the melt also failed.

Because of this dearth of information, rather than quote vibrational modes and then match frequencies to them, it is the purpose of this study to take the most prominent frequencies from the Raman and infra-red spectra, and to correlate them with the generally accepted assignments in the smaller cyclic phosphonitrilic chlorides.

The appearance of the infra-red spectrum is similar to that observed in the monocyclic chlorides, the strong broad band at 1280 cm^{-1} being characteristic of all phosphonitrilic compounds and assigned to a degenerate ring vibration. The large number of coincidences in the Raman and infra-red spectra suggest that the molecule has low symmetry. If one assumes the presence of the 3-fold axis indicated by ^{31}P n.m.r. spectrometry, the symmetries D_3, D_{3h} and D_{3d} can be excluded since these do not lead to Raman and infra-red coincidences of totally symmetric vibrations. This leaves C_3 or C_{3v} as being the only symmetries the molecule can possess. That the bridgehead chlorine atoms are all cis to one another is also indicated since, if not, the resultant C_s symmetry would produce a much more complex spectrum.

The two most prominent features of the Raman spectrum are the two intense peaks at 332 cm^{-1} and 442 cm^{-1}. In the monocyclic chlorides, the most intense peak in the Raman spectrum is the polarized band corresponding to the PCl_2 in-phase symmetric stretching vibration.

Table 3.6 shows the frequencies of these peaks in the Raman spectrum

of the monocyclic chlorides. On the basis of these assignments, the

| Compound | $(PNCl_2)_3$ | $(PNCl_2)_4$ | | $(PNCl_2)_5$ | $(PNCl_2)_6$ | $P_6N_7Cl_9$ |
		S_4	C_{2h}			
$\nu_{sym}(PCl_2)$ in-phase cm^{-1}	365	387 391	413	439	451	442
References	29,30 31,32	29,33	29,33	29	This work	This work

TABLE 3:6. Assignments for the symmetrical in-phase PCl_2 stretching vibration in phosphonitrilic chlorides.

band at 442 cm^{-1} in the Raman spectrum of $P_6N_7Cl_9$ is assigned to the

$\nu_{sym}(PCl_2)$ in-phase mode.

In $(PNCl_2)_3$,[32] the $\nu_{sym}(PCl_2)$ out-of-phase mode occurs as a very

strong band in the infra-red spectrum at 530 cm^{-1}. Although it is not

forbidden in the Raman spectrum, it does not appear there. On these

grounds the analogous mode in $P_6N_7Cl_9$ is assigned to the absorption

at 592 cm^{-1} in the infra-red spectrum. Similarly, the band at 602 cm^{-1}

in the infra-red spectrum of $(PNCl_2)_6$ is assigned to the $\nu_{sym}(PCl_2)$

out-of-phase mode in that molecule.

The strong peak at 332 cm^{-1} in the Raman spectrum is

assigned to the in-phase PCl_2 scissors vibration. The assignment of

this mode in the monocyclic series is uncertain. It is expected to

occur at a lower frequency than the symmetric stretching motion. In the trimeric chloride, Emsley[32] did not assign this mode to any frequency. Califano[30] has assigned it to a peak at 100 cm^{-1} and Hisatsune[31] to a peak at ~304 cm^{-1}. In $(PNF_2)_{3,4}$, the in-phase PF_2 scissors vibration lies about 100 cm^{-1} below the symmetric in-phase stretching mode. The intensity of the peak at 332 cm^{-1} in the Raman spectrum of $P_6N_7Cl_9$ suggests that it is an A_1 mode and that the above assignment is valid.

The next assignment that can be made concerns the strong infra-red band at 564 cm^{-1}. This is thought to be the symmetric P-Cl stretching motion of the bridgehead chlorine atoms. In $P_3N_3F_5Cl$, the P-Cl vibration is assigned to a peak at 637 cm^{-1}.[32] The corresponding vibration in $P_3N_3Br_5Cl$ occurs at 563 cm^{-1}.[34] In mononuclear phosphorus(V) compounds, ν(P-Cl) varies between 513 cm^{-1} and 567 cm^{-1}.[35] The assignment of ν_{sym}(P-Cl) at 564 cm^{-1} seems logical.

A recent review of the infra-red absorption frequencies of PN bonds[36] indicates a broad range of frequencies between 700 cm^{-1} and 950 cm^{-1} as being the stretching frequency of the PN single bond. In $P_3N_3Cl_5NMe_2$,[37] ν(P-N) occurs at 711 cm^{-1}. In $P_6N_7Cl_9$ the infra-red peak at 804 cm^{-1} weakens in solution and is a strong peak in the Raman spectrum at 807 cm^{-1}. The condensed ring PN nucleus has one more A_1 ring stretching mode than does the open ring P_6N_6 nucleus. This essentially involves the symmetric stretching motion of the internal PN bonds. On the basis of the above information, the infra-red

absorption at 804 cm^{-1} is assigned to this vibration.

Although further assignments could be made here, their validity would be questionable. The prominent features of the spectra have been given preliminary assignments, and the results are consistent with the $P_6N_7Cl_9$ molecule having C_{3v} symmetry. The shape of the molecule is therefore completely defined, and the bridgehead P-Cl bonds must all be cis to one another.

V. Base Strength Measurements

Although base strength is a chemical property, the interpretation of this property is in terms of a physical phenomenon, and therefore this discussion of the base strength of $P_6N_7Cl_9$ has been grouped with the other physical properties of the molecule.

The phosphonitrilic chlorides are weak bases, the ring nitrogen atoms acting as the basic centres. To the extent that lone pair delocalization from the ring nitrogen atoms affects the base strength of these molecules, then the measurement of the relative base strength of the condensed ring compound and the open ring $(PNCl_2)_6$ molecule gives some insight into the difference in the bonding of the two compounds.

The relative values of the base strengths of the phosphonitrilic chlorides $(PNCl_2)_n$ (n = 3-6) have been obtained by the measurement of the partition ratios of the chlorides between hexane and concentrated sulphuric acid.[38] A similar study was carried out on the condensed ring chloride, using $(PNCl_2)_6$ to standardize the sulphuric acid. By

varying the concentration of the sulphuric acid, the change in the

partition ratio was measured as a function of the concentration of

the acid. The results of these measurements, together with those found

for the monocyclic chlorides, are shown in Fig. 3.2, where the partition

ratio is shown (on the vertical axis), plotted against the Hammett

acidity function H_0. The H_0 function represents the ability of a

solvent to donate a proton to a neutral base and is defined by

equation 3.1. The physical chemistry behind this separation is not

$$H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]} \qquad \ldots\ldots\ldots\ldots (3.1)$$

fully understood, and at present there is no explanation for the

variation of the slopes in Fig. 3.2. When $\frac{[BH^+]}{[B]} = 1$, i.e. along the

x-axis, $H_0 = pK_{BH^+}$ and thus the intercept of the various lines with

the x-axis gives an approximate measure of the dissociation constant

for a particular compound. Although the quotation of absolute values

of K_{BH^+} have little meaning, the results show that the base strength

of the condensed ring chloride is less than that of the open ring

hexameric chloride by a value of $\Delta pK_{BH^+} \simeq 0.1$.

The increasing ring angle at nitrogen with increasing ring size

in phosphonitrilic chlorides (see Table 3.7) is symptomatic of

increased delocalization of the nitrogen lone pair electrons, with

a consequent weakening of their basic character. In planar molecules,

bonding of the sp^2 lone pair hybrid on nitrogen is chiefly with the
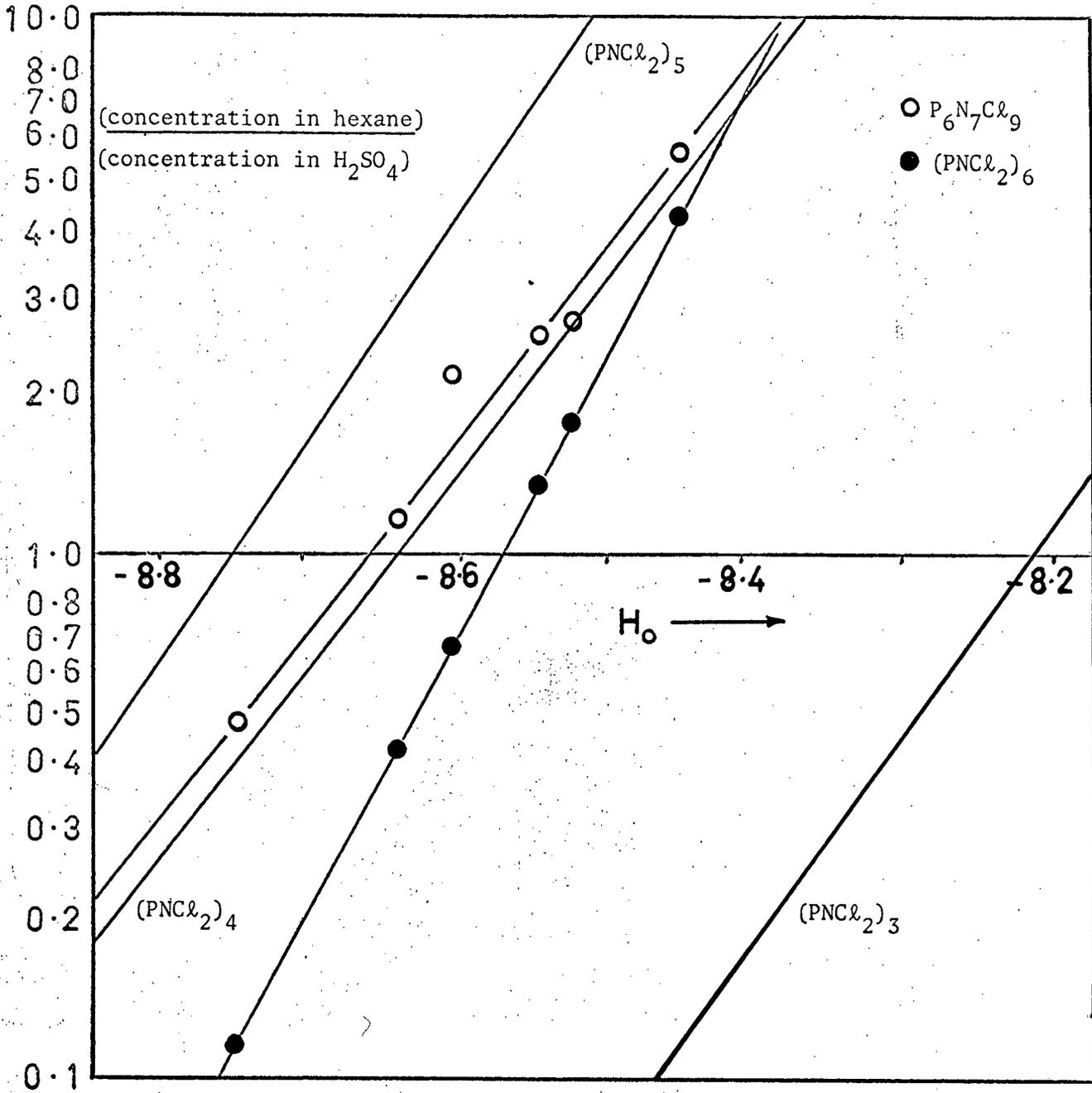
Fig. 3.2. Variation in the partition ratio of phosphonitrilic chlorides between hexane and concentrated sulphuric acid with change in concentration of the sulphuric acid.

Compound	$(PNC\ell_2)_3$	$(PNC\ell_2)_4$	$(PNC\ell_2)_5$
Ring angle at nitrogen	120°	132°	149°
Reference	39	40	41

TABLE 3:7. Average ring angle at nitrogen in the monocyclic phosphonitrilic chlorides $(PNC\ell_2)_{3-5}$.

in-plane $d_{x^2-y^2}$ orbital on phosphorus. In non-planar systems, however, overlap can also occur into the out-of-plane d-orbitals on phosphorus. Ring nitrogen lone-pair delocalization is therefore controlled by several factors, and the extent to which it occurs is a balance of these factors. A fuller interpretation of these results is given in Chapter 5.

Method:- 10^{-3} molar solutions of $P_6N_7C\ell_9$ and $(PNC\ell_2)_6$ were made up in cyclohexane solvent. The partition ratios were measured by mixing 30 ml of the cyclohexane solution with 30 ml of concentrated sulphuric acid, shaking the mixture for 2 minutes, and then finding the resultant concentration of chloride in the cyclohexane layer by evaporating a known volume of solution to dryness and weighing the residue. The concentration in the acid layer was determined by difference. All measurements were made in triplicate. Each concentration of acid was standardized by finding the partition ratio of hexameric chloride in the acid

and fitting the point so obtained onto the original plot for hexameric chloride.[38]

VI. Lewis Acid Adduct Formation

The ability of the phosphonitrilic chlorides to form Lewis acid adducts is really a measure of their base strengths, and to this extent they are only weak bases, since only a few such adducts have ever been prepared. $(PNCl_2)_3$ forms a 1:2 complex with aluminium trichloride and a 1:1 complex with aluminium tribromide.[43] The larger ring size chlorides do not form complexes and an attempt to react $P_6N_7Cl_9$ with aluminium tribromide did not produce any complex. The delocalization of the lone pair on the central nitrogen is therefore considerable, and the molecule as a whole must be viewed as being less basic than $(PNCl_2)_3$.

Method:- A solution of resublimed aluminium tribromide (0.039 g. 0.145 mmol) in 9.0 ml of carbon disulphide was added, under an atmosphere of dry nitrogen, to a stirred solution of $P_6N_7Cl_9$ (0.087 g., 0.145 mmol) in 10 ml of carbon disulphide. After half an hour, there was no visible sign of a reaction. The carbon disulphide was distilled off and 0.083 g. of the $P_6N_7Cl_9$ recovered from the residue by extraction into benzene.

CHAPTER 4

SUBSTITUTION REACTIONS OF NITRILOHEXAPHOSPHONITRILIC CHLORIDE

A series of substitution reactions was attempted in this study.
The results of these reactions show that, unlike the monocyclic phospho-
nitrilic chlorides, the condensed ring compound is not stable to sub-
stitution. The weakness of the internal PN bonds, indicated in the
mass spectrum, is apparent in the chemistry of the compound. Attempted
introduction of electron-withdrawing groups (-F, -OMe) into $P_6N_7Cl_9$
brings about a collapse of the P_6N_7 skeleton, and only when electron-
releasing groups are introduced does the condensed ring compound form
stable products. The following discussion is divided into several parts.
The first part describes the results of the fluorination and methoxyla-
tion reactions, and the second part describes the results of dimethyl-
amination of the condensed ring compound. In the third section, a
discussion is given of the spectra and structure of $P_6N_6(NH)(NMe_2)_8Cl_2$.

I(a). Fluorination of Nitrilohexaphosphonitrilic Chloride.

Monocyclic phosphonitrilic fluorides are volatile liquids,[11] and
it was consequently expected that $P_6N_7F_9$ would be similar, and hence
easy to separate from other reaction products. Its properties were
also expected to be informative, since ^{19}F has a nuclear spin, and more
structural information would be obtainable spectroscopically from the

fluoride than the chloride of the condensed ring phosphonitrile.

Because of these facts, many attempts were made to fluorinate the condensed ring chloride. A variety of reaction conditions and fluorinating agents were used. Potassium fluorosulphite has been used successfully,[11] as has argentous fluoride,[43] to fluorinate phosphonitrilic chlorides. Activated potassium fluoride[44] has been used to fluorinate phosphorus chlorides. All these reagents were used, but none produced any compound which could be properly characterized. Some of the fluorination reactions were done using open systems. In these cases, although no fluorides were isolated, the condensed ring chloride was lost in the reaction, with the formation of ionic chlorine. At first no explanation could be given for these failures. Finally, an experiment was carried out using a closed system with a liquid nitrogen trap to condense out any gaseous products.

The products of this reaction, which was carried out using silver fluoride as the fluorinating agent, were all either gases or volatile liquids at room temperature. It is thought that there are several products of this reaction, all of which are fully fluorinated, and all of which appear to have lost the condensed ring P_6N_7 nucleus. The number of products made efficient separation impossible. Trap to trap fractionation was attempted using dry ice/acetone (-97°C), dry ice/CCl$_4$ (-23°C), dry ice/chlorobenzene (-45°C) cold traps, but no fractionation was achieved. The appearance of PQR patterns in the vapour-phase infrared spectra of the volatile products indicated that some of the products

had low molecular weights, i.e. low enough to allow rotational fine structure to be observed. The magnitude of the splitting of the PQR branches was such that the distance between the maxima of the P and R branches was, in all cases, about 20 cm^{-1}. For linear molecules, the separation, $\Delta\nu$, between the maxima of the two branches is given by the formula[45]:

$$\Delta\nu = \frac{\sqrt{8kTB}}{hc} = 2.358 \sqrt{TB} \qquad \ldots\ldots\ldots\ldots (4.1)$$

where T is the absolute temperature and B is the rotational constant of the molecule ($B = \frac{h}{8\pi^2 Ic}$). This formula only holds rigorously for linear molecules, but may be used as an approximate guide for non-linear molecules. Using equation 4.1, the value of B corresponding to a $\Delta\nu$ of 20 cm^{-1} is B = 0.24 cm^{-1}. The B_o value for PF_3 is B_o = 0.26084.[46] Although a quantitative comparison is futile, the value of B = 0.24 cm^{-1} does indicate that the size of the molecule is not vastly different from PF_3.

Mass spectra results again indicated a mixture of products, mainly of low mass number, the most intense peaks corresponding to the fragments $(P_2F)^+$ and $(N_2F)^+$. The characteristic isotopic pattern of chlorine did not appear in any fragment, showing that complete fluorination had taken place, and although the average molecular weight of the product (by vapour density) was 114, fragments of mass number >400 were observed in the mass spectrum in low abundance. It is therefore likely

that a little $P_6N_7F_9$ (M = 455) was formed, but it could not be characterized because of the scarcity of peaks in the range m/e = 200-350, which made accurate mass counting impossible.

Very little positive information was obtained on the types of molecules present in the product mixture. The important conclusion to be drawn is that the fluorination reactions, as carried out in this work, break the condensed ring PN skeleton to produce volatile products of unknown composition. An attempt was made to fluorinate the condensed ring compound partially, using a method similar to that used in preparing the tetrameric chloride fluorides $P_4N_4F_xCl_{8-x}$.[47] This reaction produced only unreacted $P_6N_7Cl_9$ and a trace of volatile decomposition products of the type already discussed.

Experimental

i) Reaction of Nitrilohexaphosphonitrilic Chloride and Potassium Fluorosulphite in Cyclohexane.

A slurry of $P_6N_7Cl_9$ (3.5 g., 3.85 mmol) and potassium fluorosulphite (6.5 g., 11.0 mmol) in 125 ml of cyclohexane were heated under reflux in an anhydrous atmosphere. The reflux condenser was connected in series to a cold trap immersed in a dry ice/acetone slush bath. After 16 hours, the reaction mixture was cooled and filtered to remove insoluble salts. The cyclohexane solvent was distilled off to yield a crystalline deposit which was identified as $P_6N_7Cl_9$ (1.4 g., 2.3 mmol) by its infra-red spectrum. No other fractions were isolated in this

distillation, indicating that no $P_6N_7F_9$ was present. The insoluble

precipitate was dissolved in water and a few pellets of caustic soda

added. The solution was evaporated to dryness and the residue

dissolved in 250 ml. of water. A small aliquot of this solution gave a

positive result when tested for chloride ion, indicating that sub-

stitution of the chlorine ligands had occurred. Another aliquot of

this solution was oxidized with a few drops of conc. nitric acid, and

treated with a few drops of a solution prepared by dissolving ammonium

and magnesium chlorides in dilute aqueous ammonia. The appearance of a

white precipitate confirmed the presence of the phosphate ion in the

original solution, indicating that decomposition of the phosphonitrilic

ring had occurred.

ii) Reaction of Hexaphosphonitrilic Chloride with Activated Potassium Fluoride[44]

Freshly prepared "active" potassium fluoride (2.5 g., 43 mmol)

was added to a small 3-necked flask containing finely ground $(PNCl_2)_6$

(2.0 g., 2.8 mmol). A reflux condenser was attached to the apparatus.

The condenser was then connected in series to a cold trap (immersed in

a dry ice/acetone slush bath) which was itself connected to a silica

gel drying tube. The reaction mixture was stirred mechanically and

heated in an oil bath to a bath temperature of 145°C. The reaction

mixture soon turned into a paste which, after half an hour at 145°C,

began to bubble. After about a minute, the bubbling lessened and the

reaction was allowed to continue for 4 hours, after which time the oil bath was removed from the reaction vessel and the whole apparatus allowed to cool. No volatile products were present in the cold trap. The reaction vessel was washed with 3 x 10 ml of diethyl ether. The ether extract was fractionally distilled to yield $(PNF_2)_6$ (0.70 g., 48% of theory), boiling point 147°C.[11]

iii) Reaction of Nitrilohexaphosphonitrilic Chloride with Activated Potassium Fluoride

In an analogous experiment to that described above, $P_6N_7Cl_9$ (1.07 g., 1.78 mmol) and activated potassium fluoride (3.6 g., 62 mmol) were stirred together and heated to 150°C for 48 hours. There was no visible evidence of any reaction occurring at any time during this period. At the end of this time, no volatile products had been collected in the cold trap. The reaction mixture was extracted with diethyl ether, benzene and acetonitrile. On distillation of these solvents no other products were found. The reaction residue was completely water soluble and gave a positive test for chloride ion when treated with acidified silver nitrate, indicating that substitution of the condensed ring compound had taken place.

iv) Reaction of Nitrilohexaphosphonitrilic Chloride with Argentous Fluoride

A mixture of finely ground $P_6N_7Cl_9$ (0.800 g., 1.34 mmol) and finely ground silver fluoride (3.5 g., 27.5 mmol) were added to a 50 ml.

one-necked flask and the flask connected in series to a cold trap
(immersed in liquid nitrogen) and a vacuum system (see Fig. 4.1). At
a pressure of $\frac{1}{2}$ atmosphere, the reactants were heated to ~180°C in a
sand bath for one hour. No distillate was noticed on the walls of the
cold trap. Over a period of 15 minutes, the temperature of the sand
bath was raised to 240°C. A condensate slowly collected on the walls
of the cold trap. The heating was continued for 3 hours, at the end
of which time, the reaction mixture residue was a dark grey solid (pure
AgF is light yellow). The silver fluoride plug (see Fig. 4.1) was
heated to about 100°C with an infra-red lamp and the volatile products
of the reaction passed through this plug ten times by a series of trap
to trap vacuum distillations. The product (0.290 g.) was collected in
a sealed tube. This product was gaseous at room temperature, and its
average molecular weight was found to be 114 (the molecular weight of
$P_6N_7F_9$ is 455).

I(b). Methoxylation of Nitrilohexaphosphonitrilic Chloride

      The fully methoxylated cyclic phosphonitriles $(PN(OMe)_2)_n$
(n = 3-8) have been prepared.[48,49] These compounds are colourless
crystalline solids, except for $(PN(OMe)_2)_5$ and 7, which are both
liquids. They are soluble in most organic solvents, but not in water.
However, it is possible to extract them from an organic solution with
1N hydrochloric acid. Heated under vacuum, the methoxyphosphonitriles
undergo a thermal rearrangement, to give a hygroscopic glass, the

To Manometer

To Vacuum

AgF Plug

AgF
+
$P_6N_7Cl_9$
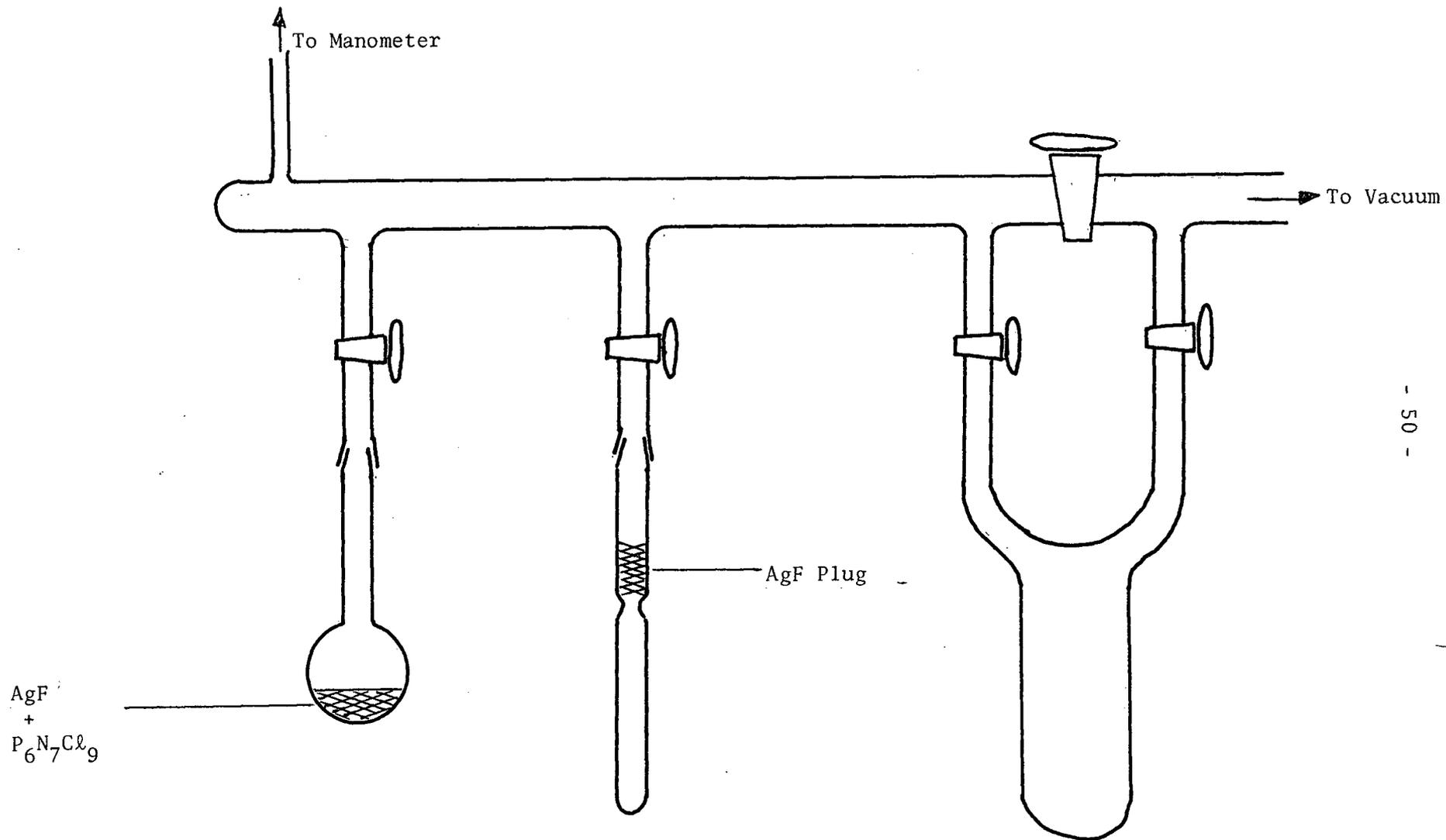
Fig. 4.1.   Apparatus used in the attempted fluorination of $P_6N_7Cl_9$.

infra-red spectrum of which indicates the presence of a P=O bond. A

Kirsanov type rearrangement is believed to take place during this reaction.

.... (4.2)
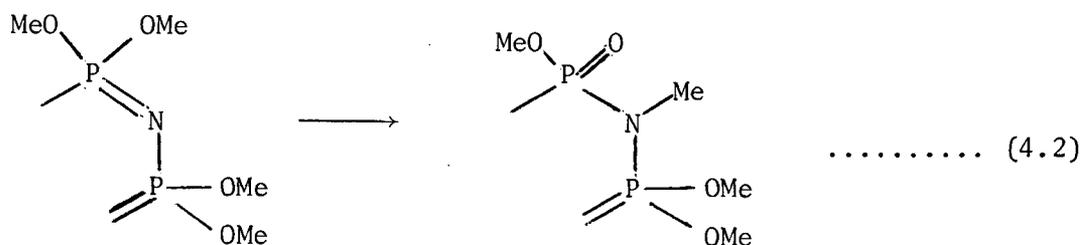
These compounds are made by a simple metathetical reaction with sodium

methoxide. Completely anhydrous reagents and conditions must be used,

since the presence of moisture drastically reduces the yield of product.

The preparation of a condensed ring methoxyphosphonitrile was attempted

in this work. ^{31}P and ^{1}H n.m.r. spectrometry would have been particularly

informative in deducing the structure of any compound isolated, and the

thermal properties of a condensed ring methoxide would be interesting in

comparison to those of the monocyclic methoxides. Despite elaborate

precautions for the exclusion of moisture in the reactants, no phospho-

nitrilic compound was obtained from the reaction. The yield of ionic

chlorine from the reaction corresponded to complete substitution of the

ring chlorine atoms. Concurrent or subsequent ring cleavage is believed

to have occurred, with the loss of the P_6N_7 skeleton.

Method:-   Anhydrous reagents were prepared as follows. "Super-dry"

methanol was produced by triply distilling 100% methanol from sodium.

Benzene (solvent) was dried by doubly distilling spectroscopic grade

benzene from sodium. Sodium methoxide was prepared[50] by dissolving

clean, dry sodium (0.150 g., 6.53 mmol) in 10 ml of "super dry"
methanol. The excess of methanol was distilled off to leave a white
powder of sodium methoxide. Under an atmosphere of dry nitrogen,
15 ml of dry benzene were added to the powdered sodium methoxide and
the mixture stirred into a slurry with a magnetic stirrer. A solution
of nitrilohexaphosphonitrilic chloride (0.300 g, 0.50 mmol) in 10 ml
of dry benzene was slowly added to the sodium methoxide slurry. The
reaction mixture was gently heated under reflux for 4 hours, after
which time the slurry was cooled and 20 ml of diethyl ether were added to
the mixture. The resulting suspension was washed with cold distilled
water (4 x 25 ml) and this water collected and analysed for Cl^- ion by
precipitation as $AgCl$. The yield of Cl^- ion was 96% of that amount
equivalent to complete substitution of the ring.

The residual ethereal solution was then extracted with 1N hydro-
chloric acid (2 x 25 ml), the extract neutralized with sodium bicarbonate,
and re-extracted with chloroform. This solution was dried over
anhydrous calcium chloride for 24 hours, decanted and allowed to
evaporate. No phosphonitrilic compound was obtained from this extract.
The original ethereal solution was also dried and evaporated, and no
phosphonitrilic compound was isolated from this solution.

II. Amination of Nitrilohexaphosphonitrilic Chloride

The reaction between phosphonitrilic chlorides and many different
types of amines has been studied. In most cases the reaction is a

simple metathetical substitution involving the elimination of the amine
hydrochloride. Partially aminated phosphonitrilic chlorides can also
be made by reaction of the two reagents in the appropriate stoichio-
metric ratio. The successive substitution of chlorine ligands by amine
groups is in a non-geminal fashion, and substitution of the ring tends
to deactivate the ring to further substitution. The fully dimethyl-
aminated phosphonitriles $[PN(NMe_2)_2]_{3-6}$ have been prepared[51] and all
are colourless crystalline solids.

Because the reaction proceeds easily at room temperature, is not
sensitive to moisture, and because the substituent deactivates the ring
to further reaction, dimethylamination of the condensed ring compound
was attempted. Even with an excess of dimethylamine, complete sub-
stitution of the chlorine ligands could not be achieved. The compound
that was isolated from this reaction was finally characterized as being
3,11,imino-3,11,dichloro-octadimethylaminocyclohexaphosphonitrile, the
molecular formula of which is $P_6N_6(NH)(NMe_2)_8Cl_2$. The course of the
dimethylamination reaction may be written simply as:

$$\cdots\cdots\cdots (4.3)$$
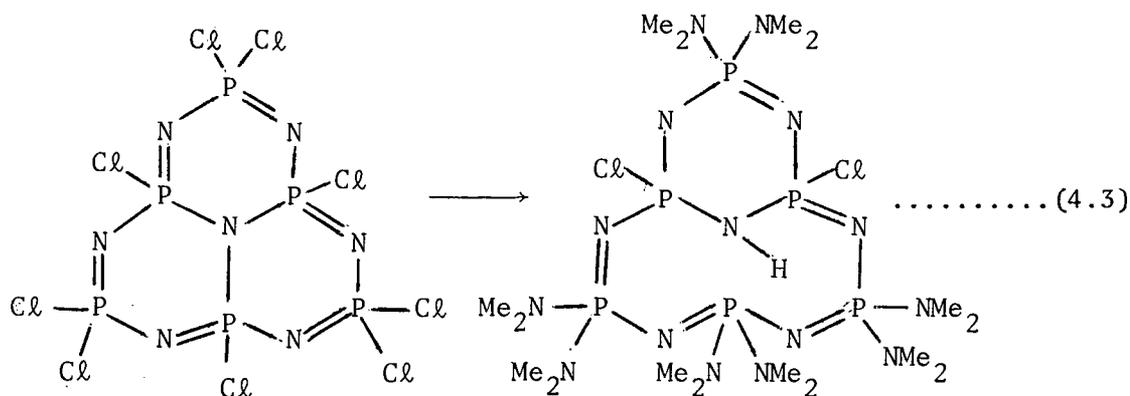
A discussion of the structure of $P_6N_6(NH)(NMe_2)_8Cl_2$ is given in the following section.

A similar reaction was attempted with diethylamine. No crystalline product could be isolated, and since the reaction was done on a small scale, purification of the residual oil could not be made. In the monocyclic phosphonitrilic dialkylamides, increasing size of the alkyl group lowers the melting point of the compound and it is thought that this is the reason that no crystalline product could be isolated from the reaction of diethylamine with the condensed ring chloride. The course of the reaction with diethylamine is thought to be the same as that with dimethylamine. The oil gives a positive test for chlorine, showing that substitution of the ring is incomplete. The infra-red spectrum of the oil was typical of a phosphonitrilic dialkylamide, with a "P=N" absorption at ~1260 cm^{-1} and a multiplet of C-H stretching peaks in the 2900-3000 cm^{-1} region. The ^1H n.m.r. spectrum (60 MHz) of the oil in carbon tetrachloride solution indicated at least partial substitution. Signals from methyl and methylene protons were observed. The former appeared as a triplet ($J_{H-H} \simeq 7$ c.p.s.) at $\delta = 1.06$ p.p.m. and the latter, as a broad unresolved multiplet (caused by ^1H-^1H and ^{31}P-^1H coupling) and making it impossible to distinguish inequivalent methylene groups appeared at $\delta = 3.1$ p.p.m.

As section III of this chapter will show, the results of the reaction with dimethylamine are very important in the understanding of the chemistry of $P_6N_7Cl_9$. In the course of this reaction the

condensed ring PN skeleton is broken. Attack by a nucleophile at the bridgehead phosphorus atoms leads either to the loss of a chlorine ligand or to the cleavage of the internal P-N bond. That the internal P-N bond is broken in preference to the P-Cℓ bond indicates the chemical weakness of the P_6N_7 nucleus to chemical substitution.

Method:- Reaction of Dimethylamine with Nitrilohexaphosphonitrilic Chloride. 12 ml of a cold (0°C) 10% solution of dimethylamine in benzene (equiv. to 0.804 g., 17.9 mmol of $HNMe_2$) were slowly added to a cold (0°C), stirred solution of $P_6N_7Cℓ_9$ (0.509 g., 0.845 mmol) in 15 ml of benzene. Immediate turbidity was noticed. After 3 hours, the reaction mixture was filtered, and the reaction mixture and precipitate washed with 3 x 5 ml of benzene. The weight of the precipitate (0.550 g.) was equivalent to 0.68 mmol of dimethylamine hydrochloride. The benzene solution was distilled to leave a pale yellow oil, which did not crystallize on cooling. The oil was dissolved in petrol ether (30°-60°C), filtered, and the solution evaporated to leave a solid product (yield 0.460 g.) which could be recrystallized from acetonitrile to produce colourless, flaky crystals (m.pt. 161-163°C) of 3,11,imino-3,11,dichloro-octadimethylaminocyclohexaphosphonitrile (calculated for $P_6N_6(NH)(NMe_2)_8Cℓ_2$:- P, 26.32; N, 29.75; C, 27.18; H, 6.94; Cℓ, 10.01. Found:- N, 29.71; C, 27.17; H, 6.91; Cℓ, 9.97.)

Unlike the parent condensed ring chloride, this compound is soluble almost to the point of miscibility in benzene, chloroform,

carbon tetrachloride and petrol ether (30°-60°). Efficient recrystall-
ization can only be made from acetonitrile. Twinning of the crystals
is evident, and the crystals are also tribo-electric.

The infra-red spectrum of the compound was recorded on samples in
a nujol mull and a carbon tetrachloride solution. The prominent peaks
in the mull spectrum are: 504 (st), 540 (m), 658 (w), 682 (w), 730 (m),
771 (m), 781 (sh), 838 (w), 863 (w), 891 (w), 929 (m), 984 (v.st),
1062 (m), 1188 (v.st), 1231 (st), 1280 (v.st), 1456 (m), 2790 (w),
2880 (w), 2920 (m).

III. The Molecular Structure of 3,11, imino-3,11,dichloro-octadimethyl-aminocyclohexaphosphonitrile

The structure of this compound, which is discussed in the follow-
ing section, is unique in phosphonitrilic chemistry. Although the actual
conformation of the molecule has not been completely established, the
structure of the molecule is believed to be that shown in Fig. 4.2.
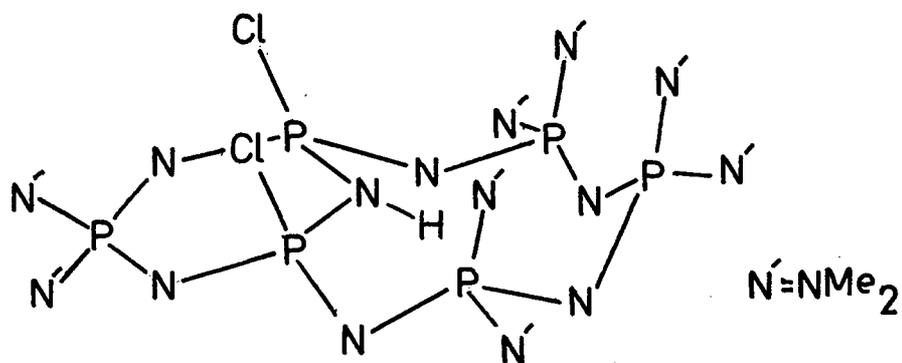
Fig. 4.2. Suggested structure of $P_6N_6(NH)(NMe_2)_8Cl_2$.

In the following discussion of the molecule, rather than use the full name of the compound, the molecular formula $P_6N_6(NH)(NMe_2)_8Cl_2$ will be used as a notation for the compound.

a) Infra-red Spectrum

The infra-red spectrum of this compound shows a complex vibrational pattern characteristic of phosphonitrilic dimethylamides. The "P=N" stretching frequency (at 1280 cm^{-1}) is considerably lower than in the open ring hexameric dimethylamide, in which $\nu(P=N)$ occurs at 1340 cm^{-1}. The large difference in frequency indicates that $P_6N_6(NH)(NMe_2)_8Cl_2$ has very different symmetry and bonding from the open ring dimethylamide and should not be regarded as a simple derivative of the open ring system. Neither the mull nor the solution spectra show an observable (N-H) vibration. The reason for the absence of this band is thought to be intramolecular hydrogen bonding, which would shift $\nu(N-H)$ to lower frequency and also broaden the absorption peak.

b) Mass Spectrum

The mass spectrum of this compound is difficult to discuss in detail, firstly because of the large number of peaks (caused by proton abstractions), which makes a detailed assignment of fragments impossible, and secondly because there are no analogous compounds with which to compare it.

The parent peak consists of a multiplet based at m/e 706. The mass number 706 corresponds to the formula $P_6N_7(NMe_2)_8Cl_2$ (taking $Cl = 35$). The mass number of $P_6N_6(NH)(NMe_2)_8Cl_2$ is 707 (taking $Cl = 35$),

but the parent ion is an odd electron species. The parent peak itself, at m/e 707, has an intensity of 24% (± 1%) of the P-1 peak. The natural abundance of ^{15}N is 0.38% and that of ^{13}C is 1.1%. On this basis, the calculated contribution to the parent peak from ^{13}C and ^{15}N in the $[P_6N_7(NMe_2)_8Cl_2]^+$ fragment is 23% that of the P-1 peak. The contribution of the parent ion to the m/e 707 peak must therefore be very small, and the N-H bond must be weak and easily broken.

The absence of a parent ion is not uncommon. The fragmentation pattern of diphenylamine[52] does not exhibit any peak corresponding to the ion $[C_6H_5-NH-C_6H_5]^+$, and the peak corresponding to the ion $[C_6H_5-N-C_6H_5]^+$ is the most intense peak in the whole mass spectrum. Presumably loss of a proton is favoured since the resulting ion fragment will be stabilized by resonance with the two phenyl groups. The mass spectrum of heptasulphur imide, S_7NH,[53] exhibits a similar phenomenon, the intensity of the $(S_7NH)^+$ ion being only 5% of that of the $(S_7N)^+$ ion.

The higher mass range part of the spectrum consists mainly of fragments of the type $P_6N_6Cl_2(NMe_2)_x$ (x = 8-2). In this part of the spectrum, loss of dimethylamine groups is more favoured than loss of chlorine, thereby indicating a stronger P-Cl bond than P-NMe$_2$ bond.

c) ^{31}P n.m.r. Spectrum

The ^{31}P n.m.r. spectrum is detailed in Table 4:1. Resolution of the 3 peaks is poor because of $^{31}P-^1H$ and $^{31}P-^{31}P$ coupling. In the case of the low-field signal at δ = -13.0 p.p.m., the peak is resolved into

Type of Phosphorus Atom	P_1	P_2, P_3	P_4, P_5, P_6
δ_p p.p.m. relative to 85% H_3PO_4	-13.7	-3.7	+1.9
Intensity ratio	1	2	3
Structure	Triplet $J_{P-P'}$ = 40 c.p.s.	broad unresolved singlet	broad unresolved singlet

TABLE 4:1.   Data from ^{31}P n.m.r. spectrum of $P_6N_6(NH)(NMe_2)_8Cl_2$.
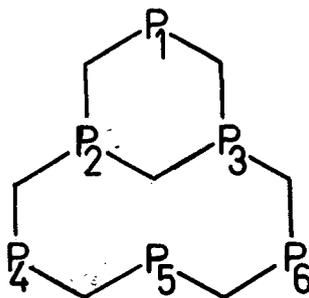
Fig. 4.3.   Gross structure of $P_6N_6(NH)(NMe_2)_8Cl_2$ indicated by ^{31}P n.m.r. spectrum.

a triplet caused by ^{31}P-^{31}P coupling $(J_{P'P} = 40 \pm 2$ c.p.s.) ^{31}P-^1H

coupling is unresolved and not measurable. The two high-field signals

are broad (half-height width $\simeq 100$ c.p.s.) unresolved peaks with no

distinguishable fine structure. The spectrum indicates the gross

structure given in Fig. 4.3. The lack of resolution in the high-field

signals is most likely caused by the fact that phosphorus atoms to which

these signals are assigned can couple with more than one type of phos-

phorus atom, thereby causing a complex coupling pattern which is

unresolvable. The P_1 phosphorus atom, however, only couples with one type

of phosphorus atom, and the simpler coupling scheme is, therefore,

resolvable. The chemical shifts of the P_4, P_5 and P_6 atoms are not

required to be equivalent by symmetry. This type of occurrence is not

unusual. In monosubstituted hexameric fluorophosphonitriles, all the

$\equiv PF_2$ phosphorus atoms, except those adjacent to the substituted phos-

phorus atom, have identical chemical shifts, even though they are not

symmetrically equivalent.

The interpretation of ^{31}P chemical shifts in terms of the electro-

negativities of ligands is unrewarding in many phosphonitrilic deriva-

tives. A ligand can affect the electron density at phosphorus in two

ways. A conjugative effect between phosphorus and the ligand can

either donate or withdraw electron density from phosphorus, whilst a

π-inductive effect can either suppress or increase the delocalization

of the lone pair electrons on the ring nitrogen atoms, thereby changing

the π-electron density at phosphorus. In fully substituted phospho-

nitriles, the ^{31}P chemical shift moves upfield with increasing electro-

negativity of the ligand.[54] Similarly, in the series $P_3N_3Cl_5X$

(X = F, OEt, Ome, Cl, NMe_2), the chemical shift of the substituted

phosphorus atom moves upfield with the increasing electronegativity

of X.[55] In these compounds, the influences of a π-inductive effect

seem to be the most important.

The correlation of the ^{31}P chemical shifts of $P_6N_7Cl_9$ and

$P_6N_6(NH)(NMe_2)_8Cl_2$ is not understood. At best, the ^{31}P n.m.r. spectrum

of $P_6N_6(NH)(NMe_2)_8Cl_2$ serves as a way of determining the gross symmetry

of the molecule, but gives only a little insight into the electronic

structure of the molecule. The positions of the three peaks in the

spectrum relative to each other are difficult to rationalize simply in

terms of a π-inductive effect. Similar difficulties arise in the

^{31}P n.m.r. spectra of partially dimethylaminated trimeric phosphonitrilic

chlorides. Fig. 4.4 shows three such derivatives and the details of

their ^{31}P n.m.r. spectra.[56] A π-inductive effect which would account

A	B	C
δ_α = -22.0 p.p.m.	δ_α = -23.9 p.p.m.	δ_α = -27.6 p.p.m.
δ_β = -20.4 p.p.m.	δ_β = -30.5 p.p.m.	
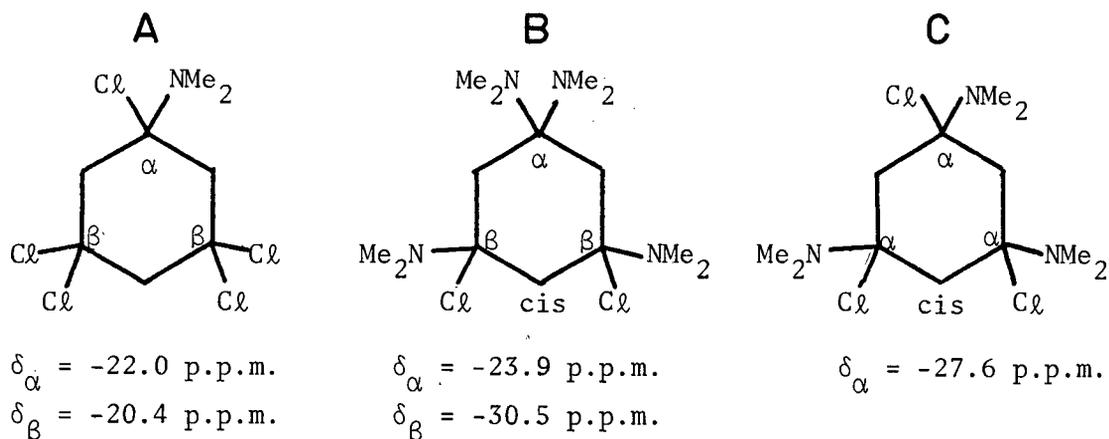
Fig. 4.4. ^{31}P chemical shifts of some trimeric dimethylamino-chlorophosphonitriles (all values relative to 85% H_3PO_4).

for the observed chemical shifts in compound A, cannot account for the shifts in compound B, where the introduction of an extra -NMe$_2$ group has increased the chemical shift of the P$_\alpha$ atom from its original value in compound C.

Anomalies, therefore do occur in the ^{31}P n.m.r. parameters of dimethylamino-chlorophosphonitriles, and the interpretation of chemical shifts in terms of π-electron density is not always rewarding.

d) ^{1}H n.m.r. Spectrum

The ^{1}H n.m.r. spectra (at 60 and 100 MHz) of P$_6$N$_6$(NH)(NMe$_2$)$_8$Cl$_2$ are shown in Fig. 4.5. The phosphorus decoupled proton spectrum is also shown, together with assignments of the various peaks.

At 100 MHz, the resolution of the peaks is much better than at 60 MHz. The signals corresponding to the H$_a$ and H$_b$ protons have collapsed into a single peak in the 60 MHz spectrum. The relative intensities of the signals in both the coupled and ^{31}P decoupled spectrum are in the ratio of H$_a$: H$_b$: H$_c$: H$_d$ = 1 : 2 : 3 : 2. In the ^{31}P decoupled spectrum, taken using a noise band with a band-width of 2000 Hz at a frequency of 40.481000 MHz, ^{31}P-^{1}H decoupling is completely achieved and the ordinary high resolution spectrum, consisting of 4 doublets, collapses into 4 single peaks, corresponding to 4 different types of proton in the molecule.

The ^{1}H spectra have been interpreted in terms of the molecular structure shown in Fig. 4.5. Although there are two conformations of the molecule which are consistent with ^{1}H n.m.r. spectra, a considera-tion of the mechanism (which will be discussed later) of the formation
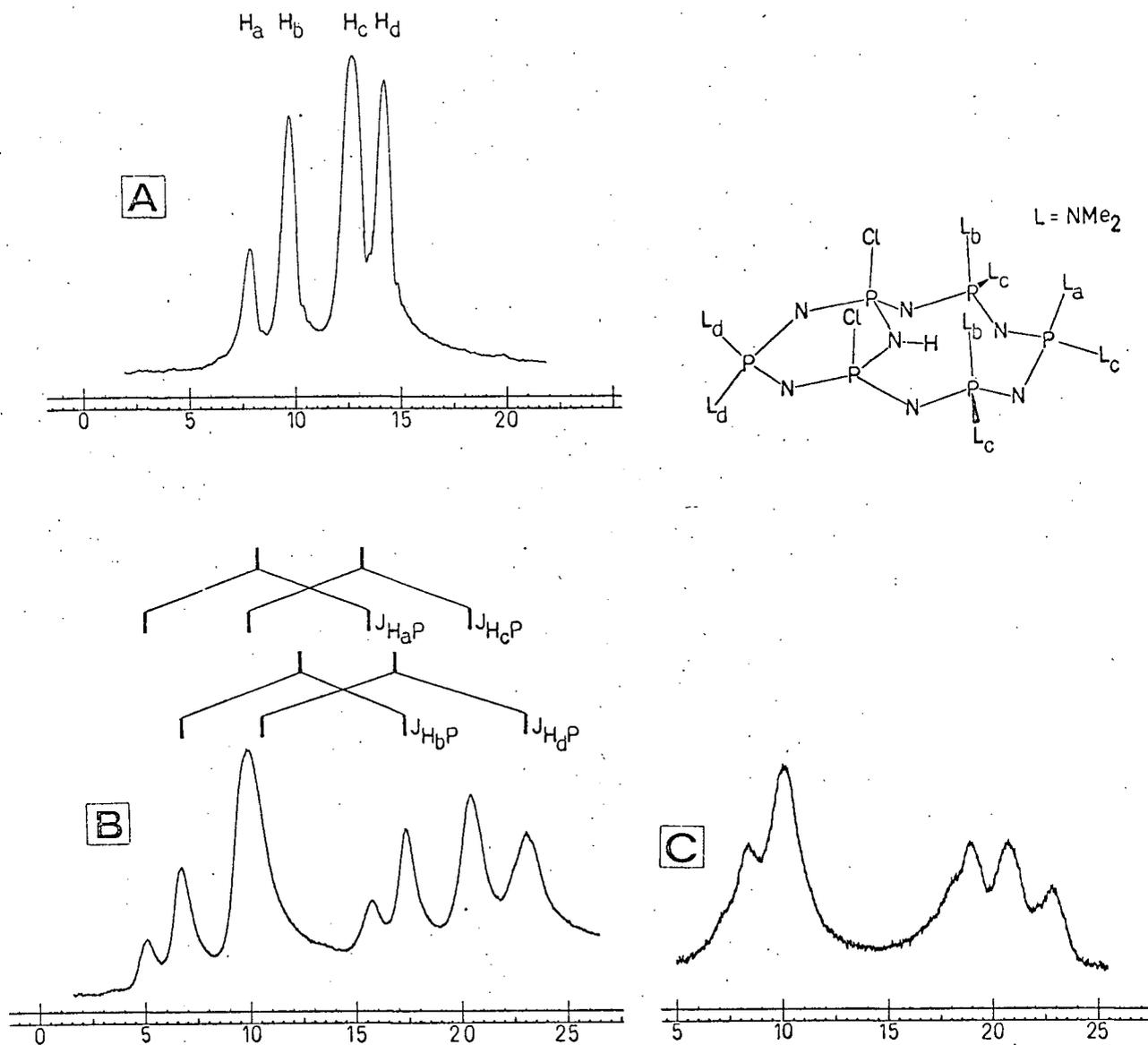
Fig. 4.5. The ^{1}H n.m.r. spectra of $P_6N_6(NH)(NMe_2)_8Cl_2$. Spectra B and C are taken at field strengths of 100 MHz. and 60 MHz. respectively. Spectrum A is the ^{31}P-^1H decoupled spectrum (taken using a 2000 Hz. noise band at 40.48100 MHz.). The figure on the top right of the diagram shows the assignments of the various peaks.

of the molecule has shown that the structure shown in Fig. 4.5 is the most probable conformation.

The chemical shifts and coupling constants of the various types of proton are given in Table 4.2. It is important to note that the largest coupling constant is J_{PH} = 12.7 c.p.s. Both in mononuclear phosphorus (V)

Type of proton	H_A	H_B	H_C	H_D
Intensity ratio	1	2	3	2
δ p.p.m.	2.626	2.606	2.576	2.551
J_{P-H} c.p.s.	10.7	10.7	10.7	12.7

TABLE 4:2. Data from ^1H n.m.r. spectra of $P_6N_6(NH)(NMe_2)_8Cl_2$

compounds,[57] and in the dimethylamino-derivatives of trimeric phosphonitrilic chloride,[56] J_{PH} values decrease with increasing aminolysis and the value of J_{PH} acts as an excellent criterion for distinguishing between $\equiv PClNMe_2$ and $\equiv P(NMe_2)_2$ groupings. For the former, J_{PH} is never below 16.3 c.p.s., and for the latter, is never above 13.9 c.p.s. In

the series $(PN(NMe_2)_2)_n$ (n = 3-6), J_{PH} decreases from 11.2 c.p.s. (for

n = 3) to 10.0 c.p.s. (for n = 6).[58] The effect of ring size on J_{PH} is

small, and the fact that in $P_6N_6(NH)(NMe_2)_8Cl_2$ $J_{PH} \leq 12.7$ c.p.s. proves

that there are no $\equiv PClNMe_2$ groups in the molecule, and is a further

confirmation of the structure shown in Fig. 4.5.

The interpretation of the ^1H n.m.r. spectra of phosphonitrilic

derivatives is in most cases hampered by complex unresolvable coupling.

For instance, the simple cyclic dimethylamides show a deviation[58] from

the simple doublet pattern which is expected from a first order treat-

ment. The spectra consist of a sharp doublet between which lies a broad

peak which, in the case of $(PN(NMe_2)_2)_3$ accounts for 25% of the total

intensity of the signal and, in the case of $(PN(NMe_2)_2)_8$, accounts for

all of the signal, with the outside doublet being completely unresolved.

The calculation of transition energies and the relative intensities

of each of the hydrogen nuclei in phosphonitrilic molecules is very

complex and has not yet been achieved. Analysis of simpler spin

systems[59] has shown that the "odd" appearance of the spectra in high

symmetrical spin systems such as cyclic phosphonitrilic dimethylamides

is due entirely to their symmetry.[60] The resolution of the ^1H n.m.r.

spectrum of $P_6N_6(NH)(NMe_2)_8Cl_2$ into separate peaks is indicative of

the lack of structural symmetry in the molecule. Long range coupling

is negligible, and the lack of chemical, and therefore magnetic,

equivalence of the phosphorus atoms in the molecule eliminates the

complexities which occur in more symmetric systems. A simple first

order treatment can therefore be used to interprete the ^{1}H n.m.r. spectrum in terms of the structure of the molecule.

Another interesting feature that this molecule shows is that some pairs of dimethylamino-groups attached to the same phosphorus atom have different chemical shifts. This distinction of dimethylamine groups differing only in their conformation at a phosphorus atom is unique in phosphonitrilic chemistry. In $(PN(NMe_2)_2)_4$, there are axial and equatorial -NMe$_2$ groups (which have different exocyclic P-N bond lengths), but all protons in the molecule resonate at the same frequency. In the monocyclic dimethylamide chlorides, when two -NMe$_2$ groups on a particular phosphorus atom are in different environments, their ^{1}H chemical shifts are still identical. The fact that there is a distinction between -NMe$_2$ groups in $P_6N_6(NH)(NMe_2)_8Cl_2$ must be a result of the molecule being held in a rigid conformation. The reason for this is thought to be intramolecular hydrogen bonding, which holds the molecule rigid. Hydrogen bonding is thought to occur between the (N-H) proton and the axial -NMe$_2$ groups on the ring. The (N-H) proton signal, which is not shown in Fig. 4.5, occurs at $\delta = 6.15$ p.p.m. at 60 MHz. It is a weak broad peak, and although intensity comparisons are difficult, the expected ratio of 1:48 is not inconsistent with the observed experimental integral curve.

Hydrogen bonding of the (N-H) proton would tend to withdraw electron density from the dimethylamino-group and thereby lower the chemical shift of the protons attached to that group. The observed chemical shifts are consistent with this theory, the extent of the hydrogen bonding depending on whether the -NMe$_2$ protons are in the

L_a or L_b position (see Fig. 4.5). The equatorial L_c -NMe$_2$ groups do not interact with the (N-H) proton and all the H_c protons resonate at a single frequency. The H_d protons are in different environments in the molecule, but as in the case of $P_3N_3Cl_2(NMe_2)_4$ (Fig. 4.4B), they have identical chemical shifts.

Some understanding of the two internal P-N bonds in $P_6N_6(NH)(NMe_2)_8Cl_2$ can be gained from an examination of the position of the chemical shift of the (N-H) proton in secondary amines. Table 4:3 shows the variation of δ_{NH} in a number of organic secondary amines. For some of the amines, the K_a is also given. The results indicate that the chemical shift of the (N-H) proton is a sensitive measure of the basic character of the nitrogen atom. Conjugation of the (N-H) group to aryl groups decreases the basic character of the nitrogen atom and at the same time lowers the chemical shift of the (N-H) proton. Alkyl groups, however, suppress lone pair delocalization, producing a stronger base and a high chemical shift for the (N-H) proton. That the chemical shift of the (N-H) proton in $P_6N_6(NH)(NMe_2)_8Cl_2$ occurs at $\delta = 6.15$ p.p.m. indicates considerable lone pair delocalization from the nitrogen atom into the phosphonitrilic π-systems. The (N-H) proton is acidic in nature, and this information, coupled with the fact that the mass spectrum of the molecule indicates that this proton is easily lost, suggests a stronger internal P-N bond in $P_6N_6(NH)(NMe_2)_8Cl_2$ than in $P_6N_7Cl_9$.

Compound	δ_{NH} p.p.m.	K_a
o-$NO_2C_6H_5NHC_6H_5$	9.39	
p-$NO_2C_6H_5NHC_6H_5$	8.20	
$CH_3CO-NH-CH_2CH_3$	8.08	
$C_6H_5-NH-C_6H_5$	5.42	1.62×10^{-1}
$C_6H_5-NH-CH_2C_6H_5$	3.78	
$C_6H_5-NH-CH_3$	3.34	1.41×10^{-5}
$C_6H_5-NH_2$	3.32	2.34×10^{-5}
$C_6H_5-NH-CH_2CH_3$	3.03	7.59×10^{-6}
$(C_6H_5-CH_2)_2NH$	1.78	
$C_6H_5-CH_2-NH-CH_3$	1.00	
$CH_3-NH-CH_3$		1.85×10^{-11}
$[(CH_3)_2CHCH_2]_2NH$	0.79	1.23×10^{-11}
Reference	61	62

TABLE 4:3. Relationship between (N-H) proton chemical shift and base strength of some secondary amines.

e) Conformational Analysis

As was mentioned above, the ^{1}H n.m.r. spectra can be interpreted in terms of two molecular conformations, both of which are shown in Fig. 4.6. The two conformations differ in the relative positions of the phosphorus and nitrogen atoms in the ten-membered ring. In structure I, the 3 adjacent ring phosphorus atoms are above the mean molecular plane and, in structure II, they are below it. In both structures, it is the axial dimethylamino-groups that are involved in hydrogen bonding, and it is this intramolecular interaction which holds the two conformations rigid. Although structures I and II both account for the observed ^{1}H n.m.r. spectrum, the former is believed, on the basis of general mechanistic considerations, to be the correct structure.

Although the stereochemical course of replacement reactions in phosphonitriles is not fully understood, the results of chlorine exchange between chloride ion and chlorophosphonitriles suggest an SN$_2$ mechanism.[63] Kinetic studies on the dimethylamination of (PNCl$_2$)$_3$ suggest[64] a penta-coordinated phosphorus atom as an intermediate, with the attacking nucleophile and the leaving group being in the axial positions. In general, most replacement reactions at phosphorus in mononuclear phosphorus compounds are accompanied by an inversion of configuration,[65] and the same inversion is believed to occur in phosphonitriles, in so far as substitution in these compounds is effected by a bimolecular reaction.
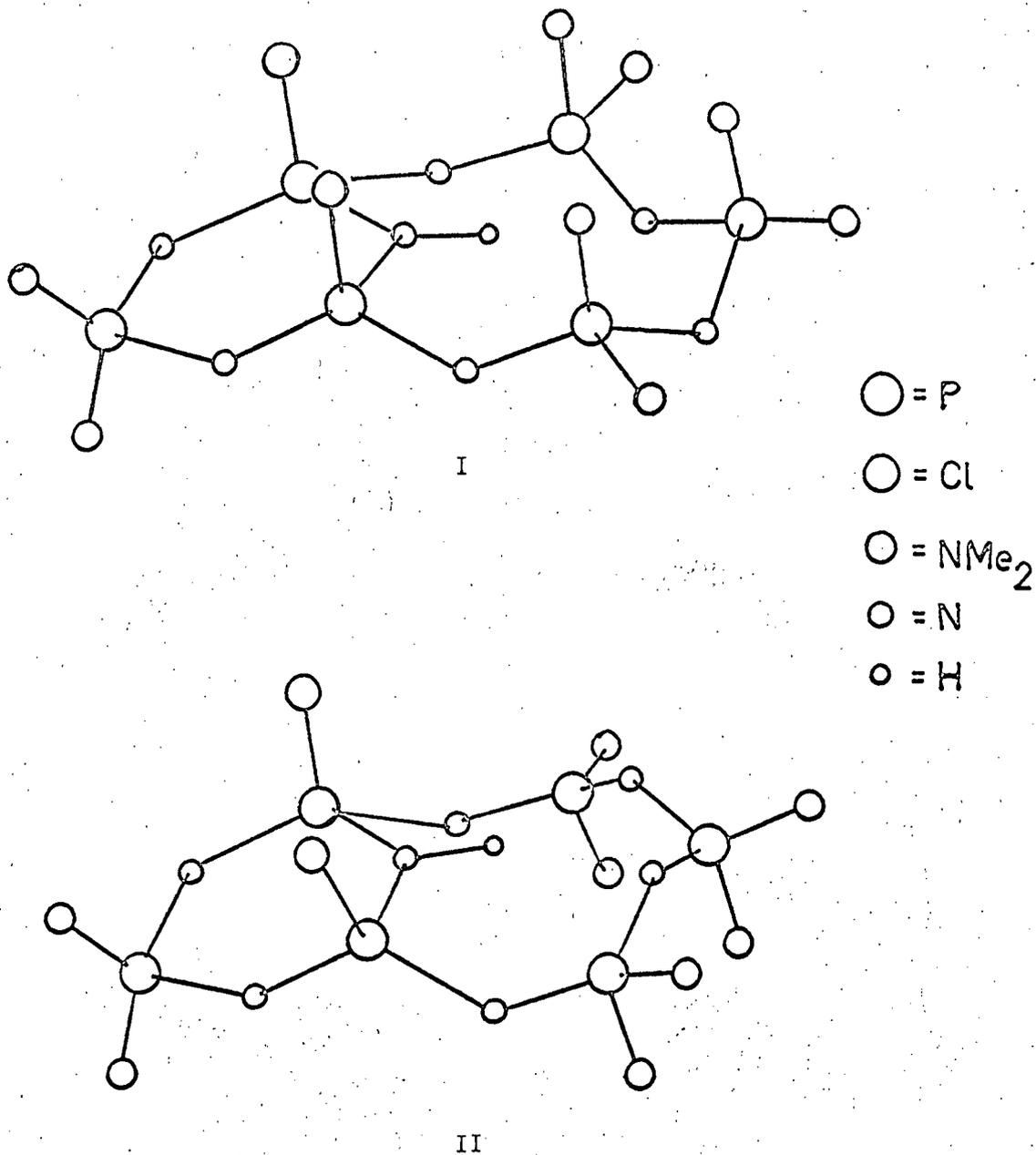
Fig. 4.6. Idealized structures for the $P_6N_6(NH)(NMe_2)_8Cl_2$ molecule. Both structures are consistent with ^{31}P and ^1H n.m.r. data, but structure I is believed to be the correct structure (see text).

The mechanism of the complete dimethylamination of $P_6N_7Cl_9$ is not known. The weakness of the internal PN bonds has already been discussed, and it is thought that attack at a bridgehead phosphorus by a dimethylamine group leads to preferential cleavage of the internal P-N bond rather than the P-Cl bond. If also the mechanism of substitution involves nucleophilic attack at these phosphorus atoms, leading to a penta-coordinated intermediate and inversion of configuration, the stereochemistry of the final product can readily be established. As Fig. 4.7 shows, nucleophilic attack at a bridgehead phosphorus atom,
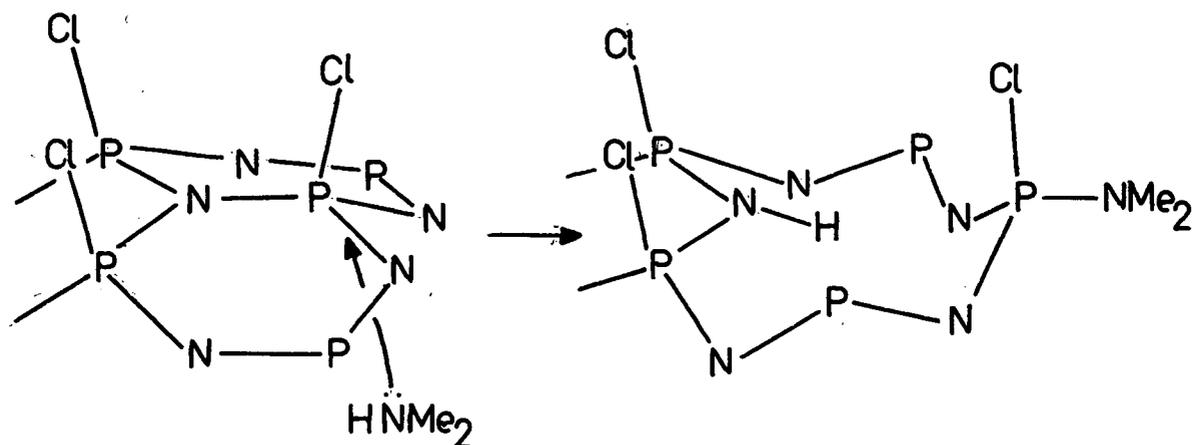
Fig. 4.7. Suggested stereochemistry of nucleophilic substitution at a bridgehead phosphorus atom in $P_6N_7Cl_9$.

with subsequent cleavage of the internal P-N bond, leads to a product where the ring phosphorus atoms are above the mean molecular plane.

Thus, the interpretation of this mechanism suggests that the conformation shown in Fig. 4.6I is the true conformation $P_6N_6(NH)(NMe_2)_8Cl_2$.

IV. Summary

The extent of this study of the chemistry of $P_6N_7Cl_9$ has been limited by the small amount of the compound that was available and by the very nature of the compound itself. Unlike the monocyclic phosphonitrilic chlorides, $P_6N_7Cl_9$ is unstable to substitution. Whether the attack of an approaching nucleophile occurs at the bridgehead or ring phosphorus atoms is not known. To the extent that lone pair delocalization from the central nitrogen atom deactivates the bridgehead phosphorus atoms, then to this extent the ring phosphorus atoms will be relatively more electrophilic in nature.

To the present time, only one derivative of the condensed ring compound has been isolated. The fact that in this compound the condensed ring skeleton has been broken, visually emphasizes the chemical weakness of the P_6N_7 skeleton. In the reaction with dimethylamine, one of the internal PN bonds is broken. That the ring cleavage process stops at this stage reflects the strengthening of the two remaining internal P-N bonds which occurs as a result of the loss of the first. The fact that substitution at the two remaining bridgehead phosphorus atoms in $P_6N_6(NH)(NMe_2)_8Cl_2$ does not occur, even with an excess of dimethylamine, must be a result of the complete deactivation of these phosphorus atoms.

In the case of ring activating nucleophiles (e.g. fluorine)
further substitution seems to occur, with subsequent collapse of the
phosphonitrilic skeleton. In organic chemistry, substitution at a
bridgehead carbon atom via an SN_2 mechanism is sterically impossible.
In $P_6N_7Cl_9$, the same situation may also occur, and the substitution
at bridgehead phosphorus atoms may be kinetically disallowed. Attack
by fluoride at the bridgehead atoms seems to break the P-N bonds rather
than the P-Cl bonds.

Further work may yet produce a fluorinated condensed ring molecule.
The appearance of high molecular weight fragments in the products of
one of the fluorination reactions attempted in this work indicate that
this may be possible. The observed characteristics of the condensed
ring molecule are entirely unexpected, and further work is necessary
before a complete understanding of this compound is achieved.

CHAPTER 5

THE MOLECULAR AND ELECTRONIC STRUCTURE

OF NITRILOHEXAPHOSPHONITRILIC CHLORIDE

The tricyclic condensed ring shape of $P_6N_7Cl_9$ was established by ^{31}P n.m.r. and vibrational spectroscopy and C_{3v} symmetry was suggested for the molecule. The recent X-ray crystal structure analysis[66] of the molecule confirmed this assignment. In the course of this study, Hückel molecular orbital calculations were carried out on an idealized planar condensed ring P_6N_7 framework. The results of these calculations, and the X-ray crystal structure analysis, are discussed in this chapter.

I. Orbital Interactions in $P_6N_7Cl_9$

Throughout the course of this work, comparisons have been made between the condensed ring $P_6N_7Cl_9$ molecule and the open ring $P_6N_6Cl_{12}$ molecule, and this comparison again becomes useful in considering the bonding in $P_6N_7Cl_9$. In phosphonitrilic compounds in general, if the valencies of phosphorus and nitrogen are taken as five and three respectively, the σ-framework of the cyclic $-PX_2=N-$ unit can be described using sp^3 hybridization at phosphorus and sp^2 hybridization at nitrogen. The formation of a π-bond, necessary to satisfy the valencies of phosphorus and nitrogen, then involves the remaining 2p orbital on nitrogen and a 3d-orbital on phosphorus.

In $P_6N_7Cl_9$, there are two types of phosphorus atom. At the non-bridgehead ($\equiv PCl_2$) type atoms, the orientations of the d-orbitals are analogous to those that occur in the monocyclic phosphonitriles. Fig. 5.1 shows the orbital overlap schemes for the d-orbitals of a $\equiv PCl_2$ phosphorus atom with valence orbitals of nitrogen. As can be seen in this diagram, two types of π-bonding can occur. Convention has it that the out-of-plane system is termed the π_a system. The d_{xz} and d_{yz} orbitals on phosphorus are involved in this system, overlap of these orbitals being (in planar systems) with the nitrogen p_z orbital. The in-plane π-system is termed the π_s system, and involves overlap of (principally) the $d_{x^2-y^2}$ and d_{xy} orbitals on phosphorus with the sp^2 lone pair hybrid on nitrogen.

At the bridgehead atoms of $P_6N_7Cl_9$, π-interactions of the phosphorus d-orbitals with the ring nitrogen atoms are the same as the non-bridgehead atoms. However, the addition of the central nitrogen atom allows a further π-interaction between the p_z orbital on that nitrogen and a phosphorus d-orbital. As Fig. 5.2 shows, the overlap of this central nitrogen p_z orbital with a phosphorus d-orbital is highly selective. The in-plane d-orbitals ($d_{x^2-y^2}$ and d_{xy}) do not interact with the out-of-plane p_z orbital. In the π_a system, the d_{xz} orbital is orthogonal to the p_z orbital, and only the d_{yz} orbital gives a non-zero overlap with the central nitrogen (see Fig. 5.2). Therefore, any π-effect that this atom has on the rest of the ring can only be made through interaction of this atom with the d_{yz} orbital on phosphorus.
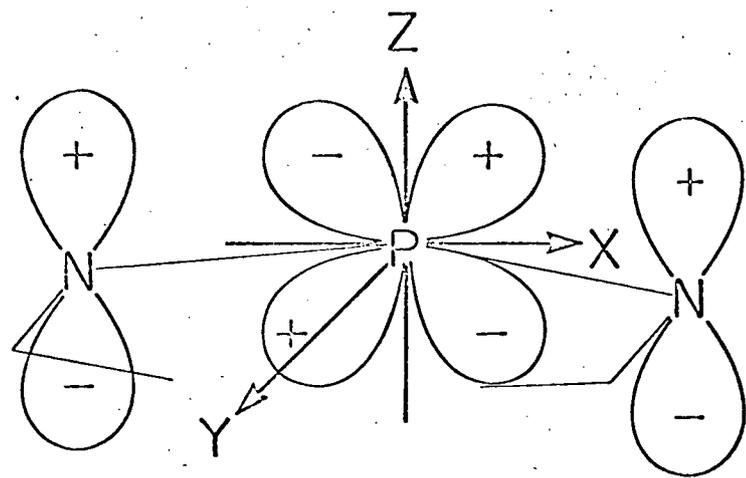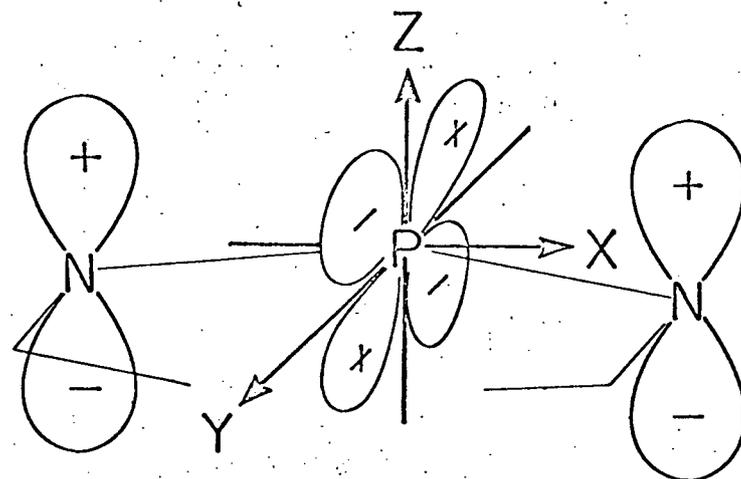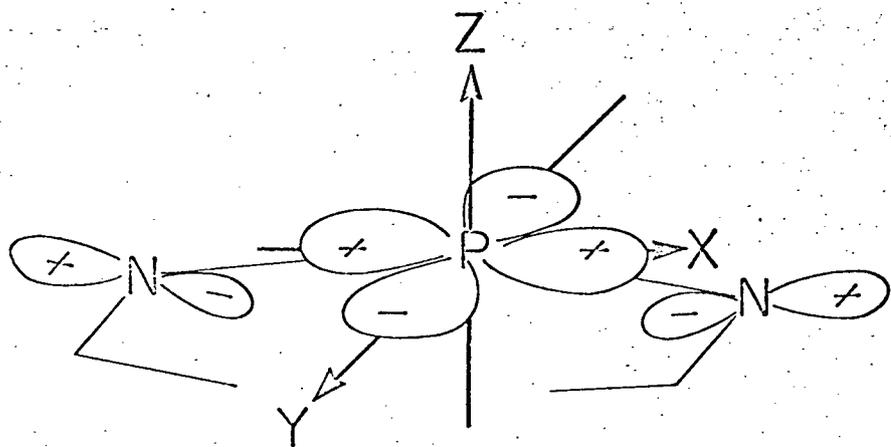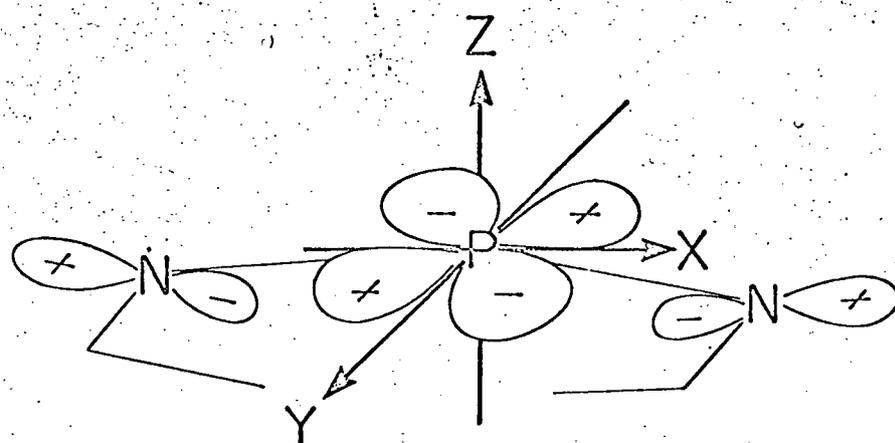
Fig. 5.1. Overlap schemes for the formation of π-bonds at a non-bridgehead phosphorus atom in $P_6N_7Cl_9$; (a) d_{xz}-p_z, (b) d_{yz}-p_z, (c) $d_{x^2-y^2}$-sp^2, (d) d_{xy}-sp^2.
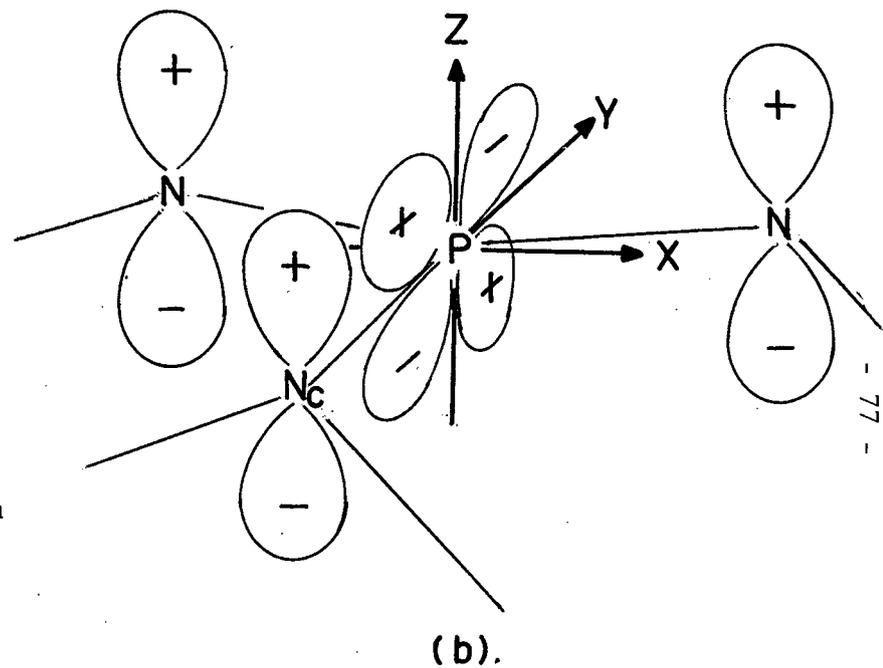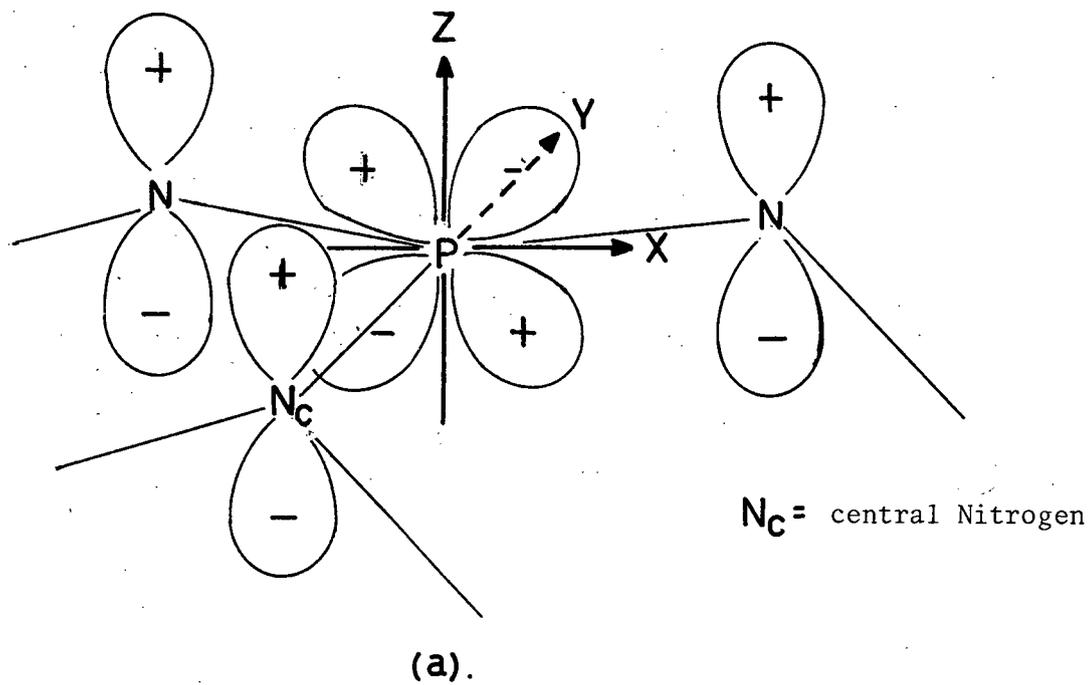
N_C = central Nitrogen

(a).

(b).

Fig. 5.2. Overlap schemes for out-of-plane orbitals at a bridgehead phosphorus atom in $P_6N_7Cl_9$.
(a) $d_{xz}-p_z$ (b) $d_{yz}-p_z$

Since the only formal difference between the $P_6N_6Cl_{12}$ system and the $P_6N_7Cl_9$ system is the insertion of this extra nitrogen, the difference in the π-bonding should not be great. The π_s systems in both molecules are formally the same and any differences in molecular bonding can only occur in the π_a system. The extent of the differences depend on the relative importance of the two components of the π_a system. Both in the π_a and π_s systems, the two separate components are not required to be equally involved, and experimentally this is found to be so. Overlap calculations,[67,68] have shown that in the π_a system, d_{xz}-p_z overlap is the more important component, and in the π_s system, $d_{x^2-y^2}$-sp^2 overlap is the more important.

II. Symmetry-based M.O. Calculations on $P_6N_7Cl_9$

Because the only difference between the open ring P_6N_6 system and the condensed ring P_6N_7 system is the addition of the central nitrogen in the latter, and because π-bonding from this nitrogen can only occur into one phosphorus d-orbital, a simple Hückel M.O. calculation was carried out on the P_6N_6 and P_6N_7 phosphonitrilic skeletons, calculations which effectively measured the difference in bond orders and charge densities between the two systems. For both molecules, a planar structure was assumed, where all ring angles were taken as being $120°$. Overlap was only considered between the phosphorus d_{yz} orbital and the nitrogen p_z orbital, and all overlaps were taken as being equivalent. For the P_6N_7 system, the energy levels that are formed are similar to

those found for the phenalenyl system.[69,70]

For any phosphonitrilic ring size, the secular equations are most conveniently set up utilizing the rotational symmetry of the molecule. For interactions involving the d_{yz} orbital at phosphorus and the p_z orbital at nitrogen, the secular determinant for an open ring system becomes:

$$\begin{vmatrix} \alpha_P - E & 2\beta\cos\dfrac{\ell\pi}{n} \\[3mm] 2\beta\cos\dfrac{\ell\pi}{n} & \alpha_N - E \end{vmatrix} = 0 \qquad \dots\dots\dots (5.1)$$

where ℓ, the ring quantum number, takes on the values $0, \pm1, \pm2 \dots \pm(n-1)/2$ (n odd) and $0, \pm1, \pm2 \dots n/2$ (n even), and n is the number of repeating PN unit in the phosphonitrilic ring. In this calculation, the two Coulomb parameters, α_P and α_N, are expressed in terms of an electronegativity difference ρ, such that $\alpha_P = \alpha_N + \rho\beta$; ρ is here arbitrarily set at $\rho = 2$. For the cyclic P_6N_6 system, the energy levels deduced from the secular determinant (equation 5.1) are:

$$E = \alpha \pm \sqrt{\cos^2\dfrac{\ell\pi}{6} + \dfrac{\rho^2}{16}} \qquad \dots\dots\dots (5.2)$$

where α is the average Coulomb parameter ($\alpha = (\alpha_P + \alpha_N)/2$). These energy levels are shown in Fig. 5.3a.

In the P_6N_7 condensed ring system, the PN skeleton has 3-fold rotational symmetry. In the C_3 point group, the central nitrogen p_z
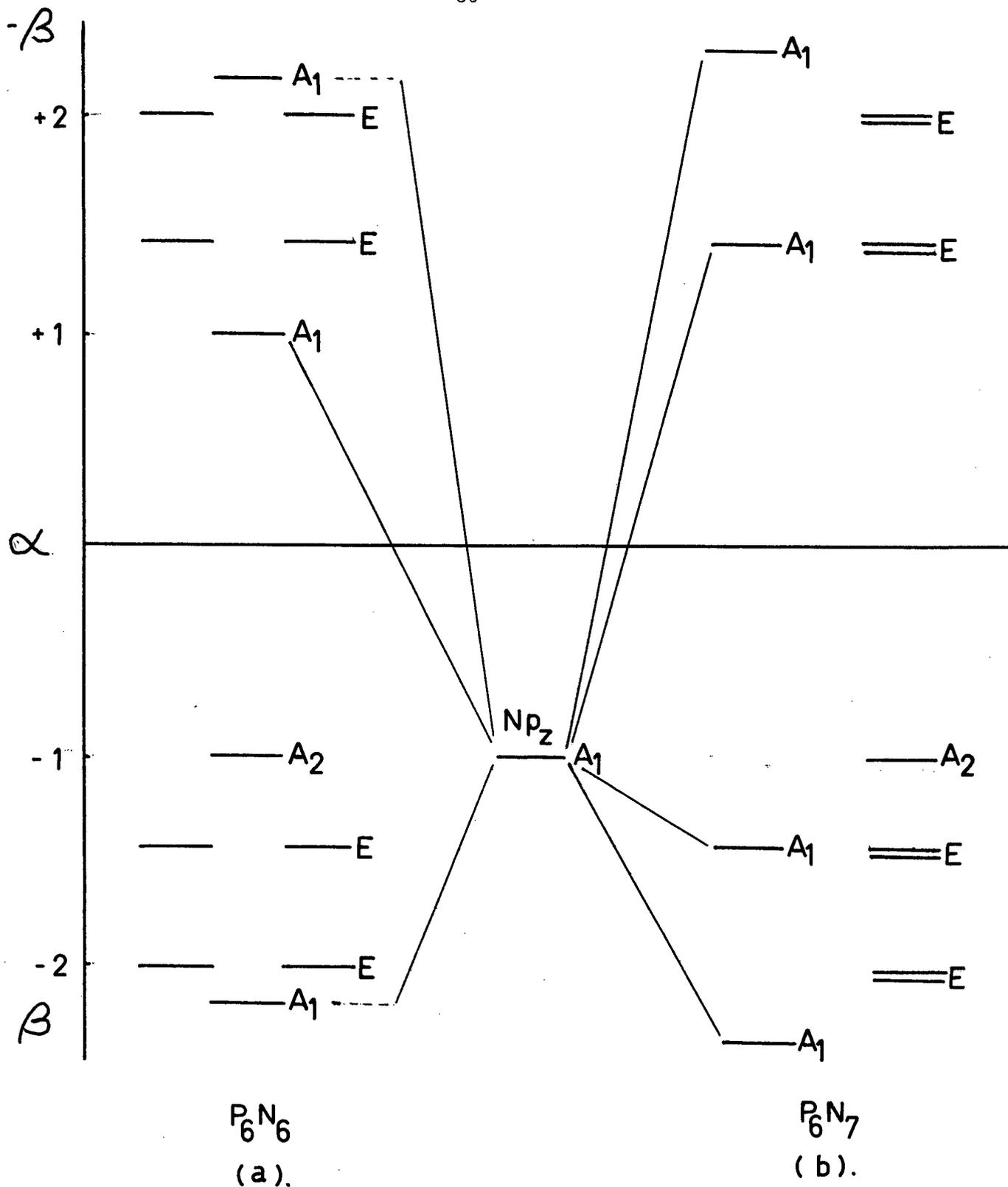
Fig. 5.3. Energy levels for the P_6N_6 and P_6N_7 systems. Overlap is is only considered between the $3d_{yz}$ orbital on phosphorus and the p_z orbital on nitrogen.

orbital has A_1 symmetry, and therefore can only combine with the three A_1 levels of the P_6N_6 system. Using the orbital nomenclature indicated in Fig. 5.4, the three A_1 intermediate orbitals with which the central
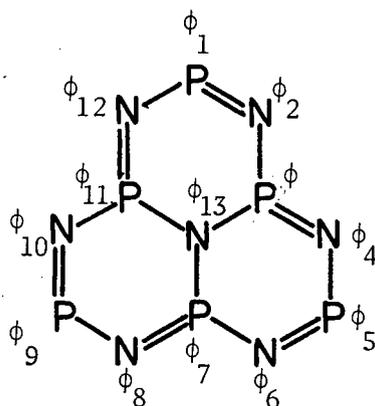
Fig. 5.4. Orbital nomenclature used in symmetry based calculations on $P_6N_7C\ell_9$.

nitrogen p_z orbital (ϕ_{13}) can combine are:

$$\text{(a)} \quad \psi_1 = \frac{1}{\sqrt{3}} (\phi_1 + \phi_5 + \phi_9)$$

$$\text{(b)} \quad \psi_2 = \frac{1}{\sqrt{3}} (\phi_3 + \phi_7 + \phi_{11})$$

$$\text{(c)} \quad \psi_3 = \frac{1}{\sqrt{6}} (\phi_2 + \phi_6 + \phi_{10} + \phi_4 + \phi_8 + \phi_{12}) . \quad \cdots\cdots\cdots (5.3)$$

Mixing of these four A_1 levels produces a new 4 x 4 A_1 secular determinant. The solution of this determinant produces the energy levels shown in Fig. 5.3b, the degenerate E levels and the non-bonding A_2

Bond	$P_A N_A$	$P_B N_A$	$P_B N_B$	
Difference between P.B.O.'s of A_1 levels in P_6N_6 and P_6N_7 systems	+0.095	+0.030	+0.444	
Atom	P_A	N_A	P_B	N_B
Difference between charge densities in A_1 levels of P_6N_6 and P_6N_7 systems	+0.027	+0.010	+0.093	-0.426

TABLE 5:1. Charge density and partial bond order (P.B.O.) differences between P_6N_6 and P_6N_7 systems as derived from symmetry based calculations. A positive difference indicates P_6N_7 > P_6N_6.
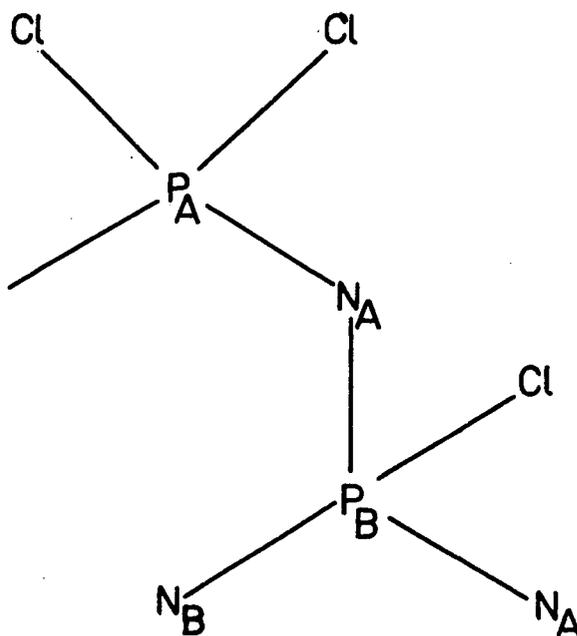
Fig. 5.5. Diagram showing the nomenclature used in describing the various types of bonds and atoms in the $P_6N_7Cl_9$ molecule.

level being unchanged from those found in the P_6N_6 system. Within this

π-system, the changes in charge densities on the ring atoms, and the

changes in partial bond orders on moving from the open ring P_6N_6 system

to the condensed ring P_6N_7 system were calculated, and the results are

shown in Table 5:1. The nomenclature used for differentiating between

the various types of atoms and bonds in P_6N_7 structure is illustrated

in Fig. 5.5.

The important conclusion which these results suggest is a

strengthening of the P_AN_A bond with respect to the P_BN_A bond (see

Fig. 5.5). A considerable π-bond order is also indicated for the

P_BN_B bond, suggesting that this bond must be quite short.

As will be discussed in the next section, the observed bond

lengths in $P_6N_7Cl_9$ are in complete disagreement with the simple argument

described above. More detailed calculations were carried out, as

described in the final section of this chapter, and they lead to a

better correlation of theory and experiment.

III. <u>The Molecular Structure of $P_6N_7Cl_9$</u>

The molecular structure[66] of this compound is shown in Fig. 5.6,

with the relevant structural data given in Table 5:2. The molecule is

not planar, the mean planes of the three six-membered rings (which are

themselves not planar) sloping down from the central nitrogen atom.

The C_{3v} symmetry of the molecule is slightly distorted in the crystal,

as one of the P-Cl bonds is almost coaxial with a two-fold axis within
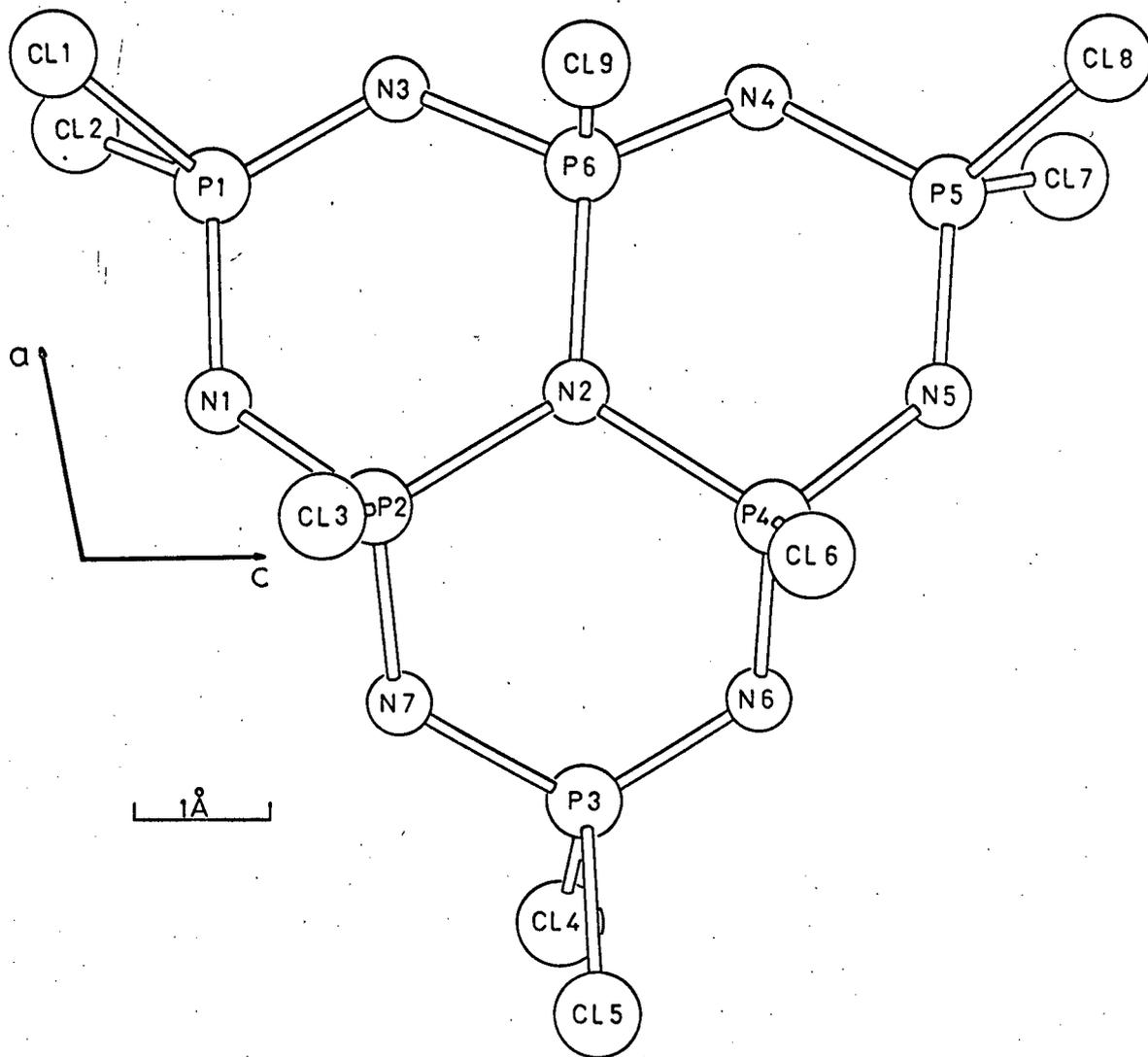
Fig. 5.6. The molecular structure of nitrilohexaphosphonitrilic chloride. Structural data for the molecule is given in Table 5.2.

BOND ANGLES		BOND ANGLES		BOND LENGTHS ($\mathring{A}$)	
	degrees		degrees		
Cℓ1-P1-Cℓ2	101.5	P5-N4-P6	123.4	P1-N1	1.569(6)
N1-P1-N3	116.5	P6-N3-P1	124.8	P1-N3	1.579(6)
Cℓ3-P2-N2	104.8	P2-N2-P4	119.0	P1-Cℓ1	1.988(3)
N1-P2-N2	110.3	P2-N2-P6	121.0	P1-Cℓ2	1.970(3)
N1-P2-N7	111.8	P4-N2-P6	119.8	P2-N1	1.549(6)
N2-P2-N7	110.2			P2-N2	1.720(6)
Cℓ4-P3-Cℓ5	101.3			P2-N7	1.568(6)
N7-P3-N6	118.1			P2-Cℓ3	2.002(3)
Cℓ6-P4-N2	104.5			P3-N7	1.557(6)
N6-P4-N2	110.1			P3-N6	1.569(6)
N6-P4-N5	113.8			P3-Cℓ4	1.977(3)
N2-P4-N5	111.4			P3-Cℓ5	1.990(3)
Cℓ7-P5-Cℓ8	101.9				
N5-P5-N4	116.1			P4-N6	1.578(6)
Cℓ9-P6-N2	102.8			P4-N2	1.733(6)
N4-P6-N2	111.4			P4-N5	1.539(6)
N4-P6-N3	111.8				
N2-P6-N3	110.8			P4-Cℓ6	2.002(3)
P1-N1-P2	125.8			P5-N5	1.574(6)
P2-N7-P3	127.3			P5-N4	1.580(6)
P3-N6-P4	123.2			P5-Cℓ7	1.970(6)
P4-N5-P5	178.6			P5-Cℓ8	1.981(3)
				P6-N4	1.560(6)
				P6-N2	1.715(5)
				P6-N3	1.553(6)
				P6-Cℓ9	2.008(3)

TABLE 5.2 . Bond angles and bond lengths in nitrolohexaphosphonitrilic chloride (see Fig. 5.6). Standard deviations for bond lengths are given in parentheses.

the unit cell, thus causing packing forces to twist the molecule out of ideal C_{3v} symmetry.

Possibly the most important fact that is seen in the crystal structure is the length of the internal PN bond, which is considerably longer than the ring PN bonds. As illustrated in Fig. 5.5, the ring PN bonds fall into two classes, the $P_A N_A$ type and the $P_B N_B$ type.

The P-N bond lengths in monocyclic phosphonitriles range between 1.50-1.60 Å. In the phosphoramidate ion, $(PO_3 NH_3)^-$ (where there is no possibility of lone pair delocalization reinforcing the σ-bond), the P-N single bond length is 1.77 Å.[71] Although the shortness of the phosphonitrilic bond is indicative of some π-bond character, the bond shortening is also contributed to by a σ-hybridization effect. The PN single bond in the $(PO_3 NH_3)^-$ ion is based on sp^3 σ-hybridization at both centres, the bond angles being close to the tetrahedral value. In phosphonitrilic compounds, the ring angle at phosphorus is usually close to 120°, and at nitrogen varies between 120° and 150°. Changing the bond angle at either atom has the effect of changing the σ-hybridization at that atom. The important point to consider is that in phosphonitriles, up to 40% of the shortening of the phosphonitrilic P-N bond with respect to a P-N single bond can be attributed to such σ-effects, and any discussion of the π-bonding in a particular molecule can only be made after σ-effects have been considered.

All the ring bond lengths in $P_6 N_7 Cl_9$ are given in Table 5:3. The actual π-contractions (with reference to the single bond length of

1.77 Å) are also given. Based on a study made of the C-C bond length in various organic compounds,[72] Craig and Paddock have calculated[73] adjusted values of the atomic radii of phosphorus (1.069 Å) and nitrogen (0.701 Å) as the σ-hybridization of the two atoms is changed. The adjustments depended on the ring angle at either atom, the size of the adjustment being that fraction of the bond length by which a C-C bond would change[72] given a similar angle change. Using the results of these calculations, the σ-corrected π-contractions for the ring PN bonds of $P_6N_7Cl_9$ have been estimated, and these values are also given in Table 5:3.

Both the actual and σ-corrected π-contractions show the same trend, namely that the P_AN_A type bonds have less π-character than the P_BN_A bonds. A smaller π-bond order is therefore indicated in the former. This experimental observation is the reverse of that predicted by the simple theoretical model described in the previous section. As has been mentioned already, the P_BN_B bond is long (1.723 Å), and when corrected for σ-hybridization, is even longer (1.748). The length of this bond suggests only a little π-character (π-contraction = 0.02 Å) for the bond, despite the fact that the sum of the bond angles at the central nitrogen is 359.8°. In tetrameric[74] and hexameric[75] phosphonitrilic dimethylamides, $[PN(NMe_2)_2]_{4,6}$, the average exocyclic PN bond lengths are 1.68 Å and 1.67 Å respectively. Thus the exocyclic PN bond in these molecules is stronger than the P_BN_B bond in $P_6N_7Cl_9$, despite the fact that the sum of the bond angles at the exocyclic nitrogen in the

	$P_A N_A$ Bond			$P_B N_A$ Bond		
Bond length Å	π-contraction Å		Bond length Å	π-contraction Å	
	Observed	σ-adjusted		Observed	σ-adjusted
1.569	0.20	0.14	1.578	0.19	0.15
1.574	0.20	0.13	1.539	0.23	0.19
1.580	0.19	0.13	1.560	0.21	0.18
1.579	0.19	0.13	1.553	0.22	0.18
1.569	0.19	0.14	1.549	0.22	0.19
1.557	0.21	0.14	1.568	0.20	0.15
1.571	0.195	0.135	1.558	0.21	0.17

TABLE 5:3.   Ring bond lengths and π-contractions in $P_6 N_7 C\ell_9$. Both observed and σ-adjusted π-contractions are tabulated (π-contractions are estimated with reference to P-N single bond length of 1.77 Å). The last figure in each column is an average value.

dimethylamides is less than 359.8°, indicating less than complete lone pair delocalization.

The exocyclic bonds in $P_6N_7Cl_9$ also show an interesting anomaly. The P-Cl bonds (2.00 Å) are slightly longer than the $\equiv PCl_2$ bonds (1.98 Å). Considering the σ-hybridization at both the P_A and P_B phosphorus atoms, the $\equiv PCl_2$ bonds have more p-character than the P-Cl bonds. Neglecting, for a moment, the π-character in these bonds, the increased s-character in the P-Cl bonds should make them shorter than the $\equiv PCl_2$ bonds. That this is not the case indicates that, in as much as exocyclic π-bonding does occur, it is much stronger at the P_A atoms than the P_B atoms.

The disparity between the simple theoretical model of the bonding and the observed structural features is therefore significant and consistent. The reversal of bond order trends between theory and experiment shows that the simple theory of the bonding is inadequate in describing the structural features of $P_6N_7Cl_9$. Because of this anomaly, further, more detailed calculations, were carried out, and are now described.

IV. Detailed Hückel M.O. Calculations on $P_6N_7Cl_9$

These molecular orbital calculations were carried out using all the phosphorus 3d-orbitals (except the $3d_{z^2}$) and the nitrogen p_z and p_y orbitals (see Figs. 5.1 and 5.2), the molecule being assumed to be planar. No explicit consideration was made of the chlorine

ligands and only the P_6N_7 nucleus was examined. The usual Hückel approximations were applied, i.e. non-nearest neighbour overlap was ignored and the motion of all the electrons was completely uncorrelated.

Suitable Coulomb parameters were chosen by reference to recent calculations on the monocyclic phosphonitrilic fluorides.[76] For all the nitrogen atoms, values of $\alpha(Np_z) = \alpha(Np_y) = -11$ e.v. were used, and for the phosphorus atoms, values of $\alpha(Pd_{xz}) = \alpha(Pd_{x^2-y^2}) = -6$ e.v. were taken. Suitable Coulomb parameters for the phosphorus d_{yz} and d_{xy} orbitals were believed to be important in the calculations, since their value was thought to depend on whether the particular phosphorus atom was a bridgehead or non-bridgehead atom. The reason for this dependence of α on the type of phosphorus atom is thought to be a result of an exchange interaction between the chlorine ligands and the various phosphorus 3d-orbitals. At the bridgehead (P_B) atoms, the chlorine ligand lies close to the z-axis and therefore does not destabilize any of the d-orbitals under consideration. At the non-bridgehead (P_A) atoms, the two (P-Cl) bonds lie close to the lobes of, and therefore destabilize, the d_{yz} orbital. Because the lobes of the d_{xy} orbital are also close to the (P-Cl) bond axes at the P_A atom, the effect of exchange interactions on this orbital were also considered. The effect of exchange destabilization on the above-mentioned orbitals was introduced into the calculations by varying the value of the Coulomb parameter.

All resonance integrals were essentially for $p\pi$-$d\pi$ interactions, and the formula used for the calculation of these integrals was:

$$\beta_{ij} = -2.4 \; S_{ij} \sqrt{\frac{\alpha_P \alpha_N}{(-6) \times (-11)}} \qquad \cdots\cdots\cdots (5.4)$$

This allowed the β's to depend on the α's, as they must, and is broadly consistent with the conclusions obtained from a recent study of the monocyclic $(PNF_2)_n$ series.[76] The overlap integrals, S_{ij}, were expressed in terms of a primitive $p\pi$-$d\pi$ overlap integral of $S(p\pi$-$d\pi) = 0.3636$, and a primitive $p\sigma$-$d\sigma$ overlap integral of $S(p\sigma$-$d\sigma) = 0.1277$. An outline of the calculation of the various S_{ij}'s is given in Appendix I.

The charge densities and bond orders derived from the solution of the 37 x 37 secular determinant are given in Tables 5:4 and 5:5. The effect of exchange interactions on the stability of various phosphorus orbitals is to produce a significant change in the trends in bond orders. Destabilizing the d_{yz} (and the d_{xy}) orbital on the P_A atoms (by setting $\alpha(d_{yz}) = \alpha(d_{xy}) = -2$ e.v.) has the effect of decreasing the π-bond order of the $P_A N_A$ bond with respect to the $P_B N_A$ bond, which is consistent with the trend observed in the actual molecule.

As the values of the partial bond orders in Table 5:5 show, the concept of orbital selectivity is valid, and some orbitals on phosphorus (d_{xz} and $d_{x^2-y^2}$) are more important in π-bonding than others (d_{yz} and d_{xy}). However, in so far as the d_{yz} orbital is used in π-bonding, it

Atom	Orbital	Charge Density	
		A^a	B^b
P_A	d_{xz}	0.07480	0.07480
	d_{yz}	0.02696	0.002945
	$d_{x^2-y^2}$	0.04818	0.04818
	d_{xy}	0.03455	0.003796
	Σ	0.18449	0.12973
P_B	d_{xz}	0.7479	0.07607
	d_{yz}	0.07155	0.07193
	$d_{x^2-y^2}$	0.06977	0.07126
	d_{xy}	0.01018	0.01043
	Σ	0.22629	0.22969
N_A	p_z	1.899	1.910
	p_y	1.919	1.933
N_B	p_z	1.860	1.860

TABLE 5:4. Calculated charge densities on various atoms in $P_6N_7C\ell_9$ using all phosphorus 3d-orbitals (except d_{z^2}).

(a) Coulomb parameters for $P_A(d_{yz}) = P_A(d_{xy}) = -6.0$ e.v.
(b) Coulomb parameters for $P_A(d_{yz}) = P_A(d_{xy}) = -2.0$ e.v.
(For other Coulomb parameters, see Text.)

Bond	Orbital Overlap	Bond Order[c]	
		A[a]	B[b]
$P_A N_A$	$d_{xz}-p_z$	0.2002	0.2002
	$d_{yz}-p_z$	0.07021	0.01348
	$d_{x^2-y^2}-p_y$	0.1262	0.1262
	$d_{xy}-p_y$	0.08986	0.01733
	Σ	0.4865	0.3572
$P_B N_A$	$d_{xz}-p_z$	0.2002	0.2024
	$d_{yz}-p_z$	0.06682	0.06757
	$d_{x^2-y^2}-p_y$	0.1851	0.1877
	$d_{xy}-p_y$	0.02617	0.02659
	Σ	0.4783	0.4843
$P_B N_B$	$d_{yz}-p_z$	0.2553	0.2551

TABLE 5:5. Calculated bond orders for the various types of bonds in $P_6 N_7 C\ell_9$.

(a) Coulomb parameters for $P_A(d_{yz}) = P_A(d_{xy}) = -6.0$ e.v.

(b) Coulomb parameters for $P_A(d_{yz}) = P_A(d_{xy}) = -2.0$ e.v.

(For other Coulomb parameters, see Text.)

(c) The definition of partial bond order differed from that used in calculations on monocyclic phosphonitriles. For the purposes of this study, the partial bond order, $(P.B.O.)_{r,s}$, between two atoms r and s, was defined as:

$$(P.B.O.)_{r,s} = 2 \sum_i c_{ir} c_{is} \beta_{rs}$$

$$i = \text{all occupied orbitals}$$

is thought that the contribution of this orbital is greater at the P_B than at the P_A atom, firstly because of exchange destabilization at the P_A atom, and secondly because the d_{yz} orbital is stabilized on the P_B atom by the influence of the central nitrogen atom.

Another interesting point concerns exocyclic π-bonding at the P_B atoms. At these atoms, exocyclic π-bonding can (by symmetry) only occur between the chlorine ligand and the d_{xz} and d_{yz} orbitals on phosphorus. The d_{xz} orbital is strongly involved in forming a ring π-system, and therefore is less involved in the exocyclic π-bonds. If the d_{yz} orbital is also strongly involved in ring π-bonding at the P_B atom, then it also will only form weak π-bonds to chlorine. That the observed values of the bond lengths of the P-Cl bonds are greater than those of the PCl_2 bonds suggests that there is little or no π-bonding in the exocyclic P-Cl bonds and adds credence to the above argument involving a strong interaction of the $P_B d_{yz}$ orbital in the ring π-systems.

The $P_B N_B$ bond order is smaller than those of the $P_A N_A$ and $P_B N_A$ bonds, but is still quite substantial and varies little with changes in the α parameters of the d-orbitals on the P_A atom. The unusually long $P_B N_B$ bond length (1.723 Å) cannot be properly explained by these calculations, and the reason for it may well be steric rather than electronic.

The base strength measurements, described in Chapter 3 are also difficult to explain in terms of electronic factors. The base strength

of any particular phosphonitrilic compound is contributed to by two electronic effects. The σ-hybridization of the lone pair hybrid on nitrogen is a function of the ring angle at nitrogen, so that the smaller the ring angle, the greater is the s-character of the nitrogen lone pair hybrid. An increase in the s-character of this lone pair orbital decreases the basic character of the lone pair. Thus, considering σ-effects alone, a decrease in the ring angle at a nitrogen atom is accompanied by a decrease in the base strength of the lone pair on that nitrogen atom.

π-effects also contribute to the basic character of the lone pair electrons. Because of this, an increasing ring angle at nitrogen, which is symptomatic of greater lone pair delocalization into the ring π_s system, is expected to be accompanied by a decrease in the base strength of the lone pair.

Thus, σ- and π-effects produce trends in the base strengths of phosphonitriles which are the opposite of each other. Whilst σ-effects increase base strength with increase in $\angle$PNP, π-effects decrease them, and the resultant base strength of any particular molecule will be a balance of these two factors.

As had already been mentioned, any formal difference in the π-bonding of the P_6N_6 and P_6N_7 system can only arise in the π_a system. Since lone-pair delocalization occurs through the π_s system, the effect of changes in the π_a system on the base strength can only be secondary (i.e. through a π_a/π_s interaction). The differences in basic properties

of $P_6N_7Cl_9$ and $P_6N_6Cl_{12}$ are therefore most likely to be caused by a σ-effect rather than a π-effect. Since the ring angle at nitrogen in $P_6N_7Cl_9$ is small (125.5°), the s-character of the lone pair hybrid is likely to be greater than that found in $P_6N_6Cl_{12}$, and thus the observed base strength of $P_6N_7Cl_9$ (which is less than that of $P_6N_6Cl_{12}$) is explainable. However, anything more than this empirical conclusion cannot be made at present, since there exists no quantitative theory for separating the σ- and π-factors which control the base strength of phosphonitriles.

APPENDIX I

Evaluation of Overlap Integrals for $P_6N_7Cl_9$

In the Huckel M.O. calculations, all overlap integrals between phosphorus and nitrogen were expressed in terms of a linear combination of a primitive pπ-dπ overlap, where $S(p\pi-d\pi) = 0.3636$ and a primitive pσ-dσ overlap, where $S(p\sigma-d\sigma) = 0.1277$. These values were based on orbital exponents of 1.95 for the 2pπ orbital at nitrogen, 1.40 for the 3dπ orbital at phosphorus and a P-N bond length of 1.52 Å (this value of the P-N bond length has been used for some studies on the phosphonitrilic fluorides, but the slightly longer phosphonitrilic bonds in $P_6N_7Cl_9$ were not considered to be important from the point of view of this study).

In the out-of-plane π-system, overlap integrals were obtained quite simply using the following formulae:

At the P_A atom, $\quad S(d_{xz}-p_z) = \pm \, S(p\pi-d\pi) \, \cos 30°$

$$S(d_{yz}-p_z) = - \, S(p\pi-d\pi) \, \cos 60°$$

At the P_B atom, $\quad S(d_{xz}-p_z) = \pm \, S(p\pi-d\pi) \, \cos 30°$

for overlap with N_A, $\quad S(d_{yz}-p_z) = + \, S(p\pi-d\pi) \, \cos 60°$

for overlap with N_B, $\quad S(d_{yz}-p_z) = + \, S(p\pi-d\pi)$

In the in-plane π-system, the evaluation of overlap integrals required a rotation of coordinates using the scheme shown below. In

this diagram (Fig. A.1), the standard coordinate scheme at the P_B and N_A
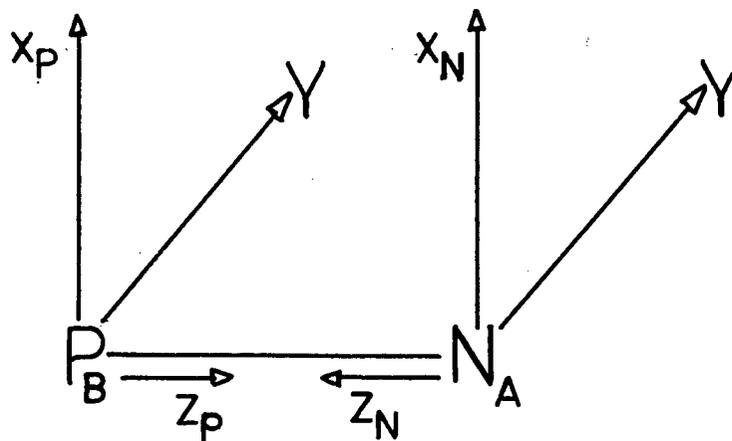
Fig. A.1. Rotated coordinate scheme used in the evaluation of overlap integrals at the P_B atoms in the π_s system.

atoms (Fig. 5.7) is rotated into a new system such that:

At N_A, $Y = -\frac{1}{2} z_N + \frac{\sqrt{3}}{2} x_N$

At P_B, $X = \frac{\sqrt{3}}{2} z_P - \frac{1}{2} x_P$

$Y = \frac{1}{2} z_P + \frac{\sqrt{3}}{2} x_P$

Therefore, the atomic orbitals in the new coordinate system have the form:

$$2p_X = R_{2p} \times X \qquad\qquad 3d_{Z^2} = \frac{\sqrt{3}}{2} R_{3d} \left(Z^2 - \frac{r^2}{3}\right)$$

$$2p_Y = R_{2p} \times Y \qquad\qquad 3d_{XY} = R_{3d} \; XZ$$

$$2p_Z = R_{2p} \times Z \qquad\qquad 3d_{YZ} = R_{3d} \; YZ$$

$$3d_{X^2-Y^2} = R_{3d} (X^2 - Y^2)$$

$$3d_{XY} = R_{3d} \; (XY)$$

Using this transformation and a similar one at the P_A atom, the overlap integrals between phosphorus and nitrogen were calculated as being:

At the P_A atom, $\quad S(d_{X^2-Y^2} - p_Y) = \frac{3}{4} \; S(p\pi\text{-}d\pi) - \frac{\sqrt{3}}{8} \; S(p\sigma\text{-}d\sigma)$ (sign +)

$$S(d_{XY}\text{-}p_Y) = \frac{\sqrt{3}}{4} \; S(p\pi\text{-}d\pi) + \frac{3}{8} \; S(p\sigma\text{-}d\sigma) \quad (\text{sign} \pm)$$

At the P_B atom, $\quad S(d_{X^2-Y^2}\text{-}p_Y) = -\frac{3}{4} \; S(p\pi\text{-}d\pi) - \frac{\sqrt{3}}{8} \; S(p\sigma\text{-}d\sigma)$ (sign +)

$$S(d_{XY}\text{-}p_Y) = \frac{\sqrt{3}}{4} \; S(p\pi\text{-}d\pi) - \frac{3}{8} \; S(p\sigma\text{-}d\sigma) \quad (\text{sign} \pm)$$

The calculation of these overlaps was a fairly simple algebraic process, e.g.

At N_A, $\quad 2p_Y = -\frac{1}{2}\ 2p_z + \frac{\sqrt{3}}{2}\ 2p_x$

At P_B, $\quad 3d_{X^2-Y^2} = \frac{1}{2}\ 3d_{z^2-x^2} - \frac{\sqrt{3}}{2}\ 3d_{xz}$

it is easy to show that $3d_{z^2-x^2} = \frac{\sqrt{3}}{2}\ 3d_{z^2} - \frac{1}{2}\ 3d_{x^2-y^2}$ and therefore overlap of $2p_Y$ at N_A and $3d_{X^2-Y^2}$ at P_B becomes:

$$\int 2p_Y\ 3d_{X^2-Y^2}\ d\tau$$

$$= \int (\frac{1}{2}\ 2p_z + \frac{\sqrt{3}}{2}\ 2p_x)\ (\frac{\sqrt{3}}{4}\ 3d_{z^2} - \frac{1}{4}\ 3d_{x^2-y^2} - \frac{\sqrt{3}}{2}\ 3d_x)\ d\tau$$

$$= -\frac{\sqrt{3}}{8}\ (p\sigma-d\sigma) - \frac{3}{4}\ (p\pi-d\pi).$$

Other S_{ij}'s were obtained similarly.

APPENDIX II

Details of the instruments and techniques used in recording the various types of spectra were not discussed in the main text of this thesis. A summary of pertinent details will now be given.

i) Infra-red spectra:- These were all recorded on a Perkin-Elmer 457 grating spectrophotometer, and calibrated against a standard polystyrene spectrum. Nujol and hexachlorobutadiene mull spectra were taken using cesium iodide plates. Solution and gas phase spectra were recorded using potassium bromide windows.

ii) Raman spectra:- These were all recorded on a Cary 81 Laser Raman spectrophotometer. No depolarization measurements were taken.

iii) Ultra-violet spectra:- These were all recorded on a Cary 14 spectrophotometer, using quartz cells and a single beam technique.

iv) Mass spectra:- These were all recorded at 70 e.v. on a A.E.I. type M.S.9 mass spectrometer, samples being admitted through conventional inlet systems.

v) N.m.r. spectra:- ^{1}H n.m.r. spectra were run at 60 MHz on a Varian T-60 n.m.r. spectrometer and at 100 MHz on a Varian HA-100 n.m.r. spectrometer. ^{31}P n.m.r. spectra were recorded at 40.1 MHz

on a Varian HA-100 n.m.r. spectrometer. ^{31}P-^{1}H decoupling experiments were carried out using a recently described double resonance technique.[a]

[a] See L.D. Hall and R. Burton; Can. J. Chem., 48, 59 (1970).

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AND ONE FLOWER