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Department of Chemistry

The University of British Columbia
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Date June 26, 1973
ABSTRACT

A study of the dielectric properties of some phosphonitrilic fluorides, chlorides and chloride-fluorides in cyclohexane solutions was carried out and evidence was found to support the hypothesis that these compounds all have a non-negligible atom polarization caused by low frequency vibrations of the molecules. The distortion polarization of one of the geminally substituted isomers of the compound $\text{N}_4\text{P}_4\text{F}_4\text{Cl}_4$ was measured and this datum was used as support for assigning the 1,1,3,3-isomer structure to the compound.
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CHAPTER I
GENERAL INTRODUCTION

Phosphonitrilic Compounds

Phosphonitrilic compounds are polymers made up of the repeating unit \((X(X')PN)\) where \(X\) may or may not be the same as \(X'\), and \(X\) and \(X'\) may be a halogen, a pseudohalogen such as azide or isothiocyanate or any of the following organic functional groups; alkyl, alkoxy, aryl, aryloxy, amino, thioalkyl. A large number of compounds where \(X = X'\) have been synthesized as well as a great many where \(X\) is not the same as \(X'\) for one or more of the monomer units in the polymer. Phosphonitrilic compounds may be either linear or cyclic polymers, of which the cyclic polymers have been more thoroughly investigated. A number of reviews\(^1\text{--}^3\) are available describing the synthesis, structure and reactions of cyclic phosphonitriles.

The first cyclic phosphonitrile was synthesized in 1834 by Liebig\(^4\) who was attempting to make the amides of phosphoric acid by reacting \(\text{PCl}_5\) and \(\text{NH}_4\text{Cl}\), but instead obtained a small amount of phosphonitrilic chloride trimer \((\text{NPCl}_3)_3\). Later, Stokes\(^5\) carried out work which showed that there existed a homologous series of phosphonitrilic chloride polymers of the formula \((\text{NPCl}_2)_n\) up to at least the heptamer \((n = 7)\). It was he who first suggested the cyclic formulae
which have since been confirmed by infrared, Raman, $^{31}$P NMR and X-ray studies. The phosphonitrilic fluorides, however, are more difficult to prepare as an attempted synthesis analogous to that used for the chlorides gives ammonium hexafluorophosphate instead. It was not until 1956 that Seel and Langer$^6$ succeeded in making the fully fluorinated cyclic phosphonitriles by reacting the cyclic chlorides and KSO$_2$F. All the cyclic fluorides are comparatively volatile, and all but the trimer and tetramer are liquid at room temperature, these last two being solids with melting points of 27.2-27.4°C and 30.4°C, respectively.$^7$ Cyclic phosphonitrilic fluorides up to (NPF$_2$)$_{17}$ have been reported in the literature$^8$ and there appears to be no reason why larger ring compounds of this type cannot be made, as all the smaller ring compounds are stable to such reactions as disproportionation at room temperature. Though in some ways these compounds are comparable to benzene and other related conjugated cyclic hydrocarbons, a major difference is that the stability of the cyclic phosphonitriles appears to be independent of ring size, for example (NPF$_2$)$_8$ is as stable as (NPF$_2$)$_5$. The lack of information on very large rings is mainly due to the problem of obtaining large enough samples of the pure compounds, which must be separated from any or possibly all of the following; mixtures of linear polymers, mixtures of chloride-fluorides, mixtures of cyclic fluorides of ring sizes other than the one of immediate interest. The most often used method of separation and purification is gas-liquid chromatography, though fractional distillation may be used to separate larger quantities of material.
Dipole Moments

The measurement of dipole moments of molecules is a relatively new technique, the earliest papers having been published in 1924. The measurement of dielectric constants, which for many methods of dipole moment determination is a necessity, has been done since 1892. From 1924 there was an immediate surge of interest in dipole moment measurements which peaked in the period 1930-32. The next upsurge started after the Second World War ended and culminated in 1949. This was due to two factors; first, the end of the war released more money into non-defence oriented research and second, the technique of microwave spectroscopy was developing rapidly and becoming sensitive enough to give accurate data for calculation of dipole moments (from the Stark effect). The microwave method has the advantage that no knowledge of dielectric constants is necessary. A third upsurge of interest in dipole moments occurred in the mid-1950's.

The bulk of dipole moment studies has always been carried out on organic compounds. This is related to the methods used to obtain the values of the dipole moment, which require data from the pure gas, or the pure liquid or a solution of the compound in a non-polar solvent. Most inorganic compounds of interest are not sufficiently volatile or else not liquid at suitable temperatures or are insoluble in non-polar solvents. It is therefore not surprising that the ratio of the number of organic compounds studied to the number of inorganic is about 12:1 and has been so for many years. The phosphonitrilic halides are good candidates for dipole moment studies owing to their high solubilities in such non-polar solvents as cyclohexane, and
therefore it may be possible to obtain information about ring size effects on the properties of phosphonitriles by studying their dielectric properties.

There are several methods available to obtain dipole moments of molecules, though not all the possible methods may be applicable to the same compounds. The most important of these methods are as follows.

1. The measurement of the dielectric constant of a known amount of the pure gaseous compound is carried out at a series of known temperatures. The polarization is then calculated and plotted against the reciprocal of the absolute temperature. The slope is directly proportional to the square of the dipole moment.

2. The measurement is carried out of the dielectric constant, density and refractive index of the pure liquid at a known temperature and the Onsager equation or one of its modifications is used to calculate the dipole moment.

3. The dielectric constant and density may be measured for each of a series of solutions of known concentrations of the compound of interest in a non-polar solvent at a known constant temperature. The Halverstadt-Kumler or Hedestrand equations are used to calculate the dipole moment.

4. The dielectric constant and refractive index of each of a series of solutions of known concentrations of the compound of interest in a non-polar solvent may be measured at a known constant temperature. The dipole moment may then be evaluated by the method of Guggenheim.

5. The dielectric constant and dielectric absorption of a solution of known concentration of the compound of interest in a non-
polar solvent may be measured at a series of known frequencies in the microwave region at a known constant temperature. From such data, a dipole moment of the compound may be calculated.

(6) The line separations in the microwave spectrum of a compound caused by the Stark effect may be measured. These line separations are a function of the dipole moment of the molecule.

(7) The absolute intensities of infrared absorption bands may be measured. These intensities are functions of the matrix elements of the dipole moment of the molecule. However, it is very difficult to obtain these integrated intensities and so the method does not find a great deal of practical use at present.

(8) Molecular beam methods are used to determine the dipole moments of compounds such as alkali halides, whose moments cannot be measured by more conventional methods. These methods are adaptations of the Stern-Gerlach experiment on magnetic moments.

(9) Electrostriction methods measure the decrease in volume of a gas at constant pressure and temperature caused by application of an electric field. This method serves only to give orders of magnitude of dipole moments because the volume changes are very small and difficult to measure accurately.

The most commonly used of these methods are the first six mentioned because from these methods it is possible to obtain fairly accurate values of the dipole moment of a molecule for a reasonable investment in cost and labour.
Object of Research

One important use of dipole moments in the past has been to study orientation effects, such as cis-trans isomerism. Orientation effects may also be studied by dipole moment measurements on substituted phosphonitrilic compounds. Koopman et al.\(^{12}\) have used dipole moment results in assigning structures to the tetrachlorobis(dimethylamino)-phosphonitrile trimer isomers as well as to the isomers of trichloro-tris(dimethylamino)phosphonitrile trimer, which are shown in Figure 1-1. Similar work has been carried out on cis and trans-tribromotriphenylphosphonitrile trimers by Nannelli and Moeller,\(^{13}\) on cis and trans-tetrafluorobisphenylphosphonitrile trimers by Allen and Moeller,\(^{14}\) on cis, trans and geminal (1,1-bis) isomers of \(\text{N}_{3}\text{P}_{3}\text{Cl}_{4}(\text{NHMe})_{2}\) by Lehr\(^{15}\) and on the 1,5-cis and trans isomers of hexaphenylidiazidophosphonitrile tetramer, \(\text{N}_{4}\text{P}_{4}(\text{C}_{6}\text{H}_{5})_{6}(\text{N}_{3})_{2}\) by Sharts et al.\(^{37}\) These last two compounds are shown in Figure 1-2.

One object of the work described in this thesis is to attempt to decide whether the geminally substituted compound \(\text{N}_{4}\text{P}_{4}\text{F}_{4}\text{Cl}_{4}\) is the 1,1,3,3 or the 1,1,5,5-isomer, both of which are shown in Figure 1-3.

There is, however, a limitation on the use of dipole moments for structural determinations in inorganic chemistry. In organic chemistry, where the method has been widely used, the compounds have very small atom polarizations (a fuller explanation will be given in Chapter IV) and thus the values of dipole moments determined by the usual methods have only a small error due to the neglect of this atom polarization. However, this is not true of many inorganic compounds and, it was
Figure 1-1a \( \text{N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_2 \) isomers

Figure 1-1b \( \text{N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_3 \) isomers
Figure 1-2 $N_4P_4(C_6H_5)_6(N_3)_2$ isomers

Figure 1-3 (NPFCI)$_4$ (gem) isomers
intended to try to determine what effect atom polarization has on phosphonitrilic compounds, whether dipole moments determined for phosphonitrilic compounds are valid and whether it is necessary to revise theories of structures of these compounds that were based on dipole moment results.
CHAPTER II
THEORY

Derivation of the Debye Equation

In order to have a better understanding of the factors affecting dipole moments, it is necessary to carry out the derivation of the equation relating dipole moment to directly measurable or calculable quantities. The derivation given below is almost entirely taken from Smyth.17

The dielectric constant of a material, \( \varepsilon \), is an electrical constant characteristic of a medium between two charges. A condenser is an electric conductor, which, is charged with a quantity of electricity \( q \) at a potential \( V \) will have a capacitance \( C \). For the case of a condenser consisting of two parallel conducting plates each of area \( A \) cm\(^2\), separated by a distance \( r \), and between which is a medium of dielectric constant \( \varepsilon \), then the capacitance \( C \) is

\[
C = \frac{\varepsilon A}{4\pi r} \text{ electrostatic units} \quad (2-1)
\]

To determine the dielectric constant of a medium, the capacitance of the condenser is measured with the medium of interest between the plates and then compared to the capacitance of the same condenser with
a standard medium between the plates. The standard chosen is a vacuum, and for a vacuum $\varepsilon = 1$, so therefore $\varepsilon$ of the medium of interest is then

$$\varepsilon = \frac{C}{C_0} \quad (2-2)$$

where $C_0$ is the capacitance of the condenser with a vacuum between the plates. The dielectric constant of a material is a dimensionless quantity.

The next situation to consider is a condenser in a vacuum where $r$ is very small compared to the plate dimensions, i.e. $r^2 \ll A$. Let one plate have a charge $+Q$, and the other a charge $-Q$ and let $\sigma$ be the surface density of charge. Inside the condenser, the intensity of the electric field perpendicular to the plates is

$$E_0 = 4\pi \sigma \quad (2-3)$$

If the space between the plates is filled with a homogeneous material of dielectric constant $\varepsilon$, the charges ($+Q$ and $-Q$) on the plates remain the same but the field strength drops to

$$E = \frac{4\pi \sigma}{\varepsilon} \quad (2-4)$$

Therefore the decrease

$$E = E_0 - E = 4\pi \sigma (1 - 1/\varepsilon) = 4\pi \sigma (\varepsilon - 1)/\varepsilon \quad (2-5)$$
This same $\Delta E$ could also be effected by reducing $\sigma$ to

$$\frac{\sigma(\varepsilon-1)}{\varepsilon} = P^*$$

(2-6)

which can be done by charging the surface of the dielectric opposite each of the plates with a charge of opposite sign to that of the plate. The surface density of this charge would then equal $P^*$, and is produced by an induced charge shift through the dielectric. $P^*$ is usually referred to as the polarization.

A quantity called the electric displacement, $D$, is defined as

$$D = 4\pi\sigma$$

(2-7)

and it can be shown that

$$D = \varepsilon E$$

(2-8)

Because

$$D-E = 4\pi\sigma(1-1/\varepsilon) = 4\pi\sigma(\varepsilon-1)/\varepsilon$$

(2-9)

it follows that

$$D = E + 4\pi P^*$$

(2-10)

By eliminating $D$ and rearranging the following result may be obtained:

$$\varepsilon-1 = 4\pi P^*/E$$

(2-11)
The charges \( +P_0^* \) on one surface of the dielectric and \( -P_0^* \) on the opposite surface resulting from charge displacement through the dielectric give an electric moment of \( P_0^* Ar \) to the dielectric slab, where \( r \) is its thickness (which also is the distance between the conducting plates). Since

\[
Ar = V
\]  

(2-12)

the volume of the slab, the total electric moment must be equal to \( P_0^* V \) and therefore \( P_0^* \) is the electric moment per unit volume. Thus the polarized slab behaves like an assembly of parallel electric dipoles, with each dipole consisting of a pair of charges equal in magnitude but opposite in sign (+e, -e) separated by a small but finite distance \( r \). The size of the moment is

\[
m = er
\]  

(2-13)

Molecular polarizability can now be defined; it is a parameter related to induced dipole moment.

Consider a charge \( e \) bound elastically to an equilibrium position. Now any displacement from equilibrium will be opposed by a restoring force \( f_r \), where \( f \) is a proportionality constant. The restoring force can be treated as a Hooke's Law type force; that is the force is proportional to the displacement. An electric field \( F \) will cause such a displacement by exerting a force \( Fe \) on the charge until the displacement is such that the two forces are equal, i.e.
Fe = fr \hspace{1cm} (2-14)

An electric moment

m = er \hspace{1cm} (2-15)

is created by this displacement so by solving for r and substituting into equation (2-14) the electric moment becomes

m = Fe^2/f \hspace{1cm} (2-16)

For a molecule containing several charged particles, each of charge e (say electrons) the total induced moment is

\[ \Sigma m = F \Sigma e^2/f \]  \hspace{1cm} (2-17)

Now the molecular polarizability can be defined as the electric moment induced in a molecule by a unit field

\[ F = 1 \text{ esu} = 300 \text{ volts/cm} \]

The symbol used for molecular polarizability is \( \alpha_o \) so then

\[ \alpha_o = \Sigma e^2/f \hspace{1cm} (2-18) \]

and \( f \) can be seen to be the force constant for the binding of the charges.
The next step is to derive the equation relating dipole moment to measurable quantities. This requires the derivation of the Clausius-Mosotti equation. Consider the following situation. Let a constant electric field, $F$, be applied to a sphere of a continuous, isotropic dielectric. The electric moment induced in the sphere is

$$m_s = \alpha_s F$$

(2-19)

where $\alpha_s$ is the polarizability of the sphere. Now it has already been shown by rearranging equation (2-11) that

$$P^* = (\varepsilon-1)E/4\pi$$

(2-20)

and the volume of the sphere is defined as

$$V = \frac{4\pi a_s^3}{3}$$

(2-21)

where $a_s$ is the radius of the sphere, so substituting into equation (2-19) gives

$$m_s = P^* V = \frac{(\varepsilon-1)E}{4\pi} \cdot \frac{4\pi a_s^3}{3} = \alpha_s F$$

$$= \frac{(\varepsilon-1)Ea_s^3}{3} = \alpha_s F$$

(2-22)

The total field $E$ produced inside the sphere is

$$E = \left[\frac{3}{(\varepsilon+2)}\right]F$$

(2-23)
This may be substituted into equation (2-22) to give

\[
\frac{\varepsilon-1}{\varepsilon+2} = \frac{a_s}{a_0^3} \quad (2-24)
\]

A molecular formula may be made by making the following substitution into equation (2-24)

\[
a_s = N_s a_o
\]

\[
4\pi a_s^3/3 = V/N_s = 4\pi a_0^3/3N_s,
\]

where \(a_o\) is the molecular polarizability, \(N_s\) is the number of molecules in the sphere of radius \(a_s\) and \(a\) is the approximate molecular radius. The formula obtained from equation (2-24) is

\[
\frac{\varepsilon-1}{\varepsilon+2} = \frac{a_o}{a^3} \quad (2-25)
\]

A more useful form of this equation may be obtained by substituting the value of \(a\) found in

\[
4\pi a^3/3 = M/Nd \quad (2-26)
\]

where \(N\) is Avogadro's number, \(d\) is the density of the substance and \(M\) is its molecular weight. The result obtained by substituting equation (2-26) into equation (2-25) is
or
\[
\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N\alpha}{3}
\]  
(2-28)

By substituting the Maxwell relation

\[
\varepsilon = n^2
\]  
(2-29)

where \( n \) is the refractive index of the material, the following equation, which is the Lorentz-Lorenz equation for molar refraction, is found:

\[
\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = \frac{4\pi N\alpha}{3} = R
\]  
(2-30)

The force \( F \) may be broken down into three components \( F_1, F_2, \) and \( F_3 \). \( F_1 \) is the force due to the charges of surface density \( \sigma \) on the condenser plates so that

\[
F_1 = 4\pi \sigma
\]  
(2-31)

\( F_2 \) is due to the polarization of the material outside the sphere under consideration. It consists of the force due to the layers of induced charge on the material facing the condenser plates \( (-4\pi P^*) \) plus the force due to the charge on the "surface" of the sphere being considered, \((+4\pi P^*/3)\) so the total force \( F_2 \) is...
\[ F_2 = -4\pi P^* + 4\pi P^*/3 \quad (2-32) \]

\( F_3 \) is the force due to the material contained within the sphere of interest and depends on the structure of the material. There is no general expression for \( F_3 \), but in cubic crystals (due to their symmetry) and in gases, \( F_3 = 0 \) and for liquids in which the molecules are randomly ordered in the absence of an electric field, \( F_3 = 0 \) approximately. The lack of a general expression for \( F_3 \) places a limitation on the types of substances for which the remainder of this discussion will apply. As an approximation, \( F_3 \) may be set to zero, i.e.

\[ F_3 = 0 \quad (2-33) \]

and thus

\[ F = 4\pi \sigma - 4\pi P^* + 4\pi P^*/3 \quad (2-34) \]

It can be shown (by substituting equation (2-6) into equation (2-4)) that

\[ E = 4\pi \sigma - 4\pi P^* \quad (2-35) \]

so

\[ F = E + 4\pi P^*/3 \quad (2-36) \]

Now

\[ P^* = \frac{1}{1}m \quad (2-37) \]

where \( n_1 \) is the number of molecules per cc so that

\[ P^* = n_1m = n_1\alpha F = n_1\alpha(E + 4\pi P^*/3) \quad (2-38) \]
If equation (2-20) is substituted into equation (2-38) the result is

\[
\frac{(\varepsilon-1)E}{4\pi} = N_1 \alpha_0 (E + \frac{4\pi}{3} \cdot \frac{(\varepsilon-1)E}{4\pi}) \tag{2-39}
\]

This can be rearranged to give

\[
\frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi N_1 \alpha_0}{3} \tag{2-40}
\]

Now in a pure substance,

\[
N_1 = \frac{N_d}{M} \tag{2-41}
\]

so therefore

\[
\frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi N_d \alpha_0}{3M} \tag{2-42}
\]

or

\[
\frac{\varepsilon-1}{\varepsilon+2} \cdot \frac{M}{d} = \frac{4\pi N_\alpha_0}{3} = P \tag{2-43}
\]

which is identical to the Lorentz-Lorenz equation (equation (2-30)) derived previously for optical wavelengths. The quantity \(P\), calculated from this equation (2-43), is the molar polarization and both \(P\) and \(\alpha_0\) have the dimensions of volume. Therefore when \(\alpha_0\) is constant, then \(P\) is constant and the expression is complete, but this is only true if the material under consideration does not have a permanent dipole. Also \(P\) is approximately independent of temperature for substances for which it and the molar refraction, \(R\) are almost equal numerically.
Equation (2-43) is the Clausius-Mosotti equation.

It was Debye who first developed the theory to explain the effect that a permanent dipole has on the molar polarization, and a brief outline of his treatment follows. Ignoring for the present the electric moment induced by the field \( \mathbf{F} \), consider the effect only of the permanent moment. For any arbitrary orientation \( \theta \) of the polar molecule with respect to the direction of the field \( \mathbf{F} \), the potential energy is

\[
U = -\mu F \cos \theta \quad (2-44)
\]

According to Boltzmann's Law, the number of molecules distributed with the axes of their dipoles pointing in the directions within a solid angle \( d\Omega \) is

\[
A \exp \left( -\frac{U}{kT} \right) d\Omega \quad (2-45)
\]

where \( A \) is a constant dependent on the number of molecules considered, \( k \) is the Boltzmann constant and \( T \) is the temperature in degrees Kelvin. By substituting equation (2-44) into (2-45) and integrating to find the total number of molecules in all possible directions, this total is found to be

\[
\text{Number} = \int A \exp \left( \frac{(\mu F \cos \theta)}{kT} \right) d\Omega \quad (2-46)
\]

The total moment is
\[ \text{Moment} = \int A \exp \left( \frac{\mu F \cos \theta}{kT} \right) \cos \theta \, d\Omega \quad (2-47) \]

Dividing equation (2-47) by equation (2-46) gives the average moment per molecule or

\[ \bar{m} = \frac{\int A \exp \left( \frac{\mu F \cos \theta}{kT} \right) \mu \cos \theta \, d\Omega}{\int A \exp \left( \frac{\mu F \cos \theta}{kT} \right) \, d\Omega} \quad (2-47) \]

In order to integrate equation (2-47) more easily, the following substitutions should be made:

\[ x = \frac{\mu F}{kT} \]
\[ z = \cos \theta \]
\[ d\Omega = 2\pi \sin \theta \, d\theta \]

Integration and simplification of equation (2-47) gives

\[ \frac{\bar{m}}{\mu} = \frac{\exp(x) + \exp(-x)}{\exp(x) - \exp(-x)} - \frac{1}{x} = \coth(x) - \frac{1}{x} = \Lambda(x) \quad (2-48) \]

the Langevin function. The series expansion of the function is

\[ \Lambda(x) = \frac{x}{3} - \frac{x^3}{45} + \ldots \quad (2-49) \]

The values of \( x \) measured in dipole moment studies are sufficiently small that it is enough to consider only the first term of the series expansion, so therefore

\[ \frac{\bar{m}}{\mu} = \frac{x}{3} \quad (2-50) \]

or

\[ \bar{m} = \frac{\mu^2 F}{3kT} \quad (2-51) \]
This effect is added to the effect of the induced moment so that the total mean moment is

\[ \bar{M} = \alpha_o F + \mu^2 F/3kT = (\alpha_o + \mu^2 \frac{1}{3kT})F \]  \hspace{1cm} (2-52)

The total polarizability \( \alpha \) is thus

\[ \alpha = \alpha_o + \mu^2 \frac{1}{3kT} \]  \hspace{1cm} (2-53)

and therefore the general expression relating dipole moment to polarizability is

\[ \mathbf{p} = \frac{\varepsilon-1}{\varepsilon+2} \cdot \frac{\mathbf{M}}{d} = \frac{4\pi N\alpha}{3} = \frac{4\pi N}{3} (\alpha_o + \mu^2 \frac{1}{3kT}) \]  \hspace{1cm} (2-54)

This above derivation is of course a classical treatment of the subject. An equation relating dipole moment to polarizability can be obtained by using quantum mechanical postulates, and when this is done, \( \alpha \) correction term \( f(T) \) appears so that the quantum mechanical equation is

\[ \frac{\varepsilon-1}{\varepsilon+2} \cdot \frac{\mathbf{M}}{d} = \frac{4\pi N\alpha}{3} + \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} (1-f(T)) \]  \hspace{1cm} (2-55)

where \( f(T) \) is a non-linear function of the dipole moment and is inversely proportional to temperature. This correction is experimentally indistinguishable from zero in all cases except for a few low molecular weight hydrides and so is not used in ordinary experimental work with solutions.
The Solution Equations and the Guggenheim Method

The Debye equation as originally given applied only to the case of pure gases, however, many compounds are difficult or impossible to vaporize at reasonably low temperatures. Therefore it becomes necessary to obtain dipole moments of compounds dissolved in non-polar solvents and to find an equation relating the measured properties of these solutions to the dipole moment of the pure solute.

Consider the situation of a polar solute, whose physical properties will be distinguished by a subscript 2, and a non-polar solvent, whose properties will be denoted by a subscript 1 (properties of the solution will be denoted by the subscript 12). It was shown by equation (2-43) that

$$ P = \frac{4\pi N}{3} \alpha $$

(2-56)

and it is known from experimental work that $P$ is closely additive for dilute solutions so for a two-component solution

$$ \frac{\varepsilon_{12}^{-1}}{\varepsilon_{12}^{+2}} = \frac{4\pi}{3} n_1 \alpha_1 + \frac{4\pi}{3} n_2 \alpha_2 $$

(2-57)

where $\alpha$ is the polarizability and $n$ the number of molecules per cc (for each component respectively). The mole fractions of each component are

$$ X_1 = \frac{n_1}{n_1 + n_2} $$

(2-58a)

$$ X_2 = \frac{n_2}{n_1 + n_2} $$

(2-58b)
and the molar polarizations are

\[ P_1 = \frac{4\pi N\alpha_1}{3} \] (2-59a)

\[ P_2 = \frac{4\pi N\alpha_2}{3} \] (2-59b)

The density of the solution is

\[ d_{12} = \frac{(n_1 M_1 + n_2 M_2)}{N} \] (2-60)

where \( M \) is the molecular weight. By solving for \( n_1 \) in equation (2-58a) and \( n_2 \) in equation (2-58b), and substituting equation (2-57) becomes

\[ \frac{\varepsilon_{12}^{-1}}{\varepsilon_{12}^{+2}} = \frac{4\pi}{3} X_1 (n_1 + n_2) + \frac{4\pi}{3} X_2 (n_1 + n_2) \] (2-61)

and equation (2-60) becomes

\[ d_{12} = \frac{(X_1 (n_1 + n_2) M_1 + X_2 (n_1 + n_2) N_2)}{N} \] (2-62)

If both sides of equation (2-61) are divided by \( d \) and rearranged, the result is

\[ \frac{\varepsilon_{12}^{-1}}{\varepsilon_{12}^{+2}} \cdot \frac{X_1 M_1 + X_2 M_2}{d_{12}} = \frac{4\pi}{3} X_1 \alpha_1 N + \frac{4\pi}{3} X_2 \alpha_2 N \]

\[ = X_1 P_1 + X_2 P_2 \]

\[ = P_{12} \] (2-63)
or, since for a two component system

\[ x_1 = 1 - x_2 \]

then

\[ P_{12} = P_1 + (P_2 - P_1)x_2 \]  \hspace{1cm} (2-64)

The polarization of the solution, \( P_{12} \), is calculated from the values of the dielectric constant and density of the solution so if \( P_1 \) is known, then \( P_2 \) can be calculated. For a solution of a polar solute in a non-polar solvent, the assumption is made that \( P_1 \) is independent of concentration and is a constant, though this is only approximately true; so that any deviation from linearity in a plot of \( P_{12} \) vs. \( x_2 \) will be attributed to a variation of \( P_2 \) due to dipole-dipole interactions which change with changing concentration, \( P_2 \) may then be plotted against \( x_2 \) and the resulting curve extrapolated to infinite dilution \((x_2 = 0)\). The value of \( P_2 \) thus obtained is referred to as \( P_{2\infty} \), from which interaction effects and any solvent effects have been approximately eliminated. The value of the dipole moment, \( \mu \), calculated by use of \( P_{2\infty} \) for the polar molecule is usually fairly close to the value of \( \mu \) (vapour).

Alternatively, instead of calculating and extrapolating the polarization to infinite dilution, the dielectric constant and density data can be extrapolated. There are two procedures that can be followed here; either \( \varepsilon \) and \( d \) can be extrapolated directly (the Halverstadt-Kumler method)\(^{18}\) or the Debye equation can be modified and \( \varepsilon \) and \( n \) (the refractive index) can be used for extrapolation (the Guggenheim method)\(^{19}\). For the Halverstadt-Kumler method the procedure is as follows.
Consider the equations:

$$\varepsilon_{12} = \varepsilon_1 + \alpha'X_2$$  
$$V_{12} = V_1 + \beta'X_2$$  

(2-65a)  
(2-65b)

where \( V = 1/d \). A plot of \( \varepsilon_{12} \) vs. \( X_2 \) and one of \( V_{12} \) vs. \( X_2 \) will give slopes of \( \alpha' \) and \( \beta' \) respectively, and intercepts of \( \varepsilon_1 \) and \( V_1 \) respectively. To determine \( P_{2\infty} \), these values should be substituted into

$$P_{2\infty} = \frac{3\alpha' V_1 M_1}{(\varepsilon_1+2)^2} + \frac{(M_2 V_1 + M_1 \beta')}{(\varepsilon_1+2)} \frac{(\varepsilon_1-1)}{(\varepsilon_1+2)}$$  

(2-66)

which is of the same form as an equation proposed by Hedestrand.

The Guggenheim method, and especially Smith's \(^{18}\) modification of it, is an easier method to use, and with the availability of highly accurate dipping refractometers is just as accurate. The derivation, given here closely follows that of Smith. \(^{20}\)

Just as

$$P_{12} = P_1X_1 + P_2X_2$$  

(2-67)

so the molar refraction is

$$R_{12} = R_1X_1 + R_2X_2$$  

(2-68)

The molar volume, \( V \), may be approximated by

$$V_{12} = V_1X_1 + V_2X_2$$  

(2-69)
Equations (2-67) and (2-68) may be rewritten as follows:

\[
\begin{align*}
\frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} V_{12} &= \frac{\varepsilon_{1} - 1}{\varepsilon_{1} + 2} V_{12} X_{1} + (P_{e} + P_{a} + P_{o}) X_{2} \\
\frac{n_{12} - 1}{n_{12} + 2} V_{12} &= \frac{n_{1} - 1}{n_{1} + 2} V_{12} X_{1} + P_{e} X_{2}
\end{align*}
\] (2-70)

where \( P_{e} \) is the electronic polarization, \( P_{a} \) is the atom polarization and \( P_{o} \) is the polarization due to the permanent dipole moment and \( P_{a} + P_{e} + P_{o} = P_{2} \). These terms will be explained in more detail in Chapter IV.

Subtracting equation (2-71) from equation (2-70) gives

\[
\begin{align*}
\frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} - \frac{n_{12} - 1}{n_{12} + 2} V_{12} &= \frac{\varepsilon_{1} - 1}{\varepsilon_{1} + 2} V_{12} X_{1} + (P_{a} + P_{o}) X_{2} \\
\frac{n_{1} - 1}{n_{1} + 2} V_{12} &= \frac{n_{1} - 1}{n_{1} + 2} V_{12} X_{1} + P_{e} X_{2}
\end{align*}
\] (2-71)

Equation (2-69) may be rearranged and substituted into equation (2-72) to give

\[
\begin{align*}
\frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} - \frac{n_{12} - 1}{n_{12} + 2} V_{12} &= \frac{\varepsilon_{1} - 1}{\varepsilon_{1} + 2} - \frac{n_{1} - 1}{n_{1} + 2} V_{12} X_{1} + (P_{a} + P_{o}) X_{2} \\
\end{align*}
\] (2-72)

Now \( \left(\frac{-1}{\varepsilon_{1} + 2} - \frac{2}{n_{1} + 2}\right) V_{12} \) is the atom polarization of the solvent.

Then a quantity \( P_{a}' \) can be defined as

\[
P_{a}' = \frac{\varepsilon_{1} - 1}{\varepsilon_{1} + 2} - \frac{n_{1} - 1}{n_{1} + 2} V_{2}
\] (2-74)

and thought of as a sort of atom polarization for the solute, and
substituted into equation (2-73) to give

\[
\frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} \left( \frac{n_{12}^2 - 1}{n_{12}^2 + 2} \right) v_{12} = \left( \frac{\varepsilon_{1} - 1}{\varepsilon_{1} + 2} \right) v_{12} + (P_a - P_a' + P_o) x_2
\]

(2-73)

If equation (2-75) is divided on both sides by \( V_{12} \) and \( x_{12}/V_{12} \) replaced by \( C \), which is the concentration of solute in moles per unit volume, the equation then becomes

\[
\frac{\varepsilon_{12} - 1}{n_{12}^2 + 2} = \left( \frac{\varepsilon_{1} - 1}{\varepsilon_{1} + 2} \right) + (P_a - P_a' + P_o) C
\]

(2-76)

and this may be simplified slightly by defining

\[
D = \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n - 1}{n^2 + 2}
\]

(2-77)

and substituting to give

\[
D_{12} = D_1 + (P_a - P_a' + P_o) C
\]

(2-78)

A plot of \( D_{12} \) vs. \( C \) gives a slope of \( (P_a - P_a' + (4\pi N U^2/9kT)) \) and an intercept equal to \( D_1 \). Guggenheim made the assumption that atom polarizations are proportional to molecular volumes and furthermore suggested that \( P_a \) and \( P_a' \) could be equated, thus eliminating atom polarizations. Equation (2-78) then becomes

\[
\lim_{C \to 0} \frac{\partial D}{\partial C} = P_o = \frac{4\pi N U^2}{9kT}
\]

(2-79)

Smith then suggests that it would be better to use weight fractions for
the concentration units and thus eliminate any need to know the
densities of the solutions. The weight fraction, \( \omega_2 \), is related to
\( C \) by \( C = \omega_2/M_2 V \) which when substituted into equation (2-78) gives

\[
D_{12} = D_1 (P_a - P_a')\omega_2 / M_2 V
\]

or assuming again that \( P_a = P_a' \)

\[
P_o = \frac{4\pi N \mu^2}{9kT} = M_2 V_1 \lim_{\omega_2 \to 0} \frac{\partial D}{\partial \omega_2} \quad (2-81)
\]

The slope \( \left( \frac{\partial D}{\partial \omega_2} \right) \) is related to the quantities \( \left( \frac{\partial \varepsilon}{\partial \omega_2} \right) \) and \( \left( \frac{\partial n}{\partial \omega_2} \right) \) by

\[
\frac{\partial D}{\partial \omega_2} = \frac{3}{(\varepsilon_1^2 + 2)} \frac{\partial \varepsilon}{\partial \omega_2} - \frac{6}{(n_1^2 + 2)^2} \frac{\partial n}{\partial \omega_2} \quad (2-82)
\]

By using the notation that \( \left( \frac{\partial \varepsilon}{\partial \omega_2} \right) \) is \( \alpha \) and \( \left( \frac{\partial n}{\partial \omega_2} \right) \) is \( \beta \), equation (2-81) becomes

\[
P_o = \left[ 3M_2 V_1 \alpha / (\varepsilon_1^2 + 2) \right] - \left[ 6M_2 V_1 \beta / (n_1^2 + 2)^2 \right] \quad (2-83)
\]

and also \( \mu = \left[ (9kT P_o) / (4\pi N) \right]^{1/2} \quad (2-84) \)

This method of calculating dipole moments has the advantage that the data
for \( \varepsilon_{12} \) and \( n_{12} \) are separately extrapolated, so that any errors in \( \varepsilon_{12} \)
and \( n_{12} \) will be easily detected. Also for a particular solvent at a
known constant temperature, the factors

\[
3M_2 V_1 / (\varepsilon_1^2 + 2) \quad \text{and} \quad 6M_2 V_1 / (n_1^2 + 2)^2
\]
are constants, therefore the calculation of the orientation polarization of the dipole moment is very much simplified.

For a laboratory equipped with a dipping refractometer, the Guggenheim method is by far the easiest way to obtain data for dipole moments. The refractometer is easy to calibrate, measurements are rapidly obtainable, and a solution from which a questionable datum was obtained can easily be remeasured. A very important thing to keep in mind about dipole moments in general, and the Guggenheim method in particular is that the absolute values of data such as temperature, dielectric constants and refractive indices need only be accurate to 0.5% to give accurate values of the dipole moment of a molecule but, the values of dielectric constants and refractive indices amongst themselves must be much more accurate. To explain more concretely, it is necessary for example to have the temperature in the thermostat controlled to \( \pm 0.02^\circ C \) because both dielectric constants and refractive indices are strongly temperature dependent, but as long as any variations in temperature can be controlled to \( \pm 0.02^\circ C \) it is of much less importance whether the mean temperature is 298.0\(^\circ K\) or 298.1\(^\circ K\).

To obtain the dipole moment \( \mu \), it is necessary to first calculate \( \mu^2 \) and then take the positive square root of this number. This process cuts the error by half, i.e. a 1% error in \( \mu^2 \) is a 0.5% error in \( \mu \). In any event, with the equipment and techniques presently available, one cannot expect accuracy in \( \mu \) greater than \( \pm 0.05 \) D and most investigators quote their results with an error of the order of \( \pm 0.10 \) D. The only method of obtaining dipole moments that can give more accurate results than those quoted is the microwave method, and
microwave work to obtain dipole moments of phosphonitrilic compounds is not feasible due to the large number of atoms in these compounds and due to the flexibility of the molecules.

Though the Guggenheim method of determining dipole moments is much easier to use, there are circumstances in which it is not applicable. It is not possible to measure the refractive index of a substance or solution accurately near an absorption band. For example, using the Na D lines as the sources of illumination, it would not be possible to measure the refractive index of a liquid that absorbed an appreciable amount of yellow light. If in dipole moment measurements the solutions used are coloured, it may become necessary to calculate dipole moments by the Halverstadt-Kumler method and to measure the densities of the solutions as accurately as possible.
CHAPTER III
EXPERIMENTAL

Materials and Equipment

Cyclohexane (Fisher, certified ACS Spectranalyzed) was stored over molecular sieves (BDH Type 13X) overnight before use. Carbon tetrachloride (Fisher, certified ACS Spectranalyzed) was also stored over molecular sieves overnight before use. Trimeric and tetrameric phosphonitrilic chlorides ($N_3P_3Cl_6$ and $N_4P_4Cl_8$) were purified by recrystallization from petroleum ether to constant melting points of 112.5°C for the trimer (lit. 112.8°C) and 122°C for the tetramer (lit. 122.8°C). Phosphonitrilic fluoride trimer ($N_3P_3F_6$) was prepared by reacting KSO$_2$F and $N_3P_3Cl_6$ in paraffin oil at 140°C. It was purified by successive trap-to-trap distillations on a vacuum line. Tetrameric phosphonitrilic fluoride ($N_4P_4F_8$) was purified by a series of trap-to-trap distillations on a vacuum line. The higher phosphonitrilic fluorides, ($NPF_n^2$)$_n$, $n = 5$ to 12, and also the mixed chloride-fluorides, ($N_3P_3F_2Cl_4$), ($N_3P_3F_4Cl_2$), ($N_4P_4F_4Cl_4$), ($N_4P_4F_6Cl_2$), ($N_5P_5F_5Cl_4$) and ($N_5P_5F_8Cl_2$) were purified by gas-liquid chromatography using a 10' x 3/8" column packed with 20% SE-30 on Chromosorb W and a helium flow rate of 55 ml per minute. The purified compounds were collected in glass collection tubes cooled in an acetone-CO$_2$ bath.
A graded series of four or five solutions of each compound were prepared using cyclohexane as the solvent. The concentrations of each of the solutions were determined by weighing the empty container, the container with added compound and the container plus compound with added solvent in order to determine the weight of solute and weight of solvent for each solution. The concentrations were then calculated as weight fractions.

A WTW Dipolemeter, Type DM01, with a DFL-1 cell, was used to measure the capacitance of each solution. The capacitances of air and of CCl$_4$ were measured as standards. Because the capacitance of the Dipolemeter cell plus contents is directly proportional to the dielectric constant of the contents, one then can use the known values of the dielectric constants of air and CCl$_4$ together with their measured capacitances to determine the conversion factor from capacitance to dielectric constant for the Dipolemeter. This conversion is best expressed in the form $\varepsilon_{12} = a \cdot $ (capacitance reading) + $b$ where $a$ and $b$ were redetermined before each set of data for a compound was collected. A capacitance reading was arrived at by taking nine separate readings for each substance or solution in the cell and using the arithmetic mean of these readings as the capacitance reading.

A dipping refractometer (Carl Zeiss) was used to measure refractive indices of the solutions. The refractometer was calibrated at the beginning of each data run using the calibrating prism supplied by the manufacturer. The refractometer has a scale engraved on the eye-piece and a reading is obtained by determining the boundary line separating the bright portion of the scale from the dimly lit portion.
A vernier scale is built into the instrument which allows scale readings to be made to four significant figures. These scale readings may be converted into refractive indices by using the tables supplied by the manufacturer. A metal-walled cell with a bayonet lock is also supplied and this cell is filled with the solution of interest and locked onto the refractometer. After allowing 15 minutes for equilibration in a thermostat bath, nine scale readings were obtained and the arithmetic mean of these was used to determine the refractive index of the solution.

In order to ensure constant temperature of the solutions when measuring their refractive indices and dielectric constants, a thermostat bath was set up and regulated to provide a constant temperature of 298°K (25°C) with maximum fluctuations of ± 0.02°. A schematic diagram of the thermostat bath is shown in Figure 3-1. It was found necessary to use a cooling coil in order to obtain constancy of temperature in the bath. Distilled water was used as the bath liquid.

Procedure

The standard procedure for obtaining a set of data from a compound was as follows. A graded series of four or five solutions of the compound in cyclohexane were prepared by weighing the components into a glass container. Figure 3-2 shows the container used for $N_3P_3F_6$ and $N_4P_4F_8$, for the other compounds a 50 ml volumetric flask was used. An analytical balance was used for weighings, with an accuracy of ± 0.0001 g. The concentrations of the solutions ranged from $4.00 \times 10^{-3}$ to $2.50 \times 10^{-2}$ in terms of weight fraction. The Dipolemeter was calibrated using air
Figure 3-1 Schematic diagram of Thermostat including connections to Dipolemeter (left) and heater-pump (right)
and carbon tetrachloride as standards. The refractometer was calibrated with the calibrating prism supplied by the manufacturer. The Dipolemeter cell was then filled with cyclohexane and was stoppered and allowed to reach the temperature of the thermostat bath. This equilibration took ten to fifteen minutes. Then nine readings of the capacitance of the cell and contents were recorded. The cyclohexane was then withdrawn from the Dipolemeter and the metal cell for the refractometer was filled and attached to the refractometer, which was then placed on a holder so that the cell was immersed in the thermostat bath. Ten to fifteen minutes were allowed for equilibration and nine scale readings were then recorded. The same procedure was then repeated with the most dilute solution of compound in solvent. This procedure was repeated as many times as necessary, each time using the least concentrated of the solutions remaining to be measured. In
this manner, data were collected for all the solutions prepared. After all data were collected, the mean capacitance readings were converted to dielectric constants and the mean refractometer scale readings were converted to refractive indices. Concentrations in terms of weight fraction were calculated for each solution and graphs of dielectric constant vs. weight fraction and refractive index vs. weight fraction were plotted. The slopes of these graphs were determined and substituted into the equation

\[ P_d = \frac{3M_2V_1\alpha}{(\varepsilon_1+2)^2} - \frac{6M_2V_1\beta}{(n_1^2+2)^2} \]

derived in Chapter II (equation (2-83)).

Data and Results

The data and results are all presented in Table I. The graphical results for a typical compound, \( N_3P_3F_4Cl_2 \) are shown in Figure 3-3. A graph of polarization vs. ring size for the phosphonitrilic fluorides is given in Figure 3-4.
Table I. Data and Results for Phosphonitrilic Halides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$10^2$ x Maximum concentration (weight fractions)</th>
<th>Maximum dielectric constant*</th>
<th>Minimum refractive index**</th>
<th>Distortion polarization in cc. ($P_d$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NPF₂)₃</td>
<td>1.88</td>
<td>2.0152</td>
<td>1.42228</td>
<td>4.4</td>
</tr>
<tr>
<td>(NPF₂)₄</td>
<td>2.25</td>
<td>2.0171</td>
<td>1.42222</td>
<td>13.4</td>
</tr>
<tr>
<td>(NPF₂)₅</td>
<td>2.60</td>
<td>2.0178</td>
<td>1.42192</td>
<td>17.2</td>
</tr>
<tr>
<td>(NPF₂)₆</td>
<td>2.37</td>
<td>2.0170</td>
<td>1.42228</td>
<td>21.9</td>
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<tr>
<td>(NPF₂)₇</td>
<td>1.50</td>
<td>2.0170</td>
<td>1.42273</td>
<td>29.4</td>
</tr>
<tr>
<td>(NPF₂)₈</td>
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<td>2.0186</td>
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<tr>
<td>(NPF₂)₉</td>
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<td>2.0182</td>
<td>1.42252</td>
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<tr>
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<td>1.42259</td>
<td>66.4</td>
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<tr>
<td>(NPF₂)₁¹</td>
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<td>2.0195</td>
<td>1.42247</td>
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<tr>
<td>(NPF₂)₁²</td>
<td>2.56</td>
<td>2.0195</td>
<td>1.42225</td>
<td>54.2</td>
</tr>
<tr>
<td>(NPC₁₂)₃</td>
<td>2.65</td>
<td>2.0239</td>
<td>1.42465†</td>
<td>17.6</td>
</tr>
<tr>
<td>(NPC₁₂)₄</td>
<td>2.55</td>
<td>2.0254</td>
<td>1.42520†</td>
<td>31.3</td>
</tr>
<tr>
<td>N₃F₃Cl₂</td>
<td>2.35</td>
<td>2.0229</td>
<td>1.42296</td>
<td>26.6</td>
</tr>
<tr>
<td>N₃F₂Cl₄</td>
<td>3.41</td>
<td>2.0297</td>
<td>1.42412†</td>
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</tr>
<tr>
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<td>2.0223</td>
<td>1.42290</td>
<td>33.2</td>
</tr>
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<td>N₄F₄Cl₄</td>
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<td>2.0272</td>
<td>1.42377†</td>
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</tr>
<tr>
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<td>2.0224</td>
<td>1.42293</td>
<td>42.9</td>
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<tr>
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<td>2.24</td>
<td>2.0271</td>
<td>1.42360†</td>
<td>61.4</td>
</tr>
</tbody>
</table>

* Minimum dielectric constant was that of cyclohexane which is 2.0150 at 25°C.

** Refractive index of cyclohexane is 1.42356 at 25°C.

† In these compounds, refractive index rose with solution concentration.
Figure 3-3a: $\varepsilon$ vs. weight fraction for $N_3P_3F_4Cl_2$

$x$: 1st run
$\circ$: 2nd run

Figure 3-3b: $\eta_0$ vs. weight fraction for $N_3P_3F_4Cl_2$

$x$: 1st run
$\circ$: 2nd run
Figure 3.4

P polarization vs. ring size for (NPF₂)ₙ

in cc.
CHAPTER IV
DISCUSSION

The Question of Atom Polarization

The total polarization, $P$, may be broken down into three components; electronic polarization, distortion polarization and atom polarization, all of which are the result of applying an electric field to a collection of molecules. The total polarization is the polarization obtained from dielectric constant data. The electronic polarization, which is due to the movement of electrons in the molecule, is obtained by optical methods, for example measurements of refractive indices. The distortion polarization is due to the orientation of the permanent dipoles, while atom polarization is the name given to the portion of the total polarization caused by the movement of atomic nuclei relative to one another in a molecule. There are a number of ways of causing such movement; by stretching of bonds joining the nuclei, by changes in bond angles and by torsional movements of nuclei with respect to one another. These movements are classed as vibrational and so evidence for them should be found in the infrared spectra of the molecules concerned. Because of its nature, atom polarization is not likely to bear any numerical relationship to the electronic polarization or to the orientation polarization, but should instead be accessible to calculation either by means of a knowledge of the force constants of bending and stretching that may be obtained via infrared spectroscopy or by means of a knowledge of the refractive index.
of the compound in the infrared portion of the spectrum. If the refractive index data are available, then a Sellmeier type of relationship can be used to calculate the refractive index at zero frequency (infinite wavelength). Using this value of the refractive index to calculate the molar refraction gives a refraction equal to the sum of the electronic and atomic polarizations, instead of just being equal to the electronic polarization, which it is if no account is taken of the infrared refractive index data. Such data are, however, not readily available, and so the most common method of dealing with atom polarization is to make an arbitrary correction for it. Smith\textsuperscript{11} quotes Van Vleck\textsuperscript{22} and Cartwright and Errera,\textsuperscript{23} who showed that low frequency modes of vibration such as bending make the greatest contribution to atom polarization because they have small enough force constants to give atom polarizations of the expected magnitude. Such vibrations will absorb in the far-infrared in the range of about $50-200$ cm$^{-1}$. Therefore, if there exist absorptions in the infrared in this range, these absorptions can be used as evidence that the molecule in question may have a considerable, non-negligible atom polarization. This sort of argument was used by Coop and Sutton\textsuperscript{24} when explaining the unexpectedly high "dipole moments" of some symmetric diketones. For benzoquinone, Hammick, Hampson and Jenkins\textsuperscript{25} carried out calculations assuming the atom polarization could be ascribed to the two carbonyl groups. It was Coop and Sutton,\textsuperscript{24} however, who showed mathematically that the high apparent orientation polarization of benzoquinone was due to atom polarization. They showed that if benzoquinone were treated as an entity consisting of two independent one-dimensional oscillators, that the frequency of the vibration calculated from the polarization was very
close to that of a vibration observed in the far infrared by Cartwright and Errera\textsuperscript{23,26} at 120 cm\textsuperscript{-1}. Coop and Sutton assumed that the two carbonyl groups vibrate in the plane of the benzene ring and perpendicular to the carbon-oxygen double bond. The atom polarization caused by two independent one-dimensional oscillators is

\[ P_a = \frac{8\pi \nu^2}{9V_o} \]

where \( \nu \) is the moment of the vibrating group and \( V_o \) is the force constant of the vibration. For benzoquinone, \( P_a \approx 9 \) cc. and \( \nu = 2.5 \times 10^{-18} \) esu-cm for a carbonyl group, which gives a value of \( V_o \) of \( 1.17 \times 10^{-12} \) erg/radian\textsuperscript{2}/molecule. This force constant corresponds to a frequency of about 111 cm\textsuperscript{-1} which is very close to the observed value of 120 cm\textsuperscript{-1}.

Because of the nature of atom polarization, it may be expected to be a roughly additive quantity for molecules of similar structure. To quote Smith\textsuperscript{27} "Atomic polarization values seem to depend principally on the nature of the dipole groups which are in opposition, and not upon the size of the groups lying between them. It must be inferred, therefore, that the effect lies in the vibrational characteristics of the polar groups". Extending this statement, then one might expect that a series of compounds made up of a repeated polar group could be expected to have atom polarizations that increased roughly proportionally to the number of repeating units. As an example, consider the \( n \)-alkanes, \( \text{CH}_3(\text{CH}_2)_n\text{CH}_3 \), as the series of compounds and the \(-\text{CH}_2-\) group as the repeated polar group. Smyth\textsuperscript{28} has tabulated the atom polarizations of
the n-alkanes (his data were obtained by measuring polarizations at different temperatures) up to n-dodecane and has calculated the increase of atom polarization per added \(-CH_2-\) group as 0.07 cc., which, considering the low polarity of carbon-hydrogen bonds appears to be a reasonable increment. For the case of the metallic acetylacetonates a similar additivity was found and it was noticed that the ratio of the atom polarizations for a series of acetylacetonates was the same as the ratio of the number of acetylacetonate groups per metal atom.\(^{24,29}\) The high residual polarizations of these compounds were not at first thought to be due to atom polarization but instead were thought to be explained by one of the following reasons:

1. the chelate rings were not fully symmetric,
2. the compounds were not fully chelated,
3. the molecules are easily bent by thermal collisions and remain this way long enough to orient in the electric field used to measure polarizations,
4. there is some sort of solvent effect.

Finn, Hampson and Sutton,\(^{29}\) however, disposed of all four of these explanations and concluded that the high residual polarizations were really atom polarizations. Application of resonance concepts eliminated the first explanation, and the second was shown to be most improbable because there was no variation of total polarization with temperature as would be expected if the second possibility were true. As far as the possibility of thermal bending is concerned, Finn, Hampson and Sutton carried out a rough calculation to show that the frequency of such bending would be too high to permit the molecule to orient itself
in the field. The fourth explanation was eliminated because the variation in total polarization with solvent was only slight and also was not in the manner predicted by the accepted solvent effect theories. Further evidence for their conclusion that the anomalous polarization of the compounds was due to atom polarization was found by Coop and Sutton who measured polarizations in the vapour phase for these and other compounds and found the polarizations constant within experimental error over temperature ranges up to 150° depending upon which compound was considered. They encountered considerable difficulty with some of the compounds due to their decomposition but were able to conclude that the metallic acetylacetonates, the symmetric diketones and most of the other compounds which they examined did have high but real atom polarizations.

A more recent discussion of atom polarizations and their effects in a series of cyclic dimethylsiloxane oligomers has been contributed by Alvik and Dale who were trying to obtain information on molecular conformations of the different oligomers by measuring their dipole moments. They found however that such information could not be obtained for the siloxanes because they had no way to accurately measure the atom polarizations. From microwave absorption work carried out by Dasgupta, Garg and Smyth it was already known that the atom polarization was of the order of 15% and 22% of the total polarization for the trimeric and tetrameric cyclic dimethylsiloxane oligomers, therefore, a very considerable error in the dipole moments of the compounds due to this atom polarization was not easily correctable. The conclusion of Alvik and Dale that the high apparent dipole moments of the cyclic
dimethylsiloxane oligomers were due to atom polarization was supported by their determination of the entropies and enthalpies of fusion and the infrared spectra of the compounds. The infrared spectra\textsuperscript{32} were very complicated, as would be expected for flexible molecules, and, molecules of high flexibility are exactly those that have high atom polarizations. When molecules are as flexible as these are, then inversion into conformations having a net dipole moment will occur due to low frequency vibrations and it is in this area of consideration that "we enter a doubtful territory in which it may be difficult or arbitrary to distinguish between dipole orientation and atom polarization."\textsuperscript{31} This same territory must also be entered when a dielectric study of phosphonitrilic compounds is carried out.

**Previous Methods of Dealing with Atom Polarization**

As has been stated previously, it is very difficult to measure the atom polarization of a molecule. Refractive index data from the infrared portion of the spectrum, used in conjunction with a Sellmeier type relationship will enable the calculation of the atom polarization or else an estimate of atom polarization can be made from force-constant data obtained in the far infrared. Usually, though, such data are not available, and the procedure then has been to estimate a value of $P_a$. There are three main approaches for such an arbitrary estimation. One can assume $P_a = 0$, i.e. that $P_a$ is so small compared to $P_e$ that it may be neglected. Another way is to assume that $P_a$ is a certain percentage of $P_e$, because it has been found for many small organic molecules that $P_a$ is about 5% to 15% of $P_e$. Evidence for this comes
from microwave studies where dipole moments can be calculated without any knowledge of $\mu_a$. A third, slightly different approach, is sometimes used when refractive index data are collected (for example when using the Guggenheim method). Refractive indices are usually measured with respect to the $n_D$ line, and the values so measured are normally a few percent higher than the refractive indices calculated for zero frequency. It is then assumed that the value of the refractive index for the $n_D$ line used in the calculations is sufficiently high enough to account for the effects of atom polarization. It has been found, however, that there are a number of compounds for which these approximations are inadequate.

Atom Polarization and Phosphonitrilic Compounds

A number of dipole moment determinations have been carried out on phosphonitrilic compounds\(^{12-16,33-37}\) in order to obtain information on their structures and, in the case of mixed substituent derivatives, distinguish different isomers from one another. An example of this is the work of Koopman et al.\(^{12}\) on the isomers of $\text{NPCl}_2 \text{Cl}_4(\text{NMe}_2)_2$ and the isomers of $\text{NPCl}_3 \text{Cl}_3(\text{NMe}_2)_3$ (see also Figure 1-1). In doing this work, no allowance was made for atom polarization effects but since such effects would be similar for all of the isomers of a particular molecular formula, this neglect probably does not invalidate their results.

As an example of a different sort of problem for which dipole moment data was used in an attempt to determine a structure, the case of $(\text{NPCl}_2)_3$ may be considered. Several determinations of its dipole
moment have been made by different workers\textsuperscript{33-36} with conflicting results. Krause\textsuperscript{33} whose determination was the earliest, found $\mu = 0.51$ D from dielectric constant and specific volume measurements at varying temperatures. Corfield's estimate\textsuperscript{34} of $\mu < 0.14$ D was carried out by measurement of the dielectric constant and dielectric absorption of a solution of (NPCl\textsubscript{2})\textsubscript{3} in benzene at different frequencies in the microwave region of the electromagnetic spectrum, all at a constant temperature. She then estimated the relaxation time of the dipole polarization and from this datum estimated a maximum dipole moment. Her method has the advantage of not being affected by atom polarization. The work of Allcock and Best\textsuperscript{35} was done by two methods, first a direct determination of the dipole moment of the pure liquid using the Onsager equation for calculations, and second a determination of dielectric constants and refractive indices of benzene solutions of known concentrations of the trimer to enable calculations of the dipole moment by means of the Guggenheim equation. The result of Kokoreva et al.\textsuperscript{36} was calculated with the Hedestrand equation using measured dielectric constants and refractive indices. As can be seen in Table II, variations in temperature notwithstanding, the agreement among the various workers is not good. None made any allowance for possible atom polarization (except for Corfield\textsuperscript{34} whose method eliminates the need for such an allowance) and none appeared to consider this necessary. At the same time, all but the Russian workers used their results to "prove" that (NPCl\textsubscript{2})\textsubscript{3} is almost planar in solution, a result justified by the infrared and Raman spectra\textsuperscript{38} but very questionable according to the dipole moment data alone.
Table II. Other Dipole Moment Results for Phosphonitrilic Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu$ (D)</th>
<th>Method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NPC$_1$)$_2$</td>
<td>0.51</td>
<td>a at $-20^\circ$ to $95^\circ$ C</td>
<td>33</td>
</tr>
<tr>
<td>(NPC$_1$)$_2$</td>
<td>0.14</td>
<td>b</td>
<td>34</td>
</tr>
<tr>
<td>(NPC$_1$)$_2$</td>
<td>0.98</td>
<td>c at $120^\circ$</td>
<td>35</td>
</tr>
<tr>
<td>(NPC$_1$)$_2$</td>
<td>0.92</td>
<td>d at $70^\circ$</td>
<td>35</td>
</tr>
<tr>
<td>(NPC$_1$)$_2$</td>
<td>0.83</td>
<td>d at $30^\circ$</td>
<td>35</td>
</tr>
<tr>
<td>(NPC$_1$)$_3$</td>
<td>0.93</td>
<td>e</td>
<td>36</td>
</tr>
<tr>
<td>(NPC$_1$)$_4$</td>
<td>0.39</td>
<td>a at $-20^\circ$ to $95^\circ$ C</td>
<td>33</td>
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<td>b</td>
<td>34</td>
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<td>c at $120^\circ$</td>
<td>35</td>
</tr>
<tr>
<td>&amp; 3.28</td>
<td>d at $70^\circ$</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>&amp; 2.84</td>
<td>d at $30^\circ$</td>
<td>35</td>
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<td>36</td>
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<tr>
<td>1,3-trans-</td>
<td>&amp; 3.28</td>
<td>e</td>
<td>36</td>
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<td>&amp; 2.44</td>
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<td>&amp; 3.67</td>
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</tr>
<tr>
<td>N$_3$P$_3$(NC$_4$H$_8$)$_6$</td>
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<td></td>
<td>36</td>
</tr>
<tr>
<td>N$_3$P$_3$Cl$_5$(NC$_5$H$_10$)</td>
<td></td>
<td></td>
<td>36</td>
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<td>Compound</td>
<td>(\mu) (D)</td>
<td>Method</td>
<td>References</td>
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<td>e</td>
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<td>1,1,3,5-cis-(\text{N}_3\text{P}_3\text{Cl}_2(\text{NC}<em>5\text{H}</em>{10})_4)</td>
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<td>e</td>
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<td>(\text{N}_3\text{P}_3(\text{NC}<em>5\text{H}</em>{10})_6)</td>
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<tr>
<td>(\text{N}_3\text{P}_3\text{Cl}_5(\text{NC}_4\text{H}_4\text{O}))</td>
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<td>e</td>
<td>36</td>
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<tr>
<td>1,3-trans-(\text{N}_3\text{P}_3\text{Cl}_4(\text{NC}_4\text{H}_8\text{O})_2)</td>
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<td>f</td>
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<tr>
<td>1,3-trans-(\text{N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_2)</td>
<td>2.61</td>
<td>f</td>
<td>12</td>
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<tr>
<td>1,3-cis-(\text{N}_3\text{P}_3\text{Cl}_4(\text{NMMe}_2)_2)</td>
<td>4.3</td>
<td>f</td>
<td>12</td>
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<td>1,3,5-trans-(\text{N}_3\text{P}_3\text{Cl}_3(\text{NMMe}_2)_3)</td>
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<td>a in benzene</td>
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<td>2.94</td>
<td>a in (\text{C}<em>6\text{H}</em>{12})</td>
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<td>(\text{1,1-N}_3\text{P}_3\text{Cl}_4(\text{NHMe})_2)</td>
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<td>a in benzene</td>
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<td></td>
<td>2.70</td>
<td>a in (\text{C}<em>6\text{H}</em>{12})</td>
<td>15</td>
</tr>
<tr>
<td>(\text{1,3-trans-}\text{N}_3\text{P}_3\text{Cl}_4(\text{NHMe})_2)</td>
<td>4.12</td>
<td>a in benzene</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>3.80</td>
<td>a in (\text{C}<em>6\text{H}</em>{12})</td>
<td>15</td>
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<tr>
<td>(\text{1,3,5-cis-}\text{N}_3\text{P}_3(\text{C}_6\text{H}_5)_3\text{Br}_3)</td>
<td>5.27</td>
<td>g</td>
<td>13</td>
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Table II (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>μ(D)</th>
<th>Methods*</th>
<th>References</th>
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<tr>
<td>1,3,5-trans-(\text{N}_3\text{P}_3\text{(C}_6\text{H}_5\text{)}_3\text{Br}_3 )</td>
<td>2.36</td>
<td>g</td>
<td>13</td>
</tr>
<tr>
<td>(\text{N}_3\text{P}(\text{o-phenylenedioxy})_3 )</td>
<td>1.9</td>
<td>d at 70°</td>
<td>16</td>
</tr>
<tr>
<td>1,5-cis-(\text{N}_4\text{P}_4\text{(C}_6\text{H}_5\text{)}_6\text{(N}_3\text{)}_2 )</td>
<td>3.7</td>
<td>not stated</td>
<td>37</td>
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<tr>
<td>1,5-trans-(\text{N}_4\text{P}_4\text{(C}_6\text{H}_5\text{)}_6\text{(N}_3\text{)}_2 )</td>
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<td>not stated</td>
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<td>1,3-cis-(\text{N}_3\text{P}_3\text{F}_4\text{(C}_6\text{H}_5\text{)}_2 )</td>
<td>4.3</td>
<td>d</td>
<td>14</td>
</tr>
<tr>
<td>1,3-trans-(\text{N}_3\text{P}_3\text{F}_4\text{(C}_6\text{H}_5\text{)}_2 )</td>
<td>2.5</td>
<td>d</td>
<td>14</td>
</tr>
<tr>
<td>1,3-cis-(\text{N}_3\text{P}_3\text{F}_4\text{(C}_7\text{H}_7\text{)}_2 )</td>
<td>4.4</td>
<td>d</td>
<td>14</td>
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</table>

* Methods used were as follows:
  a) Smith modification of Guggenheim method
  b) Dielectric constant and dielectric absorption
  c) Onsager equation, using pure melt
  d) Guggenheim method
  e) Hedestrand method
  f) Onsager and Böttcher method
  g) Halverstadt and Kumler method.
Some dipole moment work has also been done on other phosphonitrilic compounds as outlined in Table II.

As far as assignment of structural isomers to different compounds of the same molecular formula, such as \( N_3^P X^4 Y_2^2 \), is concerned, the non-allowance for atom polarization is probably not too serious a problem, at least not sufficiently serious so as to invalidate any conclusions drawn. For the three isomers of the formula \( N_3^P X^4 Y_2^2 \), the atom polarizations will be similar and may be treated as a constant factor as long as only the three such compounds are considered together. When, however, a series of compounds such as \( N_3^P X^4 Y_{6-m} \), \( m = 0-6 \) or \( (NPX_2)_n \), \( n = 3,4... \) must be considered, then some decision must be made about the best way to deal with atom polarization.

Phosphonitrilic halides are known to be flexible molecules; evidence for this coming from infrared and Raman spectra.\(^{38-41}\) It is therefore reasonable that these molecules should have high atom polarizations and that atom polarization should be roughly proportional to the number of repeating groups in the polymer. The linearity of the graph of polarization vs. ring size for the phosphonitrilic fluorides (Figure 3-4) is another piece of evidence that suggest the existence of a high atom polarization. However, before this explanation is accepted, other possible explanations for the high distortion polarization of these compounds must be shown to be unacceptable. A high distortion polarization for a compound or group of compounds might be explained in one of the three following ways. The first is that the compounds might be easily bent by thermal collisions and might remain bent long enough to orient in the electric field, producing a dipole
moment. This does not explain the proportionality of the polarization to ring size. Also if a calculation of the period of vibration of this thermal bending were carried out, for example in the manner of Finn, Hampson and Sutton,\textsuperscript{29} the period of oscillation is found to be much too small. The trimeric ring is treated as a set of three one-dimensional oscillators. The group moment for the PCl\textsubscript{2} group is of the order of $2 \times 10^{-18}$ esu-cm and for the trimeric chloride the polarization is 17.6 cc. Using equation

$$V_o = \frac{12\pi N\mu^2}{9P_\alpha}$$

the result obtained is $5.7 \times 10^{-13}$ ergs/radian\textsuperscript{2}. This would lead to vibrations with a period of oscillation of the order of $10^{-12}$-$10^{-13}$ seconds whereas for orientation effects to be significant, a period of oscillation of the order of $10^{-10}$-$10^{-11}$ seconds is required. This means that thermal bending of the molecules is not an adequate explanation of the high distortion polarization of phosphonitrilic halides. A second possible explanation is a lack of symmetry of the ring, but this can be very easily eliminated. From X-ray diffraction studies of some homogeneously substituted phosphonitrilic derivatives, it is found that all the P-N bond lengths in a particular compound are the same. This is also true of all the P-X bond lengths in any one compound.\textsuperscript{42-49} Although a variety of configurations, many with non-zero dipole moments, are in principle available to the phosphonitrilic derivatives of the larger ring sizes, in practice X-ray studies show that the configuration of highest symmetry, which usually has a zero dipole moment, is the one normally adopted. This explanation also has
the disadvantage that it does not explain the linearity of the polarization vs. ring size relationship. A third possible explanation is some sort of solvent effect but this can be eliminated for two reasons. First there are data available for phosphonitrilic chlorides for the pure liquid,\(^3\) for benzene as solvent\(^34-36\) for decalin\(^33\) and for cyclohexane, and the results obtained show greater discrepancies among different workers using the same solvent than the discrepancies among different workers using different solvents. Preliminary work in connection with this thesis was also carried out on phosphonitrilic chloride trimer using carbon tetrachloride as the solvent and the results obtained were substantially the same as those obtained using cyclohexane as solvent.

The inability of all the other proposed explanations to account for the distortion polarizations of the phosphonitrilic halides therefore leaves only one source for this polarization and that is atom polarization. Now if atom polarization is the cause of the distortion polarization of the fluorides, then it is likely also to be the cause of the high polarization of the phosphonitrilic chlorides and again should be roughly proportional to the number of monomer units. This conclusion is supported by the data obtained in this work. For the phosphonitrilic chloride trimer and tetramer there are published data for the far infrared region of the spectrum\(^38,41\) part of which are shown in Table III. The existence of vibrations in the far infrared is evidence to support the existence of high atom polarizations, as is the general flexibility of the molecules, but some mathematical backing of this hypothesis is desirable. The basic equation used by Coop and Sutton\(^24\)
Table III. Far Infrared Results for \( N_3P_3Cl_6 \) and \( N_4P_4Cl_8 \)\(^{38,61} \)

<table>
<thead>
<tr>
<th>( (NPCl_2)_3 )</th>
<th>Nujol mull</th>
<th>( CCl_4 ) solution</th>
<th>( (NPCl_2)_4 )</th>
<th>Nujol mull</th>
<th>( CCl_4 ) solution</th>
<th>Crystalline film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>140 w</td>
<td>140w</td>
<td></td>
<td>56 vw</td>
<td>141 w</td>
<td>140 w</td>
</tr>
<tr>
<td></td>
<td>162 vw</td>
<td></td>
<td></td>
<td>141 vw</td>
<td>141 w</td>
<td>156 w</td>
</tr>
<tr>
<td></td>
<td>179 w</td>
<td></td>
<td></td>
<td>150 w</td>
<td></td>
<td>158 w</td>
</tr>
<tr>
<td></td>
<td>189 w</td>
<td>188 brd,w</td>
<td></td>
<td>158 w</td>
<td>167 w</td>
<td>172 vw</td>
</tr>
<tr>
<td></td>
<td>208 vw</td>
<td></td>
<td></td>
<td>176 m</td>
<td></td>
<td>172 vw</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>189 w</td>
<td>187 m</td>
<td>197 vw</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
Pa = \frac{4\pi N\nu^2}{9V_o} \tag{4-1}
\]

may be used as a starting point. This equation applies to the case of one one-dimensional oscillator. For the phosphonitrilic halides there are \( n \) oscillators each of which is a \( PX_2 \) group. The assumption that the \( PX_2 \) groups are the oscillators is made because the low frequency vibrational modes of phosphonitrilic chlorides have been assigned as \( PCl_2 \) wagging and torsional modes.\(^{50} \) For example, for \( (NPCl_2)_3 \) with three oscillating groups, equation (4-1) must be modified to

\[
P_{a3} = \frac{36\pi N\nu^2}{9V_o} \tag{4-2}
\]
This equation still contains two unknowns (\(N\) is Avogadro's number), \(u\) and \(v_0\). The procedure here is to estimate \(u\), the moment of the \(\text{PCl}_2\) group, and calculate \(v_0\) from the measured value of \(P_a\). The moment of the \(\text{PCl}_2\) group is expected to be of the order of 1-2 Debye units. Using the value for \(u\) of 2.0 Debye units, a value for \(v_0\), the force constant, is \(1.7 \times 10^{-12}\) erg/radian². A force constant of this magnitude can be attributed to one or more vibrations in the region of 150-200 cm⁻¹. Infrared active vibrations in this region have been recorded (see Table III) and this evidence strengthens the hypothesis of the existence of high atom polarization for phosphonitrilic compounds.

**Orientation Effects in Phosphonitrilic Chloride-Fluorides**

The acceptance of the above explanation of atom polarization and its effect on phosphonitrilic compounds implies two things, first that it is possible to calculate a polarization per \(\text{PX}_2\) group for the chlorides and the fluorides and second, that such data could be used to help distinguish between geminally substituted isomers, for example those shown in Figure 1-3. In Table IV are shown the polarizations per \(\text{PX}_2\) group calculated from some of the phosphonitrilic halide results given in Chapter III.

If a vector analysis of the geminal compounds \(\text{N}_3\text{P}_3\text{F}_2\text{Cl}_4\) and \(\text{N}_3\text{P}_3\text{F}_4\text{Cl}_2\) is carried out, it can be shown that they should have the same dipole moments. The ring skeleton is almost planar so that the NPN internal angles are 120°. The \(\text{PX}_2\) group moments may be treated as vectors bisecting the NPN external angles in the plane of the ring, and can be thought of as shown in Figure 4-1.
Table IV. Polarization per Monomer Unit Calculated for Some Phosphonitrilic Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>Distortion polarization (cc)</th>
<th>Polarization per PX₂ group (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NPCl₂)₃</td>
<td>3</td>
<td>17.6</td>
<td>5.9</td>
</tr>
<tr>
<td>(NPCl₂)₄</td>
<td>4</td>
<td>31.3</td>
<td>7.8</td>
</tr>
<tr>
<td>(NPF₂)₃</td>
<td>3</td>
<td>4.4</td>
<td>1.5</td>
</tr>
<tr>
<td>(NPF₂)₄</td>
<td>4</td>
<td>13.4</td>
<td>3.4</td>
</tr>
<tr>
<td>(NPF₂)₅</td>
<td>5</td>
<td>17.2</td>
<td>3.4</td>
</tr>
<tr>
<td>(NPF₂)₆</td>
<td>6</td>
<td>21.9</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Figure 4-1 Dipole vector diagram for N₃P₃F₆Cl₂ and N₃P₃F₄Cl₂
Now for $N_3P_3F_2Cl_4$,

\[
\mu_{\text{Hor}}(PCl_2) = 0 \\
\mu_{\text{Vert}}(PCl_2) = 2\mu(PCl_2)\cos60° \\
= 2\mu(PCl_2) \cdot 1/2 \\
= \mu(PCl_2) \\
\mu(N_3P_3F_2Cl_4) = |\mu(PF_2) - \mu(PCl_2)|
\]

For the other compound, $N_3P_3F_4Cl_2$,

\[
\mu_{\text{Hor}}(PF_2) = 0 \\
\mu_{\text{Vert}}(PF_2) = 2\mu(PF_2)\cos60° \\
= 2\mu(PF_2) \cdot 1/2 \\
= \mu(PF_2) \\
\mu(N_3P_3F_4Cl_2) = |\mu(PCl_2) - \mu(PF_2)|
\]

However the two compounds have different measured distortion polarizations, for the difluoride the value is 30.1 cc. and for the tetrafluoride the value is 26.6 cc. If the atom polarization is eliminated from each compound, then the residual polarization will be due to the dipole moment of the compound. Using the symbol $P_o$ for orientation polarization as before, then

\[
P_o(N_3P_3F_2Cl_4) = P(N_3P_3F_2Cl_4) - P_a(PF_2) - 2P_a(PCl_2) \\
= 30.1 \text{ cc} - 1.5 \text{ cc} - 2(5.9 \text{ cc}) \\
= 16.8 \text{ cc}
\]
\[ F_0(N_3P_3F_4Cl_2) = P(N_3P_3F_4Cl_2) - 2P_a(PF_2) - P_a(PCl_2) \]
\[ = 26.6 \text{ cc} - 2(1.5 \text{ cc}) - 5.9 \text{ cc} \]
\[ = 17.7 \text{ cc} \]

The dipole moments for the molecules may be calculated from the equation

\[ \mu = 0.01281 \times 10^{-18} \sqrt{\rho_T} \quad (4-3) \]

For the difluoride, \( \mu = 0.91 \) D and for the tetrafluoride \( \mu = 0.93 \) D. Within the usual experimental error of \( \pm 0.05 \) D these numbers are the same.

For the tetrameric mixed chloride-fluorides studied, a slightly different problem must be discussed. It is known that substitution of chlorine by fluorine in phosphonitrilic chlorides proceeds in a geminal manner,\(^{51}\) that is after the first chlorine atom is replaced by a fluorine, the second chlorine replaced will be attached to the same phosphorus atom, in other words the replacement sequence is

\[ \text{PCl}_2 \rightarrow \text{PClF} \rightarrow \text{PF}_2 \]

Therefore, when fluorinating a phosphonitrilic chloride it is known that all the compounds with an even number of fluorines are geminal. For the compounds \( N_4P_4F_4Cl_4 \) there are two possibilities as shown in Figure 1-3 in Chapter I; the compound may be either the 1,1,3,3-isomer or the 1,1,5,5-isomer. The \(^{19}F\) NMR spectra for compounds of this type
are very complex and are not amenable to a first order treatment, therefore NMR cannot be used as a way of distinguishing one isomer from the other. By examining the NMR spectra of the compounds, $N_4P_4F_5Cl_3$ and $N_4P_4F_3Cl_5$ prepared in the same reaction, Emsley and Paddock reached the conclusion that $N_4P_4F_4Cl_4$ was the 1,1,3,3-isomer. From dipole moment data it should be possible to differentiate the two possibilities. The atom polarization for the $N_4P_4F_4Cl_4$ molecule may be determined in the same way as was done above for the trimeric compounds and then compared to the measured distortion polarization. If they are equal, then the orientation polarization of the compound is zero, the compound has a zero dipole moment and therefore must be the 1,1,5,5-isomer. If on the other hand the calculated and measured polarization values are unequal, then the compound has a dipole moment and is the 1,1,3,3-isomer. The calculation is as follows.

$$P_0(N_4P_4F_4Cl_4) = P(N_4P_4F_4Cl_4) - 2P_0(PF_2) - 2P_0(PCl_2)$$

$$= 43.5 - 2(3.4) - 2(7.8)$$

$$= 43.5 - (6.8 + 15.6)$$

$$= 21.1 \text{ cc}$$

The values of $P_0(PF_2)$ and $P_0(PCl_2)$ were chosen as the ones calculated from the tetrameric fluoride and chloride respectively in order to eliminate any possible ring size effect. The result of the above calculation supports strongly the conclusion that the $N_4P_4F_4Cl_4$ compound whose polarization was measured is the 1,1,3,3-isomer.
A similar analysis for the pentameric compound $N_5P_5F_6Cl_4$ cannot be completed because changes in the configuration of the pentameric ring could mask changes in orientation of substituents. For the two pentameric phosphonitrilic halides for which X-ray diffraction studies have been reported, a calculation by Hartsuiker and Wagner shows that $N_5P_5Cl_{10}$ can theoretically adopt the "heart-shaped" configuration adopted by $N_5P_5Br_{10}$ and that $N_5P_5Br_{10}$ could theoretically take the shape adopted by $N_5P_5Cl_{10}$, which is shown in Figure 4-2. The structure for $N_5P_5Br_{10}$ is shown in Figure 4-3. The X-ray studies showed that each molecule only adopted its own configuration in crystals. Without a knowledge of the configuration of the ring for $N_5P_5F_{10}$ and for $N_5P_5F_6Cl_4$, an analysis to determine which of two possible isomers of the $N_5P_5F_6Cl_4$ was measured is impossible.
Conclusions and Suggestions for Further Work

In conclusion, two results have been obtained from this work. First it has been shown that Guggenheim's approximation that atom polarization is proportional to molecular volume does not apply to the phosphonitrilic halides. For the phosphonitrilic chlorides and fluorides, atom polarization is a significant factor in the total distortion polarization and proper allowance must be made for it. Second, evidence has been given to strongly support the hypothesis that the compound $N_4P_4F_4Cl_4$ made by the reaction of $N_4P_4Cl_8$ and $KSO_2F$ under heat and reduced pressure is the 1,1,3,3-isomer.

For further work, a line of approach that could prove illuminating is to obtain the far infrared spectra of the phosphonitrilic fluorides and the higher phosphonitrilic chlorides. Force constants obtained from an analysis of such spectra could be used to verify and predict atom polarizations of these and related compounds.
Appendix A

There are a number of different systems of nomenclature for the compounds referred to in this thesis as cyclic phosphonitriles. The names "phosphonitrilic" or "phosphonitrile" are the oldest, and for the more simply substituted compounds have the advantages of being short and readily comprehensible. Two other nomenclature systems exist, the IUPAC system and the system used by such authors as Allcock. 52 The IUPAC system would name $N_3P_3F_6$ as 2,2,4,4,6,6-hexafluoro-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine. This system has gained little popularity among workers in the field. The other system denotes compounds containing the structural unit

$$(-P=\text{N})_R R'$$

as phosphazenes, where the phosphonitrilics are considered to be polymers and derivatives of the hypothetical compound phosphazene, $H_3P=NH$. A ring system is given the prefix "cyclo" and the number of monomer units in the ring is referred to by one of the prefixes "tri", "tetra" and so on as appropriate. The convention used for numbering the ring atoms is to start the numbering at phosphorus, which then gives the substituents the lowest possible numbers. By this convention, $N_3P_3F_6$ is called 1,1,3,3,5,5-hexafluorocyclotriphosphazene. The older naming system was used in this thesis because of its wide use in the literature and because of its simplicity.
Appendix B

At this time, in scientific literature there are still several systems of units used to label physical quantities. Though journals in physics and chemistry no longer use the British Imperial system of units, there are other systems still in use based on metric measurements. For dipole moments and other properties that may be classed under the general heading of electrical, the system used in the past was the non-rationalized three-quantity centimeter-gram-second system. It is now recommended that all physical and chemical data be expressed in the rationalized four-quantity meter-kilogram-second-ampere system, which is referred to as Systeme Internationale or SI for short. To be thorough, this requires rederiving most equations, but if such derivations are carried out the old and new equations can be compared and conversion factors for derived quantities can be calculated. This has been done for dipole moments by Hoppe. For the polarization, Hoppe obtains

\[ P = \frac{(\varepsilon - 1)}{2(\varepsilon + 2)} \cdot \frac{M}{d} = \frac{N_\alpha}{3\varepsilon_o} + \frac{N_N^2}{9\varepsilon_o kT} \]

where \( \varepsilon_o \) is the permittivity of a vacuum and \( \varepsilon \) is the relative permittivity of the dielectric. The SI units for some quantities important in dipole moment calculations are:

- \( \mu = \text{dipole moment: coulomb-meter} \)
- \( P = \text{polarization: m}^3\text{-mole}^{-1} \)
- \( \varepsilon_o = \text{permittivity of a vacuum: farad-meter}^{-1} \)
- \( \varepsilon = \text{relative permittivity of dielectric: dimensionless} \)
- \( \alpha = \text{polarizability: farad-meter}^2 \)
The conversion factor for the dipole moment is

$$1 \text{ Debye} = 3.35640 \times 10^{-30} \text{ coulomb-meter.}$$

No attempt has been made in this thesis to work in SI units, in order to facilitate comparison with the older literature.
REFERENCES

4. J. Liebig, Annalen, 11, 139 (1834).


27. See Reference 11, page 264.

28. See Reference 17, page 420.


