PhD Thesis
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ASPECTS OF THE CHEMISTRY OF COMPOUNDS CONTAINING (PNP), (PNS) AND (SNS)

Preparation of mixed phosphonitrile-sulfonitrile systems has been explored. A new preparation of *cyclo*-dichlorophosphonitrilebis(oxochlorosulfonitrile), $NPCl_2(NSOCl)_2$, based on pyrolytic decomposition of the product of reaction between amidosulfuric acid and trichlorophosphonitriletrichlorophosphonium hexachlorophosphate, $[Cl_3PNPCl_3][PCl_6]$, has been studied and the mixed ring product further characterized. Aminodiphenylphosphonitrile-aminodiphenylphosphonium ion, $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+$, forms copper(II) and cobalt(II) chloride salts which have been characterized by spectrometry. The solid state infrared spectra of linear phosphonitriles containing (PNP) and (PNS) have been assigned and interpreted for structural information.

Molecular d orbital exponents were determined for Π-bonded phosphorus and sulfur atoms in halosubstituted phosphonitriles and sulfonitriles using an approximation derived from the exchange energy dependence on the two-center, one-electron overlap integral for a localized bond. Exponents for d_{xz} and $d_{x^2-y^2}$ range from 0.92 to 1.18, while the d_{z^2}, d_{yz} and d_{xy} orbitals are uncontracted. The relationship of overlap value to bond covalent energy was used to evaluate the optimization and to interpret the chemistry of these compounds.

SHORT TITLE:

CHEMISTRY OF (PNP), (PNS) AND (SNS) COMPOUNDS

ASPECTS OF THE CHEMISTRY OF COMPOUNDS CONTAINING (PNP), (PNS) AND (SNS)

by

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ABSTRACT

Routes for the preparation of mixed phosphonitrile-sulfonitrile systems have been explored. A new preparation of *cyclo*-dichlorophosphonitrilebis(oxochlorosulfonitrile), $NPCl_2(NSOCl)_2$, based on pyrolytic decomposition of the product of reaction between amidosulfuric acid and trichlorophosphonitriletrichlorophosphonium hexachlorophosphate, $[Cl_3PNPCl_3][PCl_6]$, has been studied. The mixed ring product has been further characterized by infrared and ^{35}Cl nuclear quadrupole resonance spectrometry and related to the parent ring compounds.

The compounds, $[L]_2[CoCl_4]$, $[L]_2[CoCl_4].CH_2Cl_2$, $[L]_2[Cu_2Cl_6]$ and $[L]_2[Cu_2Cl_6].2CH_3OH$ (where L is aminodiphenylphosphonitrileaminodiphenylphosphonium ion, $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+$), have been prepared and characterized from vibrational and electronic spectra as ionic compounds of a general series of quaternary amine salts of transition metal halide anions.

The solid state infrared spectra of linear phosphonitriles containing (PNP) and (PNS) units have been assigned and interpreted for structural information: From phosphorus-chlorine stretch assignments for the trichlorophosphonitrile group, $Cl_3P=N-$, the phosphorus site symmetry is C_s rather than C_{2v}. $[Cl_3PNPCl_3][PCl_6]$ exists in two solid state forms with a probable cation configuration of distorted C_{2v} for both.

An approximate expression for optimization of orbital exponents was derived from the exchange energy dependence of the two-center, one-electron overlap integral for a localized bond. Optimum molecular 3d orbital exponents were determined for Π bonded phosphorus and sulfur atoms in phosphonitriles and sulfonitriles. Exponents for d_{xz} and $d_{x^2-y^2}$ range from 0.92-1.10

and 0.97-1.18 for chlorides and fluorides, respectively; while the molecular d_{z^2}, d_{yz} and d_{xy} orbitals are uncontracted. Π bond structures were investigated using molecular exponents in the calculation of bonded overlap values. The relationship of these values to covalent molecular and bond energies was used to evaluate the optimization expression and to interpret the structure and chemistry of phosphonitriles and sulfonitriles. The PNP chain angle of $[Cl_3PNPCl_3]^+$ in a C_{2v} configuration was estimated as 150-155 degrees.

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I. INTRODUCTION

I.1 Scope of the Work

Both phosphorus and sulfur are third-row elements and within the framework of either molecular orbital or valence bond theory, when used with an atomic orbital basis, the availability and involvement of d orbitals in their bonds with other atoms could account for much of their chemical behavior. The very active interest in compounds of phosphorus and sulfur with nitrogen has been motivated mainly by two possibilities: one, that of preparing new compounds of useful technological application; and two, that of obtaining more insight into the types of bonding which phosphorus and sulfur atoms can attain in the sense of expanded coordination or delocalized multiple bonds. This research project was undertaken in the same vein and particularly for the latter reason.

The project was a twofold attack: an experimental, preparative attempt to prepare mixed systems of sulfur and phosphorus compounds with nitrogen (II); and a quantum chemical attempt to investigate the bonding in such systems (III).

I.2 Nomenclature

The nomenclature of inorganic systems is decidedly unsystematic. And the nomenclature of compounds of phosphorus and sulfur halides with nitrogen is no exception. Even in this relatively narrow field, a comprehensive system encompassing groups such as $-N=P<$, $-N=S(O)<$ and $-N=S<$ in rings or chains is lacking.

Two systems are presently widely used for polymeric compounds made up of units of -N=P$\lessgtr$. They are referred to as phosphazenes[1] or as phosphonitriles[2]. For example, the compound in Figure I-1 would be named 2,4,6-tris(dimethylamino)-2,4,6-tris(methylamino)-*cyclo*-triphosphazatriene in the phosphazene system, or 1,3,5-tris(dimethylamino)-1,3,5-tris(methylamino)-*cyclo*-triphosphonitrile in the other. The phosphonitrile system is more familiar since it has been employed longer, but this is not sufficient reason to prefer it over a less complex or more easily extended system. Both have the ability to distinguish the extent of cyclic polymerization, but neither is easily extended to include linear compounds although perhaps the phosphonitrile system is better in this respect. The naming of ionic linear compounds, such as $[Cl_3PNPCl_3]Cl$, in some way to indicate the known equivalence of the phosphorus atoms is a problem for both. Neither has an analogy in the familiar nomenclature for sulfur-nitrogen containing polymers. Polymeric ring halides of -N=S(O)< and -N=S< units have been called sulfanuric and thiazyl halides, respectively. In comparison with the phosphorus-nitrogen polymeric system, there are fewer examples known. On the other hand, there are many compounds containing sulfur-nitrogen bonds not formally multiple, and a comprehensive nomenclature should be capable of including these as well.

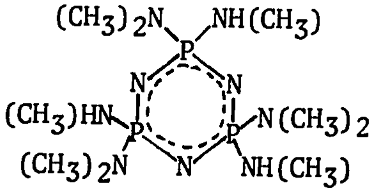


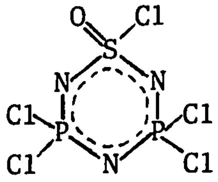
Figure I-1 A Cyclic Phosphonitrile

In this work, the arbitrary choice has been made to refer to derivatives of the -N=P⩽ unit as phosphonitriles, except when the nitrogen atom is directly bonded to a sulfur atom or an -N=S< unit as part of a chain or ring. Covalent linear systems are named as the appropriate phosphonitrile derivatives of the end groups; e.g., $Cl_3PNP(O)Cl_2$ is trichlorophosphonitrilephosphoryldichloride. Ionic linear systems are named to conform with IUPAC rules[3] for ionic compounds between non-metals; e.g., $[Cl_3PNP(Cl)_2NPCl_3][PCl_6]$ is chlorobis(dichlorophosphonitrile)trichlorophosphonium hexachlorophosphate.* Derivatives of the -N=S< unit are referred to as sulfonitriles, in general. In particular, the familiar names are used for the cyclic polymers; e.g., the α-isomer of formula $(NSOCl)_3$ is called α-sulfanuric chloride trimer.

'Mixed' systems are defined as a combination in rings or chains of two different atoms alternating with nitrogen. Rings composed of units of phosphonitrile and sulfonitrile types are called mixed phosphorus - sulfur rings. This then implies the presence of alternating nitrogen atoms in the skeleton. Mixed phosphorus - sulfur rings are named as combinations of the phosphonitrile and sulfonitrile parts; e.g., the hypothetical ring compound of Figure I-2 is called *cyclo*bis(dichlorophosphonitrile)oxochlorosulfonitrile.

* It might be better to refer to such a compound using a bridging designation: Bis(trichlorophosphorus-μ-nitrido)dichlorophosphonium hexachlorophosphate, but this would remove it from the familiar phosphonitrile system used for the other -N=P⩽ polymers and has not been adopted for that reason.

Figure I-2 A Mixed Ring, $(NPCl_2)_2NSOCl$



For the naming of other compounds, an attempt has been made to conform to IUPAC rules where possible. For the sake of familiarity, sulfuryl chloride and thionyl chloride are used for SO_2Cl_2 and $SOCl_2$, and Kirsanov's compound, Cl_3PNSO_2Cl, is called trichlorophosphazosulfonyl chloride.

I.3 Chemistry of Phosphonitriles and Sulfonitriles

I.3.1 Phosphonitriles

In general, compounds containing phosphorus-nitrogen bonds are prepared from substitution of chlorophosphoranes by $-NH_2$ or >NH containing ligands. A comprehensive review of the types of reactions resulting with amines, amides, hydrazines, etc., has been compiled by Becke-Goehring[4]. Reaction with ammonia or ammonium salts produces linear or cyclic phosphonitriles. Chlorophosphonitriles, which are the starting materials for most of the routes to other derivatives, are prepared from the reaction between phosphorus pentachloride and ammonium chloride. The products consist of a mixture of cyclic homologues, $(NPCl_2)_n$, n=3 to 17, and low chain length linear polymers. The cyclic portion is soluble in petroleum ether and can be separated from the oily linear fraction by extraction. The lower cyclic members can be isolated through fractional crystallization and sublimation. Typically, when the reaction occurs in high-boiling 'non-polar' solvents, such as *sym*-tetrachloroethane, with an excess of ammonium chloride, a ninety percent yield of cyclic product is obtained with n=3 and 4 predominant[5,6]. On the other hand, if polar solvents, such as nitrobenzene, and a controlled ratio of phosphorous pentachloride to ammonium chloride are used, the linear fraction predominates. For example, with 3:1 $PCl_5:NH_4Cl$, as much as eighty-five percent of $[Cl_3PNPCl_3][PCl_6]$ can be isolated[7]. A mechanism for the reaction has been proposed[8] and discussed[9,10]. It is suggested that an initial step is donor-acceptor addition of the nucleophilic ammonia to a tetrachlorophosphonium cation. Subsequently, further donor-acceptor reactions occur to extend the chain of phosphorus and nitrogen atoms until eventual cyclization can occur. If excess phosphorous pentachloride is present, cyclization is hindered by the formation of possibly ionic linear molecules of the type $[Cl(Cl_2PN)_nPCl_3][PCl_6]$.

Phosphonitrile reactions are typically non-stoichiometric with the accompanying problems of work-up which that implies. The most striking feature of phosphonitrile chemistry is that the system is an inorganic example of one which is as varied, while at the same time as closely interrelated characteristically, as organic systems. The cyclic halide homologues are remarkably stable to hydrolysis compared with other phosphorous halides. They polymerize above 250°C in the presence of phosphorous pentachloride to a linear polymeric product with the elastic characteristics of rubber, or in combination with metal chlorides to an oily product with good high temperature stability. Above 350°C, the high polymer depolymerizes to a mixture of cyclic polymers.

Linear phosphonitriles are much more susceptible to hydrolysis than cyclic phosphonitriles. This has resulted in a less comprehensive range of compounds studied, since they are difficult to handle experimentally. It was first suggested that they were compounds of the general series, $Cl(Cl_2PN)_nH$ n=10-15 [17]. Other attempts to characterize this fraction indicated that the series could be represented, $Cl(Cl_2PN)_nPCl_4$[5,8]. No members of the first type have been isolated, although aryl and alkyl derivatives, such as $C_6H_5NPCl_3$[18,19], have been described. Apparently no members of the second type have been isolated either. Rather, individual members of an ionic series, $[Cl(Cl_2PN)_nPCl_3][Y]$, have been characterized: $Y=Cl^-$ [7,20], PCl_6^- or BF_4^- [23], $SbCl_6^-$ [9,24] for n=1 and/or 2; and $Y=PCl_6^-$, BCl_4^- or $AlCl_4^-$ [25] for n=3,4. The ionic series represents a broad range of compounds since examples are known where some or all of the chlorine atoms are replaced by groups such as phenyl, amino and methylamino[26,27,28]. From reactions other than the general preparative one for chlorophosphonitriles, compounds of a covalent series, $Cl(Cl_2PN)_nY$; $Y=POCl_2$ or $PSCl_2$, have been prepared for n=1 or 2[7,20,21]. Phenyl derivatives of this series are also known for n=1,3 or 4[22].

Polymerization of phosphonitriles has been reviewed[11,12,13]. Several general reviews of phosphonitriles have been published since the first in 1943 [2]. A more up-to-date and complete account of the synthetic methods used, with particular emphasis on the cyclic halides and their derivatives can be obtained from two reviews by Shaw[11,14]. Preparation of mixed derivatives provides opportunity to study the types of isomerism possible for cyclic phosphonitriles and an extensive discussion of this by Corbridge is available[15]. The review by Schmulbach[12] is an excellent survey of structural and chemical information for both cyclic and linear phosphonitriles. A short account of some possibly general linear series for which examples have been characterized can be found in the review by Corbridge, while a review by Fluck[16] contains a good account of the preparation and chemistry of the ionic linear series.

Table I-1 Properties of some linear phosphonitriles.

Compound		mp°C	$\nu(PN)^a$, $\nu(PCl)$, $\nu(P\underset{S}{O})$	^{31}P δ^b	Comments and IR reference
1) $[Cl_3PNPCl_3]Cl$	7	225	1338,614		[110]ionic $n=1, Y=Cl^-$
2) $[Cl_3PNPCl_3][PCl_6]$	7	310	1298,653	-21.4	[110]ionic $n=1, Y=PCl_6^-$
3) $[Cl(Cl_2PN)_2PCl_3][PCl_6]$	20			-12.5,+13.6	ionic $n=2, Y=PCl_6^-$
4) $Cl_3PNPOCl_2$	20	36	1332,560,1261	+0.1,+14.2	[108]covalent $n=1, Y=POCl_2$
5) $Cl(Cl_2PN)_2POCl_2$	20	34		-7.1,+13.4, -20.0	covalent $n=2, Y=POCl_2$
6) $Cl_3PNPSCl_2$	20	35	1305, ,680	+2.9,-28.2	[107]covalent $n=1, Y=PSCl_2$
7) $Cl(Cl_2PN)_2PSCl_2$	20	23		-6.0,+20.6, -30.2	covalent $n=2, Y=PSCl_2$
8) $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$	26	246		-20.3	subst.ionic $n=1, Y=Cl^-$

a) cm^{-1} b) ppm from 85% H_3PO_4, [106] except 7)[209] and 8)[109], δ PCl_6^- = +305.

Table I-2 Properties of some cyclic halophosphonitriles.

Compound	mp°C	bp°C	ν(PN$^{a)}$	ν(PX)	^{31}P δ $^{b)}$	IR reference,$^{c)}$ configuration
1) $(NPF_2)_3$ ^{104}	28	51	1290	960,890	-13.9	^{101}ii planar
2) $(NPF_2)_4$ ^{104}	30	90	1438	(790)		^{104} i planar
3) $N_3P_3(C_6H_5)_2F_4$ ^{97}	69		1250 1265	916,890 914,900	-12.1^{97}	^{97} i slight boat ii
4) $(NPCl_2)_3$ ^{210}	114	256	1212	611,530	-20	^{101}ii slight chair
5) $(NPCl_2)_4$ $\bar{1}$ $^{d)}$ ^{210}	124	328	1325 1297	595,517	+7	^{127}iii chair type ii
6) $(NPCl_2)_4$ $\bar{4}$ $^{d)}$ ^{210}			1295	590,520		^{127} ii boat type
7) $(NPCl_2)_5$ ^{211}	41		1354	601,535	+17	^{100} i puckered planar
8) $N_3P_3Cl_5F$ ^{213}	50	215	1230	606,533		^{101}ii slight chair
9) $N_3P_3(C_6H_5)_2Cl_4$ ^{212}	95		1220			^{12} slight chair
10) $N_3P_3(C_6H_5)_4Cl_2$ ^{212}	142					slight boat

a) ν(PN)≡highest strong band assigned; $\nu(PX) \equiv \nu_{as}, \nu_s$; cm^{-1}.

b) ^{5} except where noted; ppm from 85% H_3PO_4.

c) i,solution; ii,solid; iii,vapor. d) $\bar{1}$,T form; $\bar{4}$,K form.

I.3.2 Sulfonitriles

Sulfur tends to form six- and eight-membered ring systems, whether made up solely of sulfur or of alternating sulfur and nitrogen atoms. This behavior has been discussed by Becke-Goehring[31,32], though reasons for it have not been established. Many rings containing dicoordinate-divalent sulfur, and also several containing tricoordinate-tetravalent or tetracoordinate-hexavalent sulfur, are known. In addition to a preparative motivation, the possible 'existence' of multiple ring bonds in the first type, and localized or delocalized multiple bonds in the latter types, has prompted recent renewed interest. Properties of the ring compound, tetrasulfurtetranitride, S_4N_4, have been discussed by Allen[33]. Recent reviews of sulfur-nitrogen-halogen compounds[34], particularly fluorides[35], are available.

In contrast to the extensive cyclic phosphonitrile system, only a few examples of cyclic sulfonitriles are known and all but one are six-membered. The parent acid system, -N=S(OH)O-, is not known, but Kirsanov isolated two isomers of the chloro derivative, the sulfanuric chloride trimers, α- and β-$(NSOCl)_3$, from the products of a pyrolytic decomposition of trichlorophosphazosulfonyl chloride[36]. The same ring can be prepared in low yield (≈4%) from chlorination by thionyl chloride of the product of the reaction of sulfuryl chloride with ammonia, sulfonyl diamide, $SO_2(NH_2)_2$[37]. Isomers of the trimeric fluoride can be obtained through fluorination of α-sulfanuric chloride trimer[38,39]. No eight-membered rings of the -N=S(O)< type are known.

Thiazylchloride, NSCl, can be prepared from chlorination of tetrasulfurtetranitride[215] or from reaction of thionyl chloride with metastable thiazyl-S-hydroxide, NSOH[41]. It rapidly polymerizes to the six-membered ring, *cyclo*-trithiazylchloride, $(NSCl)_3$. On the other hand, thiazylfluoride, NSF, is much more stable and can be prepared by reaction of mercury fluoride with tetrasulfurtatranitride in boiling carbontetrachloride[42,43]. On standing, it polymerizes to *cyclo*-trithiazylfluoride, $(NSF)_3$. An alternative route to this trimer is fluorination of *cyclo*-trithiazylchloride[215]. Mild fluorination of tetrasulfurtetranitride produces the tetramer of thiazylfluoride, $(NSF)_4$[44], which is the only eight-membered cyclic sulfonitrile known. The tetramer can be depolymerized to monomeric thiazylfluoride[45] (as can the trimeric thiazylchloride to its monomer, NSCl[46]), but the monomer, NSF, polymerizes spontaneously, and only, to the trimer.

A ring composed of thiazyl and sulfanuric units, *cyclo*-bis(chlorosulfonitrile)oxochlorosulfonitrile, $(NSCl)_2NSOCl$, has been isolated from chlorination of thiodithiazyldioxide, $S_3N_2O_2$[47]. Fluorination of this ring with silver fluoride in carbontetrachloride results in substitution at the two tricoordinate-tetravalent sulfur atoms, while the tetracoordinate-hexavalent sulfur atom is not affected. Substitution reactions, other than fluorination, of one each of the sulfanuric chloride and fluoride isomers have been investigated[38]. Substitution can be effected under very mild conditions, i.e. when the attacking agent is only weakly basic; otherwise, ring cleaveage occurs. Another reaction which leaves the ring intact is conversion of *cyclo*-trithiazylchloride to sulfanuric chloride trimer through addition of sulfurtrioxide and subsequent oxidation[48].

As for the cyclic case, there are few linear sulfur-nitrogen systems known which are not amides or imides. Polymeric sulfanuric fluoride, $(NSOF)_n$, has been reported[49], and polymeric thiazylbromide, $(NSBr)_n$, has been mentioned[50]. Compounds with the proposed ionic structure, $[R_2S{=}N{=}SR_2]X$, have been reported for $R{=}CH_3; X{=}Cl,Br$[51-53] and $R{=}C_6H_5; X{=}Cl,NO_3,I$[54]. Other isolated examples of linear sulfonitriles are dichlorosulfonitrilesulfonyl fluoride, Cl_2SNSO_2F, and its fluorine analogue, F_2SNSO_2F[55].

Table I-3 Properties of some sulfonitriles.

Compound	mp°C	Comments
1) $(NSF)_3$ [42,215]	74	^{19}F δ = 147 ppm (KF)[216]
2) $(NSF)_4$ [42,214]	153,d >128	puckered, alternating bonds ^{19}F δ = 155 ppm (KF)[216]
3) $(NSOF)_3$ [38,39]	*cis* 16	
	trans -12	
4) $(NSCl)_3$ [45,215]	162	chair, Cl's axial
5) $(NSOCl)_3$ [36,71]	α 145	chair, Cl's axial
	β 47	chair, one Cl equatorial
6) $(NSCl)_2NSOCl$ [47]	110	
7) $[R_2SNSR_2]Cl$ [54]	$R=CH_3$ 153	ionic
	$R=C_6H_5$ 182	

I.3.3 Comparison of Phosphonitriles and Sulfonitriles

The most noticeable difference in chemistry between the two systems is that the known sulfonitriles are not prepared from a reaction which can be controlled to produce either cyclic homologues or linear homologues or both, as for phosphonitriles. Also, the cyclic thiazyl halide compounds are more susceptible to hydrolysis than the cyclic phosphonitrile halides. In marked contrast to the phosphonitriles, nucleophilic or electrophilic substitution reactions of the sulfonitriles in which the rings remain intact are more restricted. Cyclic sulfonitrile halides apparently do not polymerize to long chain systems as cyclic phosphonitrile halides do. Also, the depolymerization to the monomer unit for cyclic thiazylhalides seems to be unique. Neither a monomeric phosphonitrile halide nor a monomeric sulfanuric halide have been isolated. Except for $(NSF)_4$, which has alternating sulfur-nitrogen distances, hence 'localized' double bonds, only cyclic sulfonitrile fluorides where n=3 are known, while cyclic phosphonitrile fluorides have been isolated up to n=17. Thus, the sulfonitrile skeleton is chemically less stable than the phosphonitrile skeleton, although the relative lack of experimental effort so far directed specifically to discovery of new members of the sulfonitrile series may account for most of the chemical difference.

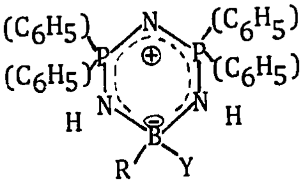
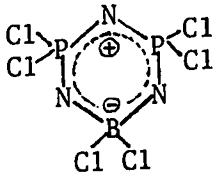
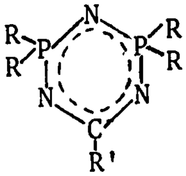
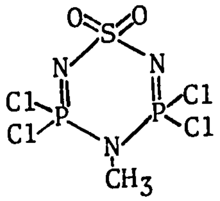
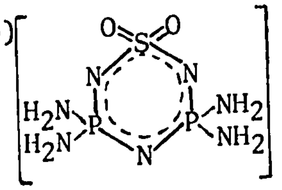
There are similarities between the two systems, however, such as the general existence of stable chains and rings. Structurally, the cyclic phosphonitrile halides have equal ring interatomic distances, and the molecules for which Xray structural determinations have been made are planar , or close to planar, except for the tetramer. Molecules of *cyclo*-trithiazylchloride and those of sulfanuric chloride are chair-shaped with equal ring interatomic distances. On the basis of ^{19}F nuclear magnetic resonance measurements, *cyclo*-trithiazylfluoride probably possesses a 'localized' double bond structure similar to that of *cyclo*-tetrathiazylfluoride[45]. The ring bond distances of the cyclic sulfonitrile chlorides and the cyclic phosphonitriles are short compared with single bond values, indicative of a delocalized Π bond system. This feature is the most striking similarity between the two series and a comparative understanding of the bonding might provide further understanding of their chemical properties.

I.3.4 Mixed Systems

The similarities between the sulfonitrile and phosphonitrile systems suggest that mixed systems could be stable. Examples of known mixed ring systems containing phosphonitrile units are shown in Table I-4. Except for one phosphorus-sulfur (Table I-4(3c)) and one carbon-phosphorus ring system, no Xray structural analyses have been reported, hence it should be noted that the cyclic structures implied in the figures are based on limited chemical and physical evidence.

The existence of long range $^{31}P-^{1}H$ coupling for molecules of the mixed linear carbon-phosphorus system, $[Cl_3PNC(R)NPCl_3][SbCl_6]$, suggests the cation charge is delocalized over the whole chain[65]. Apparently, no linear sulfur-phosphorus system containing a sulfonitrile unit has been reported. However, linear sulfur-phosphorus systems like that in trichlorophosphazosulfonylchloride are well-known. A general series of the type, $X(X_2PN)_nSO_2Y$, analogous to the covalent linear phosphonitriles might exist. Compounds of this type where n=1 are known (e.g., X=Cl,Y=Cl[66]; X=F,Y=F[67] and X=F,Y=Cl[68]). Replacement of two hydrogen atoms of an amino group by a trihalophosphorous group in a Kirsanov reaction[66] is a well-established preparative method for phosphonitrile units. Mixed linear sulfur-phosphorus systems can be prepared in this way from condensation products of sulfonyldiamide reactions[70].

Table I-4 Cyclic mixed systems.

System			mp°C	ref.	Reactants and reaction type
1. boron-phosphorus					
a) 	R	Y		56	$[H_2N(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$ + $RBCl_2$ or $RBBr_2$ ring closure of linear intermediate in solution
	Cl	BCl_4	204		
	Cl	Cl	303		
	C_6H_5	$B(C_6H_5)Cl_3$			
	C_6H_5	Cl	324		
	Br	BBr_3Cl	204		
b) 			142	57	$[Cl_3PNPCl_3][Cl]$ or PCl_5 + H_3CNH_3Cl + BCl_3 simultaneous cyclization of parent syntheses in solution
2. carbon-phosphorus	R	R′			$[Cl_3PNC(R')NPCl_3][SbCl_6]$ or $[ClR_2PNPR_2Cl][Cl]$ + $[H_2NC(NH)NH_2]Cl$ ring closure of linear intermediate in solution
	CH_3	$N(CH_3)_2$	132	58	
	C_6H_5	NH_2	214	59	
	C_6H_5	$N(CH_3)_2$	190	59	
	Cl	C_6H_5	92	60,61	
	Cl	CH_3	40	61	
	Cl	$N(CH_3)_2$	54	61	
3. sulfur-phosphorus					
a) 			177	63	$Cl_3PNS(O)_2NPCl_3$ + a) $H_3CN(Si(CH_3)_3)_2$ or NH_3 b) ring closure of linear intermediate in solution
b)  $[NH_4]$					
c) $NPCl_2(NSOCl)_2$ (Figure II-1)			96	64	Cl_3PNSO_2Cl pyrolysis

I.4 Bonding Models for Phosphonitriles and Sulfonitriles

I.4.1 Atomic Orbital Basis

There are many tricoordinate phosphorus and dicoordinate sulfur compounds where bond structure consistent with the Lewis octet theory of covalent bonding can be conceived. However, 'extended valence' compounds are not isolated examples and, for the most part, they are disconcertingly stable. The valence bond (VBMO) and the linear combination of atomic orbital molecular orbital (LCAO MO) theories of bonding, allow the use of 3d * orbitals in bond descriptions. Provided the binding energy achieved compensates for the promotion energy required to involve d orbital electrons in the valence state, hence that d orbitals of appropriate size, shape and electronic energy can be postulated, a satisfactory understanding of the bonding in expanded valence compounds is obtained. Interpretation within the VBMO formulation becomes a matter of making the appropriate combinations of covalent and ionic localized bond structures, where valence state electrons for P and S are in sp^3d and sp^3d^2 hybrid orbitals, respectively. LCAO MO theory uses all valence shell atomic orbitals in forming molecular orbitals, whether they are occupied in the atomic ground state or not. Most chemists do not realize the extent to which an atomic orbital basis formulation permeates chemical interpretation. Hybridization, d-p Π bonding, lone-pair repulsion, etc., are automatically invoked whenever one wishes to interpret or postulate structure or even reactivity at a molecular level. In fact,

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* In the remainder of the text, unless otherwise noted, s,p and d orbitals refer to the valence shell where the appropriate principal quantum number is implied.

the real success of either VBMO or LCAO MO theory lies in the conceptual grasp which the atomic orbital basis provides.

For any atomic orbital basis bonding model, the extent of participation of d orbitals unoccupied in ground state atomic configurations is difficult to assess. *Ab initio* quantum chemical calculations cannot be carried out on even the smallest molecules without considerable effort and expense, while attempts to assess d orbital participation using empirically parametrized methods are hampered by the need to know the results in order to obtain them. Further insight into d orbital parametrization is necessary before valid conclusions can be made apropos their participation in bonding.

I.4.2 Localized Bond Orbital Model

A localized bond orbital is defined as a two-centre, two-electron orbital. The VBMO approach to molecular wavefunctions is based upon the localized bond concept. It assumes that two isolated atoms combine by slightly altering their energies as bonding occurs. The ground state molecular wavefunction is therefore the antisymmetrized product of the isolated wavefunctions, while the energy is determined by a perturbation treatment.

Hybridized orbitals, for a single centre, have been used qualitatively to retain the localized bond concept in the LCAO MO approach. Recently, however, the concept of localized bond molecular orbitals has been investigated quantitatively within molecular orbital theory[161]. The highly delocalized single electron molecular orbitals may be transformed into a set of almost 'localized bond' orbitals which can be expressed as hybrids of the atomic orbital basis, providing the total determinantal wavefunction is unchanged[161,16].

There are an infinite number of such sets obtainable and the problem lies in choosing the transformation according to a desired 'localization criterion'. Symmetry considerations have traditionally been used, but where none are available, the localization must be determined in some other way. The constraint of partitionning the total electronic energy such that the maximum amount is placed in intra-orbital repulsion energy and minimum amount in inter-orbital repulsion energy conforms closely to the results obtained according to symmetry criteria[161,163].

I.4.3 A Bonding Model for Phosphonitriles and Sulfonitriles

A qualitative description of the bond structure of molecules with possible d-p Π bonding can be based on a localized bond concept for the molecular structure (σ bond framework), with the addition of 'delocalized' Π bonds formed by d orbital bonding participation[164-167]. Consider a phosphonitrile unit in a Cartesian coordinate system where the plane xy is defined by the NPN bonds and z is the axis of quantization for the phosphorus atom. (see Fig. III-1) The following discussion is concerned with contributions of orbitals of this segment to total ring molecular orbitals. The description is formulated for phosphonitriles and extended to sulfonitriles later.

To a first approximation, it is considered that the s and p valence electrons of the phosphorus and nitrogen atoms determine the bonds of cylindrical symmetry which form the σ bond system, and conform to the structural geometry in which a phosphonitrile unit or molecule exists. The question then becomes one of settling what multiple bonding could be involved, and several possibilities for it are distinguishable. The atomic orbitals from which other molecular orbitals could be formed include a set of phosphorus d orbitals which is not degenerate, since the highest site symmetry is C_{2v}, and hence, their relative contributions to bonding will not be equal. The restrictions imposed by the choice of a particular set, e.g., the conventional, real one, where z is the axis of quantization, are more than pictorial. Nevertheless, for a qualitative formulation, use of this set is acceptable.

<u>Π_a system</u> — Bonding in a system of Π symmetry with respect to the xy plane could occur through a combination of the nitrogen p_z orbital with phosphorus d_{xz} and/or d_{yz} orbitals for a planar ring[164,165]. Relative contribution of the d orbitals determines the extent of delocalization. For the special case where d_{xz} and d_{yz} contribute equally, the Π molecular orbital is a system of two-electron, three-centre 'islands' separated by a node at each phosphorus atom because of the orthogonality conditions imposed by the equal combination. Such a system has been described[166], but there is no reason to suppose that equal contribution would be likely. In this case the energy stabilization from delocalization per electron should be the same for all unit combinations regardless of number. For an unequal contribution of d_{xz} and d_{yz}, where d_{xz} predominates, cyclic delocalization would occur in a heteromorphic sense with Π stabilization energy per electron increasing steadily with increasing ring size. If d_{yz} predominates, the delocalization would be homomorphic, where the stabilization energy per electron would be greater for alternating ring sizes (n=odd>n+1=even). If the units form a non-planar ring or a linear chain, additional contributions from $d_{x^2-y^2}$ and/or d_{xy} are possible .

Π_s system — Another molecular orbital with Π symmetry can be constructed in the xy plane from the pseudo-trigonal nitrogen lone-pair orbital and appropriate phosphorus d orbitals. In a planar case, only d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals can contribute to this system, but for a non-planar case, all five d orbitals must be considered. For a cyclic Π_s system involving d_{xy} only, delocalization would be heteromorphic, while for one involving $d_{x^2-y^2}$ and/or d_{z^2} only, delocalization would be homomorphic.

Π_e system — In addition to the Π_a and Π_s systems described, it is possible that a Π system constructed from lone-pair orbitals of appropriate symmetry centered on exocyclic atoms and phosphorus d orbitals could be part of the bond structure.

Similar multiple bonding can be considered for sulfonitriles with the proviso that exocyclic Π bonding must be involved where oxygen is one of two sulfur substituents. To the extent that this exocyclic Π_e system competes with ring Π_a and Π_s systems for d orbital contribution or affects the relative d orbital energies, they will be modified.

I.4.4 Relative Contributions of Possible Π Bond Systems

The various bonding possibilities described provide a model only, and the actual electronic distribution is not necessarily related to it. However, structural evidence of multiple bonding is well-documented, although no firm conclusion has been reached concerning relative Π system contributions on this basis. Because of the shape of d orbitals, a d-p Π system is more flexible than a p-p Π system, allowing more distortion from the planar case before loss of Π stabilization energy becomes too great. Hence, bond angle considerations provide little more than a qualitative comparison, although variation in the relatively large angles observed for ring nitrogen atoms of tetrameric phosphonitrile derivatives has been cited to show the comparative strength of the Π_a system over that of the Π_s system[169].

For chloro and fluorophosphonitriles, a large difference in ^{31}P chemical shift is observed between tetramer and trimer, with only a slight increase for each succeeding ring of higher n. This was interpreted to mean that the Π_s system is weak in the trimer and of increasing importance as ring size increases[165]. ^{19}F chemical shifts for a series of pentafluorophenyl-fluorophosphonitriles suggest a homomorphic variation in conjugation between the exocyclic fluorophenyl ring Π system and a homomorphic Π_s phosphonitrile ring system effected mainly through the phosphorus d_{z^2} orbital[174].

Thermochemical evidence from heats of formation indicates only that the gain in stability from multiple bonding is ≈ 6-10 kcal/bond[168,169]. Values for relative heats of formation calculated from measured heats of polymerization for chlorophosphonitriles suggest that d_{xz} and d_{xy} predominate in the Π_a and Π_s systems, respectively, or that the Π_a system with d_{xz} is stronger than the Π_s system with $d_{x^2-y^2}$ [170]. The chlorophosphonitrile pentamer is a weaker base in sulfuric acid than either the tetramer or the hexamer[8]. It requires a greater activation energy for nucleophilic attack at the phosphorus atom than the tetramer but not the hexamer[172]. This suggests a stronger heteromorphic Π_a system, and that, given this assumption, the Π_s system is homomorphic. Further evidence for this Π system combination has been deduced from ionization potential measurements from mass spectra and from solubility measurements for HCl in solutions of halophosphonitriles[173].

Thus, the experimental evidence at present, while not conclusive, is consistent with a model of multiple bonding, at least for the phosphonitriles, which consists of a major contribution from a cyclic heteromorphic Π_a system (d_{xz}) and a less important contribution from a cyclic homomorphic Π_s system ($d_{x^2-y^2}$).

Theoretically, two characteristics determine the involvement of any atomic basis set orbital in a bond system molecular wavefunction — size and energy. When the basis set is composed of single-term, Slater-type atomic orbitals, the exponent, ξ, provides a direct measure of the relative size of the orbital as;

$r_{max} = n/\xi$ where n is the effective principal quantum number

r_{max} is the position of maximum orbital radius in bohr radii.

The sizes and energies of phosphorus and sulfur d orbitals in molecules have been the subject of much speculation, but little calculation since the initial suggestion that in molecular environments they might be sufficiently modified from the atomic values to allow bonding participation[175]. Only recently have reliable quantitative evaluations of such molecular effects been reported. Most calculations have been based on minimization of d orbital electron energy for various atomic configurations of phosphorus or sulfur in a molecular environment simulated by either a point charge field[176] or an approximate field derived from atomic wavefunctions[177]. In the presence of ligands, for neutral atoms, a P d orbital for sp^3d^1 configuration is weakly bound and diffuse[177,178], while a S d orbital in sp^3d^2 configurations contracts to nearly half its free-atom size[177]. In general, where there is more than one d orbital, or where the atom is positively charged or 'outer' orbitals are occupied, d orbital sizes are comparable to those of s and p orbitals. However, the energies of neutral atom orbitals, as determined in these calculations, remain small and unfavorable for bonding participation[179]. For outermost d orbitals of neutral atoms the effective potential energy experienced by a d electron exhibits an extremely shallow minimum with distance relative to that for an s or p electron in the same shell.

Since these investigations have been limited to free atoms in excited configurations, the molecular characteristics need further clarification. An electrostatic model based on the valence bond perfect pairing scheme[177] has been modified by Mitchell to investigate d orbitals in σ bonds for sulfur hexafluoride[180] and in Π bonds for phosphoryltrifluoride[181] and the cyclic planar phosphonitriles[182]. The basic electrostatic model predicts that all d orbital sizes in these environments could be suitable for substantial bonding participation, and that for an atom in a non-spherical 'molecular' field the single-center d orbital set would no longer be degenerate. A modification to include approximate exchange terms accounts for the effects of nonorthogonality between the optimized orbitals and non-bonded ligand orbitals, and predicts that the sizes of d orbitals are very sensitive to the specific characteristics of molecular environments. Some are contracted and important for bond participation, while others are diffuse.

The overlap value with orbitals on other centers is determined by the size of a d orbital, thus a criterion for d orbital contraction in molecular environments involves maximum bonding overlap and minimum nonbonding overlap. A test of this criterion and its use in determining appropriate molecular d orbital exponents for the investigation of relative amounts of d orbital Π bonding in sulfonitriles and phosphonitriles is reported in section III.

II. EXPERIMENTAL CHEMISTRY OF PHOSPHONITRILES AND SULFONITRILES

II.1 Preparation of Phosphorus-sulfur Mixed Systems

II.1.1 Preparation of Mixed Rings, General Considerations

Ring compound formation from linear intermediates is the culmination of a series of intermolecular addition steps, which produce a chain of sufficient or appropriate length to form the ring skeleton. This encompasses several possibilities: The starting materials could be small molecules (preparation of cyclic chlorophosphonitriles[9]), or intermediates of chain-length smaller than the eventual ring length (Table I-4,1.a), or the direct intramolecular cyclization of a linear chain molecule. For ring formation, the conditions will be a compromise between those which favor the intermolecular, chain-lengthening reaction steps, and those which favor the final intramolecular, ring-forming step.

When the starting compounds and reaction conditions for the preparation of parent system products are compatible, mixed systems could be formed through a simultaneous combination of both parent preparative reactions (Table I-4,1.b). However, the reported synthetic routes for cyclic halosulfonitriles are decidedly non-general in contrast to those for cyclic halophosphonitriles, and do not involve similar reaction conditions or starting materials. Thus, the prognosis for this approach is not hopeful.

An alternative method based on pyrolytic decomposition, such as that reported for the sulfanuric chloride trimers[66,71] or cyclic diphenylphosphonitriles[72], might be general. Ring formation occurs through decomposition of the starting material(s) into many fragments, under relatively high energy conditions, some of which may then re-combine to form mixed products, including rings. Thus, only low yields of the desired product could be expected, and a more difficult isolation problem would obtain, since many different reaction products are possible.

Preliminary results of an Xray structural analysis of a compound proposed to be the mixed ring, *cyclo*-dichlorophosphonitrilebis(oxochlorosulfonitrile), $NPCl_2(NSOCl)_2$, were reported in 1963[64]. The structure was later confirmed in a three-dimensional refinement[73]. The reported preparation was a pyrolytic decomposition of purified trichlorophosphazosulfonyl chloride (mp 32-36°C), at 8 mm, 146°C, and a reaction time of one and one-half hours under ultraviolet light. No further details were mentioned. Only the inclusion of ultraviolet light of unspecified wavelength differentiates this decomposition from one reported earlier to yield a mixture of cyclic sulfanuric chlorides[66], which was confirmed[71]. Initial attempts to duplicate the preparation reported were unsuccessful: So other cyclization attempts, both pyrolytic and in solution, were investigated for the isolation of this mixed ring or any other, with particular reference to completion of the series, $(NPCl_2)_3$, $\{(NPCl_2)_2NSOCl\}$, $NPCl_2(NSOCl)_2$, and $(NSOCl)_3$. *

II.1.2 Preparation of Mixed Ring, Skeleton $\overline{PNSNSN}$

Trichlorophosphazosulfonyl chloride, Cl_3PNSO_2Cl, and trichlorophosphonitriletrichlorophosphonium hexachlorophosphate, $[Cl_3PNPCl_3][PCl_6]$, were mixed under conditions of pyrolytic decomposition (reaction (2)).

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* Experimental details of typical procedures are outlined in II.2.3; the duplication attempt is included as reaction (1).

No reaction occurred. Since the starting compounds were widely different in nature, the former typically low-melting covalent, and the latter high-melting ionic, an additional attempt was made with more similar starting intermediates.

$$2\ Cl_3PNSO_2Cl + [Cl_3PNPCl_3][PCl_6] \overset{120\text{-}180^\circ,\ 2mm}{\not\longrightarrow} \qquad (2)$$

$$Cl_3PNSO_2Cl + Cl_3PNP(S)Cl_2 \overset{70\text{-}140^\circ,\ 2mm}{\not\longrightarrow} \xrightarrow{NH_4Cl,\ 140^\circ,\ 2mm} \text{polymeric residue} \qquad (3)$$

The simultaneous pyrolysis of trichlorophosphazosulfonyl chloride and trichlorophosphonitrile thiophosphoryldichloride, $Cl_3PNP(S)Cl_2$, was studied (reaction(3)). No cyclic or low-molecular-weight linear mixed compound could be isolated from the product, which was an intractable polymeric residue of increasing solidity, the higher the final pyrolysis temperature and longer the total reaction time.

Only cyclic trimeric sulfanuric chlorides could be obtained from the pyrolysis of purified trichlorophosphazosulfonyl chloride, so it was considered that, if addition occurs, it does so preferentially via the sulfur atom. Hence, an attempt was made to incorporate another phosphonitrile unit in the linear chain intermediate for pyrolysis starting material.

$$[Cl_3PNPCl_3][PCl_6] + H_2NSO_2(OH) \xrightarrow[(4)a]{100^\circ} \{Cl_3PNP(Cl)_2NSO_2Cl\} + POCl_3 + HCl$$

$$\Big\downarrow\ 145^\circ,\ 2mm \qquad (4)b$$

$$\underset{15\%}{NPCl_2(NSOCl)_2} + \begin{matrix}\text{polymer}\\ \text{residue}\end{matrix} + POCl_3$$

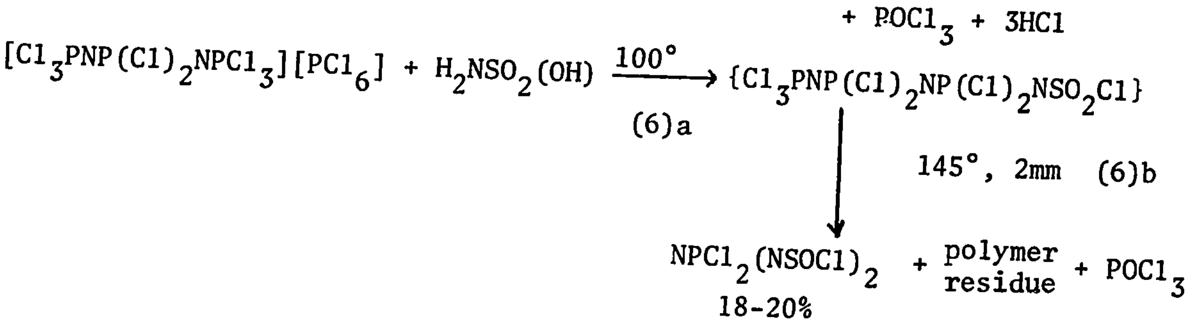
$$\text{crude } Cl_3PNSO_2Cl \xrightarrow[\substack{2mm\\ (5)}]{140\text{-}175^\circ} \underset{10\%}{NPCl_2(NSOCl)_2} + \underset{\substack{\alpha,\beta\\ 25\%}}{(NSOCl)_3} + POCl_3 + \text{polymer oil}$$

A Kirsanov reaction was carried out for amidosulfuric acid, $H_2NSO_2(OH)$, and trichlorophosphonitriletrichlorophosphonium hexachlorophosphate (reaction(4)a). The product, after removal of phosphoryltrichloride, could not be purified and hence characterized, but the mixed ring, $NPCl_2(NSOCl)_2$, in good yield (15%), was isolated from pyrolysis of the crude material (reaction(4)b).

In lower yield, the same mixed ring was prepared from pyrolysis of unpurified trichlorophosphazosulfonyl chloride slush. The product of this reaction was a mixture of the mixed ring with cyclic trimeric sulfanuric chlorides in greater abundance (reaction(5)).

II.1.3 Attempted Preparation of Mixed Ring, Skeleton $\overline{\mathrm{PNPNSN}}$

Two ring compounds are known with the skeleton $\overline{\mathrm{PNPNSN}}$ (Table I-4,3.c). Both contain an $-NS(O)_2-$ unit in the ring, however, because the starting material in their formation is sulfonyl bis(trichlorophosphonitrile),$(Cl_3PN)_2SO_2$. It is unlikely that monovalent substitution for one of the oxygens of this unit, or the removal of one by reduction, could be effected without experimental conditions strong enough to disrupt the bonds of the linear chain or ring skeleton. Hence, it is unlikely that a mixed ring of form $(NPR_2)_2NSOCl$, ultimately desired to complete the series, $(NPCl_2)_3$ — $(NSOCl)_3$, would be obtainable from any linear precursor containing an $-NS(O)_2-$ unit. By analogy with the successful incorporation of one phosphorus atom into a mixed ring skeleton $\overline{\mathrm{PNSNSN}}$ from pyrolysis of a (hypothetical) PNPNS chain, intramolecular cyclization of a PNPNPNS chain might occur under approximately similar conditions. (The analogy is a loose one only; the formation of an $\overline{\mathrm{NPNSNS}}$ ring from a PNPNS chain probably involves at least one intermolecular addition, with resulting formation of a PNPNSNS chain, or a PNPNSNPNS chain, prior to the intramolecular cyclization.) A Kirsanov reaction between chlorobis(dichlorophosphonitrile)trichlorophosphonium hexachlorophosphate, $[Cl_3PNP(Cl)_2NPCl_3][PCl_6]$, and amidosulfuric acid was carried out to produce a (hypothetical) PNPNPNS chain (reaction (6)a). From pyrolysis of the crude product (reaction (6)b), however, only the mixed ring of skeleton $\overline{SNSNPN}$ was isolated.



$$[Cl_3PNP(Cl)_2NPCl_3][PCl_6] + H_2NSO_2(OH) \xrightarrow[(6)a]{100^\circ} \{Cl_3PNP(Cl)_2NP(Cl)_2NSO_2Cl\} + POCl_3 + 3HCl$$

$$\{Cl_3PNP(Cl)_2NP(Cl)_2NSO_2Cl\} \xrightarrow[(6)b]{145^\circ,\ 2mm} \underset{18\text{-}20\%}{NPCl_2(NSOCl)_2} + \text{polymer residue} + POCl_3$$

Cyclization of a linear phosphonitrile, aminodiphenylphosphonitrile-aminodiphenylphosphonium chloride, $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$, is a preparative approach to mixed boron-phosphorus[56] or carbon-phosphorus rings. Reaction of this compound with phosphoranes produces heterosubstituted cyclic trimeric phosphonitriles[89-91]. Phosphorus- or boron-nitrogen bonds are formed, through cleavage of the chlorine bonds of the starting phosphorane or borane, by addition to an amino group of the phosphonitrile chain, with evolution of the hydrogen chloride which is produced. Thus, an appropriate sulfur compound for attempts to prepare a mixed ring in this way should contain at least two sulfur-halogen bonds (and no $>SO_2$ group). A compromise in reactivity of the initial sulfur bond towards addition cleavage of an -NH bond must be attained, since the more likely the formation of the nitrogen-sulfur link, the less time is allowed for orientation favorable to ring formation rather than linear polymerization.

Several sulfur chlorides were considered as starting compound: sulfuryl chloride was ruled out on the basis of its $>SO_2$ group; Sulfur tetrachloride is the most intuitively attractive compound to use considering the non-existence of $SOCl_4$, however, it is only stable in the solid state (below -30°C); Thionyl chloride was chosen as the compound for preliminary study. A variety of conditions, such as high dilution, polar and nonpolar solvents, addition of chlorine gas, HCl scavenger addition, and pyrolysis, were investigated (reaction (7)). When reaction occurred, only intractable polymeric material was obtained, varying from an oil to an impenetrable plastic. In all cases, the polymer reacted explosively with water. Qualitative infrared analysis of the hydrolysis products from reaction in wet *n*-hexane or acetonitrile indicated no $-NH_2$ or $>NH$ groups, although evidence that the PNP skeleton remained intact could be inferred from a comparison of the spectra and those for linear phenylphosphonitriles[22]. Possible cyclization with other sulfur-halogen compounds was not investigated.

$$[H_2N(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl \;+\; SOCl_2 \;\not\longrightarrow\; \text{ring formation} \qquad (7)$$

$$\underset{LCl}{[H_2N(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl} \;+\; \underset{CuCl_2}{CoCl_2 \text{ or}} \;\longrightarrow\; \begin{array}{ll} A & L_2Cu_2Cl_6.2CH_3OH \\ B & L_2Cu_2Cl_6 \\ C & L_2Cu_3Cl_8.2CH_3OH \\ D & L_2CoCl_4 \\ E & L_2CoCl_4.CH_2Cl_2 \end{array} \qquad (8)$$

From approximate models of the cation, $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+$, the amino groups could be oriented in *'cis'* or *'trans'* position with no 'visible' preference. For a *'trans'* orientation, formation of a linear chain might be more likely than that of a ring. (Preliminary Xray analysis of the molecular structure published subsequent to these studies confirms a *'trans'* orientation[30].) Coordination of both amino groups of a single molecule to an appropriate transition metal atom would capture the NPNPN skeleton in a ring structure, and this chelate might react with a suitable sulfur compound by insertion of a substituted sulfur atom in the ring.

The positive charge of the phosphonitrile could hinder coordination to another positively charged species. To minimize this possibility, initial chelate formation attempts were made with copper(II) salts. When crystalline solids were isolated, reactions with other transition metal salts were also investigated. Only copper(II) and cobalt(II) chloride compounds were obtained. Subsequent characterization of these indicated they are not chelates as desired, but salts containing the phosphonitrile cations and cobalt(II) or copper(II) chloride anions (II.5).

II.1.4 Summary

The possibility of ring formation by reaction of aminodiphenylphosphonitrileaminodiphenylphosphonium chloride to form a skeleton $\overrightarrow{\text{PNPNSN}}$ was by no means exhausted. However, it was shown that thionyl chloride under a variety of conditions does not react to form a crystalline solid which could be the desired ring compound. Chelate formation or ring closure reaction for this phosphonitrile is discussed further in II.5.3.5.

Results of pyrolysis reactions suggest that formation of the mixed ring, dichlorophosphonitrilebis(oxochlorosulfonitrile), or cyclic sulfanuric chlorides occurs through recombination of fragments in a complex manner. Very impure trichlorophosphazosulfonyl chloride is necessary for pyrolytic decomposition to prepare the mixed ring. Otherwise, only cyclic trimeric sulfanuric chlorides are obtained.

Pyrolysis of crude trichlorophosphazosulfonyl chloride yields a mixture of α- and β-sulfanuric chloride and the mixed ring (10%). Isolation of the mixed ring from this product is difficult. On the other hand, it can be obtained from pyrolysis of the crude product of reaction between amidosulfuric acid and chlorobis(dichlorophosphonitile)trichlorophosphonium hexachlorophosphate (reaction (6)) in greater yield (20%) than the same reaction sequence using the shorter-chain phosphonitrile (reaction (4), 15%). However, preparation of the longer-chain phosphonitrile is less efficient. Hence, of the three routes, the reaction sequence (4) is most preferable for preparation of dichlorophosphonitrilebis(oxochlorosulfonitrile).

II.2 Experimental

II.2.1 Starting Materials

Chemicals were reagent grade used without further purification except:

amidosulfuric acid— Fisher reagent grade, dried and stored over phosphorus pentoxide.

ammonium chloride— Fisher reagent grade, powdered slightly, dried at 120°C and stored over silica gel.

sulfurdioxide— Matheson lecture cylinder, anhydrous grade.

dihydrogensulfide— Matheson lecture cylinder, chemically pure grade, passed through phosphorus pentoxide powder.

chlorine gas— Matheson lecture cylinder, chemically pure grade, bubbled through reagent grade concentrated sulfuric acid, then condensed in a measured volume.

ammonia gas— Matheson lecture cylinder, anhydrous grade, a measured volume condensed over sodium metal.

thionyl chloride— Fisher purified grade, freshly distilled prior to use under dry nitrogen. A pipette flushed with dry nitrogen was used to measure the required volume of liquid which was then added to the appropriate solvent in a separatory funnel, or to the reaction flask directly under dry conditions.

diphenylchlorophosphine— Aldrich, technical grade.

copper(II) chloride and cobalt(II) chloride— dried Fisher reagent grade salts, $CuCl_2.2H_2O$ and $CoCl_2.xH_2O$, kept at 120°C for several hours, stored over silica gel.

trichlorophosphazosulfonyl chloride, Cl_3PNSO_2Cl— by modification of Kirsanov's procedure[71] from reaction between phosphorus pentachloride and amidosulfuric acid. The crude product after removal of carbontetrachloride and phosphoryltrichloride was a slush at 25°C from which a 60% yield (based on reacted amidosulfuric acid) of purified product (mp 32.5-35.0°C) was obtained without recrystallization. Recrystallization of this filtered product from *n*-hexane yielded white needles with a sharp melting point (35.0°C),(25%) which were used for analysis, infrared and ^{35}Cl nuclear quadrupole resonance measurements.

Analysis: calcd. for Cl_3PNSO_2Cl: S,12.78; P,12.35; N,5.91; Cl,56.51; O,12.76. found: S,13.0; P,12.1; N,5.9; Cl,56.6; O,11.20.

trichlorophosphonitriletrichlorophosphonium hexachlorophosphate, $[Cl_3PNPCl_3][PCl_6]$— prepared from reaction of phosphorus pentachloride and ammonium chloride in a solvent mixture of *sym*-tetrachloroethane and nitrobenzene[7]. No sodium chloride was used. The filtration was difficult as product quickly clogged the sintered glass. Hence, a repeated filtration procedure was adopted. After three or four re-solutions of the initial warm filtrate, only unreacted ammonium chloride remained as the first residue. Samples for infrared spectroscopy were recrystallized from *sym*-tetrachloroethane.

trichlorophosphonitrilephosphoryldichloride, $Cl_3PNPOCl_2$— prepared from reaction of $[Cl_3PNPCl_3][PCl_6]$ with sulfurdioxide[7], with no difficulty under moisture-free conditions; 90% yield, mp 35.0-36.5°C (lit. 35.5°C).

trichlorophosphonitrilethiophosphoryldichloride, $Cl_3PNP(S)Cl_2$— prepared from reaction of $[Cl_3PNPCl_3][PCl_6]$ with dihydrogensulfide[20], with no difficulty under moisture-free conditions; 85% yield, mp 36.0-37.0°C (lit.35°C).

trimeric sulfanuric chlorides, α-$(NSOCl)_3$ and β-$(NSOCl)_3$— prepared from pyrolysis of purified trichlorophosphazosulfonyl chloride[71] and identified by comparison of the reported infrared spectra. Samples of the β form, from vacuum sublimation separation, were used without recrystallization. Samples of the α form were purified by recrystallization; mp α-$(NSOCl)_3$, 143.5-145.0°C; β-$(NSOCl)_3$, 44.5-45.0°C (lit. 144.0-145.0 and 46.0-47.0°C, respectively).

chlorobis(dichlorophosphonitrile)trichlorophosphonium hexachlorophosphate, $[Cl_3PNP(Cl)_2NPCl_3][PCl_6]$— prepared directly from phosphorus pentachloride and ammonium chloride (2:1)[20] in a mixture of nitrobenzene and *sym*-tetrachloroethane. After two reprecipitations from *sym*-tetrachloroethane, pale yellow needles were obtained; 28% yield. Inconsistent melting points indicated an impurity remained, which was considered to be nitrobenzene, although not observed in infrared spectra. Since the product was of good morphology, it was used without further purification. The major by-product is $[Cl_3PNPCl_3][PCl_6]$, and infrared analysis indicated this was removed during the reprecipitation procedure.

aminodiphenylphosphonitrileaminodiphenylphosphonium chloride, $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$— prepared from the controlled ammonolysis of diphenyltrichlorophosphorane in chloroform solution[26]. (Diphenyltrichlorophosphorane was prepared by chlorination of diphenylchlorophosphine in controlled ratio in carbontetrachloride.) All reactions with thionyl chloride were carried out under moisture-free conditions with material recrystallized from methanol, washed in anhydrous diethylether, dried in vacuo, and stored over silica gel or phosphorus pentoxide; yield 70%, mp 242.5°C (lit. 245.0-246.5°C).

II.2.2 General Procedures

Solvents— For recrystallizations and solution spectroscopy, solvents were spectrograde quality. All solvents for reactions and work-ups were reagent grade. Carbontetrachloride, *n*-hexane, *n*-heptane,and methylene chloride were stored over calcium hydride at room temperature and filtered, or distilled after filtration, in dry atmosphere. Chloroform was washed five times with distilled water, stirred over calcium hydride for twelve hours, decanted and distilled immediately prior to use. Benzene was distilled from calcium hydride.

Dry atmosphere— All reaction products and starting materials were assumed susceptible to hydrolysis by atmospheric moisture until shown otherwise. Reactants were handled in dry atmosphere provided either by continuously circulating the air in a dry box through drierite, or in dry nitrogen atmosphere in a glove bag. Filtration was performed in either case using dry nitrogen to balance the suction. Nujol mulls of all samples susceptible to hydrolysis were prepared in dry atmosphere in the dry box or glove bag.

Analyses— Samples were analyzed for the elements reported, except cobalt and copper,by Schwarzkopf Microanalytical Laboratory. Only single determinations were made and results are quoted arbitrarily to three figures. Cobalt and copper were determined by volumetric titrations with standard EDTA solution[29]. Some chloride analyses were made as laboratory checks during reactions by Volhard method determinations on hydrolyzed samples.

Infrared Analyses— Infrared spectra were used to assess preparative reactions. Samples of liquids were prepared by placing a drop between two pieces of polyethylene film inserted between KBr discs. Solid samples were prepared as nujol mulls between KBr discs.

II.2.3 Typical Preparative Procedures

(1) Pyrolysis of purified trichlorophosphazosulfonyl chloride—

Attempts to duplicate the preparation of Van de Grampel and Vos[64] using a bath temperature of 145°C, 8mm pressure and ultraviolet light (CENCO argon mixed gas lamp, 2 watts) were unsuccessful. Only a mixture of cyclic sulfanuric chlorides was isolated. No difference in the results occurred when the ultraviolet lamp was not used;

57.0 g (0.23 moles) of Cl_3PNSO_2Cl (purified, mp 32.5-35.0°C) were placed in a 100 ml flask fitted with a nitrogen inlet, a thermometer, and a Vigreux column. The column was connected via a distillation head to a water-cooled condenser which led to a trap immersed in an ethanol-dry ice slush (-77°C), and then to a vacuum pump which was regulated to maintain the desired pressure (7-8mm). An oil bath around the flask was slowly heated until the flask contents liquefied and decomposition began(internal temperature 122°C). A colorless liquid refluxed in the column and the flask liquid slowly became more brown. Heating was continued at 145°C bath temperature, until bubbling had almost ceased (≈6 hr). The trap contained a pale yellow liquid ($POCl_3$-infrared). 9.8 g (45% crude yield) yellow solid was obtained from extraction with warm *n*-hexane, and identified as mainly α-$(NSOCl)_3$ and some β-$(NSOCl)_3$[71].

$$Cl_3PNSO_2Cl \xrightarrow{145°C,\ 8mm} \alpha\text{-},\ \beta\text{-}(NSOCl)_3 + POCl_3 + \text{polymer oil} \qquad (1)$$

(2) Pyrolysis of trichlorophosphazosulfonyl chloride and trichlorophosphonitriletrichlorophosphonium hexachlorophosphate—

30 g (0.12 moles) purified Cl_3PNSO_2Cl and 32 g (0.06 moles) $[Cl_3PNPCl_3][PCl_6]$ were placed in a 100 ml flask (as in (1)). Pressure was maintained at 10 mm while the mixture was heated at a bath temperature of 150°C. The flask contents were a refluxing liquid and an apparently

unreacting solid. The internal temperature was steady at 138°C as the colorless liquid refluxed. After cooling, the flask contents were brought to atmospheric pressure with dry nitrogen and the solid material filtered. Infrared analysis indicated that the flask contained only a mixture of starting materials. The trap contained only trace amounts of a liquid with smell of $POCl_3$. The refluxing liquid remained colorless, rather than gradually turning brown, as is typical of increasing polymerization.

(3) Pyrolysis of trichlorophosphazosulfonyl chloride and trichlorophosphonitrilethiophosphoryldichloride—

9.2 g (0.032 moles) $Cl_3PNP(S)Cl_2$ and 8.3 g(0.032 moles) purified Cl_3PNSO_2Cl were mixed in a 200 ml flask (as in (1)). Liquefaction occurred on mixing without heating. The system was maintained at 2mm, and the bath temperature gradually increased to 70°C. At 50°C, bubbling began. The mixture was maintained at 70°C for five hours ; refluxing occurred but no material was collected in the trap. The pale gold liquid remaining was a mixture of the starting materials (IR).

The flask liquid was heated again to 140°C at 2mm. The color became more brown as refluxing occurred, but no material was collected and there was no change in the liquid spectrum.

Ammonium chloride (0.030 moles) was added and pyrolysis continued at 140°C. The flask residue was a brown polymeric solid from which no crystalline material could be extracted. A yellow liquid condensed in the trap was a mixture of starting materials with small amounts of other substances which were not characterized. Distillation of this trap-liquid resulted in a brown polymeric residue, and a small amount of distillate with the same spectrum as the original trap-liquid, collected as the temperature increased.

(4)a Reaction between amidosulfuric acid and trichlorophosphonitrile-trichlorophosphonium hexachlorophosphate—

This reaction occurred in the same way as the Kirsanov reaction for the preparation of trichlorophosphazosulfonyl chloride[66]. Attempts to obtain a purified product for characterization were unsuccessful;

70.5 g (0.13 moles) recrystallized $[Cl_3PNPCl_3][PCl_6]$ and 11.6 g (0.12 moles) $H_2NSO_2(OH)$ were heated at 100°C in a 200 ml flask fitted with a condenser and drying tube, until the evolution of HCl had ceased (total 6 hr). Unreacted amidosulfuric acid (0.011 moles) was filtered from the product and phosphoryltrichloride (0.099 moles) was removed by vacuum distillation. A bright yellow liquid remained, which was vacuum distilled. However, although distillation of a colorless liquid began at 120°C and 1mm, the remaining liquid gradually became more brown, and the temperature steadily increased. It was concluded that only decomposition occurred.

Another portion of the yellow liquid product was solidified at -77°C. However, no solid could be isolated at 25°C from filtration of the solidified mass under suction during slow warming. No components of the crude product separated using techniques of thin-layer chromatography on silica plates under moisture-free conditions. Samples, applied neat or in solution, moved only with tailing. Solvents used were carbontetrachloride, benzene and anhydrous diethylether.

(4)b Pyrolysis of the crude product from (4)a—

Vacuum distillation resulted in pyrolytic decomposition, however, under controlled conditions, this decomposition produced the mixed ring, $NPCl_2(NSOCl)_2$;

120 g (0.225 moles) $[Cl_3PNPCl_3][PCl_6]$ and 21.8 g (0.225 moles) $H_2NSO_2(OH)$ were reacted as in (4)a. After filtration to remove unreacted amidosulfuric acid, the yellow liquid was transferred to a 500 ml flask fitted as in (1). It was heated slowly at approximately 1mm until most of the phosphoryltrichloride from the Kirsanov reaction had been removed. Then pyrolysis was continued at 150°C until the polymeric residue which was produced began to foam (≈15 hr). The liquid gradually became more brown on polymerization and a colorless liquid refluxed in the column, later becoming bright yellow. Crystals formed on the upper portions of the flask and lower part of the column. Phosphoryltrichloride was collected in the trap, with small amounts of an orange-yellow substance which was not characterized. The crystalline material was scraped from the column, or extracted with the flask contents in warm carbontetrachloride. After evaporation of the solvent in the atmosphere, needlelike crystals were obtained, contaminated with a colorless liquid and a white solid from hydrolysis of that portion of the polymeric residue which was soluble in the carbontetrachloride. The crude product was recrystallized from *n*-hexane or *n*-heptane; yield 15%, mp 96.5°C without decomposition. A single crystal examined with a Weissenberg camera (Cu Kα) was found to have the lattice parameters and space group of the reported structural determination[73].

Analysis: Calcd. for $NPCl_2(NSOCl)_2$: S,20.62; P,9.96; N,13.51; Cl,45.60; O,10.30; mol.wt.,310.9. Found: S,20.7; P,9.8; N,13.2; Cl,45.6; mol.wt.,311 (mass spectr.).

(5) Pyrolysis of crude trichlorophosphazosulfonyl chloride—

Crude Cl_3PNSO_2Cl (unfiltered) was pyrolytically decomposed as in (1) at 145°C initially, then gradually increasing to 175°C (total 12 hr). After cooling, crystals of unreacted Cl_3PNSO_2Cl were mixed with the amber reaction liquid. Pyrolysis was continued until no starting material remained in the reaction mixture (≈20 hr additional). During this time, the mixture became a brown oily liquid greatly reduced in volume from the starting amount. Crystals formed in the column and upper parts of the flask and phosphoryltrichloride was collected in the trap.

The column and flask contents were scraped or extracted with warm carbontetrachloride. The crude product was a pale yellow mixture of α- and β-$(NSOCl)_3$ and $NPCl_2(NSOCl)_2$. Infrared analyses indicated the column material was α- with a small amount of β-sulfanuric chloride, the solid from the upper portion of the flask was α-sulfanuric chloride with some of the mixed ring, and the extracted material from the flask residue was a mixture of α-sulfanuric chloride and the mixed ring in ≈3:1 ratio. By repeated sublimation (50°C, 1mm), the amount of mixed ring could be increased in the residue while the sublimate contained more α-sulfanuric chloride. However, complete separation was not achieved for either component. Samples of mixed ring uncontaminated by infrared-detectable amounts of α-sulfanuric chloride were only obtained after four or five sublimations and subsequent recrystallization of the residue from *n*-hexane.

(6)a and b Pyrolysis of the crude product of the reaction between amido sulfuric acid and chlorobis(dichlorophosphonitrile)trichlorophosphonium hexachlorophosphate—

8.0 g (0.082 moles)$H_2NSO_2(OH)$ and 53.5 g (0.082 moles) $[Cl_3PNP(Cl)_2NPCl_3][PCl_6]$ were reacted as in (4)a (total 4 hr). The crude yellow liquid product, after removal of unreacted amidosulfuric acid and phosphoryltrichloride, was refluxed for six hours in 100 ml *sym*-tetrachloroethane to promote possible cyclization (135-140°C, 6hr). The solvent was removed by vacuum distillation, leaving a yellow-brown liquid with no crystal formation. Extraction of this liquid with *n*-hexane and carbontetrachloride yielded a very small amount of the same oil which was not further investigated.

The hydrolytically susceptible crude product from (6)a was pyrolyzed at 1mm and 140-145°C (1 hr), then 165-175°C (2 hr). The liquid became brown but little change occurred in its infrared spectrum, and no crystalline material formed in the column. After additional pyrolysis (10 hr), the reaction was stopped and the polymeric residue extracted with warm carbontetrachloride. Only $NPCl_2(NSOCl)_2$ (18-20% uninterrupted run) and hydrolysis product impurities were obtained from the extract.

(7) Reactions of aminodiphenylphosphonitrileaminodiphenylphosphonium chloride with thionyl chloride—

To promote ring formation, a non-polar solvent is desirable. However, the ionic linear phosphonitrile is only soluble in methanol and to a much lesser extent in acetonitrile or chloroform. Both methanol and acetonitrile decompose thionylchloride with production of sulfur dioxide and were not used. Conditions and results of the reactions are shown in Table II-1. A typical procedure for the solution reactions was;

2.25 g (0.005 moles) $[H_2N(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$ was mixed in the appropriate solvent for two hours under dry nitrogen, with warming to dissolve as much as possible. Then thionyl chloride in the required amount in solution was added dropwise from a separatory funnel fitted with a teflon

Table II-1 Reactions of Thionyl Chloride with Aminodiphenylphosphonitrile-aminodiphenylphosphonium Chloride.

Mole ratio $LCl:SOCl_2$ a)	Solvent system	Other conditions	Results
1:1	*sym*-tetrachloroethane	25° 1.5 hr	LCl recovered[a)]
1:1	"	110° 2.5 hr	orange sol'n; polymer oil
1:1	carbontetrachloride	25° 1 hr	LCl recovered
1:1	"	77° 2.5 hr	LCl suspension, yellow sol'n; polymer oil
1:2	chloroform, CaO	60° 2 hr slow add'n $SOCl_2$	yellow sticky oil
1:1	chloroform	25° 3 hr slow add'n $SOCl_2$	yellow sol'n; yellow oil
1:1	chloroform, CaO	25° 2 hr slow add'n $SOCl_2$ Cl_2 bubbled into sol'n	yellow sol'n; yellow oil
1:1	pyridine	25° 10 hr	orange sol'n, white ppt; LCl + pyridine-HCl
1:14	"	25° 10 hr	orange sol'n; pyridine-HCl + brown polymer oil
1:2	benzene v. large volume	80° 3 hr slow add'n $SOCl_2$ or simultaneous slow add'n of $SOCl_2$ and LCl suspension	yellow sol'n; yellow oil + LCl
1:3	(pyrolysis)	145-150° cold finger, 1mm	hard yellow glass; LCl + polymer
1:7	"	90° 2 hr 1 mm	$SO_2\uparrow$, orange liquid; orange polymer + $SOCl_2$
		150° 4 hr 1 mm	$SOCl_2$ distilled, hard plastic residue

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a) $LCl \equiv [NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$

stopcock and a pressure-equalizing side-arm. The reaction mixture was magnetically stirred with a teflon-coated bar and temperature maintained with a heating mantle. After reaction, any solid material was filtered, washed with fresh solvent, and infrared analyzed. Solvent was vacuum distilled from the filtrate and the residue infrared analyzed, and extracted with benzene or carbontetrachloride for possible products.

(8) Reactions of aminodiphenylphosphonitrileaminodiphenylphosphonium chloride with transition metal halides—

Initial attempts to use other salts of copper(II); the nitrate, sulfate, and bromide, in a similar preparation to that for compounds of the phosphonitrile and copper(II) chloride, were unsuccessful; only copper(II) chloride in either dried or hydrated form resulted in 'complex' formation. This was also found for cobalt(II) salts. Similar preparative attempts were unsuccessful for hydrated chlorides of iron(III), iron(II), chromium(III), nickel(II), and anhydrous zinc(II) chloride. No other preparative method was tried.

Copper(II) compounds—*

A, ($CuLCl_3{:}CH_3OH$) — crystallized from methanol solution; 2.0 g (0.0044 moles) LCl and 0.57 g (0.0042 moles) dried $CuCl_2$ were added to enough methanol to just dissolve the combined substances, and the green solution warmed to 60°C. Then anhydrous diethylether was added slowly, until the point of cloudiness. The solution was allowed to stand until red-

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* empirical formulae; $L \equiv P_2N_3C_{24}H_{24}$: The phosphonitrile cation is referred to as L^+ and the chloride as $LCl \equiv [NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$.

green plates formed, which were filtered, washed with a mixture of methanol and ether, and stored in methanol atmosphere. A slight excess of LCl must be present for reprecipitation from methanol.

B, ($CuLCl_3$) — prepared by heating powdered samples of A at 100°C until constant weight, or by precipitation from acetonitrile or methylene chloride as for A. Yellow-gold needles or plates precipitated from orange solution and were filtered, washed in a mixture of solvent and ether, then in ether to dry, and stored over silica gel. A slight excess of LCl must be present for reprecipitation from methylene chloride or acetonitrile.

C, ($Cu_3L_2Cl_8.2CH_3OH$) — precipitated from methanol as for A, using a 1:2 molar ratio of LCl:dried $CuCl_2$. Red needle clusters obtained were filtered, washed in a methanol-ether mixture, and stored in methanol atmosphere. The substance lost methanol when heated to 100°C, but the product did not melt sharply. From infrared analysis, it was a mixture of B and another substance which was not anhydrous copper(II) chloride.

Cobalt(II) compounds—

D, (CoL_2Cl_4) — precipitated from methanol solution of LCl and dried $CoCl_2$ as for A (1:1 molar ratio). Royal blue diamonds formed which were filtered, washed with a mixture of methanol and ether, then ether to dry, and stored over silica gel.

E, ($CoL_2Cl_4.CH_2Cl_2$) — precipitated from methylene chloride solution as for A (1:1 molar ratio). Turquoise needles or plates were obtained and stored over silica gel at room temperature without decomposition from loss of methylene chloride. When heated above 90°C, E lost methylene chloride to become D.

Table II-2 Analytical Results for Copper(II) and Cobalt(II) Compounds of Aminodiphenylphosphonitrileaminodiphenylphosphonium Chloride.

Compound a)	mp°C	c)	Analysis, percent							
			P	N	Cl	C	H	O	M b)	wt loss
A	137.5-138.0	c	10.02	6.79	17.20	48.56	4.54	2.59	10.28	5.18
	CH_3OH↑ 90-100	f	9.87	7.28	17.4	48.7	4.48	2.61	10.4	5.16
B	137.5-138.0	c			18.18				10.84	0
		f			18.1				10.87	0.00
C	sinters 136-138	c	9.04	6.13	20.69	43.83	4.09	2.34	13.91	4.67
	decomp. by 280	f	8.81	6.20	20.5	43.7	4.01	2.68	13.9	4.76
D	155.5-157.0	c	11.99	8.13	13.72	55.80	4.65	0	5.70	0
		f	11.6	8.26	14.0	54.5	4.82	<0.5	5.61	
E	155.5-157.0	c	11.08	7.51	19.02	52.64	4.48	0	5.27	7.59
	CH_2Cl_2↑ by 90	f	11.0	7.65	18.2	52.4	4.95	<0.5	5.23	

a) as in preparative section II.2.3,(8).

b) M ≡ Cu or Co

c) calculated for: A ≡ $P_2N_3Cl_3C_{25}H_{28}OCu$, B ≡ $P_2N_3Cl_3C_{24}H_{24}Cu$, C ≡ $P_4N_6Cl_8C_{50}H_{56}OCu_3$, D ≡ $P_2N_3Cl_4C_{24}H_{24}Co$, E ≡ $P_2N_3Cl_6C_{25}H_{26}Co$.

II.2.4 Instrumental Measurements and Sample Preparation

(1) Differential scanning calorimetry— a Perkin Elmer calorimeter, Model DSC-1, was used for runs on weighed samples of $NPCl_2(NSOCl)_2$ sealed in aluminum discs. However, with slow heating (20°/min) to 200°C or above, gradual evaporation from the pellets caused complete loss of sample and a high 'noise' level for the recorded curve. During fast heating runs (80°/min) to 220°C, followed by rapid cooling to 180°C, then slower cooling

(2.5°/min), complete loss of sample was avoided , but the scale position could not be controlled to follow the curve above 200°C.

(2) <u>^{31}P nuclear magnetic resonance</u>— A Varian 19.3 Mc, high resolution spectrometer, model 4311, was used for measurements on $NPCl_2(NSOCl)_2$ in saturated solution in benzene, acetonitrile, and carbontetrachloride. The external standard was 85% phosphoric acid and samples were contained in dried, stoppered, standard 5 mm tubes. Values reported for the ^{31}P chemical shift are considered accurate to ±0.3 ppm, although precise to ±0.1 ppm for six to ten runs per sample. Temperature of measurement was ≈32°C.

(3) <u>Electron paramagnetic resonance</u>— A Varian spectrometer, model V4500-10A, was used for measurements on the copper(II) and cobalt(II) compounds in solid state and in solution. Samples were contained in dried, sealed quartz tubes of 4 mm diameter. The limit of error in g value reported was estimated as ±0.005 from three measurements per sample, for duplicate samples.

(4) <u>^{35}Cl nuclear quadrupole resonance</u>— A modified, Dean-type, externally quenched, superregenerative oscillator[62] was used with phase-sensitive detection. Interaction frequencies were determined by observation of zero beat of the oscillator fundamental with a very loosely coupled BC 221 frequency meter precalibrated against WWV. Because of limitations imposed by temperature fluctuations, values are reported with an accuracy of ±0.002 MHz. Samples of 1.0-4.5 g were sealed in pyrex tubes of 15 mm diameter under vacuum at liquid nitrogen temperature.

(5) <u>Infrared spectrometry</u>— For the mixed ring, $NPCl_2(NSOCl)_2$, solution spectra were recorded for the region 4000-420^{-1} on a Perkin Elmer 337 grating infrared spectrometer, using matched KBr cells of 0.1 mm path

length. Solution spectra for the cobalt(II) and copper(II) compounds were obtained on the same instrument, using matched IRTRAN cells of 0.5 mm path length. Solid state spectra of all compounds studied were recorded on this instrument and also on a Perkin Elmer 521 grating infrared spectrometer for the range 4000-244 cm^{-1}, using KBr or CsBr pellets and/or nujol mulls between KBr or CsBr discs or polythene film, where appropriate. Samples of compounds susceptible to hydrolysis were only prepared as mulls, and the extended range instrument was not used.

All spectra were obtained using polystyrene film bands for calibration of the wavenumber scale. Values reported for the positions of maximum absorption were reproducible to within 2 cm^{-1}. If polythene film was used, the intense, sharp doublet at 725 and 734 cm^{-1} also provided a check on the wavenumber scale.

When the main bands observed were 'symmetric' (within limitations of instrument resolving power, and sample preparation technique), the wavenumber value for maximum absorption was used directly. If there was an obvious shoulder, the band was resolved qualitatively for values of the components' maxima. These values were reproducible to ±3 cm^{-1}. When very broad bands were observed, with more or less obvious complex structure, values of the components' maxima were estimated to ±5 cm^{-1}. Relative intensities for all spectra reported were estimated visually from absorbance scale curves.

(6) Ultraviolet, visible, and near-infrared spectrometry— Solution spectra for the copper(II) and cobalt(II) compounds were obtained using matched silica cells of 10 mm path length on a Beckman DU manual spectrophotometer or a Unicam SP 800 recording spectrophotometer (13,500-47,500 cm^{-1}), and on the former or a Perkin Elmer 350 spectrophotometer (4000-

16,800 cm^{-1} solvent-permitting).

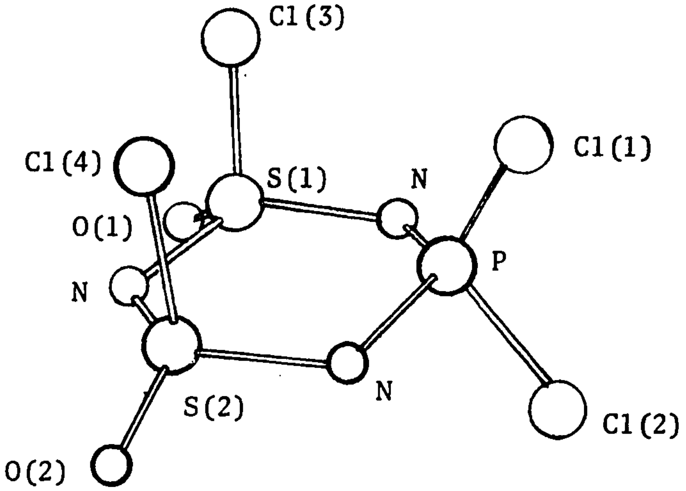
Solid state spectra were obtained on these instruments using nujol mulls on Whatman no.1 filter paper strips held in place by matched silica cells[69]. A strip painted with nujol was used as reference. Spectra obtained in this way are necessarily qualitative, since values of molar extinction coefficient cannot be calculated. However, this technique is as reproducible as reflectance measurements on powdered samples, and as useful for solid state spectra where samples can be ground sufficiently fine to make a good mull suspension.

II.3 *Cyclo*-dichlorophosphonitrilebis(oxochlorosulfonitrile) — Comparison With Dichlorophosphonitrile and Sulfanuric Chloride Trimers

II.3.1 Some Physical and Chemical Properties

Mixed ring* molecules are in a distorted chair configuration with both sulfur chlorine substituents axial[73]. A molecule in the crystal does not have the symmetry implied by the structural formula shown (Figure II-1), and expected for the vapor phase. Comparison of the molecular dimensions of the mixed ring, dichlorophosphonitrile trimer, $(NPCl_2)_3$, and α-sulfanuric chloride trimer, α-$(NSOCl)_3$, is shown in Table II-3.

Figure II-1 The mixed ring, $NPCl_2(NSOCl)_2$



The mixed ring possesses similar stability and chemical properties to those of its 'parents', $(NPCl_2)_3$ and α-$(NSOCl)_3$. It has an appreciable vapor pressure at room temperature, resulting in the disappearance of

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* In this section, *cyclo*-dichlorophosphonitrilebis(oxochlorosulfonitrile) is referred to as the mixed ring, $NPCl_2(NSOCl)_2$.

Table II-3 Molecular Dimensions of $NPCl_2(NSOCl)_2$, $(NPCl_2)_3$ and α-$(NSOCl)_3$

Compound and reference	Bond lengths (Å) a)				
	PN	SN	PCl	SCl	SO
1) $NPCl_2(NSOCl)_2$[73]	1.585(13)	1.540(13) 1.578(13)	1.957(6)	2.007(6) 2.028(6)	1.421(13)
2) $(NPCl_2)_3$[77,78]	1.590(17)		1.975(8)		
3) α-$(NSOCl)_3$[79]		1.569(8)		2.003(4)	1.407(8)

(cont.)	Bond angles (degrees) a)					
	NPN	NSN	PNP or PNS	SNS	ClPCl	ClSO
1)	115.3(7)	115.0(7)	123.5(8) 120.6(8)	120.3(8)	104.4(3)	106.0(5)
2)	119.6(12)		119.4(10)		101.9(4)	
3)		113.0(6)		122.0(6)		107.0(5)

a) estimated standard deviation in brackets in units of the last figure quoted.

single crystals exposed to the atmosphere, and can be easily sublimed in vacuo (45°C, 0.5-1.0 mm). However, attempts to obtain a vapor-phase infrared spectrum were unsuccessful. (A sample of 10 mg, loosely wrapped in aluminum foil, was placed in a gas cell (RIIC GR-5, 7cm, NaCl), which was evacuated to 0.001 mm at room temperature. On heating slowly to temperatures above the melting point, vaporization was insufficient for a spectrum. Eventually vapor condensed on the cell windows to a liquid with a spectrum similar to mixed ring non-polar solution spectra.)

Differential scanning calorimetry indicated that no 'phase' change occurred between 25 and -110°C. On heating, then cooling to 25°C, within the experimental limitations (II.2.4,(1)), no discernable 'phase' change except melting occurred (95-96°C). Recrystallization during cooling occurred at 56±5°C. (Samples recrystallized from non-polar solvents melted at 95.5-96.0°C.)

The mixed ring is soluble in organic solvents, but after several hours in polar solvents, decomposition occurred, which was more rapid on exposure to the atmosphere. It is very stable to hydrolysis, as are $(NPCl_2)_3$ and α- or β-$(NSOCl)_3$: No weight change was observed for a sample exposed to atmospheric moisture up to ten hours. Samples could be recrystallized from wet *n*-hexane or carbontetrachloride, in the presence, or absence, of hydrochloric acid, with no noticeable decomposition (infrared analysis), except after prolonged heating (3 hr at 80°C) when a brown color indicated polymerization decomposition.

II.3.2 Spectrometric Results

Details of measurements reported in this section are included in II.2.4.

Table II-4 ^{31}P Chemical shift (δ); $NPCl_2(NSOCl)_2$ in saturated solution

Solvent	δ ppm from 85% H_3PO_4
benzene	-28.0
carbontetrachloride	-27.3
acetonitrile	-28.0

Table II-5 ^{35}Cl Nuclear quadrupole resonance frequencies (MHz); $NPCl_2(NSOCl)_2$, α- and β-$(NSOCl)_3$ and $(NPCl_2)_3$ at 21°C [a)]

$NPCl_2(NSOCl)_2$	α-$(NSOCl)_3$	β-$(NSOCl)_3$ [b)]	$(NPCl_2)_3$ [c)]
28.660	36.138*	36.134	27.880*
29.836	36.454	36.445	27.812
34.521		37.55	27.684
35.472			27.608*

a) All interactions for each compound are of equal intensity except those marked with an asterisk which are of twice the intensity of others for that compound.

b) As the temperature of observation approaches that of the melting point, the signals become less sharp and intense. The highest frequency interaction is most affected.

c) M.Kaplansky, PhD Thesis, McGill Univ.,(1967).
H.Negita and S.Satou, Bull.Chem.Soc., Japan, <u>29</u> 426 (1956).
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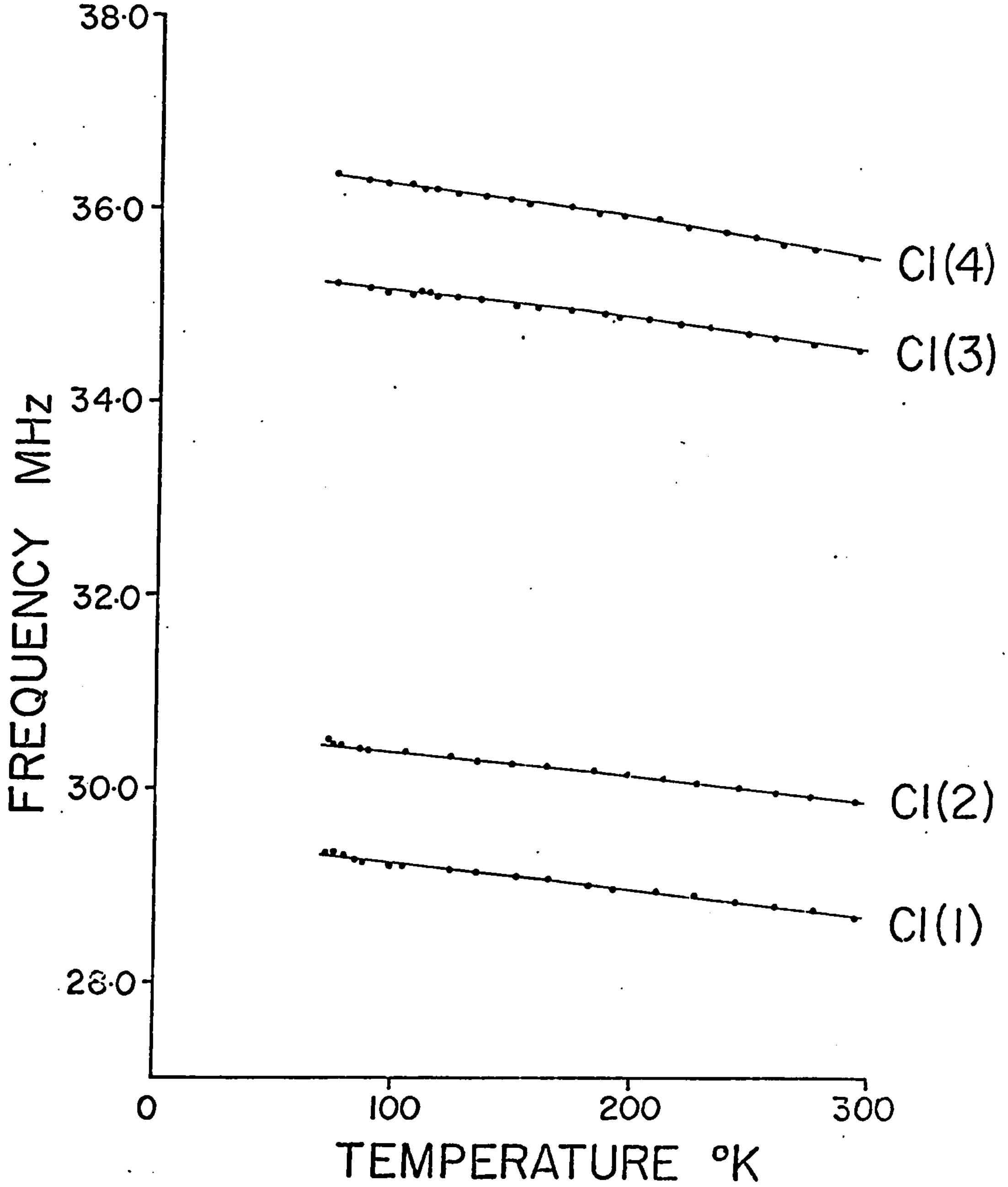

Figure II-2 Temperature Dependence of ^{35}Cl Nuclear Quadrupole Resonance Frequencies of $NPCl_2(NSOCl)_2$.
(ref. 40)

Table II-6 Infrared spectra of $NPCl_2(NSOCl)_2$ a) c)

Solid	Solution	
	Cyclo-hexane	Acetonitrile
1348 w,sh b)	1348 s	1340 sh
1336 s	1335 s	1328 s
1312 w,sh		1280 w
1179 vs,br	1177 vs	1182 vs
1138 s,br	1142 s	1139 s
1028 ms	1035 m	1029 s
855 sh		915 m
840 m	840 mw	841 mw
722 s	720 ms	724 ms
666 w	666 w	668 w
		650 w,sh
640 s	624 s	635 s
562 s	558 s	564 s
488 mw	484 mw	487 mw
442 w	437 w	435 w
410 w		
348 w		
310 w		

a) Values (in cm^{-1}) of maximum absorption for main bands observed.

b) Abbreviations: vw, very weak; w, weak; mw, medium weak; m, medium; ms, medium strong; s, strong; vs, very strong; sh, shoulder; br, broad; Relative intensities were estimated from absorbance scale.

c) Reference 40.

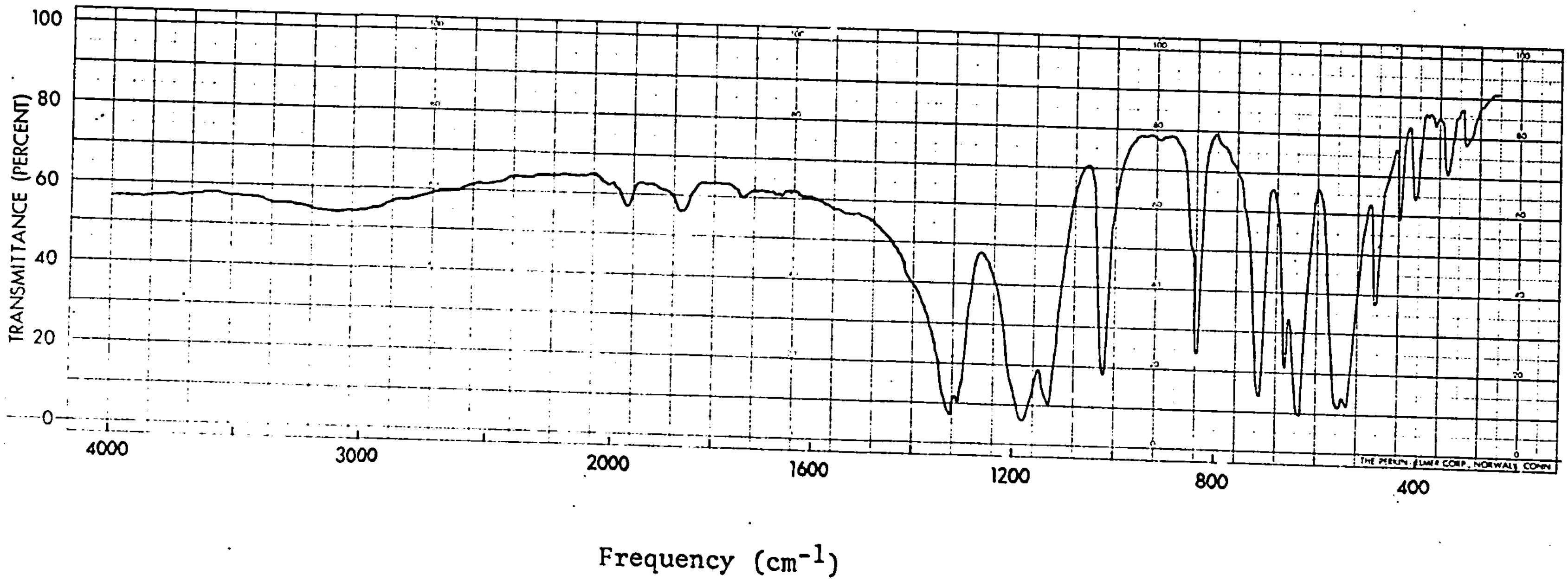

Figure II-3 Infrared Spectrum of $NPCl_2(NSOCl)_2$, Solid State (CsBr pellet).

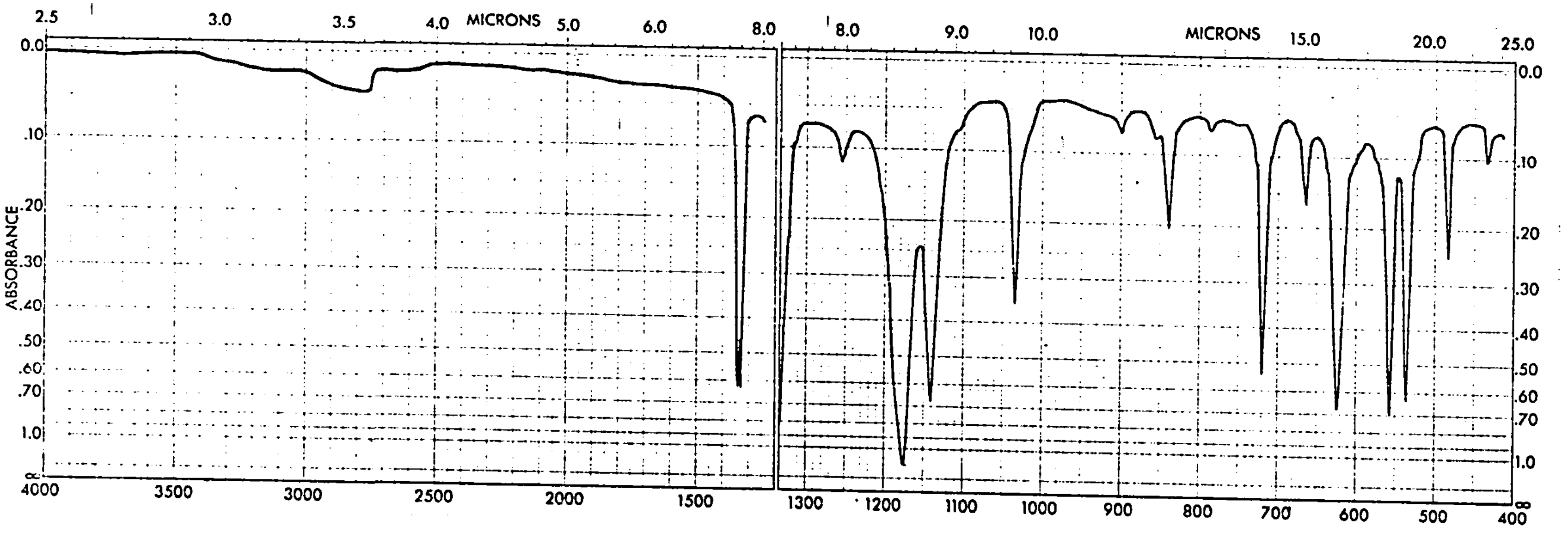

Figure II-4 Infrared Spectrum of $NPCl_2(NSOCl)_2$, Cyclohexane Solution (0.1 mm KBr).

II.3.3 Discussion

II.3.3.1 ^{31}P Chemical Shift

Within estimated experimental error, there is no solvent effect on the chemical shift which lies approximately 8 ppm downfield from that for dichlorophosphonitrile trimer (Table II-4). A downfield shift represents less shielding for the mixed ring with respect to that for $(NPCl_2)_3$ phosphorus nuclei. According to a theoretical treatment of ^{31}P nmr chemical shifts, based on an LCAO MO formulation[80], the relative occupation numbers of phosphorus p and d orbitals in the ground state electronic wavefunctions is the determining contribution to the shift variation for a series of tetra-coordinate phosphorus-containing compounds. Thus, the sum of atomic populations for the phosphorus p and d orbitals in the wavefunction for $NPCl_2(NSOCl)_2$ should be less than that for $(NPCl_2)_3$. In terms of the bonding model(I.4.3), given a constant sigma population, the variation must originate in the total Π population difference. This would mean increased bonding contribution for the Π_a system, and/or a decreased contribution for the Π_s system in the mixed ring, depending upon the relative importance of these systems. A comparison of the phosphorus exocyclic and ring angles for the two rings (Table II-3), indicates that the sigma system cannot be assumed to be the same, however, so no inference about relative Π system bonding can be made. (see section III.2.6 for further discussion in terms of bonded overlap values)

II.3.3.2 ^{35}Cl Nuclear Quadrupole Resonance Frequencies

The frequencies observed (Table II-5) can be assigned to ^{35}Cl nuclei of the mixed ring molecules by comparison with the frequencies observed for the other ring molecules, and because detailed structural information is available, a specific assignment can be made. The published report of this work[40] contains a bonding interpretation consistent with the assignment.

The spectrum of the mixed ring consists of four intense interactions of equal magnitude. Comparing the spectra for sulfur chlorines of α-$(NSOCl)_3$ and β-$(NSOCl)_3$ and for phosphorus chlorines of $(NPCl_2)_3$, the lower frequency pair of interactions for $NPCl_2(NSOCl)_2$ can be assigned to phosphorus chlorines, and the higher frequency pair to the sulfur chlorines. For m molecular symmetry, the sulfur chlorines are chemically equivalent (i.e. in the same bonding environments). However, the molecule in the solid state is distorted from m symmetry, hence observation of two interactions for sulfur chlorines and for phosphorus chlorines is not unexpected.

Without making a temperature dependence parametrization of the nqr frequencies, the relative temperature dependence observed for the two pairs of interactions (Figure II-2) allows a further assignment of each pair of chlorines using the results of the Xray structural determination. From the temperature factor corrections necessary during the structural refinement, two of the chlorine atoms, (2) and (3) (Figure II-1), are more restricted to thermal motion than the others. The higher frequency phosphorus chlorine interaction and the lower frequency sulfur chlorine interaction have smaller slopes (lower dependence on temperature variation) than the other interactions of each pair. Thus, these frequencies can be assigned to the phosphorus chlorine (2) and the sulfur chlorine (3), respectively.

II.3.3.3 Infrared Spectra; Group Frequency Assignments for α- and β-Sulfanuric Chloride Trimers and Dichlorophosphonitrilebis(oxochlorosulfonitrile)

The infrared spectrum of $(NPCl_2)_3$ has received considerable attention, and several attempts have been made to assign the bands and to clarify anomalies[81,82,100,101]. The assignment is shown for the main bands observed(Table II-8). Molecular symmetry indicated is D_{3h} for all states, although specific assignments, particularly for PCl_2 stretching and ring out-of-plane deformation motion,are still controversial.

No assignments have been reported for spectra of the trimeric sulfanuric chlorides[71]. For these molecules, it is probable that relative motion of the sulfonitrile ring bonds and exocyclic sulfur-oxygen bonds would not be independent. Coupled motion has been attributed to -N=S=O groups in sulfinyl compounds, and suggested for -N=S(O)< containing compounds, on the basis of a linear correlation between assigned 'antisymmetric' and 'symmetric' NSO stretch frequencies[83]. In general, S=O stretch frequencies assigned are very dependent upon the bonding involved, since delocalization occurs readily with appropriate adjacent bonds and affects the stretch frequency 'observed'. (i.e. coupled motion occurs so characteristic bands are only nominally S=O stretch). For the sulfur-nitrogen bond lengths determined (α-$(NSOCl)_3$, 1.57Å and $NPCl_2(NSOCl)_2$, 1.54 and 1.58Å), the corresponding SN stretch frequencies should be approximately 1040, 1090 and 1000 cm^{-1}, respectively[83]. If the bands at 1110, 1140 and 1180 cm^{-1} observed for the two rings are related to sulfur-nitrogen stretching motion only, the differences could indicate that ring motion is not independent of S=O motion for these compounds. However, characteristic bands do occur (Table II-8), so an approximate assignment has been made.

Modes expected for 'coupled' unit motion[104] were derived for three $NPCl_2$ or NSOCl units in a ring (Table II-7). Further discussion of this approach for tentative assignment of group frequencies is included in section II.4. For bond stretching and ring deformation motion only,

Table II-7 Modes Expected for Bond Stretching and Ring Deformation Motion; Three Phosphonitrile (NPX_2) or Sulfonitrile (NSOX) Units in a Ring Molecule.

Unit motion	Number and description of modes derived[a]		
	Description	D_{3h}	C_{3v}
PN or SN bond stretching	ring stretch as	$2E' + (A_2')$[b]	$2E + (A_2)$
	s	(A_1')	A_1
	ring deformation		$2A_1 + 2E$
	in-plane	$(A_1') + E'$	
	out-of-plane	$A_2'' + (E'')$	
PX bond stretching	PX_2 stretch as ip	A_2''	A_1
	op	(E'')	E
	s ip	(A_1')	A_1
	op	E'	E
SO or SX bond stretching	SO or SX stretch ip		A_1
	op		E

a) as,antisymmetric; s,symmetric; ip,in phase; op, out of phase: symmetry notation according to Cotton[208].

b) modes in brackets infrared inactive

$(NPCl_2)_3$ (D_{3h}) should have 6 and α-$(NSOCl)_3$ (C_{3v}) should have 11 IR active fundamentals in the energy region observed. If the symmetry is distorted from C_{3v} in a related sense (e.g., β-$(NSOCl)_3$ — suggested as the chair-form isomer with one chlorine substituent equatorial[71]), the degeneracy of some or all of the C_{3v} E modes might be removed and the A_2 mode might become weakly IR active, resulting in 12 to 18 observable fundamentals.

By assuming that the 1100 cm^{-1} sulfanuric chloride bands involve primarily ring antisymmetric stretching and can be correlated to the band

Table II-8 Infrared Spectra of α- and β-$(NSOCl)_3$ and $NPCl_2(NSOCl)_2$; Tentative Group Frequency Assignments Compared with $(NPCl_2)_3$ Spectrum.

$(NPCl_2)_3$	assignment a)	α-$(NSOCl)_3$ b)		β-$(NSOCl)_3$ b)		$NPCl_2(NSOCl)_2$ c)		Tentative assignment e)
		sol'n	solid	sol'n	solid	sol'n	solid	
		1356 vs 1344	1357 vs 1345	1340 vs d)	1340 vs,b	1348 s 1335 s	1338 s 1315 ms	SO stretch(op E, ip A_1)
1218 vs 1200 m	ring $\nu_{as}E'$	1110 vs d)	1165 w,sh 1110 vs,b	1100 vs d)	1170 w,sh 1100 vs,b	1177 vs 1142 s	1185 vs,b 1140 s,b	ring as stretch(E)
						1035 m	1031 s	ring as stretch((A_2))
875 vw	ring $\nu_{as}E'$	816 m	837 vw,sh 818 ms	822 s	863 vw,sh 828 s	840 mw	858 w,sh 844 ms,sp	ring as stretch(E)
782 vw	ring $\nu_s A_1'$	700 vs	723 708 s	702 w	710 m	722 s,sp	723 s	ring s stretch(A_1)
675 vw	ring δ A_1	665 s	679 mw,sp 673 s,sp	665 s	673 ms	666 w	669 m,sp	ring deformation(A_1)
612 s	PCl_2 $\nu_{as}ip$ A_2''*		(637 vw,sp)*		(640 vw)*	624 s	643 s	PCl_2 as stretch
527 ms	PCl_2 $\nu_s op$ E'	530 m 520 w	552 vs,b 531 ms,sp	562 m 540 w	590 vs,b 567 m	558 s 537 s,sp	566 s,b 549 ms,b	SCl stretch(E,A_1) PCl_2 s stretch
						484 mw	490 mw,b	SCl stretch(long bond)
410 vw	ring δ E'	430 w	432 w	440 w 415 vw		437 w	435 vw 410 w	ring deformation(E)
336 vw 315 vw	PCl_2 δ op E'	347 w		380 w,b 340 w			370 vw 345 w 310 w,b	SOCl bending(E) PCl_2 bend op

*) ? ring δ A_2'' – see text. a) D_{3h}[101], sol'n bands[81], (A_1' IR inactive, Table II-7); rel. intensities cf. other solid spectra. b) sol'n[71]; solid, nujol mull; b, broad; sp, sharp; other abbreviations, Table II-6. c) Table II-6; solid CsBr pellet. d) possibly a closely spaced doublet. e) symmetry notation for C_{3v} (Table II-7) does not apply to $NPCl_2(NSOCl)_2$.

at 1212 cm^{-1} for $(NPCl_2)_3$ (and, as a corollary, that the sulfanuric chloride bands at 1350 cm^{-1} involve primarily SO stretching), other ring bands would be expected for α-$(NSOCl)_3$ at 780-820(E), 715(A_1), 670(A_1) and 405(E) cm^{-1}. On the basis of assignments made for other phosphonitriles, the A_2 ring mode (IR inactive D_{3h},C_{3v}) would be expected at ≈1040 cm^{-1} [101]. The assignments for ring motion have been made accordingly (Table II-7), leaving bands at 520, 530 and 347 cm^{-1} to be assigned to SCl stretch motion (A_1 and E expected), or other possible deformation modes, of which two additional ring modes (transferred from planar ring out-of-plane deformation A_2'',E'') remain unassigned. If assignment of the A_2'' ring deformation mode to a component of the $(NPCl_2)_3$ band at 612 cm^{-1} is correct[82], the transferred band should occur at ≈600 cm^{-1} for α-$(NSOCl)_3$. This may account for the very weak band observed in the solid state spectrum at 637 cm^{-1}.

Assignments of SCl stretch frequencies for S(O)Cl and NSCl compounds have been the subject of some speculation[84], and generally fall into two regions: 390-420 and 560-620 cm^{-1}. Characteristic bands cannot be so readily assigned to 'pure' SCl stretch as has been assumed[85]. Nevertheless, consistent with the approximate terminology used for the other assignments, bands at 520 and 530 cm^{-1} have been assigned to SCl stretch,and that at 347 cm^{-1} to SOCl bending.

This tentative assignment for α-$(NSOCl)_3$ is easily related to the solution spectrum of β-$(NSOCl)_3$, in further support of the symmetry being very close to C_{3v}. For solid state spectra of both α- and β- forms, more distortion from C_{3v} is evident in the removal of the degeneracy for the ring as stretch modes(E). The origin of the 'splitting' of bands assigned for ring s stretch modes(A_1) for solid state α-, and not observed for β-$(NSOCl)_3$, is not obvious.

The relative intensity of an observed band depends upon the change in dipole moment for the vibration to which it corresponds. Thus, it is not reasonable to transfer relative intensities for ring bands, as well as energies, from planar $(NPCl_2)_3$, even when the motion can be entirely attributed to ring modes. Given the approximate band descriptions for the sulfanuric chlorides, no attempt has been made to predict specific component assignments for the symmetric and antisymmetric ring modes derived from the C_{3v} E modes.

The assignments for $(NPCl_2)_3$ and the sulfanuric chlorides have been transferred to corresponding main bands observed for $NPCl_2(NSOCl)_2$, for which there should no longer be any degenerate modes, as the molecular symmetry is further reduced to distorted m (C_s). The notation corresponding to modes derived for C_{3v} symmetry does not apply, but the descriptions can be retained. No attempt has been made to differentiate ring motion into possible PN and SN components, as it is unlikely such motion would be independent.

At first glance, the bands at 624 and 484 cm^{-1} of the mixed ring spectrum, which have no counterparts in the sulfanuric chloride spectra, could be assigned as the PCl_2 as and s stretch modes expected. ^{31}P nmr measurements (Table II-5, I-1, and I-2) indicate that the charge density at the phosphonitrile phosphorus atoms is similar for $(NPCl_2)_3$, $NPCl_2(NSOCl)_2$, and $[Cl_3PNPCl_3]^+$. The PCl bond distances for the two cyclic compounds are 1.95 and 1.97 Å, respectively. By comparison with the ring and linear phosphonitrile PCl_2 as stretch assignments (section II.4, Table II-11), the PCl_2 as stretch for the mixed ring would be expected at 612-633 cm^{-1}. Thus, the 624 cm^{-1} band has been assigned to this mode. Also in comparison with other cyclic phosphonitriles, the corresponding PCl_2 s stretch should then occur at 528-550 cm^{-1}. So the relatively strong band at 537 cm^{-1} has been assigned to this mode.

The two sulfur-chlorine distances in the mixed ring are crystallographically inequivalent, and one is longer than that for α-$(NSOCl)_3$ (Table II-3). So, at least in the solid state, the 490 cm^{-1} band may involve relatively more 'long bond' SCl stretching, and the other SCl stretch mode expected has been assigned to the band at 566 cm^{-1}.

II.4 Infrared Spectra of Linear Phosphonitriles

II.4.1 Definition and Group Frequency Assignment Approach

Energies corresponding to vibrational motion for a molecule can be obtained from its infrared absorption spectrum. It is possible to assign a particular vibration to an observed band as if that vibration involved relative motion of only one atom or group of atoms, and could be described as only one type of motion (e.g. bond stretching). Because molecular vibrations actually involve motion of all the atoms, the description of the vibrational mode assigned to an observed band is only a name, and the molecular vibration which corresponds to the energy absorbed is not necessarily that which is implied. However, whatever the motion involved, it may still be attributable to a certain atom or group, and thus be characteristic and transferable to other similar bonding situations for that atom or group. In this sense, group frequencies* have been tentatively assigned for some of the linear phosphonitriles prepared.

The problem is twofold – first, to find the observed bands, if any, which can be associated with (independent) group motion and second, to name them according to the most likely type of vibration involved. The linear phosphonitriles possess at most minimal symmetry (possibly C_s for the covalent three-atom chains, C_{2v} for the three-atom chloro-cation or C_2 for the five-atom cation). Thus, 3N-6 fundamentals are expected (except for C_{2v}, none degenerate), all of which are both Raman and infrared active.

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* Frequency is used in the conventional sense referring to wavenumber of maximum absorption for a characteristic vibration.

Table II-9 Vibrational Modes Expected for Covalent Linear Phosphonitrile and Mixed Systems Derived from Unit Motion (4000-425 cm^{-1}).

Unit and site symmetry	Original motion	Modes expected, number and description[a)]
Chain:		
PNS	stretching	one P=N stretch one S-N stretch
	deformation	one PNS chain bend[b)]
PNP, C_s	stretching	one P=N stretch one P-N stretch }or{ two PN chain stretch; as(A"), s(A')
	deformation	one PN chain bend (A')
PNPNS	stretching	two P=N stretch one P-N stretch }or{ one P=N stretch two PN chain stretch; as(A"), s(A') one S-N stretch
	deformation	two chain bend[b)]
Sulfur or phosphorus atom groups:		
$-S(O)_2Cl$, C_s	stretching	two S=O stretch; as(A"), s(A') one SCl stretch
	deformation	one SO_2 bend (A')
$=PCl_3$, C_{3v}	stretching	two PCl stretch; as(E), s(A_1)
C_s	stretching	three PCl stretch; as(A',A"), s(A')
$>PCl_2$, C_s	stretching	two PCl stretch; as(A"), s(A')
$-P(O)Cl_2$, C_s or $-P(S)Cl_2$, C_s	stretching	two PCl stretch; as(A"), s(A') one P=O stretch or one P=S stretch

a) symmetry notation refers to corresponding site symmetry elements; as, antisymmetric; s, symmetric

b) may not be high enough energy to occur in region observed.

Table II-10 Vibrational Modes Expected for Ionic Linear Phosphonitriles Derived from Unit Motion (4000-425 cm^{-1})

Bond or group	Original motion	Modes expected, number and description[a)]
Cations:		
$P(NP)_n$	PN stretching	n=1 two PN chain stretch; as(B_1), s(A_1)
		n=2 four PN chain stretch; as, ip(B) and op(A) s, op(B) and ip(A)
	PNP deformation	n=1 one PN chain bend (A_1)
		n=2 three PN chain deformation (2A, B)
$=PCl_3$(two units)	PCl stretching	two PCl_3 s stretch; ip(A_1) and op(B_1)
		four PCl_3 as stretch; ip(B_2, A_2) and op(B_1, A_1)
$>PCl_2$	PCl stretching	two PCl_2 stretch; as(B), s(A)
$=P-NH_2$(two units)	PN stretching	two P-N stretch; op(B), ip(A)
	NH stretching	four NH_2 stretch; as, op(B) and ip(A) s, op(B) and ip(A)
	NH_2 deformation	two NH_2 bend; ip(A) and op(B)
Anions:		
$[PCl_6]^-$	PCl stretching	one as stretch (O_h, F_{1u})

a) notation for cation symmetry C_{2v}; for application to C_2, ignore subscripts 1 and 2; ip,in phase; op,out of phase; as,antisymmetric; s,symmetric.

Table II-11 Frequencies Expected for Inorganic[a)] Phosphorus and Sulfur Groups for Liquid or Solid State Vibrational Spectra.

Bond type and assigned mode	Expected range, cm^{-1}	References and comments
Phosphorus-oxygen:		
P=O stretch	1275-1400, general 1250-1330, phosphorylhalides	[86,87] $\tilde{\nu} = 35.0\ \Sigma\chi_i + 975$ cm^{-1}(liquids) (χ_i = group electronegativity of ith substituent at P atom; i ≠ oxygen)
Phosphorus-sulfur:		
P=S stretch	610-770, general 660-740, thiophosphorylhalides	[86,87] P=S stretch couples with symmetric stretch of other P substituents; frequency of latter lower than expected, and of P=S stretch higher; calculated for isolated bond, 675 cm^{-1} [88,89,102].
Phosphorus-nitrogen:		
P=N stretch	1170-1440, general 1325-1400, localized	[90] lower if delocalization of Π system likely over adjacent bonds.
P-N stretch	875-1055	[90]
P(NP)$_n$ PN chain	1170-1350, as[b)] 700-900, s 470-530	[90,104] modes expected as derived for C_2 PN stretch — PN chain def'n n=1 two(as,s) — one n=2 four(2as,2s) — three
Sulfur-oxygen, SO_2:		
S=O stretch	1350-1440, as 1160-1220, s	[91,92] ratio ≈ 1.16-1.18 [93]
SO_2 deform'n	400-700	[94] ≈500 cm^{-1} [95]
Sulfur-nitrogen:		
S=N stretch	780-1500, general 1350-1430, localized	[96] variable since delocalization with SN bond occurs readily, depending on other sulfur substituents.
S-N stretch	680-930	[96]

(continued)

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a) halo-substituents at P or S; in general, for a given mode, frequency for chlorine substituent is expected lower than for fluorine[86].

b) as, antisymmetric; s, symmetric.

Table II-11 (continued)

Bond type and assigned mode		Expected range,cm^{-1}		References and comments	
Sulfur-chlorine:					
SCl stretch		450-655,general		86	
		570-610, >NSO_2Cl		95	
Phosphorus-chlorine:					
PCl stretch					
		as	s	ratio (as/s)	
ionic	$[PCl_6]^-$	450	(360)$^{c)}$	1.25	98
	$[PCl_4]^+$	630	(450)	1.40	98
covalent	$RN{=}PCl_3$	580-615	465-485	1.23-1.30	103,105,107
	$P(O)Cl_2$	530-590	460-515	1.10-1.17	99,108
	$P(S)Cl_2$	510-610	430-550	1.12-1.27	102,107
	N_2PCl_2	590-620	510-535	1.15-1.20	101,102,127

c) values in brackets for modes Raman active only (regular configuration).

Motion of the chain and the end groups was treated as independent, and modes assigned for corresponding frequencies expected, as derived for the separate chain and phosphorus or sulfur atom groups as units (Table II-9, II-10; modes expected, and Table II-11; frequencies expected). Where the molecule or ion contains repeating units, the phase conditions for 'coupling' were used to determine the number and types of associated motion expected[104]. Only the main bands of a spectrum were considered, and they were treated as fundamentals. (This ignores overtone or combination bands as relatively weak and possible accidental degeneracy-induced Fermi resonance.) Deformation modes of all but very strong bond groups were not considered.

II.4.2 Solid State Infrared Spectra and Group Frequency Assignments

Group frequencies were assigned to the main bands of the solid state infrared spectra of:

$Cl_3PNPOCl_2$, trichlorophosphonitrilephosphoryldichloride; Figure II-5 and Table II-12(i).

$Cl_3PNPSCl_2$, trichlorophosphonitrilethiophosphoryldichloride; Figure II-6 and Table II-12(ii).

Cl_3PNSO_2Cl, trichlorophosphazosulfonyl chloride; Figure II-7 and Table II-12(iii).

$[Cl_3PNPCl_3][PCl_6]$, trichlorophosphonitriletrichlorophosphonium hexachlorophosphate; Figure II-9 and Table II-13(i).

$[Cl_3PNP(Cl)_2NPCl_3][PCl_6]$, chlorobis(dichlorophosphonitrile)trichlorophosphonium hexachlorophosphate; Figure II-10 and Table II-13(ii).

$[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$, aminodiphenylphosphonitrileaminodiphenylphosphonium chloride; Figure II-11 and Table II-14.

The liquid spectrum of the product from the reaction (4)a, II.2.3, has also been assigned on the basis of the (hypothetical) formula $\{Cl_3PNP(Cl)_2NSO_2Cl\}$; Figure II-8 and Table II-12(iv). Details of compound preparation and spectral measurement are included in II.2.1 and II.2.4,(5), respectively.

Some band position values have been tabulated[107,108] (Table I-1) for $Cl_3PNPOCl_2$ and $Cl_3PNPSCl_2$, and values from this work agree within experimental error, except for the band at 1355 cm^{-1} for the phosphoryl chloride, which is reported at 1332 cm^{-1}. As observed, this band is very broad and could not be resolved into possible components (Figure II-5). Isolated values have been reported for $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$[26,109], and agree with those reported here. The Raman and infrared spectra of $[Cl_3PNPCl_3]Cl$ and $[Cl_3PNPCl_3][PCl_6]$ have been reported and assigned[110] (discussed in II.4.4).

Table II-12 Main Bands Observed and Tentative Group Frequency Assignments for Some Covalent Linear Phosphonitrile and Mixed Systems.

Compound, bands observed[a)]		Tentative assignment[b)]
i $Cl_3PNPOCl_2$	ii $Cl_3PNPSCl_2$	
1355 vs,b[c)]	1315 vs,b	P=N stretch
1270 s		P=O stretch
778 s,b	811 s	P-N stretch
	692 s	P=S stretch
615 s,b * 597 s	609 s,b 591 s	}PCl_3 as stretch (A', A")
570 m	533 ms	$POCl_2$ or $PSCl_2$ as stretch (A")[d)]
525 m		$POCl_2$ s stretch (A')
505 w,sh}	515 mw	PN chain bend
477 ms	470 ms	PCl_3 s stretch (A'),and $PSCl_2$ s stretch (A')
iii Cl_3PNSO_2Cl	iv $Cl_3PNP(Cl)_2NSO_2Cl$	
1375 1360 vs[e)]	1360 vs,b	SO_2 as stretch (A")
	1263 w	
1230*	1190-1205*	P=N stretch, and PN chain as stretch
1173} vs,b	1165 sh} vs,b	SO_2 s stretch (A')
	822 ms,sh	PN chain s stretch
770 s	773 s,sp	S-N stretch
	710 vw	
	675 vw	
630 ms 604 s	615 * 600 vs,b	}PCl_3 as stretch (A', A")
	590 sh}	PCl_2 as stretch (A")
572 ms	565 m,sh	SCl stretch
538 w	535 w,sh	SO_2 bend (A')
	510 ms,sp	PCl_2 s stretch (A')
510 s,sp	475 ms,b	PCl_3 s stretch (A') and PN chain deform'n

* composite . a) position of maximum absorption, cm^{-1}; solid state. b) symmetry notation refers to approximate site symmetry of group as in Table II-9. c) vs,verystrong; s,strong; m,medium; w,weak; sh,shoulder; b,broad; sp, sharp. d) PCl_2 stretching motion. e) nujol absorption interference.

Table II-13 Main Bands Observed and Tentative Group Frequency Assignments for Ionic Linear Phosphonitriles, $[Cl_3PNPCl_3][PCl_6]$ (i), and $[Cl_3PNP(Cl)_2NPCl_3][PCl_6]$ (ii).

Compound, bands observed[a)c)] i	ii	Tentative assignment[b)]
1325 vs (2)		
1310 s (1)	1312 vs,b	PN chain as stretch B_1 [ip(B)]
1285 sh	1280 sh	[op(A)]
	1230 sh	
837 mw	846 mw	[ip(A)]
	787 s	PN chain s stretch A_1 [op(B)]
	760 w,sh	
662 ms (1) 655 ms (2)	633 s *	PCl_3 as stretch ip(B_2)
	620 ms	[PCl_2 as stretch op(B)]
637 s (1) 626 s (2)	609 s	PCl_3 as stretch op(B_1)
(612 sh)	598 mw	PCl_s as stretch ip(A_2)(IR inactive, C_{2v})
595 w	590 ms,sp	op(A_1)
	550 sh	[PCl_2 s stretch ip(A)]
502 m,sp	518 ms,sp	PCl_3 s stretch op(B_1) and ip(A_1)
470 sh	475 vw,sh	PN chain bend A_1 (see text)
455 ms (1) 437 s (2)	438 s,b	$[PCl_6]^-$ as stretch

---

* composite.

a) position of maximum absorption, cm^{-1}, solid state.

b) [] brackets refer to assignments for the five-atom chain cation, symmetry C_2; for modes expected for both cations, symmetry notation listed is C_{2v} which corresponds to that for C_2 if the subscripts 1 and 2 are ignored.

c) abbreviations as for Table II-12.

Table II-14 Main Bands Observed and Group Frequency Assignment for $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$.

Bands observed a)	Phenyl bands b)	PN chain and P-NH_2 bands
3160 s		NH_2 as stretch (B, A)
3052 s	CH stretch	NH_2 s stretch (B, A)
1970 w	CH deformation out-of-plane combinations	
1890 w		
1810 w		
1765 w		
1602 w	C=C stretch	
1578 mw		NH_2 bend (A, B)
1555 w,sh	C=C stretch	
1480 m,sp	"	
1437 ms,sp	"	
1308 w,sh	combination	
1292 w,sh	CH deformation in-plane	
1250 s,b		PNP as stretch (B)
1176 mw	CH deformation in-plane	
1158 w	"	
1118 1114 }s	X-sensitive ring deformation	
1068 w	CH deformation in-plane	
1025 w	"	
995 mw,sp	ring breathing	
968 s		P-N stretch, P-NH_2, (A) and (B)
935 m	CH deformation out-of-plane(w)	
747 744 }ms	CH deformation out-of-plane	
715 ms	X-sensitive ring deformation in-plane	
695 ms		PNP s stretch (A)
686 w	ring deformation out-of-plane	
538 mw	X-sensitive ring deformation (out-of-plane C-P bend)	
528 s		
507 m		(PNP deformation)
443 mw	X-sensitive ring deformation in-plane	
420 w		

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a) position of maximum absorption in cm^{-1}; solid state; abbreviations as in Table II-12. b) description as in references 113 and 114; X-sensitive ≡ P-sensitive.

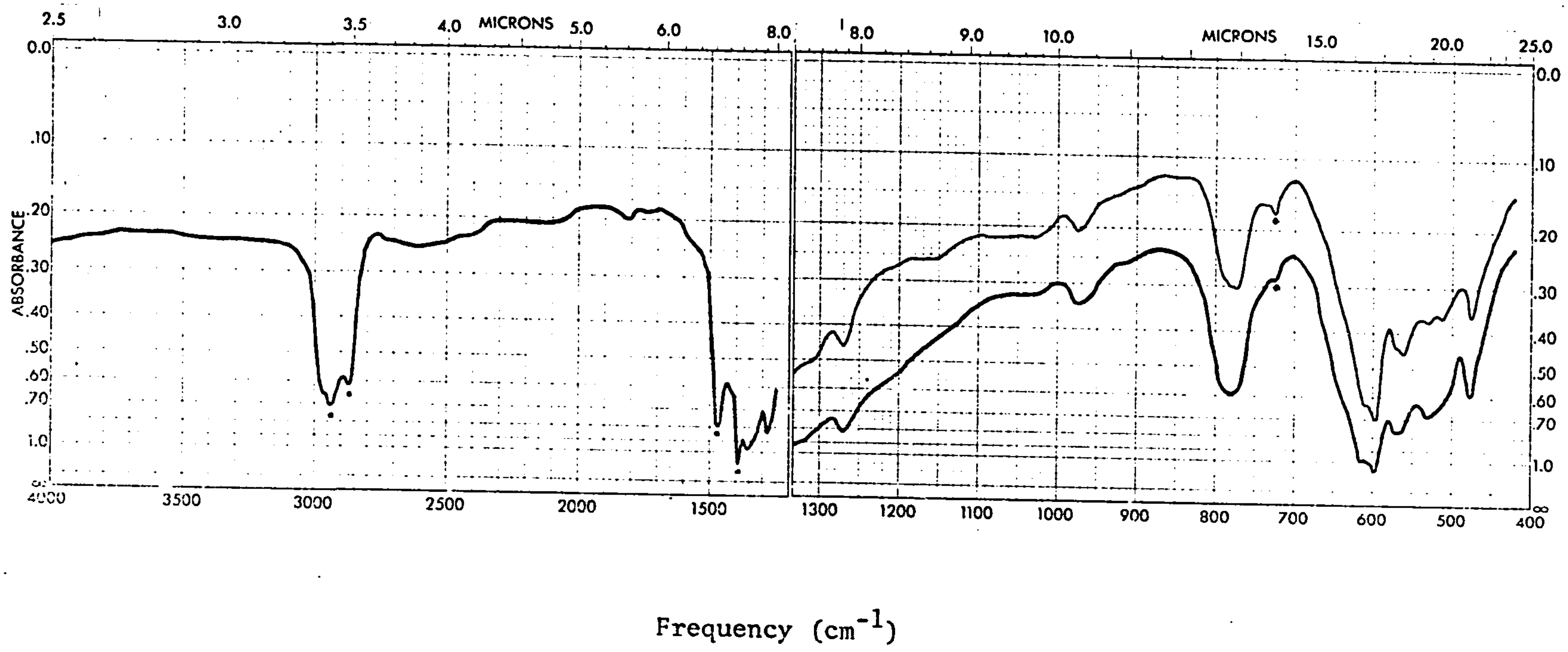


Figure II-5 Infrared Spectrum of $Cl_3PNPOCl_2$, Solid State (nujol mull, KBr*).

*nujol bands marked with an asterisk.

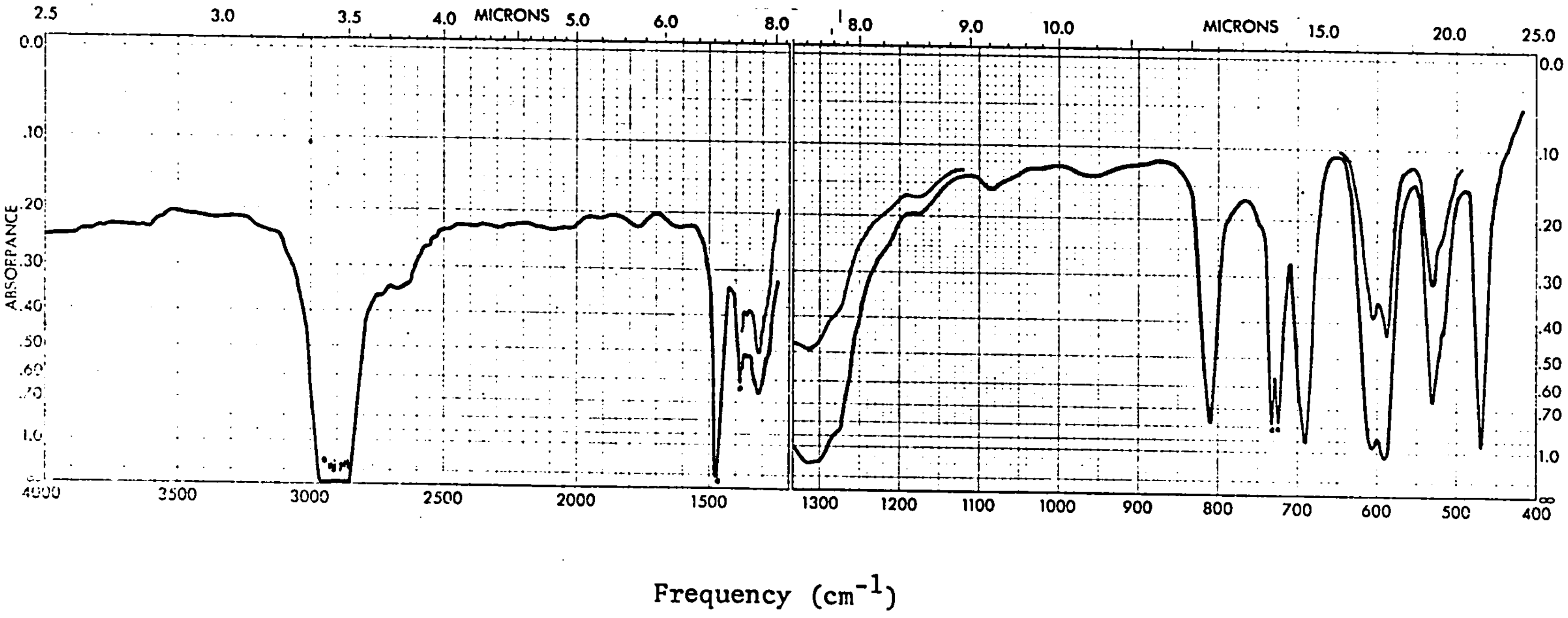
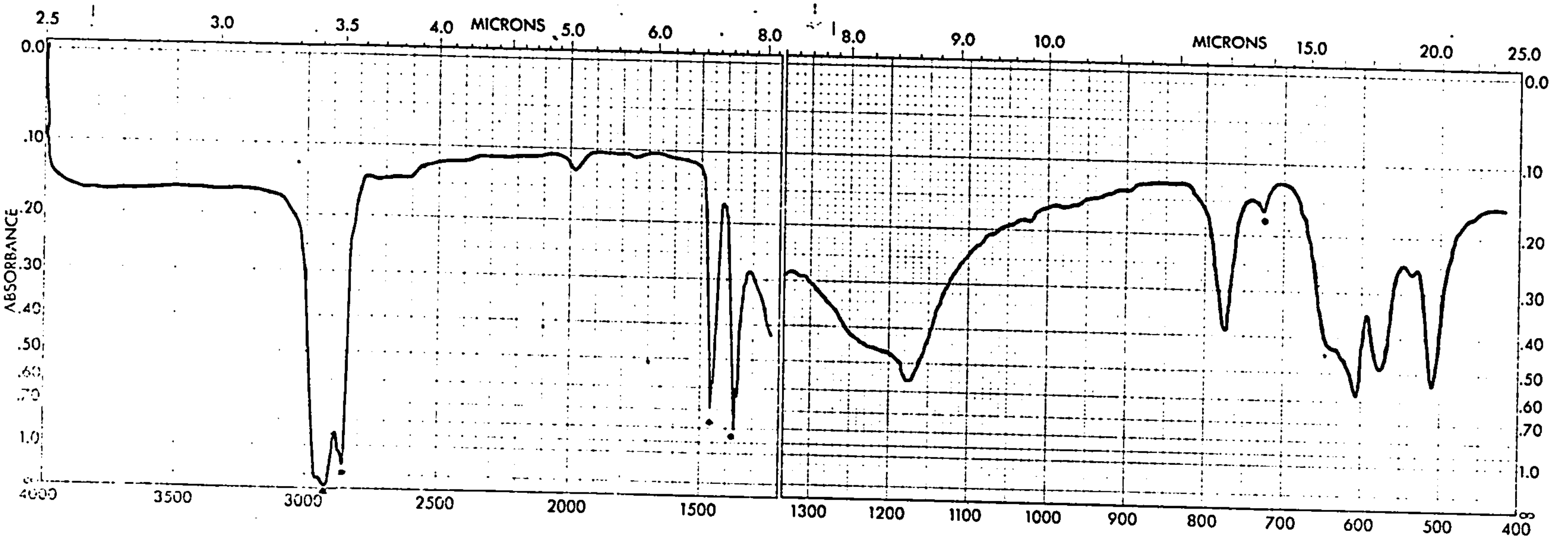


Figure II-6 Infrared Spectrum of $Cl_3PNPSCl_2$, Solid State$^{a)}$ (nujol mull, polythene film*).

* nujol and polythene bands marked with an asterisk.

a) Samples were molten in the heat of the cell compartment.



Frequency (cm^{-1})

Figure II-7 Infrared Spectrum of Cl_3PNSO_2Cl, Solid State (nujol mull, KBr*).

*nujol bands marked with an asterisk

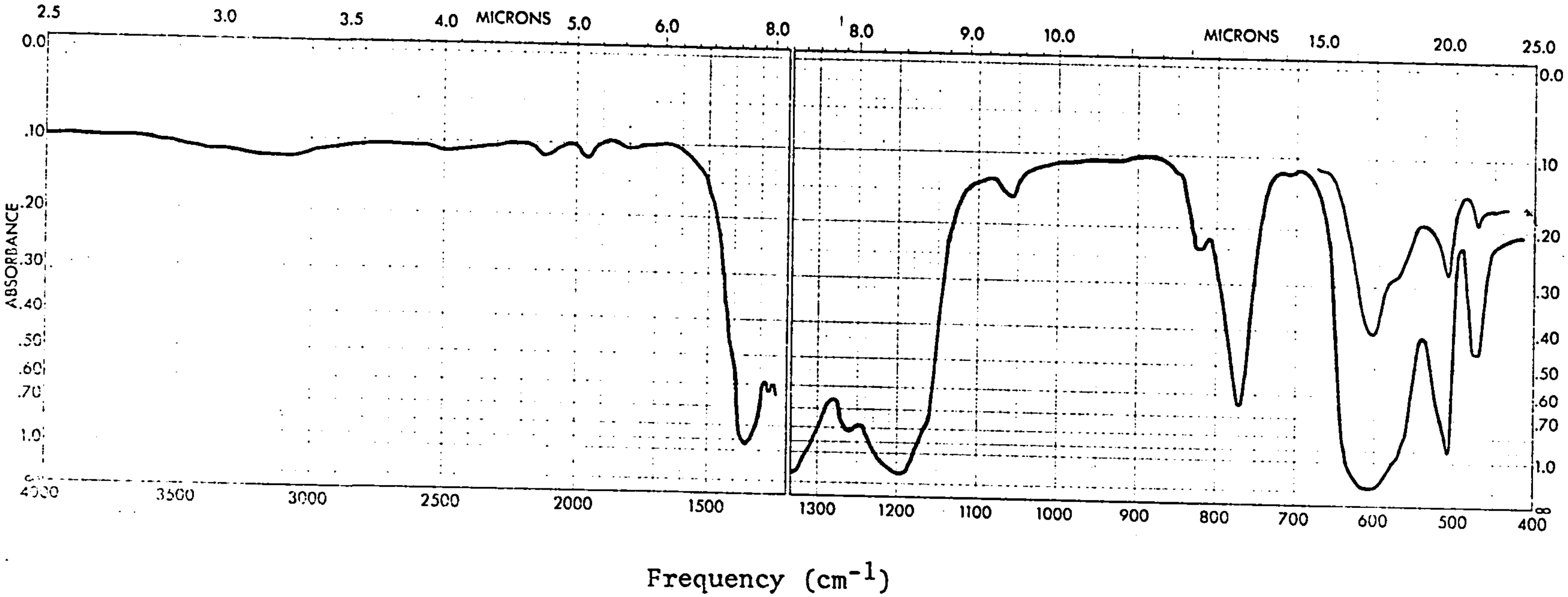


Figure II-8 Infrared Spectrum of the Product of the Reaction Between NH_2SO_2OH and $[Cl_3PNPCl_3][PCl_6]$; $\{Cl_3PNP(Cl)_2NSO_2Cl\}$, Liquid.

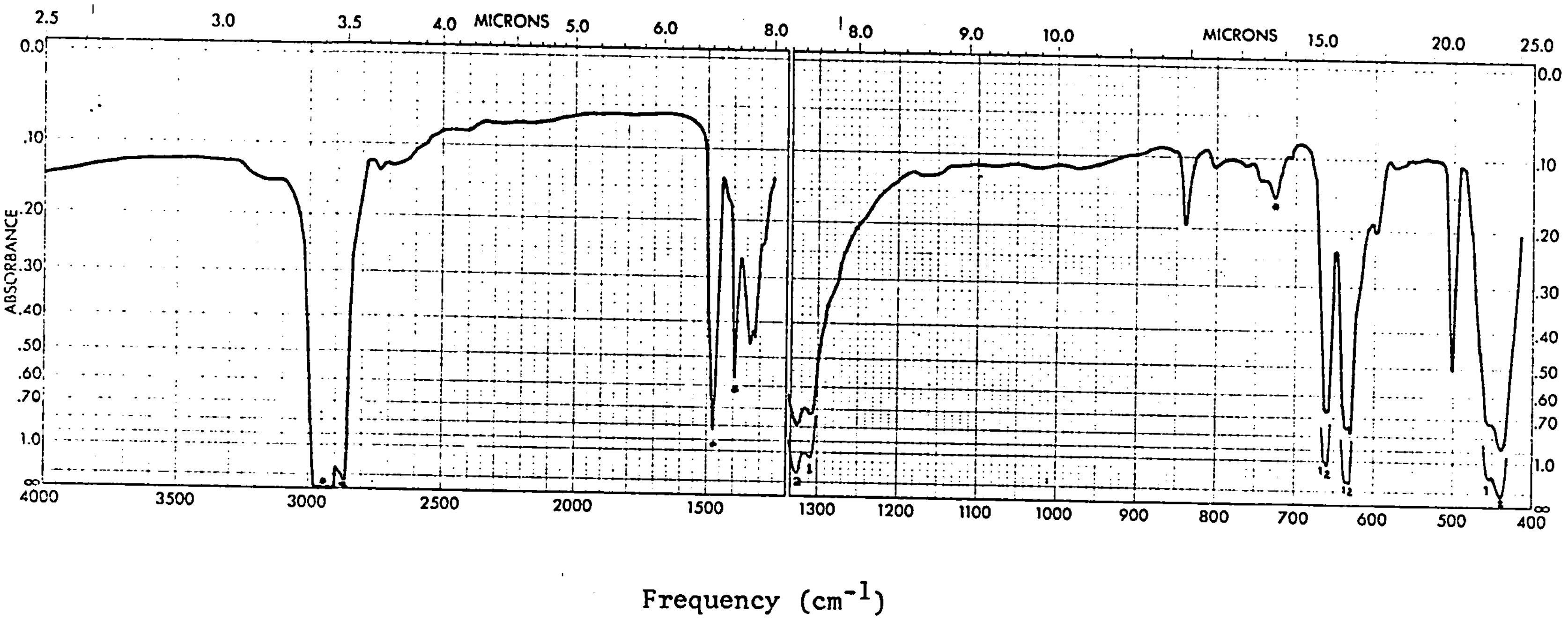


Figure II-9 Infrared Spectrum of $[Cl_3PNPCl_3][PCl_6]$, Solid State (nujol mull, KBr*).

*nujol bands marked with an asterisk.

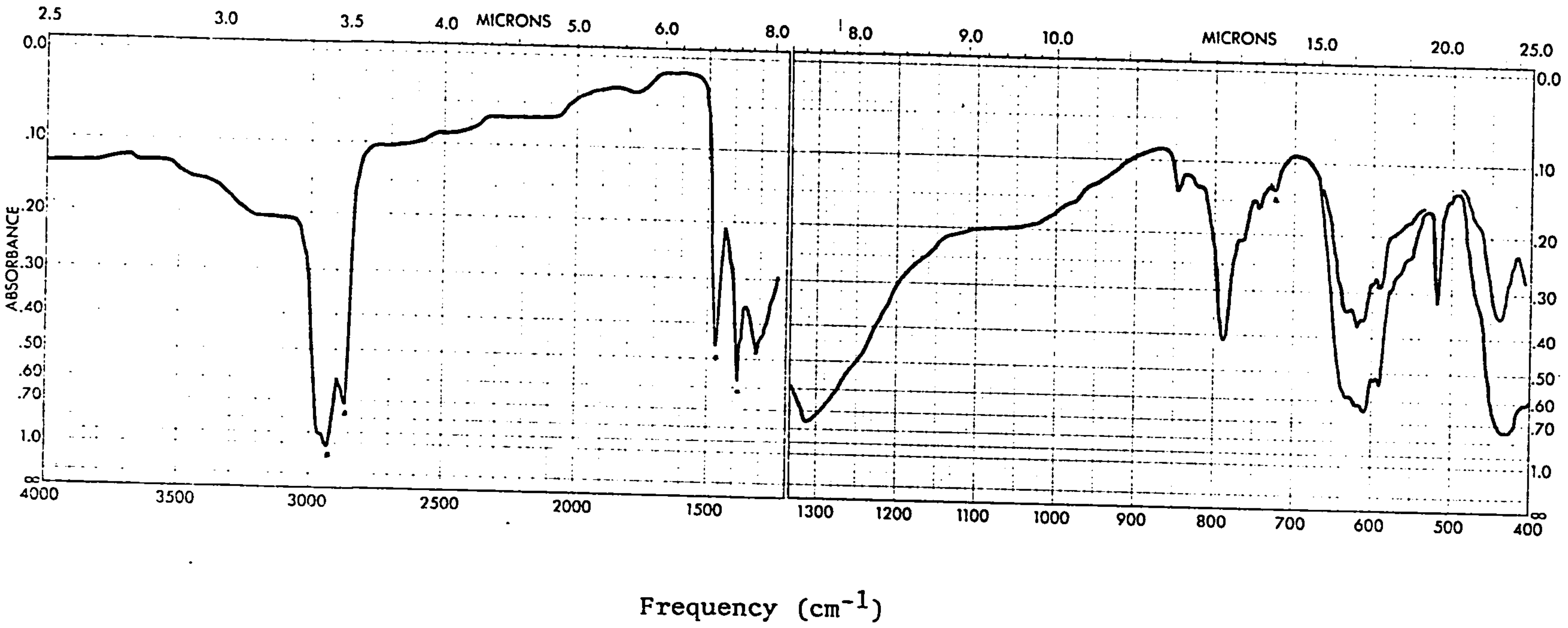


Figure II-10 Infrared Spectrum of $[Cl_3PNP(Cl)_2NPCl_3][PCl_6]$, Solid State (nujol mull, KBr*).

*nujol bands marked with an asterisk

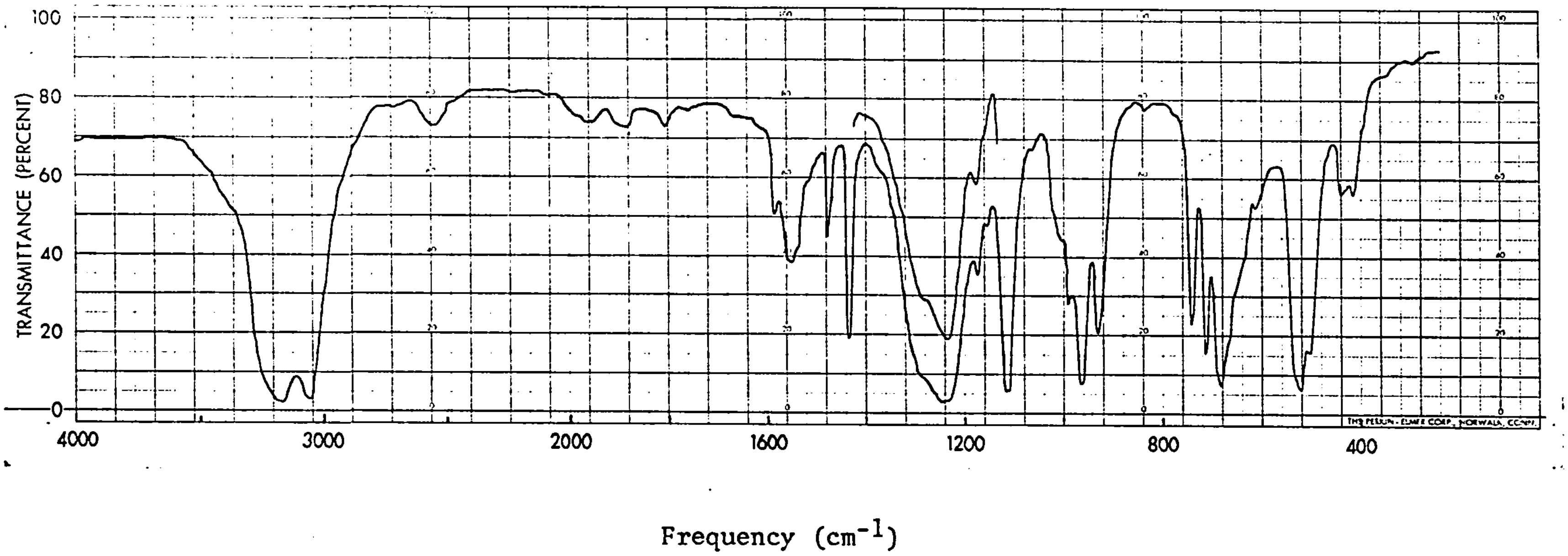


Figure II-11 Infrared Spectrum of $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$, Solid State (CsBr pellet).

II.4.3 Discussion

Covalent Molecules

The two bands assigned to PCl_3 antisymmetric stretch (A', A") were not considered to be the degenerate antisymmetric stretch (E) and the symmetric stretch (A') bands expected for C_{3v} site symmetry, because their relative intensities are invariably reversed to that expected (E > A') in all spectra, including those for similar $RN{=}PCl_3$ compounds reported elsewhere[103,105]. On the basis of the assignment made, the site symmetry at phosphorus in linear phosphonitriles containing $N{=}PCl_3$ groups is not C_{3v}, but possibly C_s.

For the linear phosphonitrile sulfonylchlorides, the assignment of P=N and S=O stretch modes was based mainly on the relative regions expected for the latter antisymmetric and symmetric modes. In the composite band at 1190-1220 cm^{-1} of the spectrum of trichlorophosphazosulfonyl chloride, the higher wavenumber component is broader, which is consistent with its assignment as P=N stretch.

The band at 1270 cm^{-1} for trichlorophosphonitrilephosphoryldichloride was assigned to P=O stretch rather than that at 1355 cm^{-1}, because the P=O stretch frequency for chlorine substituents is expected in the lower portion of the range listed (Table II-11). This is consistent with the empirical fit for liquid state[86], $\tilde{\nu} \simeq 1280$ cm^{-1}. Similar assignments have been made for phosphonitrilephosphorylchloridefluorides on the same basis[108]. The assignment of P=S stretch to the band at 692 cm^{-1} for the thiophosphoryldichloride, agrees with those made for other phosphonitrile halide analogues (630-695 cm^{-1})[111]. This value, compared with a 'single bond' value, 675 cm^{-1} (Table II-11), indicates that coupling occurs, as expected.

Ionic Phosphonitriles

Apparently trichlorophosphonitriletrichlorophosphonium hexachlorophosphate, $[Cl_3PNPCl_3][PCl_6]$, exists in two solid state forms. All the antisymmetric stretch bands are doubled with not-quite-equal intensities, and bands pertaining to the different forms have been labelled (1) and (2) on this relative intensity basis. There is no mention of any doubling of bands in the published report of the spectrum[110], nor is there any indication of whether the infrared spectrum was obtained for solid state samples, solution, or both. From a comparison, it is not obvious whether the results reported correspond to one of the forms ((1) or (2)), or an unresolved average spectrum, but making allowance for a scale shift of 10 cm^{-1}, the published values are within experimental error of those found for form (1). The antisymmetric stretch bands are doublets of almost equal intensity components, and the PN as stretch mode should contain only one component, which indicates that the doubling is real. The presence of more than one solid state molecular form in samples of this compound was also inferred from nqr measurements[112]: The signals (and side bands) observed overlap considerably, making it impossible to decipher the fundamentals and define the nqr spectrum. However, there is an unusual doublet fine structure which indicates two inequivalent solid state forms.

The reported assignment[110] was discussed on the basis of C_{2v} symmetry using erroneous arguments. The PN chain s stretch mode was reported to be infrared inactive for C_{2v}, although assigned to an infrared active band. This mode belongs to the A_1 representation, and would be both infrared and Raman active. The stretch mode expected to be inactive in C_{2v} symmetry (A_2) can be considered (within the 'unit' approach used in this work) to be one derived from coupling of the PCl stretch motion, PCl_3 as stretch, ip(A_2), which would be relatively weakly infrared active if the symmetry were lowered to C_2. The assignment for the solid state spectrum, forms (1) and (2), of the three-atom chain cation fits either C_{2v} or C_2, although the latter would be the more likely solid state symmetry.

The suggestion of a shoulder on the high wavenumber edge of the very strong, doubled $[PCl_6]^-$ antisymmetric stretch band has been assigned to the PN chain deformation mode (A_1), and the more intense band at 502 cm^{-1} to the PCl_3symmetric stretch mode (B_1). This is the only difference from the reported assignment, for the region considered. Both modes should be infrared and Raman active. The relatively strong band in the Raman spectrum at ≃470 cm^{-1}, and not noted in the infrared spectrum, is most likely to be a combination of the PCl_3 symmetric stretch (A_1) mode and the PN chain deformation mode (A_1), which is obscured in the infrared spectrum by the $[PCl_6]^-$ antisymmetric stretch (Raman inactive).

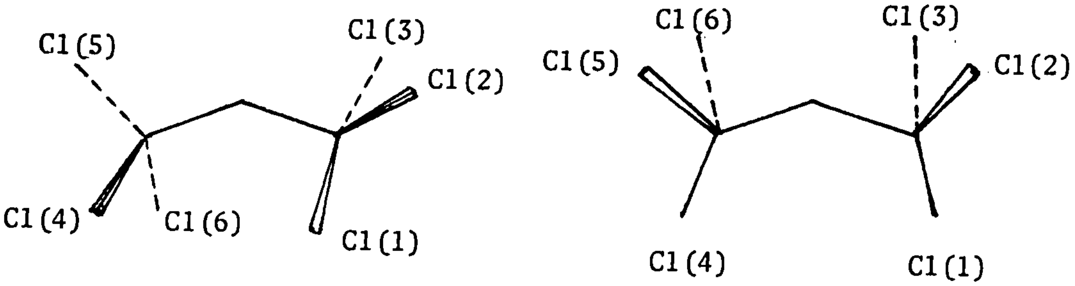
Assignment of phenyl group frequencies to the bands observed for $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$ was based on a discussion of the normal vibrations of monosubstituted benzenes[113] and assignments made for phenyl-substituted phosphonium ions[114,115]. The phenyl bands for which the modes assigned involve major contributions from motions of the phosphorus atom (X-sensitive) occur at positions expected for phosphonium ions; 1116_{av}, 715, 520_{av} and 430_{av} cm^{-1} for $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+$ compared with 1110, 718, 500 and 419 (±12, split) cm^{-1} for $[(C_6H_5)_4P]^+$ or 1089, 700, 499_{av} and 428_{av} cm^{-1} for $(C_6H_5)_3P$ [116]. The remaining bands were assigned to modes expected for the phosphonitrile skeleton and the amino groups. The terminology chosen was based on a combination of PNP chain motion and P-NH_2 group motion, rather than on a fully delocalized NPNPN chain, consistent with the observation of relatively greater shifts in bands between 900 and 1000 cm^{-1} on formation of transition metal chloride compounds, which were thus assigned to $P-NH_2$ group modes (II.5.4).

II.4.4 Structural Information From Assignment Comparison

A linear correlation exists for SN stretch frequency and sulfur-nitrogen bond distance[96], from which the sulfur-nitrogen bonds in the mixed systems, Cl_3PNSO_2Cl and $\{Cl_3PNP(Cl)_2NSO_2Cl\}$, are predicted to be approximately single (≃1.73 Å). The P=N stretch frequency is relatively low (≃1200 cm^{-1}), compared with that suggested (1325 cm^{-1}) for a localized double bond[90]. If both these observations are interpreted as indications of the bonding, it is possible that the electron charge density at the phosphorus atom is high, and greater than that at the sulfur atom. This corroborates the experimental observation that formation of rings from pyrolytic decomposition of these compounds appears to occur via addition reactions involving electron lone-pair donation to the sulfur atom.

The PN antisymmetric stretch frequency for $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+$ is high (1250 cm^{-1}) and closer to values for the cyclic phosphonitrile tetramers, where Π_s bonding is expected to compensate for weaker Π_a bonding in non-planar ring structures[165] (phenyl substitution — 1190 and 1213 cm^{-1}, amino substitution — 1170 and 1240 cm^{-1} for trimer and tetramer, respectively).[12] A similar assignment (1245 cm^{-1}) has been made for $[CH_3(C_6H_5)_2PNP(C_6H_5)_2CH_3]I$[117]. The PN chain antisymmetric stretch frequencies for the ionic linear chlorophosphonitriles are also high (≃1315 cm^{-1}) and similar to those of the $\bar{I}$ form of $(NPCl_2)_4$ (1315 cm^{-1}, $P\hat{N}P$=131°), or the almost planar $(NPCl_2)_5$ (1355 cm^{-1}, $P\hat{N}P_{av}$=149°). ^{31}P nuclear magnetic resonance measurements have shown that the phosphonitrile cations contain equivalent end group phosphorus atoms, so the multiple bond system must be delocalized[106]. They are unlikely to exist in a small nitrogen angle configuration (≤ 120°) because of steric requirements of the substituents, thus the strong PN bonds indicate appreciable Π_s bonding in addition to the Π_a bonding (further discussion in II.5 and III.2).

The doubling of the $[PCl_6]^-$ band at 450 cm^{-1} indicates that molecules of $[Cl_3PNPCl_3][PCl_6]$ are associated in the solid state. That is, ion-pairing occurs rather than a mixed crystal situation where the anions would be independent of the cations except in the overall crystal lattice sense. This also suggests that the anion is intrinsically involved in the formation of the two solid state forms. From the difference in PN chain antisymmetric stretch for $[Cl_3PNPCl_3]^+$ for Cl^- and $[PCl_6]^-$ anions (1338 [110] and (1),1310 or (2), 1325 cm^{-1}), the smaller counterion is associated with a stronger phosphorus-nitrogen bond. This can be interpreted in the bonding model as follows: The most probable configuration is C_2 (distorted C_{2v}) for minimum intra-ionic chlorine-chlorine repulsion (Figure II-12).



a) C_2 b) C_{2v}

Figure II-12 Possible Configurations for the Trichlorophosphonitrile-trichlorophosphonium Ion, $[Cl_3PNPCl_3]^+$

For C_{2v}, a wider angle increases chlorine-nitrogen lone-pair interaction slightly,but a smaller angle increases intra-ionic chlorine-chlorine interaction to a much greater extent, and thus a wider angle accompanies a closer approach to C_{2v}. Distortion reflects the compromise for maximum stability. The Cl^- anion can approach closer 'sideways' for the same amount of distortion due to inter-ionic chlorine-chlorine repulsion, than can the bulkier $[PCl_6]^-$. Hence, the smaller anion allows a larger Π_s contribution to the PN bond strength than $[PCl_6]^-$ for a given crystal lattice stability.

Form (2) is probably in a configuration closer to C_{2v} than (1) (PN antisymmetric stretch (2) > (1)), because crystal lattice stabilization allows more distortion from inter-ionic repulsion to remain uncompensated (by a lowered angle to that of form (1)). (This is consistent with the observation that the reported spectrum corresponds most closely to that of form (1) assuming that it refers to a solution measurement.) However, the concomitantly greater cation chlorine-lone-pair interaction in form (2) would cause slightly longer phosphorus-chlorine bonds, reflected in the small decrease of the PCl bond strength from that of form (1) (PCl_3 antisymmetric stretch ip(B_2) (1), 662 and (2), 655 cm^{-1}; Table II-13(i)).

For $[Cl_3PNP(Cl)_2NPCl_3]^+$, intra-ionic interaction probably determines the configuration. A distorted form with wide nitrogen angles is favored. Thus, the Π_s contribution should be larger than that for $[Cl_3PNPCl_3]^+$ for the same anion. However, there is a lower Π_a contribution to the chain bonding because of the non-coplanarity of the PNP 'halves' at the center phosphorus atom. Thus, the PN bond strength, as a net result, is almost the same as that for form (1) of the three-atom phosphonitrile cation.

II.5 Copper(II) and Cobalt(II) Chlorides of Aminodiphenylphosphonitrile-aminodiphenylphosphonium Ion

II.5.1 General Considerations, Possible Compound Types

In this section, the phosphonitrile cation, $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]$ is designated L^+, and the phosphonitrile chloride as LCl. The copper compounds are referred to as A, B, and C; and the cobalt compounds as D and E, following the outline and formulae indicated in the description of their preparations (II.2.3,(8)).

There have been no reports of complex formation for the phosphonitrile chloride from which a chelate was desired. However, preparation of a blue compound, $Cu(HN(C_6H_5)_2PNP(C_6H_5)_2NH)_2$ (mp 178-180°C with decomposition), from methanol solution of the ionic phosphonitrile and $CuCl_2.2H_2O$, has been reported[118]. After treatment with sodium methoxide, a green precipitate was obtained which became the copper compound on hydrolysis. It was insoluble in water and could be crystallized from polar organic solvents or benzene.

When compounds are formed by amino group nitrogen atom coordination to copper(II) or cobalt(II) halides, they usually contain polymeric distorted octahedral copper(II), and octahedral or tetrahedral cobalt(II) in a non-ionic structure[119,120]. Cobalt(II) halides form complex ionic compounds for some ligands, particularly at low metal:ligand ratios, where the cations are ligand-coordinated cobalt(II) ions and the anions are tetrahedral tetrachlorocobaltate(II)[121]. Similar behavior occurs for copper(II) halides[121,122].

The donor properties of positively charged ligand quaternary amines and phosphines have been studied[123,124], and it has been suggested that a positive charge on a ligand does not necessarily prevent its coordination to a positively charged metal ion, but may stabilize unusual stoichiometries and structures. Tetracoordinate cobalt(II) and nickel(II) complexes containing monoquaternized ditertiary phosphines have been reported with stoichiometry $MX_2.\P X$, where ¶ is the monocharged phosphonium ion. Although these compounds are supposed to contain non-ionic, monomeric transition metal species, they have high thermal stabilities and low solubilities in non-polar solvents, which has been attributed to high lattice energies from interaction of polar $\P^{\delta+}\text{-}MX_3^{\delta-}$ sites of neighboring units.

On the other hand, there are many examples of ionic compounds containing bulky quaternary amine[125,126] or other cations[128] and transition metal halide anions, including tetracoordinate copper(II) and cobalt(II) chlorides[126,129,130].

From the solubility, conductivity, and melting point characteristics (II.2.3,(8) and II.5.2), and the similarity of their electronic spectra to those of anionic copper(II) and cobalt(II) chlorides (II.5.3.1), the compounds prepared could be ionic compounds of the last type. However, the possibility that they are of the pseudo-tetrahedral 'polarized' phosphonium type must also be considered.

II.5.2 Some Physical and Chemical Properties

All the prepared compounds were soluble in polar and insoluble in non-polar organic solvents. In aqueous solution or in wet organic solvents, decomposition occurred with formation of the phosphonitrile chloride and octahedral aquo copper(II) or cobalt(II) ions. Decomposition also occurred

Table II-15 Comparison of Analytical Results Found and Calculated for Copper(II) and Cobalt(II) Chlorides of $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+$ (=L$^+$).

Compound	Analysis, percent						
	Cu or Co	P	N	Cl	C	H	O
A	10.36	9.87	7.28	17.4	48.7	4.48	2.61
B	10.87			18.2			
C	13.94	8.81	6.20	20.5	43.7	4.01	2.68
$CuLCl_3$	10.84	10.57	7.17	18.14	49.18	4.10	0
$CuLCl_3.2H_2O$	10.21	9.96	6.75	17.09	46.33	4.51	5.14
$CuLCl_3.CH_3OH$	10.28	10.02	6.80	17.20	48.58	4.54	2.59
$Cu_3L_2Cl_8$	14.59	9.48	6.43	21.70	44.12	3.68	0
$Cu_3L_2Cl_8.4H_2O$	13.83	8.98	6.08	20.57	41.81	4.07	4.64
$Cu_3L_2Cl_8.2CH_3OH$	13.91	9.04	6.13	20.69	43.83	4.09	2.34
D	5.61	11.6	8.26	14.2	54.6	4.88	<0.5
E	5.23	11.0	7.65	18.2	52.4	4.95	<0.5
CoL_2Cl_4	5.70	11.99	8.13	13.72	55.80	4.65	0
$CoL_2Cl_4.H_2O$	5.61	11.78	7.99	13.49	54.85	4.76	1.52
$CoL_2Cl_4.CH_3OH$	5.53	11.63	7.89	13.31	55.25	4.89	1.50
$CoL_2Cl_4.CH_2Cl_2$	5.27	11.08	7.51	19.02	52.64	4.48	0
$CoLCl_3$	10.05	10.65	7.23	18.28	49.57	4.13	0

in pyridine with formation of the phosphonitrile chloride and copper(II) or cobalt(II) pyridine complexes.

The solid state copper(II) compounds exhibited color changes on variation of temperature. For example, B changed from brown, through gold, to yellow as the temperature was lowered from the melting point, 430°K, to 77°K. The change was gradual, with no evidence of a sharp transition. Single crystals of all the copper(II) compounds were pleochroic: When viewed in one direction, plates of A appear green-brown, while in an approximately perpendicular view, they are deep red.

Qualitative conductance measurements indicated B was more ionic in solution than the phosphonitrile chloride[131] for the solvent nitrobenzene. However, solvation occurred to a varying extent for all compounds. For each metal ion, the same solution spectrum was obtained for all compounds, and because of their insolubility in solvents with low coordination[132], no further conductance studies were attempted.

II.5.3 Spectrometric Results

(1) ^{35}Cl nuclear quadrupole resonance – Solid samples of A and B were scanned through 9-54 MHz. No interactions were detected.

(2) Electron paramagnetic resonance –

Table II-16 G-values From Electron Paramagnetic Resonance Measurements for Some Copper(II) Chloride Compounds.

	Compound[a)b)]	g value	
		294°K	124°K
A	$CuLCl_3.CH_3OH$	2.098	2.092
B	$CuLCl_3$	2.107	2.113
C	$Cu_3L_2Cl_8.2CH_3OH$	2.096	2.094
	dried $CuCl_2$	2.096	2.089

a) empirical formulae, $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+ = L^+$

b) polycrystalline

(3) Infrared spectra — Few changes in solid state or solution spectra occur on compound formation. Those which are observed are minor shifts or 'splitting' of bands assigned to phosphonitrile amino or P-NH_2 group vibrations, which could be attributable to a solvent shift or crystal packing effect[133].

Table II-17 Main Bands Observed for Solid State Infrared Spectra of Copper(II) and Cobalt(II) Chlorides of $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+$. a) ($cm^{-1}$)

LC1	A	B	C	D	E	Tentative assignment
	3425 sh				3495 w	
					3420 vw	
		3352 m,sp	3385 m	3385 m	3375 w	NH_2 as stretch. s
	3295 sh					
	3285 ms,b	3270 m,sp	3280 m			
	3215 m,b		3200 ms	3220 b	3200 m,b	(OH stretch, CH_3OH)
3160 s						
3052 s	3095 w		3085 w			CH stretch.
	3065 w,sp	3074 w	3075 vw	3055 w	3068 mw	
		3054 w	3055 w		3050 mw,sp	
			3025 w	3040 w		
1970 w	1970	1965	1970	1970	1965	CH deformation,
1890 w	1900	1900	1905	1895	1900	out-of-plane
1810 w	1815	1817	1810	1817	1815	combinations.
1765 w	1770	1776		1775	1772	
1602 w,sp	1585 w,sp	1588 w,sp	1585 w,sp	1587 w,sp	1586 w,sp	C=C stretch.
1578 mw,sp 1555 w,sh	1560 ms	1550 mw,sp	1550 1545 } m	1545 m,b	1540 m,b	NH_2 deformation and C=C stretch.
1480 m,sp	1480 w,sp	1482 w,sp	1485 w,sp	1478 w,sp	1478 w,sp	C=C stretch.
1437 ms,sp	1440 ms,sp	1437 ms,sp	1440 ms,sp	1437 ms,sp	1436 ms,sp	"
1308 w,sh	1309 w,sh	1306 w,sh	1310 w,sh	1303 w,sh	1308 w,sh	phenyl combination.
1292 w,sh	1294 w	1281 w	1288 w	1287 w,sh	1290 w,sh	CH deformation, in-plane.
1250 s,b	1254 vs	1258 s	1255 s	1240 vs,b	1252 1208 } vs,b b)	PNP chain as stretch.
1176 mw 1158 w	1178 mw	1177 mw	1177 w,sh 1157 w,sh	1178 w 1158 vw	1178 w 1158 w	CH deformation, in-plane.
1118 1114 } s	1122 1116 } s	1122 1118 } s	1122 s	1116 s	1114 s	X-sensitive ring deform'n.

(continued)

Table II-17 (continued)

LCl	A	B	C	D	E	Tentative assignment
1068 w	1068 w	1069 vw	1070 w	1070 w	1068 w	CH deformation,
1025 w	1026 w	1027 w	1025 w	1020 vw	1025 w	in-plane.
	1008 m,sp$^{c)}$		1010 ms,sp$^{c)}$			
995 mw,sp	994 mw,sp	995 mw,sp	995 mw,sp	993 mw,sp	993 mw,sp	ring breathing.
	970 w,sh	979 w	978}vw			
	964 w,sh		973			
968 s	960 ms				963 s	P-N stretch,
			945 s	955 ms,b		($P-NH_2$) and
		947 s,sp				
935 m	933 w		930}w,sh		929 mw	CH deform'n,
	925 w	919 w	913		923 sh	out-of-plane.
		905 w				
748}ms,sh	750 m	748 sh	777 w	750 sh	755 sh	
744			765 mw			CH deform'n,
	744 w,sp	743 ms	752 ms			out-of-plane.
			742 mw			
717 ms	718 ms	718 ms	727 ms	718 m	716 m	X-sensitive.
695 ms	694 mw	688 s	691 s	690}s	686 s	PNP chain s
686 w	684 m			687		stretch and
				670 w,sh		ring def'n(w).
	614 w$^{c)}$		615 w$^{c)}$			
538 mw	544 m	530 ms	545 ms	538 m	535 w	X-sensitive.
528 s	524 ms	516 s			522 s	
507 m	507 m	508 mw	513 ms	512 s	508 w	PNP chain def'n?
		494 mw	492 ms	498 m,sp		
443 mw	456 w	460 vw	460 w	435 vw	447 w	
	438 w		448 w			X-sensitive ring
420 w	d)		d)			in-plane def'n.
		402 m		410 w	410 w	
		315 w		304 vw	303 vw	Cu(Co)Cl stretch.
		303 mw		290 w	292 w	"

---

a) Compounds as in II.2.3,(8); assignment for $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl \equiv LCl$ in II.4, Table II-14; abbreviations as for Table II-12.

b) possibly CH_2 deformation, CH_2Cl_2 (1265 s for methylene chloride).

c) CH_3OH, C-O stretch (1035 vs for methanol).

d) loses methanol in cell compartment of PE521; lower region not examined.

(4) Ultraviolet, visible and near-infrared spectra — Dried $CuCl_2$ and $CoCl_2$ were insoluble in methylene chloride or nitromethane. All cobalt(II) and copper(II) compounds prepared were soluble in both these solvents, and in the absence of moisture no changes in their solution spectra occurred during periods of two hours.

Table II-18 Electronic Spectra of Some Cobalt(II) Chlorides.[a)]

LCl	D, L_2CoCl_4		$(NH_4)_2CoCl_4$[134]	$((C_4H_9)_4N)_2CoCl_4$[125]
solution, CH_2Cl_2	solution, CH_2Cl_2[b)]	solid	solid	solid
	6300-4500 (55_{av})	4545-6250	4250-6600	4780-5920
	14,500 (565)	14,550	14,450	14,300
	15,100 (535)	15,000	15,040	14,900
	15,750 sh	15,700 sh	15,500	15,750
	15,850 (385)	15,800	15,870	
	16,500 sh	16,250 sh	16,210 sh	16,230 sh
				17,300 sh
			18,182 sh	18,100 sh
	19,000 (5-10)	19,000 w	18,760	18,900
	23,000 (<5)	23,000	22,220	22,000
			24,390	
36,340 (2240)[c)]	36,400 (2240)[c)]	36,230[c)]	31,250 sh	
37,200 (2890)	37,250 (2880)	37,200		
38,000 (2430)	38,100 (2380)	38,000		
38,950 sh	39,050 sh	sh		
		42,200	45,450	

---

a) positions of maximum absorption in cm^{-1} ($\pm$ 200 cm^{-1});
$L^+ \equiv [NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+$.

b) molar extinction coefficient in brackets based on formula L_2CoCl_4 (±5 l/molecm), values low compared with $CoCl_4^{2-}$[125] because excess Cl^- not present.

c) phenyl bands, 36,200 — 39,000 cm^{-1}.

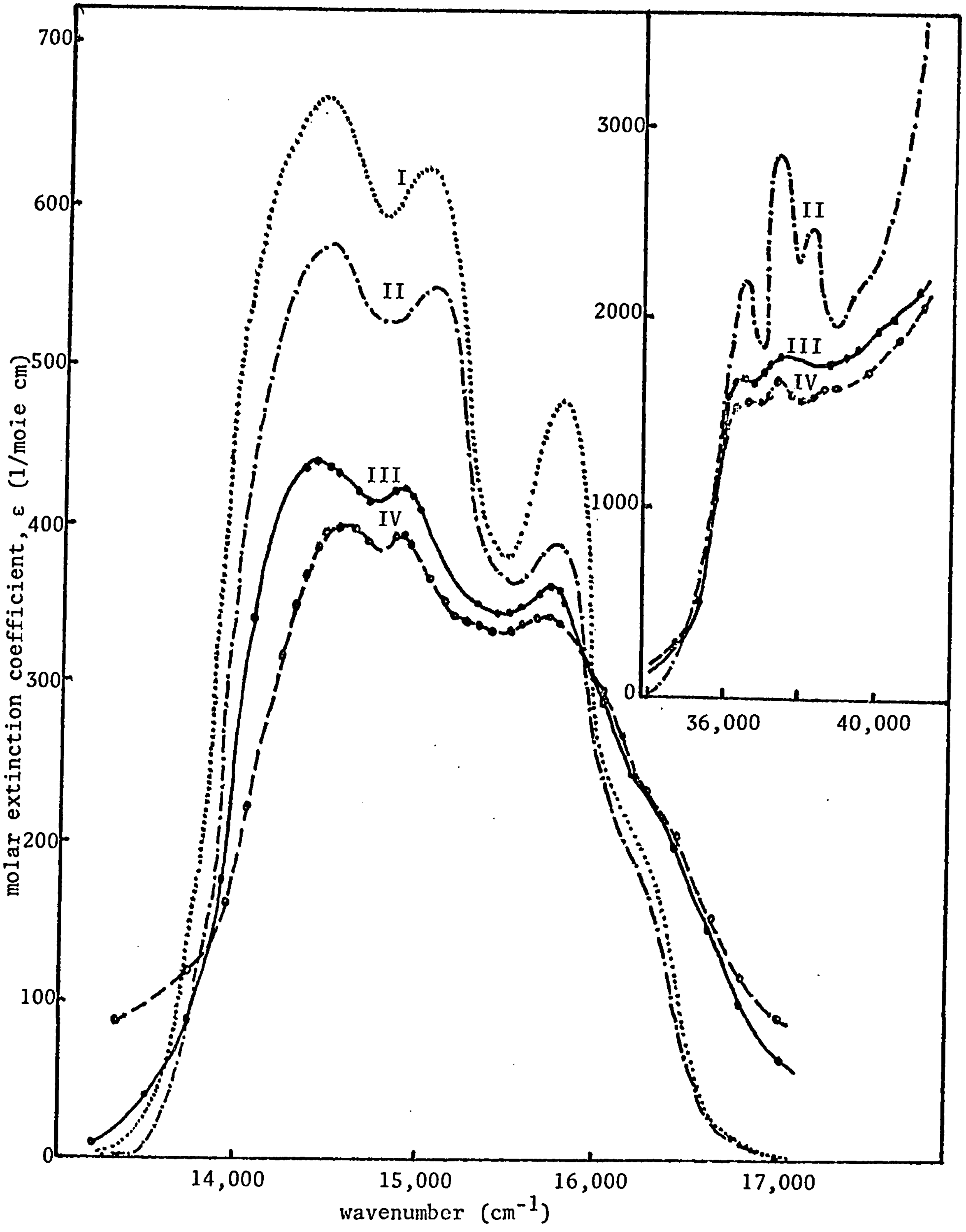


Figure II-13 Electronic Spectra of Some Cobalt(II) Chlorides.
I, $[(C_4H_9)_4N]_2[CoCl_4]$ in methylene chloride[125]; II, D or E in methylene chloride; III and IV, D and E nujol mulls (arbitrary vertical scale).

Table II-19 Electronic Spectra of Copper(II) Chlorides; Solid State, $L^+ \equiv [NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+$. a)

A $LCuCl_3.CH_3OH$ b)	B $LCuCl_3$	C $L_2Cu_3Cl_8.2CH_3OH$
10,500 c)	10,000 sh d)	9,800 sh e)
12,000 sh	12,500	12,100
18,600		18,800
23,800	22,700	23,600
f)	25,700 (w,sh)	25,600 (w,sh)
	27,000 (vw,sh)	f)
	32,000	
	36,400	
	37,500	
	f)	

a) position of maximum absorption in cm^{-1}; see also Figure II-14.

b) empirical formulae. c) broad, slightly asymmetric to higher cm^{-1}.

d) v.broad, at least two components, asymmetric to lower cm^{-1}, 9,000-14,000 cm^{-1} spread.

e) intermediately broad, slightly asymmetric to lower cm^{-1}.

f) higher energy components not distinguishable.

Table II-20 Solution Electronic Spectrum of Copper(II) Compounds of $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+$, L^+. a)

Maximum absorption, cm^{-1}	A,B, or C
11,300	slightly asymmetric to lower cm^{-1} broad band
17,500	
24,200	
31,600	
36,400	phenyl bands
37,200	
37,600	
39,100 sh	

a) methylene chloride solution; A, B, and C as in Table II-19.

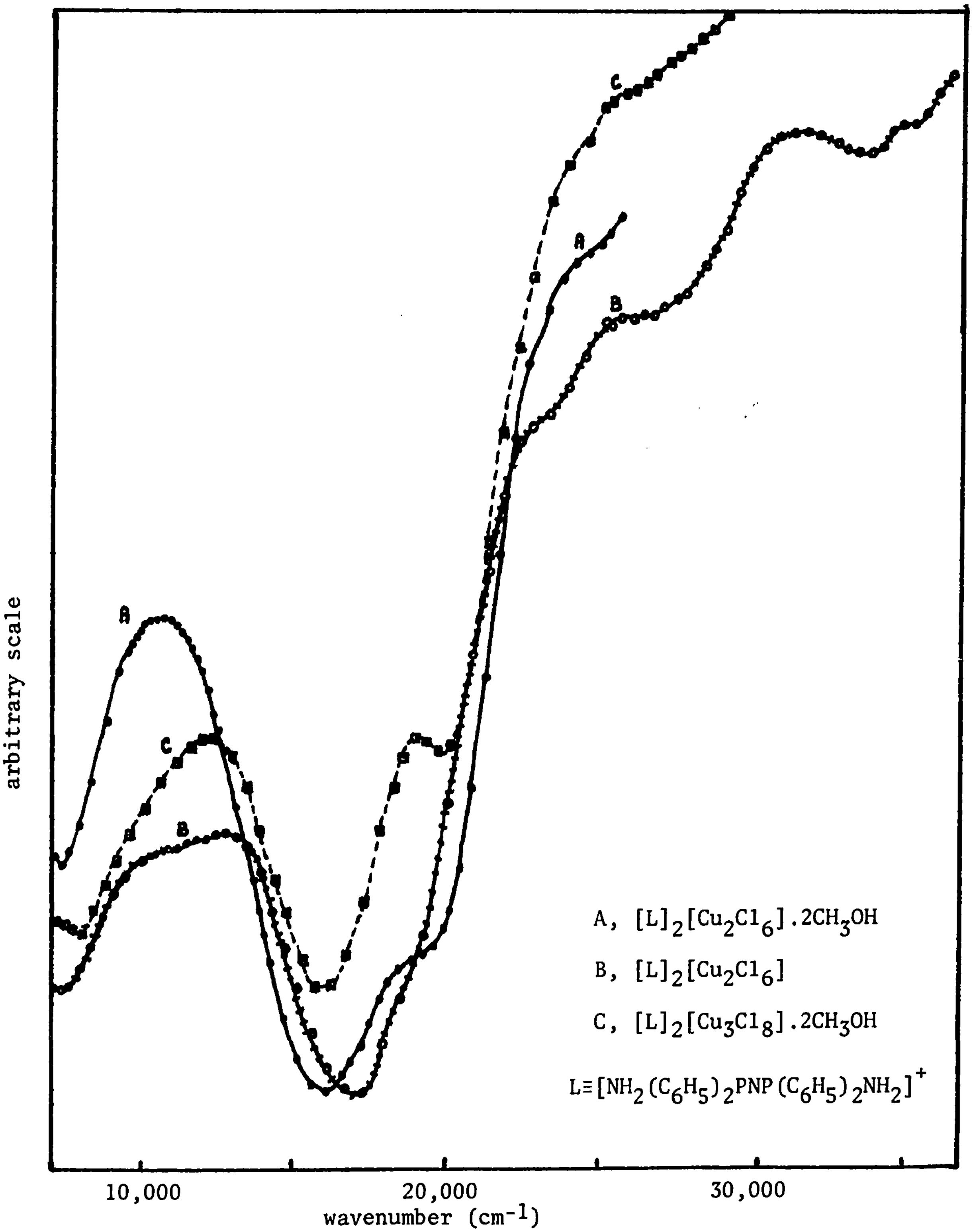


Figure II-14 Electronic Spectra of Copper(II) Chlorides of $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]^+$ (solid state, nujol mull).

II.5.4 Discussion

II.5.4.1 Empirical Formulae

From solution infrared spectra of A and C, they are probably methanolates. Melting point characteristics of A, C and E also indicate these compounds are solvates. From a comparison of the analytical results (Table II-15), the empirical formulae for A,B and C are $CuLCl_3.CH_3OH$, $CuLCl_3$ and $Cu_3L_2Cl_8.2CH_3OH$, respectively; and A and C are methanolates rather than hydrates. Empirical formulae concluded for D and E are less certain. Infrared spectra indicate neither is a methanolate. Low percent oxygen values for both compounds are also evidence that neither is a methanolate or a hydrate. From its analysis, E is most likely to be a solvate of methylene chloride with the empirical formula $CoL_2Cl_4.CH_2Cl_2$, and comparing spectral characteristics and other behavior with E, the empirical formula of D is CoL_2Cl_4.

II.5.4.2 Cobalt(II) Compounds; Ionic Type $[L]_2[CoCl_4]$

Solid state and solution electronic spectra for D and E indicate the cobalt(II) species in both is tetracoordinate (Figure II-13, Table II-18). Comparison of the solid state spectra of D and E suggests that the latter contains a more distorted ligand arrangement: That is, the minor shifts in band shape observed are similar to those expected for a more 'solvolyzed' structure[135]. Given the empirical formula, CoL_2Cl_4, for D, the possibilities which must be considered for the solid state structure are: (a), $[CoL_2^{4+}][Cl^-]_4$; (b), a eutectic mixture of $CoLCl_3$ and LCl; and (c), $[L^+]_2[CoCl_4^{2-}]$;in a crystal lattice which is ionic ((a) or (c)) or pseudoionic (b). Possibility (a) is least likely because of the high formal charge of the cobalt cation, and can be ruled out because major spectral changes would be expected on solution. The electronic spectrum of pseudotetrahedral $CoCl_3¶$, where ¶ is a monoquaternized phosphine cation, has been described as very similar to that of tetrahedral $CoCl_4^{2-}$ [123b]. Thus, the electronic spectral evidence is consistent with either (b) or (c). Possibility (b) is less likely on the basis of infrared spectra, as the solid state spectrum would then be a superposition of unchanged phosphonitrile chloride and the pseudo-tetrahedral complex spectra. This is not observed. Thus, the most likely structure for D is a lattice of phosphonitrile cations and somewhat distorted tetrahedral $CoCl_4^{2-}$ anions. E can then be considered as a solvate containing methylene chloride 'of crystallization', which further distorts the solid state $CoCl_4^{2-}$ anions from a strictly tetrahedral arrangement. A pentacoordinate cobalt(II) arrangement for E is not likely by comparison of its electronic spectrum with that reported for pentacoordinate arrangements[123a]. (The relatively strong band expected at ≈10,500 cm^{-1} is not observed.)

II.5.4.3 Copper(II) Compounds; Ionic Type $[L]_2[Cu_2Cl_6]$

From the similarity to the cobalt compounds in their infrared spectra and solubility, and the qualitative conductivity of B, the copper compounds are also ionic and possibly contain analogous copper(II) chloride anions. The same preparative system was used for monoalkylammoniumtetrachlorocuprates(II)[136] and acetamidinium tetrachlorocuprate(II)[137], which is chemical evidence for the ionic formulation as well as for the possible presence of tetracoordinate copper(II) anions.

Several tetracoordinate copper(II) chloride anions are known, and there is Xray structural evidence for the existence of the types: discrete distorted tetrahedral, $CuCl_4^{2-}$ [139,129b]; trigonal bipyramidal, $CuCl_5^{3-}$ [140]; square planar ('long'-bonded, tetragonally distorted octahedral), $CuCl_4^{2-}$; and dimeric square planar, $Cu_2Cl_6^{2-}$ [138,141,142]. Electronic d-d bands and some charge-transfer bands observed for compounds containing these anions have been used to differentiate between possible arrangements. From comparison of the spectrum of B (or A, Table II-19) with the spectra for these types (Table II-21), it is apparent that neither is tetrahedral or trigonal bipyramidal as the d-d bands occur at too high energies. The solid state electronic spectrum of A indicates the copper absorbing species may be very similar to that which exists in methylene chloride in the absence of excess chloride ion. That is, the copper species in compound A is probably a 'solvated' form of that in B. Both solids probably contain square planar or distorted square planar anions.

Table II-21 Electronic Spectra for Some Copper(II) Chloride Anions.a)

$CuCl_4^{2-}$ discrete tetrahedral[143]	$CuCl_5^{3-}$ bipyramidal[144]	$Cu_2Cl_6^{2-}$ dimeric square planar[145]	$CuCl_4^{2-}$ square planar[145]	B b)
4,800				
5,550				
7,900	8,330-8,500c)	10,800-11,500sh	10,500 sh	10,000 sh
9,050	9,900-10,200	12,900-12,500b	12,800 b	12,500
23,000 sh		18,800-18,500		
24,800	23,800-24,400sh	22,700-25,000	24,000	22,700
29,000	27,030-27,470	34,000 b	33,000 b	25,700
34,000	39,060-37,000		38,500	27,000
34,500		44,500		32,000
42,400		49,000	49,000	
d) R_2CuCl_4 $R=Cs^+, R_4N^+$	$M(NH_3)_6CuCl_5$ M(III)=Cr,Co	$RCuCl_3$ $R=R_2NH_2^+, K^+, Cs^+$	R_2CuCl_4 $R=RNH_3^+, NH_4^+$	

a) solid state; position of maximum absorption in cm^{-1}. b) see Table II-19 and Figure II-14 for spectra of A, B and C. c) more intense. d) compound type, empirical formulae.

Thermochromic and pleochroic behavior similar to that observed for A, B and C (II.5.2) has been noted for solid state compounds containing tetragonal copper(II) chloride anions, either approximately square planar[137, 146-148], or distorted square planar, $Cu_2Cl_6^{2-}$ [145], and cited as evidence for the existence of this arrangement[137]. However, dichroism has also been noted for compounds containing discrete flattened tetrahedral anions[149,129b]. Thus, it is likely that on more close examination the use of such behavior as a diagnostic tool will not prove applicable.

But the empirical formulae of A and B or C, indicate that a discrete tetracoordinate anion arrangement anologous to that proposed for D and E does not occur, and that A and B, at least, are probably similar to the dimeric square planar compounds (Table II-21, compound types).

The presence of a band at 18,500-18,800 cm^{-1} has been used to distinguish between dimeric ($Cu_2Cl_6^{2-}$) and discrete ($CuCl_4^{2-}$) square planar arrangements as indicative of the former[145]. On the 'dimer' band basis however, A (and C) should be considered to contain $Cu_2Cl_6^{2-}$ ions and B should not. This is unlikely considering the ease with which B and A can be interconverted in the solid state. It is more probable that a dimeric arrangement exists for both A and B, and the 'dimer' band is not an indication of the $Cu_2Cl_6^{2-}$ arrangement, per se, but is related to the distortion from square planar symmetry in some other way.

The possibility remains that instead of a lattice of discrete anions, a pseudotetrahedral system occurs, such as that for quaternary phosphines (II.5.1). The electronic spectra reported for these compounds resemble those of tetrahedral cobalt(II) and nickel(II) species, so a pseudotetrahedrally coordinated metal ion structure is proposed. A similar quaternary phosphine of copper(II) would be even more distorted from this arrangement, and might possess the d-d band spectra observed for A and B. On chemical grounds, however, since the compounds reported are cobalt(II) and nickel(II) halides and required rigorously anhydrous preparative conditions as well as excess halide ion, this system is very different from that used to prepare the copper(II) phosphonitrile compounds (and the cobalt (II) compounds). Thus, it is preferable to formulate B and A as the ionic compounds, $[L^+]_2[Cu_2Cl_6^{2-}]$ and $[L^+]_2[Cu_2Cl_6^{2-}].2CH_3OH$.

II.5.4.4 The Copper(II) Compound, $Cu_3L_2Cl_8.2CH_3OH$

The solid state electronic spectrum of C suggests that two forms of copper(II) could be present – both tetragonally distorted from square planar, and one more so than the other. It is possible that C is a methanolate containing trimeric anionic groups $Cu_3Cl_8^{2-}$, analogous to the dimeric structures proposed for A and B. Such a compound would have a similar solid state electronic spectrum to A with smaller components from copper(II) in a completely bridged environment. The latter would also be derived from square planar symmetry and this is consistent with the electronic spectrum of C. Considering the infrared spectra of the phosphonitrile cation on replacement of the Cl^- counterion by $Cu_2Cl_6^{2-}$ and $CoCl_4^{2-}$, similar changes would be expected on replacement by $Cu_3Cl_8^{2-}$ to those observed. The crystal structure of a compound containing molecules with a related trimeric structure, $Cu_3Cl_6(CH_3CN)_2$, has been reported[150]. Melting point behavior of C indicates that on drying decomposition occurs, so that the remaining substance is not a single compound. Thus, instead of discrete $Cu_3Cl_8^{2-}$ ions, C may contain a more complex ionic structure involving three-dimensional bridging to form infinite chains which decomposes on loss of methanol to a mixture containing units of B.

II.5.4.5 Further Evidence

Electron paramagnetic resonance — Several dimeric copper(II) compounds exhibiting anomalous magnetic behavior at room temperature, or a temperature dependent demagnetization, are known, and electron paramagnetic resonance (epr) studies have been used to investigate the nature of the magnetic interaction between the bridged copper atoms[151]. Superexchange has been suggested as the dominant mechanism[152,153].

G-values from epr measurements on polycrystalline samples of A, B and C and dried copper(II) chloride are almost the same, and within the accuracy of measurement a temperature independent paramagnetism is observed. (Table II-16) The average g-value is 2.10 ± 0.01, which is within the range expected for an 'unpaired' copper(II) electron in a complex molecule. However, this does not rule out the dimeric anion arrangement. No anomalies in the magnetic susceptibility of $CsCuCl_3$ due to exchange interactions have been observed down to 80°K[151a], and g-values from epr measurements at room temperature on other compounds containing $Cu_2Cl_6^{2-}$ dimers are similar to those for square planar[147] or trigonal bipyramidal[153] chloride anion arrangements, and lie within the 'normal' range.

Recent single crystal measurements have enabled a closer study of the slight differences in copper(II) g-values for compounds with discrete anion structures[154,155] or chloride ion bridges[137,148], and similar studies of the phosphonitrile compounds and dimerically bridged copper(II) chlorides might provide information about the anion arrangement and its nature.

Metal-chlorine vibrational stretching modes — Bands assigned to transition metal-halide stretching modes have been used to assess possible structural arrangements[156-159]. Some assignments for copper(II) and tetrahedral cobalt(II) chloride anions for solid state measurements are

Table II-22 Some Copper(II) and Cobalt(II) Chloride Stretching Frequency Assignments for Solid State Infrared Spectra.

Anion	Compound	M-Cl stretch (cm^{-1})	Reference
bipyramidal $CuCl_5^{3-}$	$Co(NH_3)_6CuCl_5$	273	144
tetrahedral $CuCl_4^{2-}$	Cs_2CuCl_4	298 sh, 268 s, 247 m	135
tetragonal square planar $Cu_2Cl_6^{2-}$	$CsCuCl_3$	terminal bridging 293 s, 287 s, 263 s	158
	NH_4CuCl_3	311 s, 280 s, 230 m	
	$KCuCl_3$	301 s, 278 s, 236 m	
	$LiCuCl_3.2H_2O$	295 s, 272 s, 222 m	
square planar $CuCl_4^{2-}$	$CuCl_2$	328 m, 275 s	158
tetrahedral $CoCl_4^{2-}$	R_2CoCl_4	300 s, 281 sh	135
		297 s	159
	B $LCuCl_3$	315 w, 303 mw	Table II-17
	D L_2CoCl_4	304 w, 290 w	"
	E $L_2CoCl_4.CH_2Cl_2$	303 vw, 292 w	"

shown in Table II-22 in comparison with tentative assignments for the ionic phosphonitrile compounds prepared. Assignment of bands at 304 and 290 cm^{-1} to cobalt(II) chloride stretching modes agrees with those reported for tetrahedral tetrachlorocobaltate(II) compounds. Considering that the anion arrangement for D is flattened tetrahedral in the solid state, it is not unlikely that two bands in the expected region are observed. Thus, the ionic structures suggested for D and E are substantiated. If B contains dimeric $Cu_2Cl_6^{2-}$ anions, a third band (attributable to a bridging chloride mode) should occur at lower energy, though the limits of measurement may have precluded its observation. The positions of the bands which are observed, 315 and 300 cm^{-1}, suggest that the arrangement for B could be tetragonally distorted square planar. At most, it can be concluded that these assignments are consistent with other evidence in support of the ionic structures proposed.

II.5.5 Chelate Formation for Aminodiphenylphosphonitrileaminodiphenylphosphonium Ion Reassessed

Initially, it was considered that the positive charge repulsion hindrance to chelation or coordination via the amino groups might not prevent formation of covalent bonds with a positive transition metal ion. Based on the observation of a single ^{31}P nmr interaction and only a single broad interaction attributable to the nitrogen hydrogen atoms, the phosphorus atoms are equivalent, and the positive charge can be considered as delocalized over the PNP portion of the skeleton[109].

The recent preliminary crystal structure report[30] indicates a possible reason for the non-occurrence of chelation or coordination. The phosphorus-nitrogen interatomic distances for the PNP portion are equal and short (1.57Å), comparable with those of cyclic phosphonitriles, as expected for a delocalized multiple bonding system. However, the phosphorus-nitrogen distances for the P-NH$_2$ bonds are also short (1.65Å) compared with that usually considered as the single bond value (1.78Å). They are of the order calculated for a phosphorus-nitrogen 'pure' double bond (1.64Å)[160]. This is evidence for a Π_s-type bond system involving the whole phosphorus-nitrogen skeleton. Thus, the amino group lone-pairs must be even less 'available' for donation to any external acceptor site. This substantiates the proposal of ionic structures for the copper(II) and cobalt(II) compounds prepared. It also indicates that formation of a covalent bond to a sulfur atom, for example, through an addition mechanism, would require substantial rearrangement of the charge distribution for the phosphonitrile, possibly resulting in a destabilized skeleton. This might favor chain polymerization, thus contributing to the problem of obtaining an experimental compromise between conditions necessary for reaction and also favorable to intramolecular cyclization.

III. QUANTUM CHEMISTRY OF PHOSPHONITRILES AND SULFONITRILES

III.1 Molecular d Orbital Exponents for Phosphonitriles and Sulfonitriles; Determination by an Exchange Overlap Variation

III.1.1 Statement of the Problem and Valence Bond Perfect-pairing Scheme for Exchange Optimized Orbital Energies

A simplification of the exchange-included valence bond perfect-pairing scheme for energy optimization of d orbital exponents has been made to find environment dependent exponent sets suitable for use in simple LCAO MO calculations, when suitable energy parameters can also be derived, without the computational effort involved in an exchange optimized calculation. The derivation is expressed for d orbital exponent optimization but applies for any valence shell orbital where no 'outer' orbitals are occupied.

In the VBMO approach, where the bond structure of a molecule is formulated as a series of two-centre,two-electron localized bonds, the bonding energy contributed by any two-electron pair can be written,

$$\frac{Q_{ij} + J_{ij}}{1 + S_{ij}^2}, \qquad \text{(III.1)}$$

and the total covalent energy of the molecule is,

$$E_c = \sum_r \overset{o}{E}_r + \sum_{ij} \frac{Q_{ij} + J_{ij}}{1 + S_{ij}^2} + \text{bond interaction terms} \qquad \text{(III.2)}$$

E_r^o represents the energy of the rth separated atom,

$\sum_{ij}$ is over all bonds,

Q_{ij} and J_{ij} are valence bond coulomb and exchange integrals, respectively, and

S_{ij} is the two-centre, one-electron overlap integral.

If the separated atom wavefunctions are ϕ_i and ϕ_j, these integrals are;

$$Q_{ij} = \int\phi_i(1)\phi_j(2)H^1\phi_i(1)\phi_j(2)d\tau_1 d\tau_2 \qquad \text{(III.3)}$$

$$J_{ij} = \int\phi_i(1)\phi_j(2)H^1\phi_j(1)\phi_i(2)d\tau_1 d\tau_2 \qquad \text{(III.4)}$$

$$S_{ij} = \int\phi_i(1)\phi_j(1)d\tau_1 \qquad \text{(III.5)}$$

where the hamiltonian is $H = H^0 + H^1$, and H^1 represents the interaction perturbation on bonding.

The interaction operator for a system composed of a central atom A surrounded by ligand atoms, B_i, includes nuclear-nuclear, and electron-electron repulsions as well as electron-nuclear attractions between A and all B_i. To a first approximation, only interactions affecting the valence shell orbitals of A need be considered in an energy minimization to determine the orbital exponents. In particular, for the determination of molecular d orbital exponents, only those interactions involving d orbitals are needed in the minimization, since the effect of d orbital exponent variation on other valence shell orbitals is small[180]. If the bond interaction terms and $(1 + S_{ij}{}^2)$ are also neglected, then d orbital contribution to the total energy gained on bond formation is,

$$E_c(d) = \sum_{ij} Q_{ij} + \sum_{ij} J_{ij} \qquad \text{(III.6)}$$

as for (III.2) where ϕ_i refers to a d orbital at A.

The exchange portion of (III.6) is composed of bonded (paired spins) and non-bonded (random oriented spins) contributions;

$$E_c(d) = \sum_{ij} Q_{ij} + \sum_{m,n} J_{mn} - 1/2 \sum_{p,q} J_{pq} \qquad \text{(III.7)}$$

m and p refer to orbitals on A, ϕ_i,
n refers to atomic orbitals on all B_i, ϕ_j, which
  form localized two-electron bonds (AB_i) with ϕ_i, and
q refers to non-bonded orbitals, ϕ_j.

When d orbitals participate in delocalized molecular orbitals, the localized bond perfect-pairing scheme breaks down, and a factor, ε, is included for bonding exchange terms, J_{mn}, to account for this.

The inclusion of non-bonded exchange terms ensures that minimum inter-orbital repulsion energy and maximum intra-orbital repulsion energy are maintained in the minimization to optimize d orbital exponents (I.4.2).

The variation of the covalent energy contribution of a d orbital electron with the d orbital exponent, ξ, is

$$\frac{\partial E_c(d)}{\partial \xi} = \frac{\partial}{\partial \xi} \sum_{ij} Q_{ij} + \frac{\partial}{\partial \xi}\left[\sum_{m,n} \varepsilon J_{mn} - 1/2 \sum_{p,q} J_{pq}\right] \qquad \text{(III.8)}$$

The coulomb integral portion, ΣQ_{ij}, varies with ξ_i implicitly but slowly compared with the exchange integral portion, for values in the bonding range, due to compensation between the electron repulsion and nuclear attraction terms[183]. As ξ_d becomes larger and ϕ_i is contracted, Q_{ij} goes through a minimum for maximum bonding. If, at the same time, the exchange integral portion passes through the same minimum ($\Sigma Q/\Sigma J$ is constant), the position of maximum value for the exchange terms can be used to determine an optimum orbital exponent. By considering only the exchange terms, kinetic energy effects and some potential energy effects (interactions between the d electrons and the central atom field) are neglected. This is acceptable for exponent values corresponding to maximum overlap at reasonable bond distances.

Although ΣQ is commonly assumed as $\approx$15% of ΣJ for the total binding energy[103], it may reach as much as 50%[184]. The ratio $\Sigma Q/\Sigma J$ has not been tested for sulfonitrile and phosphonitrile bond participation for d orbitals, since appropriate energy integral values are not readily available. The constant relationship has been useful in estimating relative energies where molecular bond structures were similar[185], and this is assumed to be true for the chemically similar bond systems studied by the exchange overlap variation method derived below.

III.1.2 An Exchange Overlap Variation (EOV) Method for Determination of Molecular d Orbital Exponents

The exchange integrals, J_{ij}, can be approximated[180] as;

$$J_{ij} = (\phi_i\phi_j|\phi_i\phi_j) + S_{ij}\int\phi_i\phi_j[V(A-\phi_i) + V(B-\phi_j)]d\tau + S_{ij}^2(A-\phi_i|B-\phi_j) \qquad \text{(III.9)}$$

ϕ_i and ϕ_j are atomic orbitals as defined in III.1.1,
$V(A-\phi_i)$ represents the electrostatic potential of the charge distribution at A minus the contribution from an electron in ϕ_i, and
$(A-\phi_i|B-\phi_j)$ represents the interaction of the charge distributions $A-\phi_i$ and $B-\phi_j$.

When $S_{ij} \neq 0$, the second term usually dominates and is negative, thus causing bonding. The variation in the exchange portion of (III.8) is determined by variation of the second term in (III.9), and is thus proportional to the variation in overlap between ϕ_i on A and ϕ_j on B. Minimum energy corresponds to a maximum value of (III.10);

$$\frac{\partial}{\partial\xi}E_c(d) = \frac{\partial}{\partial\xi}\{\varepsilon \sum_{m,n} S_{mn}\int\phi_m\phi_n[V(A-\phi_m) + V(B-\phi_n)]d\tau - 1/2 \sum_{p,q} S_{pq}\int\phi_p\phi_q[V(A-\phi_p) + V(B-\phi_q)]d\tau\} \qquad \text{(III.10)}$$

If the B's and ϕ_i's (ϕ_m,ϕ_p) are equivalent centers and A orbitals, (III.10) reduces to

$$\frac{\partial}{\partial\xi}E_c(d) \propto \frac{\partial}{\partial\xi}\{\varepsilon \sum_{m,n} k_{mn}|S_{mn}| - 1/2 \sum_{p,q} k_{pq}|S_{pq}|\} \qquad \text{(III.11)}$$

where all $k_{nm} = k_{pq}$. In general, neither the

ϕ_i's nor B's are equivalent and only if relative amounts of $| S |$ are considered (determined by relative k's) will this strictly hold. The integral which the k's represent (from the second term in (III.9)) is a measure of the binding energy exchange interaction of an electron associated with the charge density distribution represented by S_{ij}, in the net simultaneous potential at A and B. It is approximately proportional to the average 'valence state' ionization potential of ϕ_i and ϕ_j. If this is not very different for all pairs of ϕ_i and ϕ_j, constant proportionality to S_{ij} can be assumed, and expression (III.11) used in the simplified form. The effects of this simplification for d orbitals in phosphonitrile and sulfonitrile bonding are discussed in III.2.4.

In the approximate molecular environment provided for central atom A by B_i which includes only, and all, atoms directly bonded to A, the exchange overlap variation (EOV) method determines that value of ξ for which (III.11) is maximum. In the EOV method, the localized bond model for the fragment (AB_i) system is chosen to maximize the bonding overlap, and minimize the non-bonding overlap to the optimum extent, unless various localized models are to be examined. This ensures that $\Sigma Q/\Sigma J \approx$ constant.

III.1.3 Application of EOV Method to Fragment-Simulated Molecular Environments

The problem is to approximate the molecular orbitals as a series of two-center, two-electron localized bond orbitals, and to simplify the calculation by considering a representative fragment of the molecule. The ring or chain phosphorus or sulfur atom is atom A and all immediate bonded neighbor atoms, B_i, approximate the molecular environment. The EOV method optimizes the d orbital exponent by applying the variation of (III.11) to each d orbital, $A_d \equiv d_{z^2}$, d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{xy}.

III.1.3.1 Fragment Systems

The bond structure for each phosphonitrile or sulfonitrile fragment (N(1)N(2)AE(1)E(2), Figure III-1) is specified by the sigma bond framework of localized bonds between valence shell s and p orbital hybrids on A and B_i, directed for maximum overlap and conforming as closely as possible to the molecular geometry. A_d orbitals are considered to participate in localized Π bonds only (of the types outlined in I.4.3). Molecular fragment bond systems are made up of the localized two-center, two-electron bonds of a given bond type formed from localized atomic orbitals, which may be valence shell hybrids or 'pure' atomic orbitals. The nomenclature is summarized in Table III-1.*

A fragment coordinate system (x,y,z) is chosen with origin at A, and atomic orientation such that atom A and its ring neighbors N(1) and N(2) lie in the xy plane, with y bisecting the angle N(1)$\hat{A}$N(2), θ, and N(1) in the positive x direction. (Figure III-1)* To a first approximation, the site symmetry is C_{2v} at A for the sigma system localized atomic orbitals ($h_{N(1)}$,$h_{N(2)}$,$h_{E(1)}$ and $h_{E(2)}$), whose coefficients are specified by the ring angle θ. The ring and exocyclic angles at A fit this restriction for most cyclic molecules considered, but when the substituents E(1) and E(2) differ, the $h_{E(1)}$ and $h_{E(2)}$ orbitals might not be exactly equivalent.

The ring nitrogen atom localized atomic orbitals (h_A,$h_{A'}$) for the ring σ system bonds were also specified by the geometry, with coeffients determined by the ring angles A$\hat{N}$(1)A'(1), γ_1, and A$\hat{N}$(2)A'(2), γ_2.

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* A foldout sheet is included on the back page for ease of later reference to Table III-1 and Figure III-1.

Table III-1 Nomenclature of Localized Bonds for Sulfonitrile and Phosphonitrile Fragments, N(1)N(2)AE(1)E(2), With Orientation Specified in Figure III-1.

Bond system	Localized bond type	Localized atomic orbitals	
		at A or A'	at N or E
Ring Π			
Π(AN)	Π_a(AN)	$A_d \equiv A_{d_{z^2}}, A_{d_{xz}}, A_{d_{yz}}, A_{d_{x^2-y^2}}, A_{d_{xy}}$	$N_{\Pi_a} \equiv h_p$
	Π_s(AN)	A_d as for Π_a(AN)	$N_{\Pi_s} \equiv h_L$
Ring σ			
σ(AN)	σ_A(AN)	$A_\sigma \equiv h_{N(1)}, h_{N(2)}$	$N_{\sigma_A} \equiv h_A$
	$\sigma_{A'}$(AN)	$A'_\sigma \equiv h'_{N(1)}, h'_{N(3)}$	$N_{\sigma_{A'}} \equiv h_{A'}$
Exocyclic Π			
Π(AE)	Π_e(AE)	$A_d \equiv A_{d_{z^2}}, A_{d_{yz}}, A_{d_{x^2-y^2}}$	$E_\Pi(1), E_\Pi(2)$
	Π'_e(AE)	$A_d \equiv A_{d_{xz}}, A_{d_{xy}}$	$E_{\Pi'}(1), E_{\Pi'}(2)$
Exocyclic σ			
σ(AE)	σ_E(AE)	$A_{\sigma E} \equiv h_{E(1)}, h_{E(2)}$	$E_\sigma \equiv h_{E\sigma}$

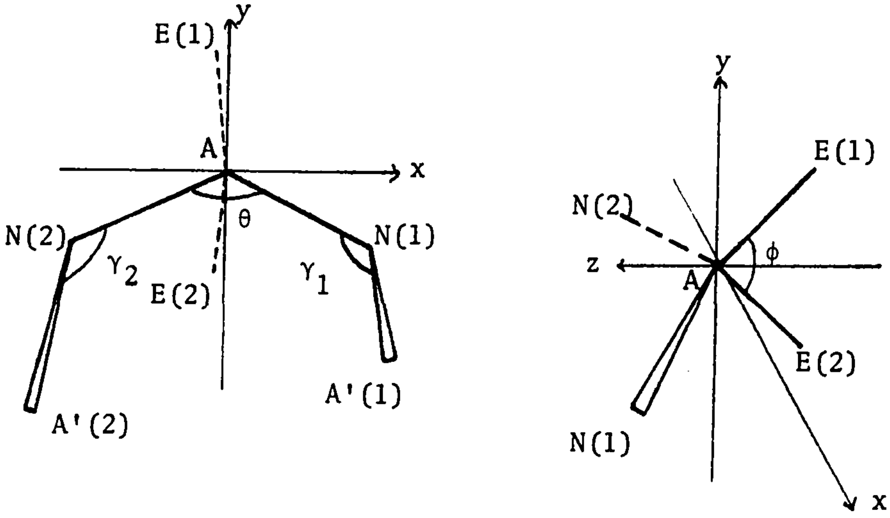

Figure III-1 Fragment N(1)N(2)AE(1)E(2) and Next-bonded Neighbors, A'(1) and A'(2).

Ring Π system nitrogen localized atomic orbitals (h_L, h_P) were taken as the remaining trigonal-type hybrid specified by the direction, $\vec{L}$, which bisects the angle γ in the plane formed by ANA', and a 2p atomic orbital directed perpendicular to this plane at N. This direction, $\vec{P}$, will not be parallel to z for a non-planar ring molecule, in general.

Exocyclic localized atomic orbitals for sigma bonds with $h_{E(1)}$ and $h_{E(2)}$ were assumed to be sp hybrids for all E's $(h_{E\sigma})$. For the exocyclic Π system bonds, localized atomic orbitals at each E $(E_{\Pi}(1), E_{\Pi}(2) E_{\Pi'}(1)$, and $E_{\Pi'}(2))$ consist of two mutually perpendicular p orbitals; 'lone-pair' orbitals for halogen substituents, and one 'lone-pair' and one formally Π bonded for oxygen substituents. The best approximation for this combination is not readily chosen, particularly for sulfur with two different exocyclic substituents. To a first approximation, the Π_e bond system can be neglected except for non-bonded exchange interactions for the halogen substituent cases, but the sulfur-oxygen substituent must be included explicitly as formally Π bonded in the localized bond model. The combination was specified as one directed in the yz plane perpendicular to the exocyclic bond at E (E_{Π}), and one parallel to the x axis $(E_{\Pi'})$.

III.1.3.2 Specific Formulation

For each A_d, the non-zero overlaps for the fragment system neighbor atom localized orbitals can be divided into bonding or non-bonding depending upon the sign correspondence with ring Π systems. The ring Π system was considered bonded in all cases. This is easily specified for planar rings, where d_{xz} and d_{yz} participate in the Π_a system, and d_{z^2}, $d_{x^2-y^2}$, and d_{xy} in the Π_s system. For non-planar cases, where all d orbitals may participate in each system, the sign convention was chosen so that the net contribution (for the sum of Π_a and Π_s overlap values) over each ring bond was bonding. Then, for a given neighbor atom, the correspondence of sign for all non-zero overlaps with a particular d orbital, to the chosen sign convention, determines whether such overlap is bonding or non-bonding. D orbital participation in sigma bonds is neglected, so inclusion of bonding-oriented overlaps for nitrogen or exocyclic localized atomic orbitals in these systems as non-bonding will introduce an artificial non-bonded exchange destabilization. Hence, these overlaps were not included. All overlaps for nitrogen localized atomic orbitals, $h_{A'}$, were included as non-bonding. Two exponent sets were determined from maximization of (III-11) according to these specifications, labelled EOV and EOVΠ in subsequent discussion:

EOV — all Π_e bonding overlaps were neglected, except with oxygen, $E_\Pi(O)$, for which they were included as bonding.

EOVΠ — all Π_e overlaps were included as bonding or non-bonding according to the sign convention.

Subject to these specifications, (III-11) can be written for a phosphonitrile fragment, for example;

$$\frac{\partial}{\partial\xi} E_c^f(d) \propto \frac{\partial}{\partial\xi}\Big(\varepsilon[m \sum_{N_{\Pi_A}} k_{\Pi_a}|S_{A_d\Pi_a}| + \sum_{N_{\Pi_s}} k_{\Pi_s}|S_{A_d\Pi_s}|] - 1/2[\sum_{E_\sigma} k_{\sigma_E}|S_{A_dE_\sigma}| - \sum_{N_{\sigma_A}} k_{\sigma_A}|S_{A_dN_{\sigma_A}}| - \sum_{N_{\sigma_{A'}}} k_{\sigma_{A'}}|S_{A_dN_{\sigma_{A'}}}| - \sum_{E_{\Pi,\Pi'}} k_{\Pi_e,\Pi_e'}|S_{A_dE_{\Pi,\Pi'}}|]\Big) \qquad \text{(III.12)}$$

where the S terms refer to overlap values for a given A_d exponent, ξ, for overlaps between A_d and the appropriate neighbor atom localized atomic orbital h_P, h_L, E_σ, N_{σ_A}, $N_{\sigma_{A'}}$, and E_Π, respectively. The sums are over all neighbor atoms N(1), N(2), E(1) and E(2). The k's relate overlap integrals to the exchange interaction energy (III.1.2). Since the variation was carried out for the total fragment,and non-bonding overlap values are either relatively small or an approximately equal proportion of the bonding overlap values for each A_d orbital, the simplified expression with all k's equal to one was used.

The expression for a sulfonitrile case is similar, but the $\sum_{E_\Pi}$ terms for $E_\Pi(O)$ are included as bonding and multiplied by a factor -2.

The factor m must be included to account for the phase change which occurs in the ring molecular Π_a system when it is approximated by a series of localized two-center bonds. For a maximum delocalization sign system, a phase change 'node' remains where n is odd, if n is the number of sulfonitrile or phosphonitrile units in the ring. m represents the average amount by which the sum of two localized Π_a bond overlaps must be decreased in order to consider their contribution to the fragment bond structure as a fraction of the total molecular structure. For the fragment system,

$$m = \frac{n - \Delta/2}{n} \qquad \text{where } \Delta = 1;\ n,\text{odd} \qquad \Delta = 0;\ n,\text{even.}$$

III.1.3.3 EOV Calculation; Formulae for d Orbital Overlaps, Molecular Coordinates, and Calculation Details

(1) Formulae for d orbital overlap values for the localized bond model fragment system:

a) localized atomic orbitals — The formulae for the localized atomic orbitals in the coordinate system (III.1.3.1) for appropriate valence shell atomic orbital basis sets for each atom (s, p_x, p_y, p_z, d_z2, d_{xz}, d_{yz},

$d_{x^2-y^2}$, d_{xy}), neglecting chlorine d orbitals, are:

i) <u>at A(σ system)</u>

$$h_{N(1)} = \lambda s(A) + \mu[\sin(\theta/2)p_x(A) - \cos(\theta/2)p_y(A)]$$

$$h_{N(2)} = \lambda s(A) - \mu[\sin(\theta/2)p_x(A) - \cos(\theta/2)p_y(A)]$$

$$h_{E(1)} = \alpha s(A) + \beta[\cos(\phi/2)p_y(A) + \sin(\phi/2)p_z(A)]$$

$$h_{E(2)} = \alpha s(A) + \beta[\cos(\phi/2)p_y(A) - \sin(\phi/2)p_z(A)]$$

where $\lambda^2 = 1/2(1 - \cot^2(\theta/2))$

$\mu^2 = 1/2(\sin^2(\theta/2))^{-1}$

$\alpha^2 = 1/2(1 - \cot^2(\phi/2))$

$\beta^2 = 1/2(\sin^2(\phi/2))^{-1}$

ii) <u>at N(1) or N(2)</u> where $\gamma = \gamma_1$ or γ_2, respectively

$$h_A = \lambda' s(N) + \mu'[a_1 p_x(N) + a_2 p_y(N) + a_3 p_z(N)]$$

$$h_{A'} = \lambda' s(N) + \mu'[b_1 p_x(N) + b_2 p_y(N) + b_3 p_z(N)]$$

$$h_L = \alpha' s(N) + \beta'[c_1 p_x(N) + c_2 p_y(N) + c_3 p_z(N)]$$

$$h_P = d_1 p_x(N) + d_2 p_y(N) + d_3 p_z(N)$$

where $\lambda'^2 = (-\cos\gamma)/(1 - \cos\gamma)$

$\mu'^2 = (1 - \cos\gamma)^{-1}$

$\alpha'^2 = (1 + \cos\gamma)/(1 - \cos\gamma)$

$\beta'^2 = (-2\cos\gamma)/(1 - \cos\gamma)$ and

a's, b's, c's, and d's are direction cosines for the appropriate localized atomic orbital direction ($\vec{A}$, $\vec{A}'$, $\vec{L}$, and $\vec{P}$) with respect to the fragment coordinate system (x,y,z), and are obtained from atomic coordinates and distances (R) in the usual way as;

	1	2	3
a	$(x_A-x_N)/R_{AN}$	$(y_A-y_N)/R_{AN}$	$(z_A-z_N)/R_{AN}$
b	$(x_{A'}-x_N)/R_{A'N}$	$(y_{A'}-y_N)/R_{A'N}$	$(z_{A'}-z_N)/R_{A'N}$
c	$\pm t_1 t_2$	t_2	$t_3 t_2$
d	$\pm(a_2b_3-a_3b_2)/\sin\gamma$	$\pm(a_3b_1-b_3a_1)/\sin\gamma$	$\pm(a_1b_2-b_1a_2)/\sin\gamma$

$$\text{and } t_1 = \frac{d_2(a_3-b_3) - d_3(a_2-b_2)}{d_3(a_1-b_1) - d_1(a_3-b_3)}$$

$$t_2 = (1 + t_1{}^2 + t_3{}^2)^{-1/2}$$

$$t_3 = -1/d_3(t_1d_1 + d_2)$$

The + sign applies to N(1), the - sign to N(2), to specify positive directions away from the ring and in the positive z direction for the Π_s and Π_a system orbitals, respectively. All localized atomic orbitals for a given center have been chosen to form an orthonormal set.

b) overlaps between localized atomic orbitals — Overlap integrals for the localized atomic orbitals can be expressed in terms of primitive overlap integrals for the local coordinate system defined by the interatomic axis. The calculation of primitive overlap values is outlined in Appendix A. Overlaps are then obtained from the following formulae, where $\tilde{S}\sigma$'s and $\tilde{S}\Pi$'s represent appropriate primitive overlap values,and all localized atomic orbital coefficients $(\lambda,\mu,\alpha,\beta)$, direction cosines (a,b,c,d) and angles (θ,ϕ,γ) are as previously specified ((1)a)).

i) overlaps not involving d orbitals (for reference in III.2)

Ring σ; $\sigma_A(AN)$

$$S_\sigma(AN) = \lambda\lambda'\tilde{S}s(A)s(N)\sigma + \lambda\mu'[\cos(\theta/2)-\sin(\theta/2)]\tilde{S}s(A)p(N)\sigma$$
$$+ \mu\lambda'[\sin(\theta/2)-\cos(\theta/2)]\tilde{S}p(A)s(N)\sigma - \mu\mu'\tilde{S}p(A)p(N)\Pi.$$

Exocyclic σ;$\sigma_E(AE)$

$$S_{\sigma_E}(AE) = \frac{\lambda}{\sqrt{2}}[\tilde{S}s(A)s(E)\sigma + \tilde{S}s(A)p(E)\sigma] + \frac{\mu}{\sqrt{2}}[\tilde{S}p(A)s(E)\sigma + \tilde{S}p(A)p(E)\sigma].$$

ii) overlaps involving d orbitals

These are obtained via the appropriate transformation matrix, T, discussed in appendix A for the calculation of overlap values, such that

$$S_{A_dh} = T\tilde{S}_{A_d\sigma} \text{ or } T\tilde{S}_{A_d\Pi} \text{ ; and}$$
$$\tilde{S}_{A_d\sigma} \equiv \tilde{S}_{A_dN_{\sigma_A}}, \tilde{S}_{A_dN_{\sigma_{A'}}}, \tilde{S}_{A_dE_\sigma} \text{ or}$$
$$\tilde{S}_{A_d\Pi} \equiv \tilde{S}_{A_d\Pi_a}, \tilde{S}_{A_d\Pi_s}, \tilde{S}_{A_dE_\Pi}$$

represent the appropriate combination of primitive overlap values, where T and $\tilde{S}_{A_d\sigma}$ or $\tilde{S}_{A_d\Pi}$ components are:

with exocyclic σ system orbitals —

$$T_{\sigma_E}(AE) = \begin{pmatrix} \frac{3}{2}\sin^2(\phi/2) - \frac{1}{2} \\ 0 \\ \sqrt{3}\cos(\phi/2)\sin(\phi/2) \\ -\frac{\sqrt{3}}{2}\cos^2(\phi/2) \\ 0 \end{pmatrix} \qquad \tilde{S}_{A_d\sigma} = \frac{1}{\sqrt{2}}[\tilde{S}d(A)s(E)\sigma + \tilde{S}d(A)p(E)\sigma]$$

with exocyclic Π system orbitals —

$$T_{\Pi_e}(AE) = \begin{pmatrix} \sqrt{3}\sin(\phi/2)\cos(\phi/2) \\ 0 \\ \cos^2(\phi/2) - \sin^2(\phi/2) \\ \cos(\phi/2)\sin(\phi/2) \\ 0 \end{pmatrix} \qquad \tilde{S}_{A_dE_\Pi} = \tilde{S}d(A)p(E)\Pi$$

$$T_{\Pi_e'}(AE) = \begin{pmatrix} 0 \\ \sin(\phi/2) \\ 0 \\ 0 \\ \cos(\phi/2) \end{pmatrix} \qquad \tilde{S}_{A_dE_{\Pi'}} = \tilde{S}d(A)p(E)\Pi$$

with ring nitrogen atom orbitals; Π systems —

$\underline{\Pi_a(AN)}$ $\quad S_{A_d\Pi_a} = d_1S_{A_dp_x}(N) + d_2S_{A_dp_y}(N) + d_3S_{A_dp_z}(N)$

where, for example, if $A_d \equiv d_z2$ and $p_x(N) \equiv p_x$, etc.,

$$S_{d_z2\Pi_a} = d_1S_{d_z2p_x} + d_2S_{d_z2p_y} + d_3S_{d_z2p_z}$$

$\underline{\Pi_s(AN)}$ $\quad S_{A_d\Pi_s} = \alpha' S_{A_d}s(N) + \beta'[c_1S_{A_dp_x}(N) + c_2S_{A_dp_y}(N) + c_3S_{A_dp_z}(N)]$

The values for $S_{A_dp(N)}$ terms were obtained directly from the calculation of overlap values for the fragment systems(part (3) of this section), and represent overlap values between d orbitals at A and s or p orbitals at N in the fragment coordinate system.

with ring nitrogen atom orbitals; σ systems —

$$T_{N\sigma_A} = \begin{pmatrix} -\frac{1}{2} \\ 0 \\ 0 \\ \frac{\sqrt{3}}{2}[\sin^2(\theta/2) - \cos^2(\theta/2)] \\ \mp\sqrt{3}\sin(\theta/2)\cos(\theta/2) \end{pmatrix} \qquad \tilde{S}_{A_dN_{\sigma_A}} = \lambda'\tilde{S}d(A)s(N)\sigma + \mu'\tilde{S}d(A)p(N)\sigma$$

and $S_{A_d N_{\sigma A'}} = T_{N_{\sigma A'}} \tilde{S}_{A_d N_{\sigma A'}}(\mathrm{sigma}) + T_{N_{\sigma A'}} \tilde{S}_{A_d N_{\sigma A'}}(\mathrm{pi})$; where,

$$\underset{(\mathrm{sigma})}{T_{N_{\sigma A'}}} = T_{N_{\sigma A}} \qquad \underset{(\mathrm{sigma})}{\tilde{S}_{A_d N_{\sigma A'}}} = \{\lambda' \tilde{S}d(A)s(N)\sigma - \mu'[\pm b_1 \sin(\theta/2) - b_2 \cos(\theta/2)]\tilde{S}d(A)p(N)\sigma\}$$

$$\underset{(\mathrm{pi})}{T_{N_{\sigma A'}}} = \begin{pmatrix} 0 \\ \pm b_3 \sin(\theta/2) \\ -b_3 \cos(\theta/2) \\ 2\sin(\theta/2)\cos(\theta/2)[\pm b_1 \cos(\theta/2) + b_2 \sin(\theta/2)] \\ [\sin^2(\theta/2) - \cos^2(\theta/2)][b_1 \cos(\theta/2) \pm b_2 \sin(\theta/2) \end{pmatrix}$$

and

$$\underset{(\mathrm{pi})}{\tilde{S}_{A_d N_{\sigma A'}}} = \mu' \tilde{S}d(A)p(N)\Pi$$

(2) Molecules and related fragments, atomic coordinates from Xray crystallography:

The EOV method was used to determine molecular exponent sets for all cyclic molecules containing chlorine or fluorine substituted phosphonitrile or sulfonitrile units for which Xray crystallographically determined geometries were available (Table III-2). To specify the ring nitrogen localized atomic orbital directions completely, the coordinates of the next-bonded (A') atoms must be known (Figure III-1). For planar rings, this presents no difficulty, and the appropriate atomic coordinates can be found from interatomic distances and angles reported. However, to use the reported distances and angles in the same way for a non-planar ring fragment, the distances between A and A'(1) or A'(2) are required to specify the angles between the N(1)AN(2) plane and the AN(1)A'(1) or AN(2)A'(2) planes. These are not given directly, so the atomic coordinates for each fragment must be derived from the fractional atomic coordinates reported, by a series of transformations

Table III-2 Fragment Geometries From Xray Structural Determinations for Cyclic Phosphonitriles and Sulfonitriles.

Fragment	Molecule and reference		Details of Geometry; bond distances and angles$^{a)}$						
			R_{AN}(Å)	R_{AE}(Å)	θ	γ_1	γ_2	φ	b)
N_2PF_2	$(NPF_2)_3$	186	1.560(11)	1.521	119.4	120.3		99.1	planar
	$(NPF_2)_4$	187	1.510	1.51	122.7	147.0		99.9	planar
	$N_3P_3(C_6H_5)_2$	188	1.555(4),1.539(5)	1.531(5)	120.6(3)	120.1	120.8	96.9(2)	
N_2PCl_2	$(NPCl_2)_3$	77	1.590(17)	1.98	120.0	120.4(8)		102	planar
	"		1.590(17)	1.97(2)	120.9(1.1)	118.3(8)	120.9(8)	101.8(5)	
	$(NPCl_2)_4$ $\bar{1}$	189	1.555,1.562(12)	1.992(4)	120.5(7)	137.2(8)	133.6(8)	103	
	$(NPCl_2)_4$ $\bar{4}$	190	1.569(9)	1.989(4)	121.2(5)	131.3		102.8(2)	c)
	$(NPCl_2)_5$	191	1.521(15)	1.961	118.4	159.0(10)	133.6(10)	102.2	planar$^{d)}$
	$N_3P_3Cl_5F$	192	1.563(7)	1.963(5)	118.5(5)	121.9(3)		100.5(2)	
	$N_3P_3(C_6H_5)_2Cl_4$	193	1.554,1.579(5)	1.998	117.5	122.4(3)	119.2(3)	100.3(1)	
	$N_3P_3(C_6H_5)_4Cl_2$	194	1.554(9)	2.017	118.2(5)	120.3(5)	121.4(5)	98.5(2)	
	$NPCl_2(NSOCl)_2$	73	1.585(13)	1.957(6)	115.3(7)	122.1(8)		104.4(3)	
N_2SOCl	α-$(NSOCl)_3$	79	1.569(8)	2.003(4),1.407(10)$^{e)}$	112.9(5)	120.0(6)		107.0(5)	
	$NPCl_2(NSOCl)_2$	73	1.538,1.577(13)	2.007(6),1.415(14)	115.6(7)	123.4(8)	120.3(8)	105.7(6)	S(1)
	"		1.579,1.542(13)	2.028(6),1.427(12)	114.3(7)	120.3(8)	120.6(8)	106.3(5)	S(2)
N_2SCl	$(NSCl)_3$	195	1.607(7)	2.117(4)	113.4(4)	123.0(4)	124.9(4)		
N_2SF	$(NSF)_4$	196	1.66(1),1.54(1)	1.602	111.7(6)	123.9(6)			

a) see Figure III-1 for meaning of symbols; angles in degrees. b) planar; coordinates derived for assumed planar geometry, otherwise coordinates obtained from fractional atomic coordinates reported. c) The symmetry centre of the molecule as reported is 1/4,1/4,3/4. Cl atom coordinates are reported for another molecule, so values used were calculated from R_{PCl} and φ for site symmetry C_{2v}. d) average R_{PN} and extreme ring angles γ. e) E≡oxygen for second value listed, otherwise E≡halogen.

to convert them into the fragment coordinate system.

To check the variation between results obtained for an assumed planar geometry and the crystallographically-derived geometry, coordinates for both cases were used for $(NPF_2)_4$ and $(NPCl_2)_3$. Molecules of the former are planar within crystallographic error, and the difference in results for this case was used to estimate an uncertainty range for optimum exponent values.

(3) Calculation details:

a) A program was coded in FORTRAN IV to use the subroutine OVERLP (discussed in Appendix A) to calculate overlap values for the atomic orbital basis set specified at each atom for the fragment coordinate system. Valence shell s and p orbital exponents used are shown in Table III-3. Average exchange optimized exponents for phosphorus and sulfur orbitals were obtained from Mitchell's results[180,181], and other exponents used were Clementi and Raimondi best atom exponents[197].

Table III-3 Valence Shell s and p Orbital Exponents for Fragment Overlap Calculations

Atom	ξ_s	ξ_p	
N	1.924	1.917	
O	2.246	2.227	
F	2.564	2.550	
Cl	2.356	2.039	
P	1.65	1.42	chloro substituents
S	1.93	1.64	
P	1.65	1.48	fluoro substituents
S	1.94	1.68	

The main program was coded to calculate d orbital overlap values for variation of ξ_d in the fragment system for the nitrogen localized atomic orbitals, from the formulae in part (1)ii of this section. Values for $S_{A_d\Pi_a}$ and $S_{A_d\Pi_s}$ were calculated for phosphorus and sulfur exponents from 0.050 to 2.200 and 0.050 to 2.500, respectively.

b) For the same exponent ranges, primitive overlap values obtained from the overlap variation calculation were used with formulae in part (1)ii to calculate values for $S_{A_dE_\sigma}$, $S_{A_dE_{\Pi,\Pi'}}$, $S_{A_dN_{\sigma_A}}$, and $S_{A_dN_{\sigma_{A'}}}$.

c) For each fragment, the value of ξ_d which corresponded to a maximum in expression(III.11) was determined, either by a large scale plot of the results, or by linear extrapolation based on relative rate of increase to the maximum. Results were obtained for ε values of 0.85 and 1.00, and compared with exchange optimized exponents for $(NPF_2)_3$, $(NPF_2)_4$ and $(NPCl_2)_3$ (III.1.5). The values calculated for $\varepsilon = 1.00$ are listed in Table III-4 (III.1.4), and discussed in section III.1.5.

Overlap values for d orbital exponent variation for a typical molecule are included in Appendix B.

III.1.4 Results; Molecular d Orbital Exponent Sets

Table III-4 EOV Optimized P and S d Orbital Exponents for Cyclic Halo-Phosphonitriles and Sulfonitriles.[a)]

Molecule		Phosphorus or sulfur d orbital exponent, ξ.				
	A_d:	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
$(NPF_2)_3$	MO	0.93	1.12	1.13	1.03	0.75
planar	EOV	(0.57)[b)]	1.12	0.55	0.90	0.19
	EOVΠ	0.15	1.16	0.55	0.97	0.19
$(NPF_2)_4$	MO	0.90	1.15	1.15	1.08	1.58
planar	EOV	—	1.15	0.65	1.08	—
	EOVΠ	—	1.18	0.65	1.14	—
$(NPF_2)_4$	MO	0.90	1.15	1.15	1.08	1.58
	EOV	—	1.15	0.64	1.09	—
	EOVΠ	—	1.16	0.64	1.12	—
$N_3P_3(C_6H_5)_2F_4$	MO	0.92	1.13	1.12	1.02	0.76
	EOV	(0.65)	1.14	0.57	0.94	—
	EOVΠ	0.20	1.16	0.57	0.95	—
$(NPCl_2)_3$	MO	0.91	1.12	1.11	1.13	0.77
planar	EOV	(0.40)	1.12	0.21	0.90	—
	EOVΠ	—	0.99	0.21	0.97	—
$(NPCl_2)_3$	MO	0.90	1.12	1.11	1.01	0.75
	EOV	(0.50)	1.11	0.18	0.83	—
	EOVΠ	—	1.02	0.18	0.89	—

(continued)

a) from (III.11) for k's equal, ε=1.0; where no maximum occurred before ξ→0, no value is listed. EOV, EOVΠ are sets specified in III.1.3.2 and MO is the set derived from maximum m $|S_{Ad\Pi_a}| + |S_{Ad\Pi_s}|$, without non-bonded contributions. b) values in brackets determined for neglect of non-bonding $S_{Ad\Pi_e}$; for EOV set as in III.1.3.2 use value shown in EOVΠ.

Table III-4 (continued)

Molecule	Phosphorus or sulfur d orbital exponent					
	A_d:	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
$(NPCl_2)_4$ $\bar{1}$	MO	0.90	1.13	1.14	0.95	0.85
	EOV	(0.13)	1.13	0.40	0.96	—
	EOVII	—	1.09	0.40	0.92	—
$(NPCl_2)_4$ $\bar{4}$	MO	0.90	1.12	1.12	1.05	≈1.70
	EOV	(0.22)	1.11	—	1.01	—
	EOVII	—	0.97	—	0.98	—
$\{(NPCl_2)_4\}$ planar	MO	0.88	1.14	1.14	1.05	1.55
	EOV	(0.10)	1.14	0.30	0.95	—
	EOVII	—	1.01	0.30	1.01	—
$(NPCl_2)_5$	MO	0.90	1.15	1.15	1.06	0.95
	EOV	—	1.15	0.23	1.04	—
	EOVII	—	1.02	0.23	0.98	—
$N_3P_3FCl_5$ (Cl subst.)	MO	0.90	1.13	1.13	1.02	0.75
	EOV	(0.37)	1.12	0.20	0.92	—
	EOVII	—	1.00	0.20	0.93	—
$N_3P_3(C_6H_5)_2Cl_4$	MO	0.92	1.12	1.13	1.04	0.78
	EOV	(0.48)	1.11	0.17	0.91	—
	EOVII	—	0.98	0.17	0.90	—
$N_3P_3(C_6H_5)_4Cl_2$	MO	0.90	1.12	1.13	1.03	0.75
	EOV	(0.50)	1.14	—	0.91	—
	EOVII	—	0.98	—	0.93	—
$NPCl_2(NSOCl)_2$ (P)	MO	0.90	1.12	1.12	1.04	0.76
	EOV	(0.40)	1.13	0.14	0.92	—
	EOVII	—	0.96	0.14	0.93	—

(continued)

Table III-4 (continued)

Molecule	Phosphorus or sulfur d orbital exponent					
	A_d:	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}
$NPCl_2(NSOCl)_2$	MO	0.93	1.13	1.14	1.03	0.82
(S(1))	EOV	(0.42)	1.16	—	0.95	—
	EOVII	—	1.07	—	0.93	—
	MO	0.92	1.14	1.13	1.02	0.82
(S(2))	EOV	(0.46)	1.19	—	0.99	—
	EOVII	—	1.05	—	0.97	—
α-$(NSOCl)_3$	MO	0.92	1.13	1.14	1.02	0.82
	EOV	(0.43)	1.18	—	0.98	—
	EOVII	—	1.00	—	0.96	—
$(NSCl)_3$	MO	0.86	1.06	1.09	1.01	0.78
	EOV	(0.42)	1.09	—	0.92	—
	EOVII	—	0.97	—	0.92	—
$(NSF)_4$	MO	1.09	1.08	1.09	1.11	1.04
	EOV	—	1.11	0.61	1.09	—
	EOVII	—	1.11	0.61	1.09	—

III.1.5 Discussion

(1)Accuracy of Results and Uncertainty Range for Optimized Exponents:

The precision of the calculated overlap values is at least six figures. However, the accuracy is determined by the coordinate input, and by approximations inherent in the evaluation of overlap integrals(Appendix A). When the exponent is considered to be a variable parameter, the coordinate input uncertainty can be used to establish an overlap value uncertainty range. This is ±0.0005 units,from a comparison of fragment overlap values for crystallographic geometries where AN(1) and AN(2) bond distances are equal within experimental error.

Exponent value uncertainty introduced by the approximations of the exchange overlap variation method cannot be assessed except by comparison with results reported for an actual exchange-included energy minimization[182], which also involves approximation uncertainty. The variation in results for crystallographically-determined and assumed-planar geometries is ±0.01 units for bonding d orbital exponents. Total bonded overlap values calculated using the molecular exponent sets (III.2) are not insensitive to this exponent uncertainty range, but trends obtained for a series of molecules are.

(2) Comparison of the Molecular Exponent Sets Determined:

A comparison of EOV method exponents with exchange energy optimized exponents (ME, Table III-5) shows that the former are in general agreement as an indication of which orbitals remain important for bonding (considering size characteristics only), when non-bonded orthogonality is taken into account. There are two criteria which may be used to determine which EOV

Table III-5 Optimized d Orbital Exponents for Planar Cyclic Phosphonitriles.

Molecule		Phosphorus d orbital exponent				
		A_d: d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
$(NPCl_2)_3$	MO[a)]	0.91	1.12	1.11	1.13	0.72
	MQ	1.07	0.96	0.95	1.11	1.21
	ME	0.25	1.34	0.23	1.24	0.21
	EOV	0.40(0.34)	1.12	0.21(0.12)	0.90(0.90)	—
	EOVΠ	— (—)	0.99(0.97)	0.21(0.12)	0.97(0.98)	—
$(NPF_2)_3$	MO	0.91	1.12	1.13	1.03	0.75
	MQ	1.18	0.89	1.19	1.18	1.21
	ME	0.36	1.15	0.31	1.05	0.24
	EOV	0.57(0.50)	1.12	0.55(0.42)	0.90(0.86)	0.19(0.10)
	EOVΠ	—	1.16(1.16)	0.55(0.42)	0.97(0.90)	0.19(0.10)
$(NPF_2)_4$	MO	0.90	1.15	1.15	1.08	1.58
	MQ	1.18	1.02	1.20	1.18	1.21
	ME	0.32	1.23	0.32	1.13	0.25
	EOV	—	1.15	0.65(0.60)	1.08(1.08)	—
	EOVΠ	—	1.18(1.18)	0.65(0.60)	1.14(1.14)	—

a) MO — maximum overlap, $(m|S_{A_d\Pi a}| + |S_{A_d\Pi s}|)_{max}$.
MQ — Mitchell electrostatic approximation, $\varepsilon=0.85$ [182].
ME — Mitchell exchange optimized approximation, $\varepsilon=0.85$ [182].
EOV,EOVΠ — Exchange Overlap Variation approximation, $\varepsilon=1.0$ ($\varepsilon=0.85$).

method set is in better agreement with exchange optimized values: 1) The correspondence for each d orbital, and 2) the ratio of 'bonding' orbital exponents, $\xi_{d_{xz}}/\xi_{d_{x^2-y^2}}$. For 1), there is little difference between using $\varepsilon=0.85$ and $\varepsilon=1.0$ to account for delocalization breakdown of perfect-pairing, except for the chlorine case, where the latter value gives closer results.

With either ε value, the ratio, $\xi_{d_{xz}}/\xi_{d_{x^2-y^2}}$, is in better agreement for the EOVΠ sets (where Π_e bonding overlaps have been included). This does not imply that exocyclic Π bonding is important necessarily, but does imply that it should not be excluded as a possibility in the halophosphonitriles. The improved ratio agreement for EOVΠ sets is slight, however, and may be a result of the particular simplifications inherent in this method. Since it was not established *a priori* that, for 'non-planar' molecular environments, the 'destabilization' effects of non-bonding exchange overlap would occur to the same extent as for these planar cases, both EOV and EOVΠ optimized sets were determined. From Table III-4, it can be seen that similar 'destabilization' effects do occur for all cases for both sets. (Both were used in subsequent bonded overlap calculations (III.2) to further test for differences.) Exchange energy optimized exponents were insensitive to an ε range of 0.6-1.0 [182]; and since it is an arbitrary parameter, a value of 1.0 was used in all subsequent exponent determinations as providing sets in better agreement with exchange energy optimized results for the chlorophosphonitrile in particular.

The simplification which is of greatest importance is that of assuming the same exchange overlap integral proportionality for each d orbital in overlaps with different substituent localized atomic orbitals, and a constant proportionality over the applicable overlap range. The latter will not likely affect the maximum position, since the proportionality can be approximated as an implicit linear function of the overlap value. The former should be important only where non-bonding overlaps are large compared with bonding overlaps (d_{z^2}, d_{yz}, and d_{xy}). However, approximate weights for non-bonding overlap values relative to those for Π bonding overlap values are ≤ 1.0 for all cases except chlorine E_{Π} (Table III-6, III.2.4), where the relative weight is 0.9. Thus, the same or greater destabilization would be introduced for all orbitals if this weighting scheme were used. Since the agreement for $(NPCl_2)_3$ with exchange energy optimized exponents would then be worse, it is more likely that neglecting some of the overlap values as bonding compensates for the equal-weight simplification for the fluorophosphonitriles, and may over-compensate for the chlorophosphonitrile. The actual relative weight which should be used depends upon the appropriate exchange energy integral values which this level of approximation was designed to detour, and the agreement obtained with energy-minimized results indicates that the EOV method optimization for exponents is successful in this context.

The exchange overlap variation is applicable only where overlap values are large enough to maintain the exchange integral proportional to the overlap integral(III.1.2). As the orbital exponent approaches zero (expanded orbital), the overlaps involving that orbital approach zero, and the approximation no longer holds. In some cases (Table III-4), the d_{z^2}, d_{yz}, and d_{xy} orbitals are completely 'destabilized' on the inclusion of non-bonding overlaps (compare sets labelled MO and EOVII, for example). At the low overlap value range where maxima for these diffused orbitals do occur, only relative significance can be attached to the actual value. That is, the EOV method provides a good indication of which d orbitals can be expected to be important for bonding (d_{xz} and $d_{x^2-y^2}$ for the phosphonitrile and sulfonitrile molecular environments investigated), and which may be destabilized when the non-bonded orthogonality requirement is considered. A relative indication of the bond covalent energy contributed by d orbital Π bonding can also be obtained from the value of the EOV method expression (III.11) at optimum exponent, and this is discussed and applied in section III.2.

The assumption that the d orbitals at A can be considered as participating in the ring and exocyclic Π bond systems only may also be an important limitation. The d_{z^2} orbital, especially, is oriented for considerable overlap in both the exocyclic Π and ring σ ($N_{\sigma A}$) systems, and d_{xy} is oriented for relatively large bonding overlaps with the latter system for some cases. If such overlaps were included as bonding, the optimized exponents might be higher for these orbitals, although for d_{xy} non-bonding ($N_{\sigma A'}$) overlaps are also large and account for its complete 'destabilization' in most cases. On an equal weight basis, only very large bonding overlaps would counteract this. The extent to which the d orbitals should be included as bonding cannot be finally assessed without an energy-minimized calculation for a complete molecule. Therefore, it is noted that these exponents are optimum for one particular choice of localized bond structure, and should be used accordingly. This restriction is not so limiting as it first appears, as considerable experimental evidence can be successfully interpreted within this localized bond model (I.4.4). For energy level calculations by a simple approximate LCAO MO method, the choice of exponent for orbitals which are otherwise determined to be diffuse is not a major factor, if any, affecting the results, since the energy of an electron in such an orbital would be correspondingly less favorable for bonding. It is more important to use a consistent set for examining trends in calculated values for a series of molecules. Hence, the molecular phosphorus and sulfur d orbital exponents determined by the EOV method (Table III-4) are proposed for use in investigations of bond structure in these molecules.

III.2 Bond Structure of Phosphonitriles and Sulfonitriles From Localized Bond Overlap Values

III.2.1 Introduction and Previous Calculations

Use of the localized bond model fragment overlap values in the study of bond structure does not imply that the question of either 'island' or cyclic Π system delocalization is settled in favor of localization. It merely provides an approach through which possible molecular bond system contributions to the total covalent bond structure can be assessed.

Although the bond structure of phosphonitriles and sulfonitriles has been discussed qualitatively using this model, the lack of good molecular orbital sizes and energies has restricted 'quantitative' calculations. Overlap values for several possible configurations of an eight-membered cyclic phosphonitrile have been calculated[165]. Use of a d orbital exponent of 0.47 in all cases precluded any quantitative conclusion. However, the principal qualitative conclusion, that other d orbitals, besides those oriented for bonding overlap in the 'classical' Π system (Π_a), must be considered for the d-p Π bond structure, remains valid. This was shown most conclusively by Mitchell[182] who calculated ring bond overlap values for cyclic trimeric and tetrameric phosphonitriles for a generalized planar geometry (R_{PN}=1.58Å, θ=120°, γ=120 or 150°; n=3 or 4) and a d orbital exponent range, 0.25-1.25. Ring bond overlap values were also reported for $(NPCl_2)_4$ $\bar{4}$ for the same exponent range. No extension to the prediction or comparison of molecular energy associated characteristics was made from these overlap values or from the exchange energy optimized d orbital exponent sets.

The relative importance of various bond systems in terms of molecular bonding energy and charge separations cannot be more fundamentally assessed without reliable estimates of valence shell orbital energies, particularly for d orbitals in the molecule. However, overlap value calculations for the localized bonds should provide insight into bond structures. The overlap values on which the present work is based represent a substantial advance on previous calculation, and, with the d orbital exponent sets proposed from the Exchange Overlap Variation calculation, provide an estimate of covalent bond system contributions to the total bond structure.

III.2.2 Bonded Overlaps As a Measure of Covalent Bond Energies

If bond energy is loosely defined as the relative gain in electronic energy on formation of a bond, it can be partitioned into the sum of covalent and ionic contributions. The sum, neglecting bond interaction terms, of localized covalent bond energies over all such bonds of a molecule is proportional to its covalent energy, E_c (III.1.1). In the localized bond model, the exchange energy contribution is proportional to the total covalent energy. A total 'bond' between two atoms, A and B, is made up of all the localized two-electron bonds between them, and within the exchange overlap approximation, the sum of appropriately weighted overlap values over all the localized bonds, including non-bonding overlap values, is proportional to the molecular covalent energy (III.1.2). The sum of appropriately weighted overlap values over localized bonds between A and B is proportional to the covalent energy contribution of the total 'bond' AB to the molecular covalent energy. Such localized bond overlap values are here termed <u>bonded overlaps</u> with the implication that these are <u>maximum</u> when the overlap integrals are evaluated for EOV optimized exponents.

For a series of molecules with chemically similar bond structure, bonded overlaps for the various bond types, systems and total structure are proportional to the relative covalent energy contributions to the localized bond structure. Thus, the minimum total covalent energy corresponds to the maximum total bonded overlap for each molecule and for each localized bond. The localized atomic orbital basis must meet this requirement. The criterion of maximum total overlap has been investigated for a localized basis atomic orbital set[202,203], and shown to be good if all valence shell electrons participate in bonds[204,205]. Since the localized bond model used (III.1.3.1) to investigate phosphonitriles and sulfonitriles does not strictly maximize bonding overlap,and minimize non-bonding overlap energy, other factors may have to be taken into account when minimum-energy properties, such as molecular configuration, are studied.

III.2.3 Experimentally Observed Properties Related to Bonded Overlaps

For a series of molecules formed of predominantly covalent, chemically similar bonds, such as the cyclic halophosphonitriles, and for which experimentally determined geometry is used to specify the localized atomic orbital directions, the ionic contributions per bond may be considered as constant. Variations in relative total bonded overlaps per bond type should reflect the bond energy associated properties for the series.

Infrared stretching frequencies are a measure of total bond energies (covalent plus ionic). When the ionic energy contribution is 'known' for a localized bond, or is a constant proportion of the total bond energy for similar bonds for an atom pair AB, the infrared stretching frequency of AB is proportional to the covalent energy. The total bonded overlap for a phosphonitrile or sulfonitrile ring bond should be linearly proportional to the infrared frequency assigned to ring stretching modes (positive slope).

The bonded overlap value establishes the participation of a particular bond system on an energy basis. Hence, d orbital charge density at the nucleus cannot be directly considered in this model, and no correlation of individual Π_a or Π_s bonded overlaps with ^{31}P chemical shift is expected. If the bonded overlap for each of the Π_a and Π_s bond systems is indeed a measure of its contribution to the bond structure at phosphorus, the total Π system may be considered as it affects the value of the ^{31}P chemical shift. For the same exocyclic substituent (e.g. for chlorophosphonitriles), assuming a constant sigma system framework at each phosphorus atom in a series, the chemical shift observed should be a linear function (with positive slope) of the total Π bonded overlap. Where possible exocyclic d orbital Π bonding, p orbital Π bonding and d orbital σ bonding are neglected, this correlation should exist for the total ring Π bonded overlap.

The bond model predicts the larger, non-planar rings to be stable because the wider ring nitrogen angle allows Π_s system bonding to compensate for the loss in Π_a system bonding due to non-planarity. If the ring Π system were the only covalent energy contribution determining the molecular configuration, Π_s system bonded overlap should be a linear function of ring nitrogen angle for each series (positive slope).

The expected correlations can be tested within the limits of the experimental measurement and the theory. They will be used as a framework within which the use of optimized molecular d orbital exponents and the exchange overlap approximation can be evaluated, and bonded overlap values used to investigate bond structure of phosphonitriles and sulfonitriles.

III.2.4 Bonded Overlaps; Calculation and Estimated Weighting Factors For Their Comparison

It is assumed that the crystallographically-determined geometry defines a maximum bonded overlap criterion for the sigma framework localized bonds which is a good approximation to the optimum localized sigma bond structure.

(1) Bonded overlaps:

Including non-bonding exchange overlap for d orbitals, expressions for the calculation of bonded overlaps were derived from EOV method formulae and localized bond sigma overlap formulae (III.1.3.3(1)). For optimized d orbital exponents in a total fragment (two AN and one or two AE bonded pairs), bonded overlaps are;

$$\Pi_a^f(AN) = \sum_{N_{\Pi_a}} \sum_{A_d} \Bigl(mk_{\Pi_a}|S_{A_dN_{\Pi_a}}| - \frac{Y}{2}\,[\sum_{E_\sigma} k_{\sigma_E}|S_{A_dE_\sigma}| - \sum_{N_{\sigma_A}} k_{\sigma_A}|S_{A_dN_{\sigma_A}}| - \sum_{N_{\sigma_{A'}}} k_{\sigma_{A'}}|S_{A_dN_{\sigma_{A'}}}|] - X\,[\sum_{E_{\Pi,\Pi'}} k_{\Pi_e,\Pi'_e}|S_{A_dE_{\Pi,\Pi'}}|]\Bigr) \qquad \text{(III.13)}$$

$$\Pi_s^f(AN) = \sum_{N_{\Pi_s}} \sum_{A_d} \Bigl(k_{\Pi_s}|S_{A_dN_{\Pi_s}}| - \frac{Y}{2}\,[\sum_{E_\sigma} k_{\sigma_E}|S_{A_dE_\sigma}| - \sum_{N_{\sigma_A}} k_{\sigma_A}|S_{A_dN_{\sigma_A}}| - \sum_{N_{\sigma_{A'}}} k_{\sigma_{A'}}|S_{A_dN_{\sigma_{A'}}}|] - X\,[\sum_{E_{\Pi,\Pi'}} k_{\Pi_e,\Pi'_e}|S_{A_dE_{\Pi,\Pi'}}|]\Bigr) \qquad \text{(III.14)}$$

$$\sigma^f(AN) = \sum_{N_{\sigma_A}} S_\sigma(AN) \qquad \text{(III.15)}$$

$$\sigma^f(AE) = \sum_{E_\sigma} S_{\sigma_E}(AE) \qquad \text{(III.16)}$$

where bonding A_d overlap with $N_{\sigma A}$ and E_σ are neglected,

$X = 2$ or 0 for EOVΠ and EOV determined d orbital exponents, respectively, for A_d bonding overlaps; otherwise, $X = \frac{Y}{2}$.

For $E_{\Pi,\Pi'}(0)$, $X = 2$ in both cases; and

Y is a factor to proportionate the total non-bonding overlap integrals into bonding Π system contributions for a given d orbital.

All other symbols are as defined in III.1.3.1, and the k's are appropriate weighting factors discussed below.

The values calculated per fragment unit are divided by the number of fragment bonds of a particular bond type to obtain bonded overlaps per bond (represented in further discussion without the superscript ^{f}).

(2) Estimated weighting factors:

The factors which relate an overlap integral to its exchange energy contribution can be approximated as noted in III.1.2 as;

$$k_{\phi j}(A_{\phi i}B_{\phi j}) \propto \frac{Z_{\phi i} + Z_{\phi j}}{2} \tag{III.17}$$

where Z's are valence state ionization potentials for orbitals ϕ_i and ϕ_j of the overlap integral, centred at A and B, respectively.

Thus, $\phi_i \equiv A_d$ and

$\phi_j \equiv N_{\sigma A}, N_{\sigma A'}, E_\sigma, E_{\Pi,\Pi'}, N_{\Pi_a}, N_{\Pi_s}$

and for each orbital A_d, the relative weights can be written,

for Π_a bond system;

$$\frac{k_{\phi j}(A_d\phi_j)}{k_{\Pi_a}(A_dN_{\Pi_a})} = \frac{Z_{A_d} + Z_{\phi_j}}{Z_{A_d} + Z_{N_{\Pi_a}}} = k'_{\Pi_a}(A_d\phi_j) \tag{III.18}$$

for Π_s bond system;

$$\frac{k_{\phi j}(A_d\phi_j)}{k_{\Pi_s}(A_dN_{\Pi_s})} = \frac{Z_{A_d} + Z_{\phi_j}}{Z_{A_d} + Z_{N_{\Pi_s}}} = k'_{\Pi_s}(A_d\phi_j) \tag{III.19}$$

Table III-6 Estimated Weighting Factors For Exchange Overlap Approximation. (Z_{A_d} = 2.00ev; A≡P or S [a])

ϕ_j	Localized atomic orbital b)	Relative weighting factor; $k'_{\Pi_a}(A_d\phi_j)$	$k'_{\Pi_s}(A_d\phi_j)$	Average k'_{Π}
N_{Π_a}	p	1.00		1.00
N_{Π_s}	sp^2		1.00	
N_{σ_A}	sp^2	1.26	1.00	1.13
$N_{\sigma_{A'}}$	sp^2	1.26	1.00	1.13
F_{Π}	p	1.40	1.11	1.26
F_{σ}	sp	2.00	1.60	1.80
Cl_{Π}	p	1.00	0.79	0.90
Cl_{σ}	sp	1.40	1.10	1.25
O_{Π}	p	1.20	0.94	1.07
O_{σ}	sp	1.69	1.34	1.52

a) Average neutral atom Z_{A_d} for P,S used with neutral atom Z_{ϕ_j}[206] and linear extrapolation for s-p hybrids[207]; k' calculated from (III.18) and (III.19).

b) s-p hybrid type for ϕ_j.

Valence state ionization potentials, Z_{A_d}, may be different for each d orbital depending upon the molecular environment. Molecular Z's are not known, though expected in the range 2-9 ev for phosphorus and sulfur atomic d orbitals[206]. For most cases calculated, the total of Π_a and Π_s overlap values for a given d orbital over both nitrogen bonds was found to be approximately the same. So estimated weighting factors (Table III-6) and non-bonding/bonding overlap contributions were considered; and it was noted that the simplified expression (III.11 with all k's equal to one) could be used to derive the optimized exponent sets (III.1.3).

However, when the sum of Π_a and Π_s bonded overlaps is compared for a series of structures, the weighting factors must be re-assessed, since the difference between $k'_{\Pi a}$ and $k'_{\Pi s}$ may be important. That is, the use of equal weights for non-bonding overlap values remains an acceptable simplification for a given bond type, Π_a or Π_s, but the relative weights of Π_a and Π_s (summed over all d orbital contributions) should be included to compare total bonded Π overlaps for a series of structures where the ratio of the two Π system contributions may not be constant.

Table III-7 Estimated Weighting Factors For Bonded Overlap Comparison Between Different Bond Types and Atom Pairs (AB)

Bond type and atom pair	Z_{ϕ_i}(A) (ev)	Z_{ϕ_j}(B) (ev)	Relative weighting factor, k' a)
Π_a(PN)	1.9	14.4	1.00
Π_s(PN)	1.9	18.7	1.26
σ (PN)	13.0	18.7	1.94
Π_a(SN)	2.0	14.4	1.01
Π_s(SN)	2.0	18.7	1.27
σ (SN)	15.3	18.7	2.09
σ_E(PCl)	13.0	20.9	2.08
σ_E(PF)	13.0	31.2	2.71
σ_E(SCl)	15.3	20.9	2.22
σ_E(SF)	15.3	31.2	2.85
Π_E(SO)	2.0	17.6	1.20
σ_E(SO)	15.3	25.8	2.52

a) $k' = k_t(AB)/k_{\Pi a}(PN)$ from expression (III.18); neutral atom Z's[206]; t represents the bond type.

Estimated weights relative to that for bonded overlap in the phosphonitrile Π_a system (Table III-7) indicate that individual phosphonitrile and sulfonitrile Π system overlaps can be compared on an equal weight basis. Exocyclic σ bonded overlaps for phosphorus and sulfur chlorine or phosphorus and sulfur fluorine, but not for both, can be compared with almost equal weight. Using the estimated weighting factors, comparable totals for bonded overlap for ring atom pairs (Σ_{ring}, Σ_{Π}) and for total molecule or fragment units (Σ_T) are;

$$\Sigma_{\Pi}(AN) = \Pi_a(AN) + 1.26\Pi_s(AN) \qquad AN \equiv PN \text{ or } SN \qquad \text{(III.20)}$$

$$\Sigma_{ring}(AN) = \Sigma_{\Pi}(AN) + k_A' \,\sigma(AN) \;;\; k_A' = \begin{matrix} 1.94, & A=P \\ 2.09, & S \end{matrix} \qquad \text{(III.21a,b)}$$

$$\Sigma_{exo}(SO) = 1.20\Pi_e(SO) + 2.52\sigma_E(SO) \qquad \text{(III.22)}$$

$$\Sigma_T = \sum_n [\Sigma_{ring}(PN) + k_E' \,\sigma_E(PE)] \;;\; k_E' = \begin{matrix} 2.08, & E=Cl \\ 2.71, & F \end{matrix} \qquad \text{(III.23a)}$$

or

$$\Sigma_T = \sum_n [\Sigma_{ring}(SN) + \Sigma_{exo}(SO) + k_E' \,\sigma_E(SE)];\; k_E' = \begin{matrix} 2.22, & E=Cl \\ 2.85, & F \end{matrix} \qquad \text{(III.23b)}$$

n = the number of bonded pairs per molecule or unit,
$\Pi(AB)$ and $\sigma(AB)$ terms are bonded overlaps as defined in III.2.4(1).

These estimates apply only to an approximation for relative covalent bond energies: Ionic bond energy contributions are not considered.

III.2.5 Details of Bonded Overlap Calculations and Results

III.2.5.1 Cyclic Phosphonitriles and Sulfonitriles, Crystallographic Configurations

Individual overlap values for each atom pair, using molecular exponent sets, EOV and EOVΠ, for d orbitals (Table III-4), were determined from the overlap variation calculation (III.1.3.3), and the bonded overlap for each bond system was calculated per fragment from formulae (III.13)-(III.17) with all k's equal to one. (Typical calculation figures for planar and non-planar molecules are included in appendix B.) These were converted to an average per bond basis and are listed in Tables III-8 and III-9 for EOV and EOVII exponent sets, respectively. Bonded overlap totals were calculated using the estimated weighting factors in formulae (III.20)-(III.23b) and are shown in Table III-10.

III.2.5.2 Cyclic Molecules, Hypothetical Configurations

(1) Planar chlorophosphonitrile tetramer

For a planar octahedron, all the ring angles must equal 135°. However, a geometry of alternating ring angles, θ and γ, can be specified for arbitrary, equal ring bond distances. Since the ring phosphorus angles for all known cyclic phosphonitrile cases are close to 121° (117-123°), θ was fixed at this value and γ then specified as 149°. Average bond distances for $(NPCl_2)_4$ $\bar{1}$ and $\bar{4}$ were used; R_{PN} and R_{PCl} = 1.56 and 1.98 Å, respectively.

An exchange overlap variation calculation was applied to this configuration, and optimized d orbital exponents derived as in III.1.3 (results in Table III-4). Bonded overlaps were calculated as for the crystallographically determined configurations, $(NPCl_2)_4$ $\bar{1}$ and $\bar{4}$ (III.2.5.2), and included in Tables III-8 and III-9 for comparison.

(2) Bis(dichlorophosphonitrile)oxochlorosulfonitrile,{$(NPCl_2)_2NSOCl$}

The missing link in the series, $(NPCl_2)_3 \rightarrow (NSOCl)_3$, was approximated as a molecule composed of one average sulfonitrile and two phosphonitrile units based on the known mixed ring, dichlorophosphonitrile bis(oxochlorosulfonitrile). Total bonded overlaps were calculated for EOVII exponent set results and are shown in Table III.10 for comparison.

Table III-8 Bonded Overlaps For Phosphonitriles and Sulfonitriles Using EOV Optimized d Orbital Exponents. (average per bond per unit [a])

Molecule	Ring bond systems (AN ≡ PN or SN)					Exocyclic bond systems (AE ≡ PCl,F or SCl,F,O)		
	σ(AN)	Π_a(AN)	Π_s(AN)	Σ_Π(AN)	Σ_{ring}(AN)	Π_e(AE)	σ_E(AX)	σ_E(SO)
$(NPF_2)_3$	0.6750	0.2948	0.2414	0.5990	1.9085		0.5404	
$(NPF_2)_4$	0.7241	0.4035	0.2703	0.7441	2.1488		0.5412	
planar	0.7230	0.3900	0.2942	0.7607	2.1633		0.5412	
$N_3P_3(C_6H_5)_2F_4$	0.6794	0.2575	0.2748	0.6037	1.9217		0.5365	
$(NPCl_2)_3$	0.6623	0.2466	0.2025	0.5017	1.7866		0.6152	
planar	0.6612	0.2681	0.2245	0.5509	1.8336		0.6152	
$(NPCl_2)_4$ $\bar{1}$	0.6943	0.0678	0.3926	0.5624	1.9093		0.6085	
$\bar{4}$	0.6857	0.3614	0.0642	0.4424	1.7726		0.6128	
planar	0.7029	0.3337	0.2794	0.6857	2.0493		0.6106	
$(NPCl_2)_5$	0.7102	0.3034	0.2925	0.6720	2.0498		0.6288	
$N_3P_3FCl_5$ (Cl)	0.6713	0.2659	0.2351	0.5624	1.8647		0.6235	

(continued)

a) Except for Σ_Π and Σ_{ring}, values are unweighted and must be combined with factors from Table III-7 for overall comparison on an energy basis. Details of geometry in Table III-2.

Table III-8 (continued)

Molecule	σ(AN)	Π_a(AN)	Π_s(AN)	Σ_Π(AN)	Σ_{ring}(AN)	Π_e(AE)	σ_E(AX)	σ_E(SO)
$N_3P_3(C_6H_5)_2Cl_4$	0.6692	0.2334	0.2358	0.5305	1.8288		0.6110	
$N_3P_3(C_6H_5)_4Cl_2$	0.6739	0.2843	0.2153	0.5556	1.8630		0.5990	
$NPCl_2(NSOCl)_2$ (P)	0.6642	0.2385	0.1925	0.4810	1.7700		0.6338	
(S(1))	0.6722	0.1954	0.2594	0.5222	1.9271	0.3430	0.5539	0.6648
(S(2))	0.6684	0.1787	0.2189	0.4545	1.8514	0.3295	0.5369	0.6616
$(NSOCl)_3$ α	0.6765	0.1936	0.2274	0.4801	1.8940	0.3467	0.5539	0.6712
$(NSCl)_3$	0.6405	0.1741	0.2347	0.4698	1.8084		0.4938	
$(NSF)_4$	0.6503	0.3565	0.1671	0.5670	1.9261		0.4903	

Table III-9 Bonded Overlaps For Phosphonitriles and Sulfonitriles Using EOVΠ Optimized d Orbital Exponents. (average per bond per unit [a])

Molecule	Ring bond systems (AN ≡ PN or SN)					Exocyclic bond systems (AE ≡ PCl,F or SCl,F,O			
	σ(AN)	Π_a(AN)	Π_s(AN)	Σ_Π(AN)	Σ_{ring}(AN)	Π_e(AX)	Π_e(SO)	σ_E(AX)	σ_E(SO)
$(NPF_2)_3$	0.6750	0.3075	0.2697	0.6473	1.9568	0.2791		0.5404	
$(NPF_2)_4$	0.7241	0.4264	0.2883	0.7897	2.1944	0.2918		0.5412	
planar	0.7230	0.4048	0.3095	0.7948	2.1974	0.3016		0.5412	
$N_3P_3(C_6H_5)_2F_4$	0.6794	0.2818	0.3006	0.6606	1.9786	0.2713		0.5365	
$(NPCl_2)_3$	0.6623	0.2530	0.2542	0.5733	1.8582	0.3588		0.6152	
planar	0.6612	0.2690	0.2770	0.6180	1.9007	0.4217		0.6152	
$(NPCl_2)_4$ $\bar{1}$	0.6943	0.1022	0.4161	0.6265	1.9734	0.3928		0.6085	
$\bar{4}$	0.6857	0.3897	0.1114	0.5301	1.8604	0.3935		0.6128	
planar	0.7029	0.3440	0.3042	0.7273	2.0909	0.4180		0.6106	
$(NPCl_2)_5$	0.7102	0.3050	0.3152	0.7022	2.0800	0.4435		0.6288	
$N_3P_3FCl_5$ (Cl)	0.6713	0.2708	0.2718	0.6133	1.9156	0.3903		0.6235	

(continued)

a) Except for Σ_Π and Σ_{ring}, values are unweighted and must be combined with factors from Table III-7 for overall comparison on an energy basis. Details of geometry in Table III-2.

Table III-9 (continued)

Molecule	σ(AN)	Π_a(AN)	Π_s(AN)	Σ_Π(AN)	Σ_{ring}(AN)	Π_e(AX)	Π_e(SO)	σ_E(AX)	σ_E(SO)
$N_3P_3(C_6H_5)_2Cl_4$	0.6692	0.2421	0.2744	0.5878	1.8860	0.4133		0.6110	
$N_3P_3(C_6H_5)_4Cl_2$	0.6739	0.2859	0.2512	0.6024	1.9098	0.4123		0.5990	
$NPCl_2(NSOCl)_2$ (P)	0.6642	0.2528	0.2320	0.5451	1.8336	0.4237		0.6338	
(S(1))	0.6722	0.2027	0.2734	0.5472	1.9521	0.4078	0.3492	0.5479	0.6648
(S(2))	0.6684	0.1905	0.2304	0.4808	1.8778	0.3833	0.3412	0.5369	0.6616
$(NSOCl)_3$ α	0.6765	0.2013	0.2418	0.5060	1.9199	0.4053	0.3522	0.5539	0.6712
$(NSCl)_3$	0.6405	0.1918	0.2464	0.5023	1.8409	0.3760		0.4938	
$(NSF)_4$	0.6503	0.4153	0.1804	0.6426	2.0017	0.1465		0.4903	

Table III-10 Bonded Overlap Totals As a Measure of Covalent Energy For Phosphonitriles and Sulfonitriles a)

Molecule	Σ_{ring}(AN)		Σ_{exo}	Σ_T	$\Delta H_{gc}^{17.0\,b)}$ (kcal/ monomer mole)	Σ_T /molecule *
		(AX)	(SO)			
$(NPF_2)_3$	3.914	2.929		6.843		20.592
$(NPF_2)_4$	4.389	2.933		7.322		29.288
$N_3P_3(C_6H_5)_2F_4$	3.957	2.908		6.865		
$(NPCl_2)_3$	3.716	2.559		6.276(0)$^{b)}$	4.863(0)	18.827
$(NPCl_2)_4$ $\bar{1}$	3.947	2.531		6.478(0.2)	4.052(0.8)	25.912
$\bar{4}$	3.721	2.549		6.270		25.080
planar	4.182	2.540		6.722		26.888
$(NPCl_2)_5$	4.160	2.616		6.776(0.5)	3.750(1.1)	33.880
$N_3P_3FCl_5$ (Cl)	3.831	2.594		6.455		
$N_3P_3(C_6H_5)_2Cl_4$	3.772	2.542		6.314		
$N_3P_3(C_6H_5)_4Cl_2$	3.820	2.492		6.323		
$NPCl_2(NSOCl)_2$ (P)	3.667	2.637		6.304		
(S(1))	3.904	1.216	2.094	7.214		
(S(2))	3.756	1.192	2.077	7.025		
$(NSOCl)_3$ α	3.856	1.230	2.114	7.100		21.300
$(NSCl)_3$	3.682	1.096		4.778		14.334
$(NSF)_4$	4.003	1.397		5.400		21.600
totals;						
$(NPCl_2)_3$	*11.148	7.677				18.827
$\{(NPCl_2)_2NSOCl\}$	*11.164	6.478	2.086			19.728
$NPCl_2(NSOCl)_2$	*11.327	5.045	4.171			20.543
α-$(NSOCl)_3$	*11.568	3.690	6.342			21.300

a) per unit except where noted *. b) difference from $(NPCl_2)_3$ in brackets.

III.2.5.3 Linear Trichlorophosphonitriletrichlorophosphonium Ion, C_{2v} Symmetry

The ion, $[Cl_3PNPCl_3]^+$, was approximated as a fragment, Figure III-1, with N(2) as the in-plane chlorine (atom 4, Figure II-12; E(1) and E(2) are atoms 5 and 6), and $\theta = 115°$. EOVII optimized d orbital exponents were calculated for this C_{2v}-derived configuration for PNP chain angles, γ_1, from 120° to 160°, in increments of 5°. The sign convention and method of including non-bonding overlap was employed as described (III.1.3). The major difference from the variation as applied to a ring fragment is that only one in-plane atom pair (PN) was considered as Π bonding.

Table III-11 Exchange Overlap Optimized d Orbital Exponents For $[Cl_3PNPCl_3]^+$, C_{2v} Symmetry

	Orbital and exponent				
	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{yz}
MO[a)]	0.85-0.89	1.13	1.13	1.04-1.08	0.65-1.60
EOVII	—	0.93	0.43	0.91-0.95	—

a) MO; maximum bonding overlap only.
EOVII; non-bonding overlap included as in III.1.3.
The range shown refers to $P\hat{N}P$ = 120° to 160°.

Using the optimized exponents determined, bonded overlaps were calculated as described (III.2.4) (Table III-11). The change in distance of close-approach for the chlorine atoms in the C_{2v} configuration (and C_2 configuration (Figure II-12)) was calculated from the variation in interatomic distances with chain angle, γ = 120°- 160°.

Table III-12 Bonded Overlaps Calculated For $[Cl_3PNPCl_3]^+$, C_{2v} Symmetry

$P\hat{N}P$ (γ)a) degrees	σ(PN)	Π_s(PN)	Σ_Π(PN)	Σ_{chain}(PN)	Π_e(PCl)	Σ_T/unit
120	0.6642	0.2706	0.6903	1.9788	0.4911	5.8810
130	0.6809	0.2894	0.7139	2.0348	0.4954	5.9371
135	0.6867	0.2952	0.7212	2.0534	0.4977	5.9557
140	0.6913	0.3002	0.7276	2.0687	0.4995	5.9710
145	0.6950	0.3053	0.7340	2.0823	0.5015	5.9846
150	0.6979	0.3078	0.7372	2.0911	0.5030	5.9934
155	0.7002	0.3063	0.7353	2.0937	0.5021	5.9960
160	0.7019	0.2983	0.7252	2.0869	0.4981	5.9892
maximum 152 ±2	0.699	0.308	0.738	2.094	0.503	5.996

a) Values per bond except where noted; additional values constant for angle variation:

σ_E(PCl) in-plane	0.6297
σ_E(PCl) out-of-plane	0.6232
Π_a(PN)	0.3493.

III.2.6 Evaluation of the EOV Bonded Overlap Calculation

When bonded overlaps per bond type for crystallographically determined geometries of $(NPCl_2)_3$ and $(NPF_2)_4$ are compared with those for assumed planar geometries (Tables III-8 and III-9), the discrepancy can be attributed to coordinate input uncertainty (III.1.3.3(2)). The discrepancy range, ±0.015 units, is termed calculation error in the following discussion.

Bonded overlap results using EOV and EOVΠ optimized d orbital exponent sets were tested for correlation against experimental observables (Tables I-1 and III-2; Values used were for solid state if available,and the average for a fragment unit to compare with overlap per bond.). Results from the EOV set were consistently lower than those from the EOVΠ set; however, both showed the same correlations. Since the latter set makes fewer approximations in including bonded exocyclic Π overlap more explicitly, better when assessing properties of the sulfanuric halides, only correlation plots for results of this set have been included (Figures III-2 to III-5).

Bonded overlaps for ring sigma bonds are similar for the phosphonitriles (mean 0.68 ±0.02, 2.4%) and phosphorus-nitrogen bond distances for the molecules are within 1.5% of the mean. Theoretically, only the total bonded overlap can be assumed proportional to a covalent bond energy, and, of the ring unit types (phosphonitrile, sulfanuric chloride, thiazyl chloride), sufficient points to establish a correlation are only available for the phosphonitriles (Figure III-2). The correlation is inversely linear as expected (standard deviation in overlap entirely, ±0.03), and suggests that the localized bond model including ring Π bonds is acceptable, so that total system bonded overlaps can be compared as an indication of possible σ and Π bonding contributions to the total covalent energy.

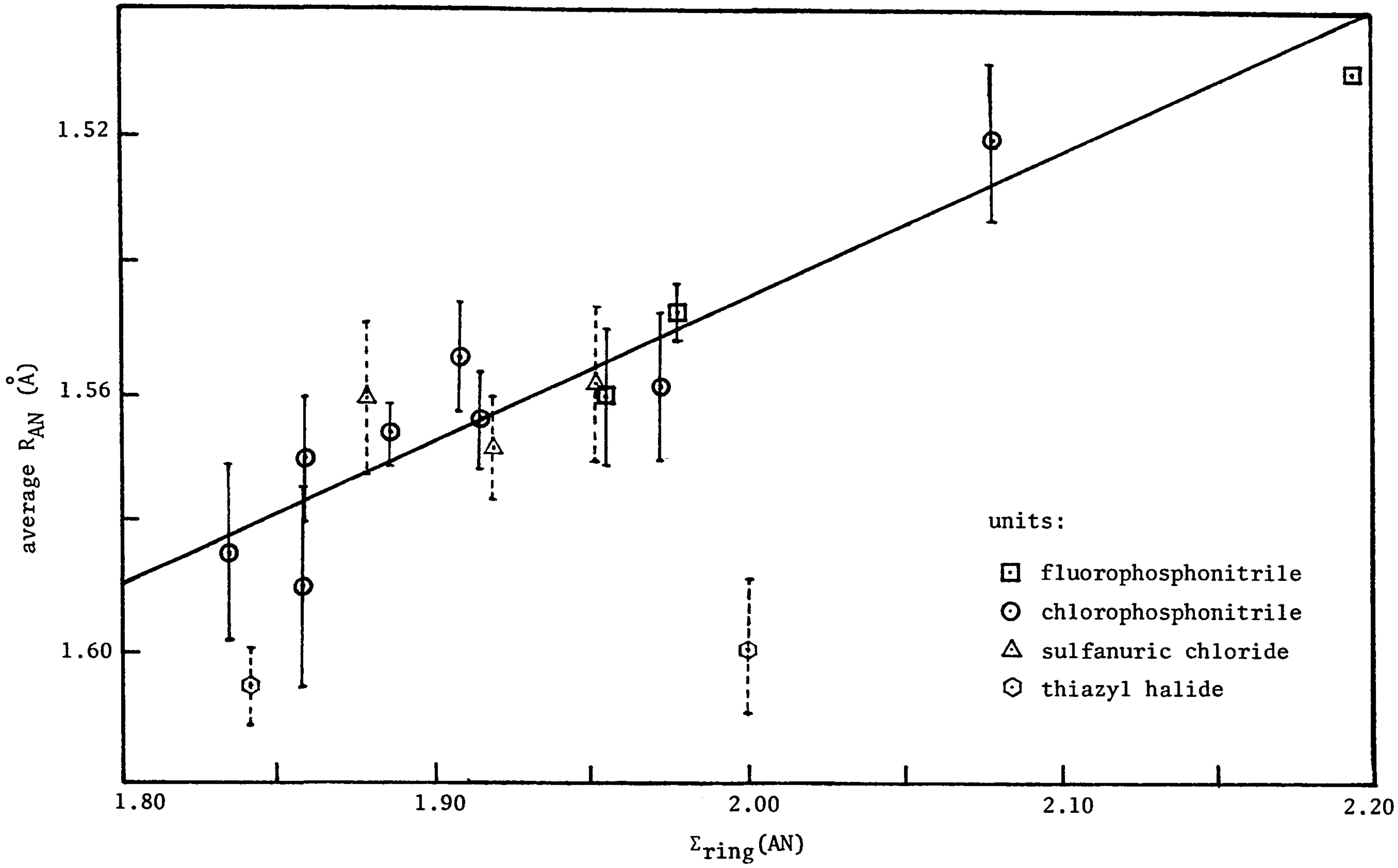

Figure III-2 Ring Bond Distance, R_{AN}, Compared With Total Bonded Overlap, $\Sigma_{ring}(AN)$ For Cyclic Phosphonitriles and Sulfonitriles.

It is more desirable to use experimentally observed properties which, although they should also correlate with bond distances and angles, are not explicitly included as input for the calculation. Total bonded overlaps (Σ_{ring}) for the phosphonitriles show a linear correlation with a positive slope for infrared ring stretching frequencies except for $N_3P_3(C_6H_5)_2F_4$ and $(NPCl_2)_4$ $\bar{4}$ (Figure III-3; standard deviation in overlap ±0.015 including $N_3P_3(C_6H_5)_2F_4$ but excluding $(NPCl_2)_4$ $\bar{4}$). The former differs from the other fluorophosphonitriles in its phenyl group substitution, which might result in a lower 'average' ring stretching frequency observed from that for complete fluorine substitution, through a decrease in ionic character for the ring bonds. The assignments for both solid state forms of $(NPCl_2)_4$ are not well-established, but it is unlikely that the value for $\bar{4}$ would be lowered sufficiently for a fit. Application of the bonded overlap calculation as used for these non-planar molecules is discussed further in (III.2.7).

Few of the phosphonitrile ^{31}P chemical shift measurements apply to molecules for which overlaps were calculated. However, there is a possibly linear correlation for total Π bond system overlap and chemical shift for the chlorophosphonitriles except $(NPCl_2)_4$ (Figure III-4). (This deviation is discussed in III.2.7).

These correlations as expected where bonded overlaps can be 'theoretically' related to experimental observables, indicate that as calculated they are a measure of relative covalent bond energies within the localized bond model used.

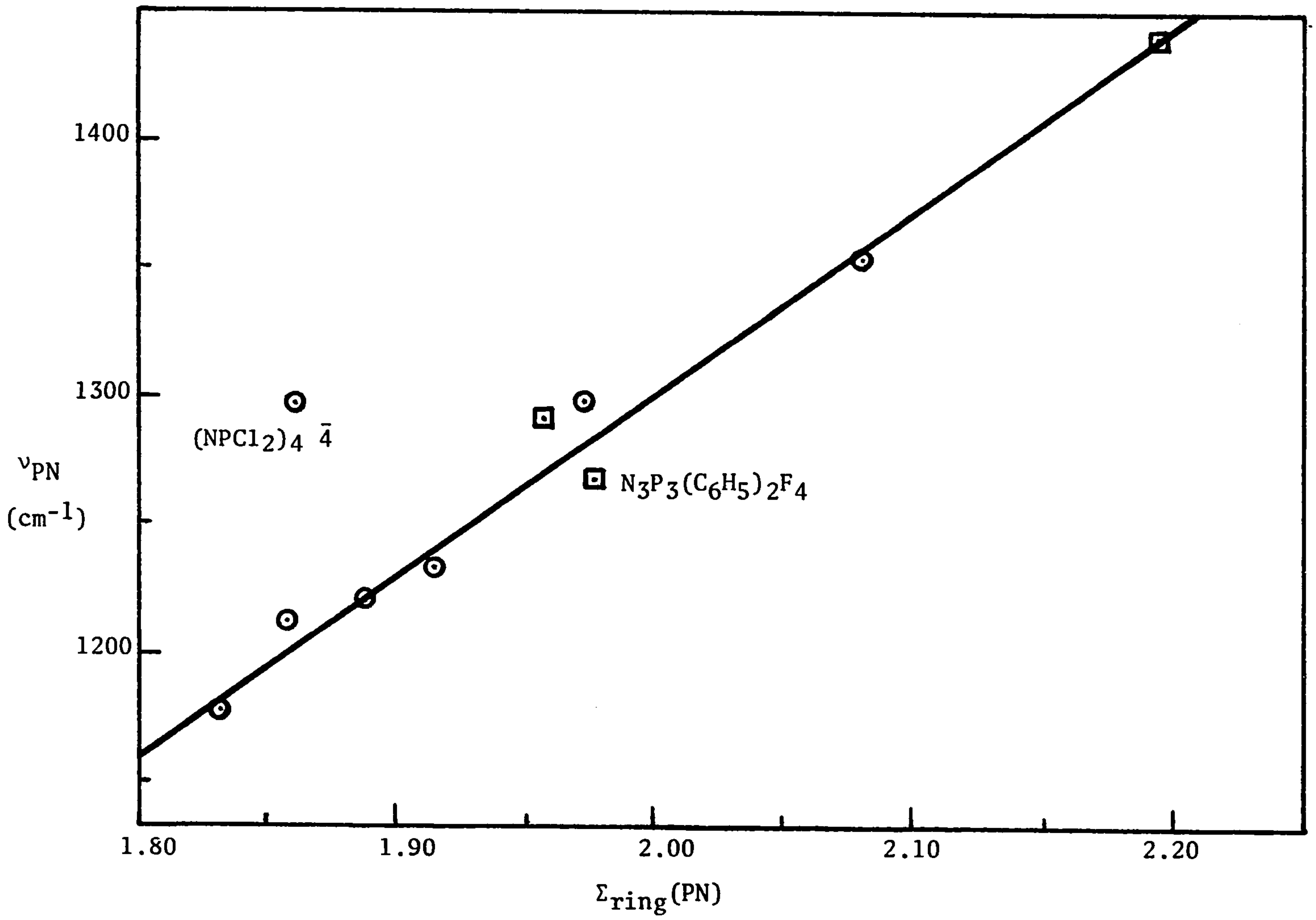

Figure III-3 Ring Bond Infrared Stretching Frequency, ν_{PN}, Compared With Total Ring Bonded Overlap, $\Sigma_{ring}(PN)$, For Cyclic Phosphonitriles.

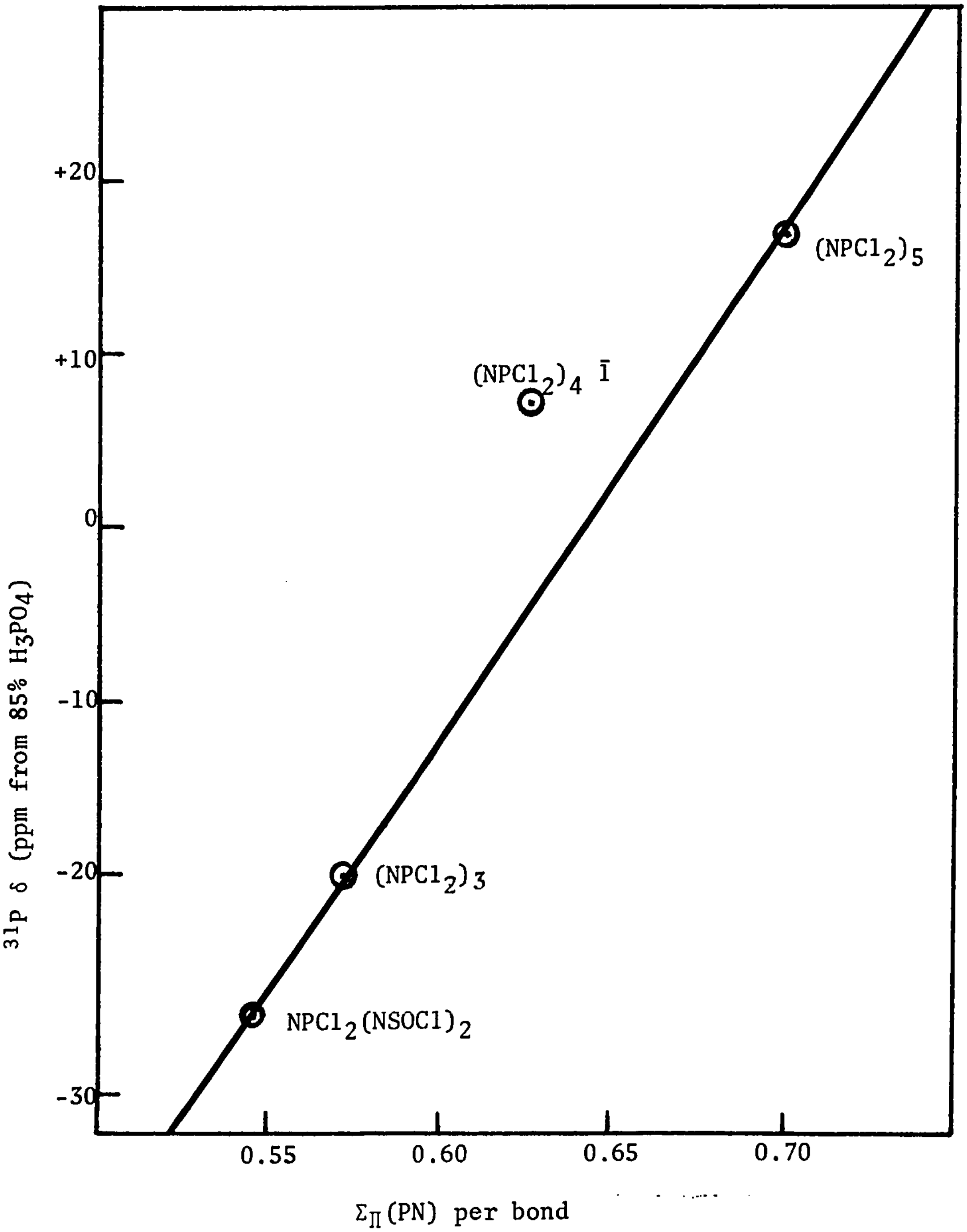

Figure III-4 ^{31}P Chemical Shift, δ, Compared With Total Π Bonded Overlap, $\Sigma_\Pi(PN)$, For Chlorophosphonitriles.

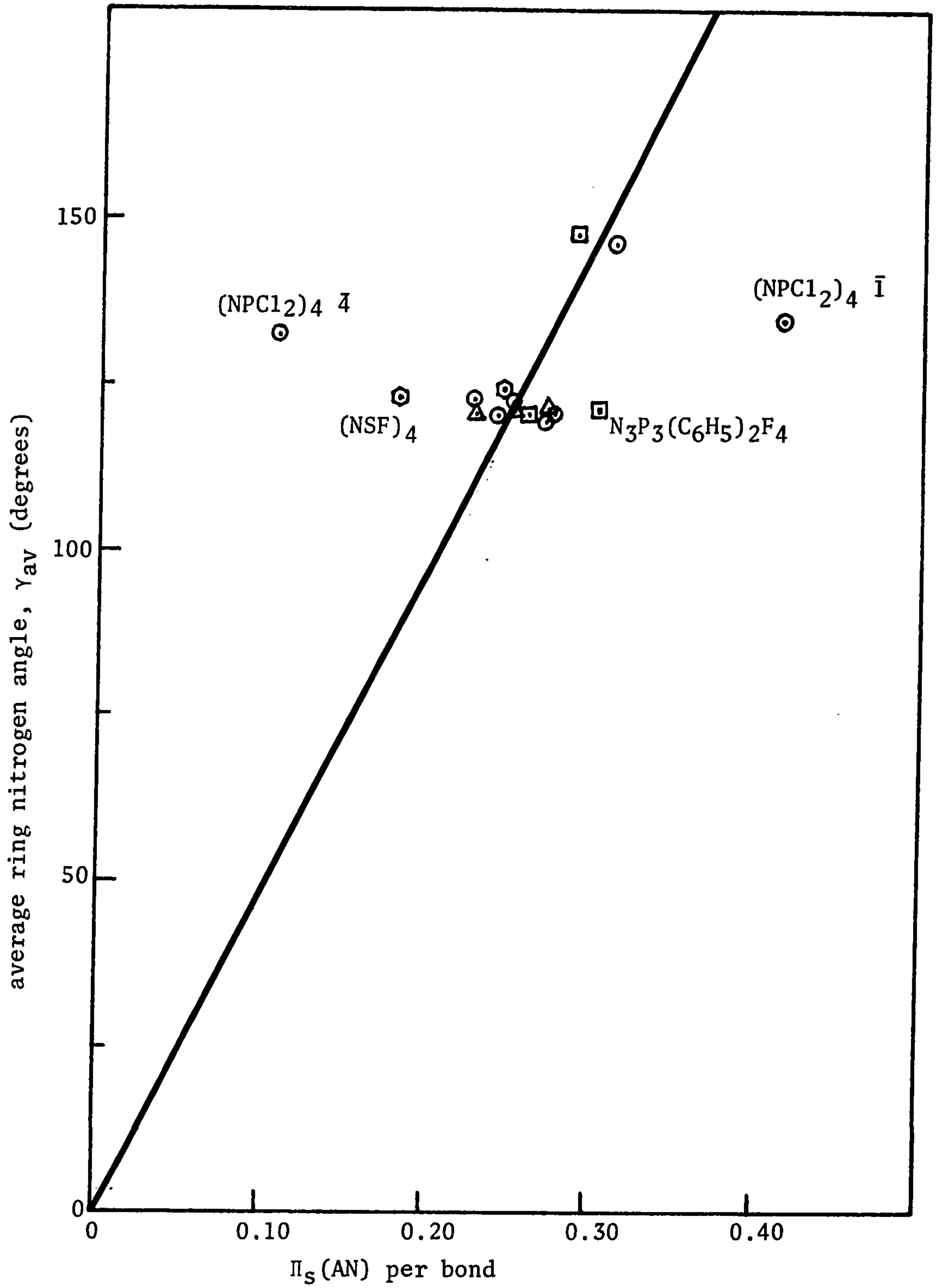

Figure III-5 Ring Nitrogen Angle, γ, Compared With Π_s Bonding For Cyclic Sulfonitriles and Phosphonitriles, Π_s(AN).

III.2.7 Discussion

III.2.7.1 Trends For Individual Bond Systems

The variation in phosphonitrile ring Π system values (Σ_Π) is greater than that for the σ system (III.2.6 and Table III-9), although approximately constant for each series (fluoro or chloro), compared with the component Π_a and Π_s system variations. On an equal weight basis, Π_a and Π_s bonding contributions are the same (within calculation error) for each of the planar chlorophosphonitriles. For non-planar chlorophosphonitrile tetramers, $(NPCl_2)_4$ $\bar{1}$ and $\bar{4}$, there are large differences; a greater Π_a contribution for $\bar{4}$ and a greater Π_s contribution for $\bar{1}$. The Π bonding component difference is also marked for the fluoride tetramer, but not the trimer, and the sulfonitrile rings. For sulfanuric units and the thiazyl chloride trimer, $\Pi_s > \Pi_a$, though only slightly more so than calculation error, but for thiazyl fluoride and phosphonitrile fluoride tetramers, $\Pi_a \gg \Pi_s$. The experimentally determined geometry accounts for this difference in the thiazyl tetramer compared with other sulfonitriles, as it is made up of alternating long and short bonds. The latter can be interpreted within the bond model as strong, alternate, Π_a type double bonds.

For 'delocalized Π system' ring molecules, however, where equal bond distances are observed, the Π bonding model predicts that as the rings become larger, and the ring nitrogen angles wider to absorb the strain, a resulting larger Π_s contribution can compensate for the loss in Π_a bonding. Π_s system bonded overlaps compared with ring nitrogen angle, γ, (Figure III-5) show qualitative agreement when a line is drawn through the origin and the trimeric molecules. However, values for $(NPCl_2)_4$ $\bar{1}$ and $\bar{4}$, and $N_3P_3(C_6H_5)_2F_4$ (and $(NSF)_4$) deviate from the trend. These molecules are the most non-planar of the phosphonitriles (and sulfonitriles) studied.

If the Π systems alone account for the behavior, these results indicate that either the covalent energy gain from increased Π_s contribution does not compensate for the lost Π_a contribution (this affects k'), or the coulomb(Q)/exchange(J) ratio for the total covalent bonding energy can be assumed constant for all planar phosphonitriles, but not for non-planar cases (III.1.1). The ring bonds for $(NPCl_2)_4$, $\bar{1}$ or $\bar{4}$, or $N_3P_3(C_6H_5)_2F_4$ are not chemically anomalous; so the ratio Q/J is probably constant for both non-planar and planar phosphonitriles. Linear correlations exist for $\Sigma_{ring}(PN)$ with R_{PN} for the phosphonitriles and also with the infrared ring stretching frequencies (except $(NPCl_2)_4$ $\bar{4}$) (Figures III-2 and III-3). This suggests that the Π_s non-planar deviation is due to relative weighting for Π_a, Π_s and the σ systems. The weights of Σ_{Π} and σ may be the same as assumed for each bond type (SN and PN), but the relative weight of Π_a and Π_s system contributions could be in error. Where bonded overlaps for Π_a and Π_s systems are approximately the same (e.g. cyclic planar phosphonitriles), the linear correlation for total bonded overlap (Σ_{ring}) will not be affected, but Π_s bonded overlap correlation would be.

The deviation may be due to the relative bonding d orbital contributions to the Π systems. The basic assumption of equal weights for all d orbital overlap values in each component (Π_a,Π_s) was made because relative molecular d orbital energies are not known. For planar cases, the set of d orbitals involved in Π_a is independent of that in Π_s, and the systems are composed mainly of d_{xz} and $d_{x^2-y^2}$ overlaps, respectively, because non-bonding exchange interaction 'destabilizes' the other potentially Π bonding orbitals. 'Destabilization' of these orbitals also occurs for non-planar cases according to the EOV method approximation. However, for these cases, d_{xz} and $d_{x^2-y^2}$ are both involved in each ring Π system. Thus, the exchange interaction for these orbitals, which may be different, should be included as a possible difference in $k_{d_{x^2-y^2}}$ and $k_{d_{xz}}$.

Interpretation of experimental results (I.4.4) is consistent with a relatively weaker Π_s system contribution to the ring Π energy. This conclusion neglects σ system changes, and for planar cases infers that the molecular energy of $d_{x^2-y^2}$ is lower than that of d_{xz}. A relative weighting scheme of $k_{d_{x^2-y^2}} < k_{d_{xz}}$ decreases Π_s with respect to Π_a for $(NPCl_2)_4$ $\bar{1}$ and increases the separation between Σ_{ring} (i.e. Σ_{Π}) or Σ_T for $\bar{1}$ and $\bar{4}$.* For $\bar{1}$ there is better agreement with ^{31}P chemical shift and ring nitrogen angle correlations. The $\bar{4}$ deviation from infrared stretching frequency correlation is not improved, but the fit for $N_3P_3(C_6H_5)_2F_4$ is.

Qualitatively better agreement for the phenylfluorophosphonitrile, but not $(NSF)_4$ or $(NPCl_2)_4$ $\bar{4}$, would be found for the ring angle correlation. This deviation is not unexpected for the thiazyl fluoride tetramer, where Π_a system bonding determines the molecular configuration 'entirely'. It suggests that the stabilization of the $\bar{4}$ form originates as well in the large contribution to Π_a of $d_{x^2-y^2}$ bonded overlap. This contribution, by definition, is not included in the Π_s bonded overlap, which in turn is lower than expected for the ring nitrogen angle of $(NPCl_2)_4$ $\bar{4}$ or $(\bar{N}SF)_4$. For the $\bar{1}$ form, there is a relatively large contribution to the Π_s system of d_{xz} bonded overlap, and both forms have similar total Π contributions which are sufficient to make the total ring bond contribution greater than, or equal to, that of the trimer $(NPCl_2)_3$.

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* The effects of this weighting scheme can be visualized from the example calculations in appendix B.

The assumption of different energies (and thus different amounts for exchange overlap contributions) for d_{xz} and $d_{x^2-y^2}$ (and possibly d_{z^2},d_{yz} and d_{xy}) can only be checked by accurate *ab initio* energy minimization for molecular cases and remains a question for the future. However, results of the bonded overlap calculations agree with other interpretations in suggesting that the net bonded exchange energy contribution of $d_{x^2-y^2}$ electrons is less than that of d_{xz} in these molecular environments, and hence that for planar molecules,the in-plane Π bonding is weaker than the out-of-plane Π bonding.

III.2.7.2 Bonded Overlap Totals; Relative Covalent Energies and Configurational Stability

The trends in bonded overlaps have been noted for individual bond systems for bonds between like pairs of atoms (e.g. PN or SN). Within the weighting scheme (III.2.4), total bonded overlaps can be compared as a measure of relative total covalent energies per molecule or unit (Table III-10). The only experimental data are from a differential thermal analysis study of the relative heats of polymerization of $(NPCl_2)_n$ n=3-7[170]. These were converted and reported as heats of formation for vapor phase molecules (shown in Table III-10 for comparison). Bonded overlap totals per unit for these molecules increase as expected for n=3-5.

From interpretation of the reported heats of formation[170], the contribution of a 'weaker' Π_s system accounts for the slower increase in relative heat of formation with increasing n than expected from changes in the Π_a system only. Variations in the σ system were neglected. However, differences in ring and exocyclic σ system bonded overlaps account for a substantial part of the variation in total overlaps for these molecules, indicating that the σ system should be neglected only with caution. Calculated overlap values, combined with reliable estimates of actual energy contributions corresponding to the different localized bond types, would provide a check on the validity of this assumption.

(1) Chlorophosphonitrile tetramer configurations:

Molecules of the chlorophosphonitrile tetramer exist in two solid state forms; $\bar{1}$, the stable form at room temperature and $\bar{4}$, a metastable form unstable above 70°C. Rings of both forms are non-planar although phosphorus-nitrogen bond distances are equal for each within experimental error[189,190].

The total bonded overlap (Σ_T) for the $\bar{1}$ form is greater than that for the $\bar{4}$ form, consistent with the experimental evidence (Table III-10; 6.48 and 6.27). The value per unit for $\bar{4}$ is approximately that for the trimer, $(NPCl_2)_3$ (6.28). The exocyclic bond system differences (2.53, 2.55, 2.56) are much less than those for the ring bond systems, indicating that relative ring energy differences account for the covalent bond contribution to configurational stability. However, bonded overlaps calculated for a planar geometry ($\Sigma_T = 6.72$) are larger than those calculated for either observed geometry, indicating that other factors (steric considerations) also contribute to the actual configuration. 'Steric considerations' are responsible for the Q/J ratio, and unless all overlap values are considered explicitly in the calculation, this ratio can only be assumed constant for chemically similar molecules of known geometry (III.1.2). These results for the hypothetical planar geometry reinforce this point.

(2) Covalent energy contributions to stability for the series, α-$(NSOCl)_3 \rightarrow (NPCl_2)_3$ and for sulfanuric or thiazyl sulfonitriles:

Bonded overlap totals per molecule (Table III.10) suggest that the missing link in the series, $\{(NPCl_2)_2NSOCl\}$, should be at least as stable as the other known members. The ring bonded overlap totals for the series are; 11.15, 11.16, 11.33 and 11.57 for $(NPCl_2)_3 \rightarrow \alpha$-$(NSOCl)_3$, respectively. Even if $k_{d_{x^2-y^2}} < k_{d_{xz}}$ were incorporated in the calculation, qualitatively little difference in the trend would be obtained, since deviation from planarity and consequent d orbital Π system 'mixing' is not large for the known mixed ring and should be less for $\{(NPCl_2)_2NSOCl\}$. The total values also suggest that the exocyclic oxygen Π system makes a substantial contribution to the total covalent energy for molecules containing a sulfanuric unit.

In this connection, it is interesting to note the results for thiazyl chloride trimer compared with those for the sulfanuric chloride trimer and the thiazyl fluoride tetramer. The ring totals per unit for these molecules are 3.68, 3.86 and 4.00, respectively; but the molecular totals per unit are 4.78, 7.10 and 5.40. The difference in total exocyclic sigma bonding for the chlorosulfonitriles is ≃ 12 % ($\sigma_E(SCl)$ for α-$(NSOCl)_3 > (NSCl)_3$), but leaves a minimum additional energy conferred by the oxygen substituents of 85 % of the difference between the sulfanuric chloride and the thiazyl chloride, and 30 % of the total for the sulfanuric chloride. The ring energy per unit provides 75 % of the total for both thiazyl compounds, compared with 54 % for the sulfanuric chloride. Although this is an approximate comparison, it is consistent with the chemistry of these sulfonitriles (I.3.2) and with the observation that a chloro-sulfanuric unit is readily formed from a thiazyl chloride unit[47,48]. The ring energy per unit contributes 60 % of the total for the chlorophosphonitrile trimer compared with 54% for the sulfanuric chloride trimer, in agreement with chemical evidence that the phosphonitrile ring is more stable than the sulfanuric chloride ring (I.3.3).

The exchange overlap application of the Π bonding model successfully correlates with chemical and physical properties for sulfonitriles as well as phosphonitriles. Thus, the Π bonding model is acceptable for sulfonitriles. These calculations related to covalent bonding energies apply to ground state configuration molecules and relative reaction stabilities cannot be assessed. However, the possibility that the missing member of the series, bis(dichlorophosphonitrile)oxochlorosulfonitrile, might be stable if a suitable preparative route could be found, has not been negated.

(3) The ionic linear phosphonitrile, $[Cl_3PNPCl_3]^+$, C_{2v} symmetry:

From infrared spectra of compounds of $[Cl_3PNPCl_3]^+$, the ion may possess C_{2v},or distorted C_{2v}, symmetry (II.4.4). Possible configurations can be considered in the bonding model for phosphonitriles as the result of a balance between gain in Π_s system bond energy with wider chain angle $P\hat{N}P$ (γ), and steric requirements. The latter can be estimated from the relative distances of close approach of the chloro-substituents. (Π_a and Π_s bonding is defined with respect to the plane formed by the chain PNP bonds).

Optimized d orbital exponents (Table III-11) indicate similar non-bonding overlap destabilization for d_{z^2}, d_{yz}, and d_{xy} as in the cyclic units. A slight variation occurs in the ratio of d orbital exponents for the bonding orbitals, d_{xz} and $d_{x^2-y^2}$, which is ≈ 1.0 for the range compared with 1.1 for the cyclic chlorophosphonitriles. The non-bonding ($N_{\sigma A'}$) overlap destabilization for $d_{x^2-y^2}$ in the linear ion fragment is less than that of a ring fragment, because the angle γ is larger.

The infrared assignment (II.4.4) indicates a stronger phosphorus-nitrogen bond for the ionic phosphonitrile compared with that of the cyclic phosphonitrile, $(NPCl_2)_3$. In the bonding model this is explained in terms of a strong Π_a system and an additional Π_s contribution which results in a total bond strength similar to that of the chlorophosphonitrile tetramer, $\bar{I}$ form. In agreement with this, Π_a and Π_s bonded overlaps are 0.308 and 0.349, 0.254 and 0.253 for optimized γ $[Cl_3PNPCl_3]^+$ and $(NPCl_2)_3$, respectively. Π_s bonding for the ionic phosphonitrile is slightly overestimated by the assumption of C_{2v} symmetry. (Distortion allows a smaller angle to balance the steric requirements of inter-ionic chlorine-chlorine interaction, II.4.4). However, the total bonded overlap is 2.09, 1.86 and 1.90 for $[Cl_3PNPCl_3]^+$, $(NPCl_2)_3$ and $(NPCl_2)_4$ $\bar{I}$, respectively; which is in qualitative agreement with the infrared stretching frequencies assigned (1325, 1212 and 1297 cm^{-1}).

Although the variation in bonded overlap values in the angle range is not large compared with estimated calculation error, it can be considered as 'real' since the error is coordinate input determined. This calculation treats such input as a parameter by varying the angle γ. A maximum in bonded overlap occurs for the Π_s system and the total covalent energy contribution per unit (Σ_T) between 150° and 155° (152°±2°)(Figure III-6 and Table III-12). A force constant estimation for C_{2v} symmetry[110] predicts an angle of 140°, rather than 120 or 180°. As the angle is widened, C_{2v} becomes a more favored configuration than C_2 because only one chlorine-chlorine distance is less than 5.0 Å compared with two for C_2. The most important non-bonded neighbor atom interaction for C_{2v} (intra-ionic distance of close approach) is that between Cl(1) and Cl(4) (Figure II-12), the in-plane chlorine substituents for the fragment calculation. From the change of this interatomic distance in C_{2v}, the angle should be wider than 147° to accommodate the sum of the Van der Waals radii for two chlorine atoms, 3.62 Å (Figure III-7). The solid state configuration is probably slightly distorted C_{2v}, but little change in PNP angle from the C_{2v} value is expected; and this bonded overlap approximation to covalent energy predicts a chain angle of 150-155 degrees for the trichlorophosphonitriletrichlorophosphonium ion.

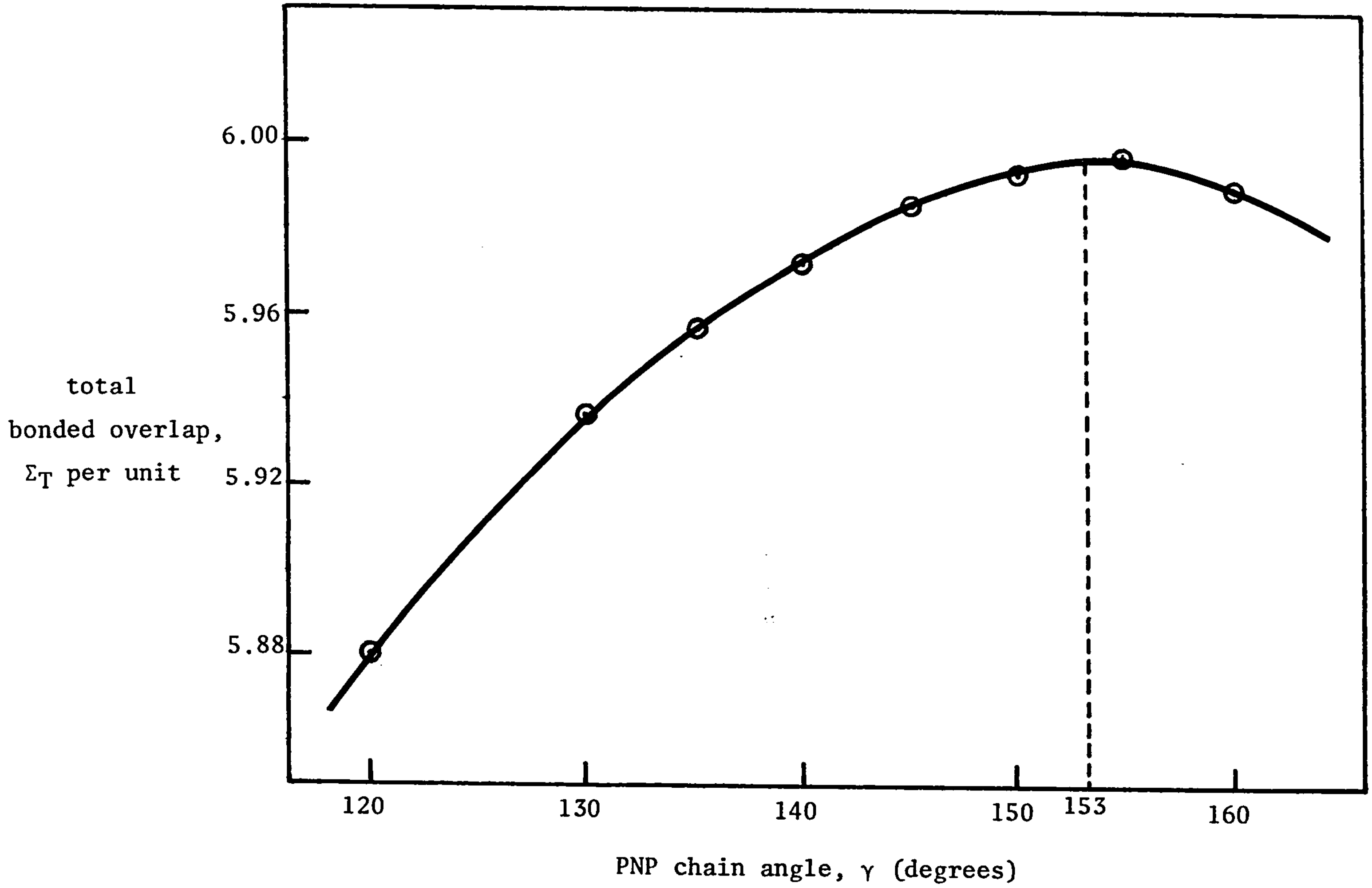

Figure III-6 Total Bonded Overlap Variation With Chain Nitrogen Angle For Trichlorophosphonitrile-trichlorophosphonium Ion, $[Cl_3PNPCl_3]^+$, C_{2v} Configuration.

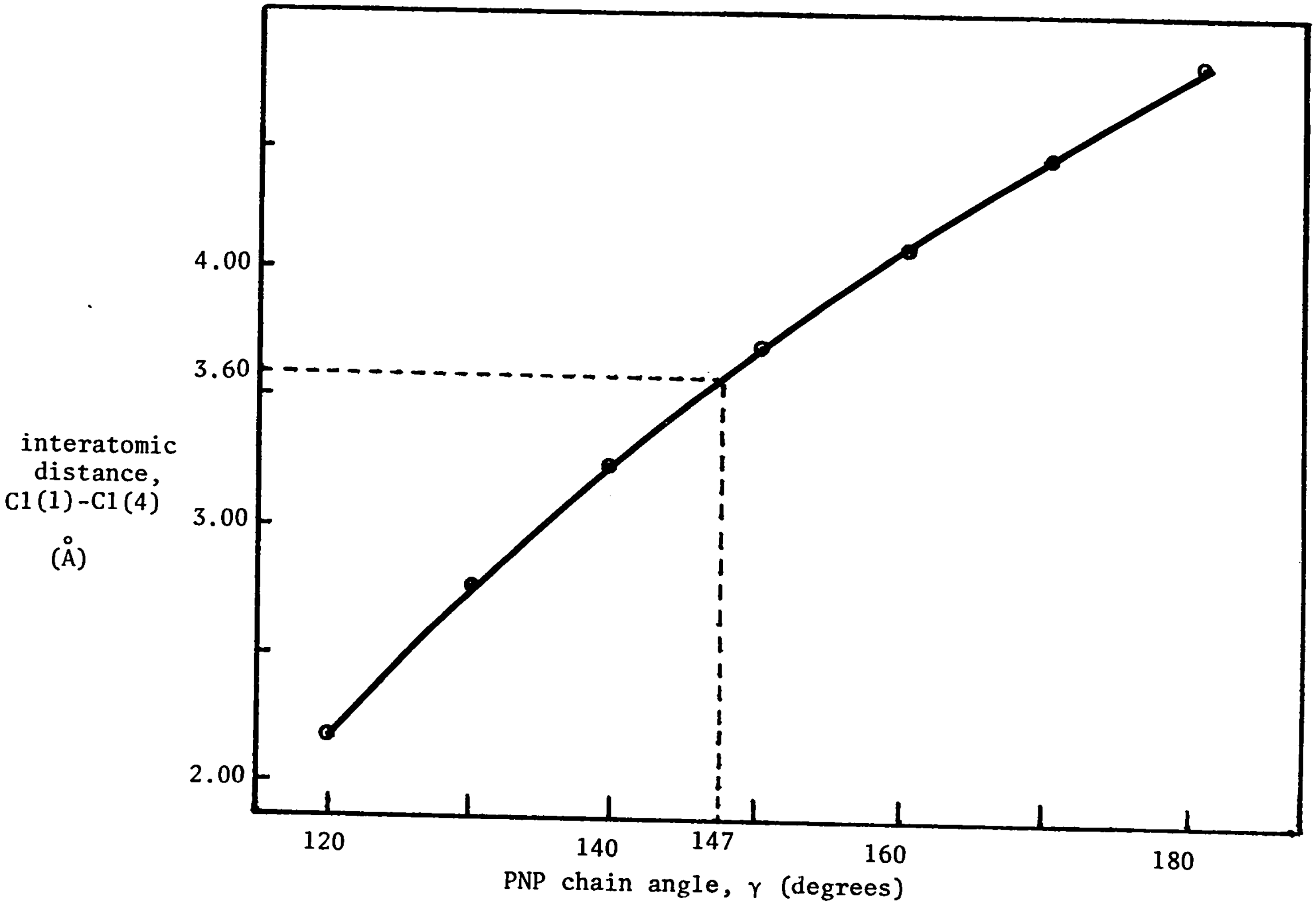

Figure III-7 Variation of In-plane Chlorine-chlorine Distance of Close Approach With Chain Nitrogen Angle For $[Cl_3PNPCl_3]^+$, C_{2v} Configuration.

SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

Possible reaction routes have been investigated for the preparation of mixed phosphonitrile and sulfonitrile compounds. An improved preparation of *cyclo*-dichlorophosphonitrilebis(oxochlorosulfonitrile), $NPCl_2(NSOCl)_2$, has been described based on the pyrolytic decomposition of the product of a reaction between trichlorophosphonitriletrichlorophosphonium hexachlorophosphate and amidosulfuric acid. (II.1,2)

Properties of the mixed ring compound, $NPCl_2(NSOCl)_2$, have been further investigated. ^{35}Cl nuclear quadrupole resonance frequencies observed have been assigned to specific chlorine atoms using the results of a published Xray diffraction study. Group frequencies have been assigned for the main bands in the infrared spectrum of the mixed ring and those reported for α- and β- sulfanuric chloride trimers based on a comparison and the reported assignment for *cyclo*-dichlorophosphonitrile trimer. (II.3)

Group frequencies have been assigned for the solid state infrared spectra of the linear compounds, Cl_3PNSO_2Cl, $[Cl_3PNP(Cl)_2NPCl_3][PCl_6]$ and $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]Cl$; and the assignments for $Cl_3PNPOCl_2$, $Cl_3PNPSCl_2$ and $[Cl_3PNPCl_3][PCl_6]$ have been reassessed for the region 425-4000 cm^{-1}. Assignments were interpreted on the basis of a bond structure model for phosphonitriles. (II.4)

Two new compounds, $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]_2[CoCl_4]$ and $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]_2[CoCl_4].CH_2Cl_2$, have been isolated and characterized by spectrometry as examples of the general series of quaternary amine transition metal chloride salts. Three other compounds containing the same cations, with empirical formulae, $CuP_2N_3C_{25}H_{32}OCl_3$ (I), $CuP_2N_3C_{24}H_{28}Cl_3$ (II) and $Cu_3P_4N_6C_{50}H_{64}O_2Cl_8$ (III), have been isolated and studied by spectrometry. The formulae, $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]_2[Cu_2Cl_6]$ and $[NH_2(C_6H_5)_2PNP(C_6H_5)_2NH_2]_2[Cu_2Cl_6].2CH_3OH$, are proposed for II and I, respectively, by comparison with the cobalt compounds and interpretation of the electronic spectra. (II.5)

An optimization method for the determination of molecular orbital exponents has been derived from the relationship of the two-center, two-electron exchange integral to the two-center, one-electron overlap integral for a localized bond (EOV Method). Molecular d orbital sets for two variations of a Π bonding model for cyclic fluoro and chlorophosphonitriles have been determined and compared with the results of Mitchell's exchange energy optimization for the planar molecules; $(NPCl_2)_3$, $(NPF_2)_3$ and $(NPF_2)_4$. (III.1)

Molecular exponent sets derived for phosphonitriles and sulfonitriles were used in a calculation of bonded overlap values from the exchange overlap approximation, and the relationship of these values to covalent bond and molecular energies discussed. The EOV optimization method was evaluated from correlation of the calculated results with experimental properties and shown to be an acceptable approximation for the molecules investigated. The method applied to the ionic linear phosphonitrile, $[Cl_3PNPCl_3]^+$, for C_{2v} configurations predicts a chain nitrogen angle of 150-155 degrees. (III.2)

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APPENDIX A. CALCULATION OF OVERLAP VALUES

A subroutine, OVERLP, was coded to determine overlap integral values for specified types (quantum number ℓ) of valence shell single-term Slater-type atomic orbitals for any number of atoms, from two to a main program-specified dimension for the overlap value array. Orbitals which may be included for a principal quantum number n of 1,2 or 3,are s, sp, and spd sets, respectively. Orbital exponent values are required for each atom and a different value for each orbital type for a given atom may be specified, although a single-center, orthonormal, degenerate set is assumed for each orbital type.

The set of orthonormal valence shell atomic orbitals at each atom a, Φ_a, is defined with respect to a molecular coordinate system, x,y,z. Additional subroutine input requires numbers of atom types (defined according to the orbital types to be included in the valence shell), atomic numbers, and z,x,y coordinates for each atom.

Overlap integrals in a local coordinate system, $\tilde{x},\tilde{y},\tilde{z}$ (defined by the interatomic axis $\tilde{z}$) between orbital sets on each pair of atoms, a,b ($a \neq b$), are considered in turn. The method proposed by Mulliken *et al*.[198] was used to calculate primitive overlap integral values, and these are temporarily stored for transfer to the molecular coordinate system. Formulae employed were derived from tables reported by Lofthus[199]. The coordinate system transformation is accomplished by a subroutine, SPRING, which determines the elements of a rotational transformation matrix, T, which takes the local coordinate system orbital set($\tilde{\Phi}_a$) into the molecular coordinate system set(Φ_a), for each atom pair.

Thus, since the overlap integrals are defined as S_{ij}, where

$S_{ij} = \int\phi_i(a)\phi_j(b)^{\dagger}d\tau$ and

$\Phi_a = T\tilde{\Phi}_a$

i and j refer to atomic orbitals at atoms a and b, respectively in x,y,z and

$\tilde{\Phi}_a$ defines the atomic orbital set at a with respect to $\tilde{x},\tilde{y},\tilde{z}$.

$$S_{ij} = \int T_{ij}\tilde{\phi}_i(a)\tilde{\phi}_j(b)^{\dagger}T_{ij}^{\dagger}d\tau$$
$$= T_{ij}\tilde{S}_{ij}T_{ij}^{\dagger} \quad \text{where } \tilde{S}_{ij} = \tilde{\phi}_i(a)\tilde{\phi}_j(b)^{\dagger}d\tau$$

$\tilde{S}_{ij}$ is the primitive overlap integral between atomic orbitals, $\tilde{\phi}_i$ and $\tilde{\phi}_j$ (in the local coordinate system),

$\dagger$ denotes the transposed matrix and its elements.

The rotational transformation matrix for p orbitals, T_p, is that for the coordinate system itself;

$$\underset{T_p}{\begin{pmatrix} \cos\Theta & \sin\Theta & 0 \\ \sin\Theta\cos\Omega & -\cos\Theta\cos\Omega & -\sin\Omega \\ \sin\Theta\sin\Omega & -\cos\Theta\sin\Omega & \cos\Omega \end{pmatrix}} \begin{pmatrix} p_{\tilde{z}} \\ p_{\tilde{x}} \\ p_{\tilde{y}} \end{pmatrix} = \begin{pmatrix} p_z \\ px \\ p_y \end{pmatrix}$$

The angles Θ and Ω are Euler angles for the coordinate system rotation, and correspond to those in Goldstein[200] with $\Psi=0$, $\Theta=\Theta$ and $\Phi=\Omega + \pi/2$. The transformation matrix for d orbitals, T_d, was derived from the appropriate radial functions of the real set, d_{z2}, d_{xz}, d_{yz}, d_{x2-y2} and d_{xy}; It is shown at the end of this section.

The overlap value transformation formulae are expressed in terms of primitive overlap values ($\tilde{S}\sigma$, $\tilde{S}\Pi$, $\tilde{S}\delta$) and transformation matrix elements, TP_{ij} and TD_{ij}, as;

s with s $\quad S_{s(a)s(b)} = \tilde{S}_{ss\sigma}$

p with p $\quad S_{pi(a)pj(b)} = \sum_{m=1,3} TP_{im}TP_{jm}S'_m \qquad S'_1 = -\tilde{S}_{pp\sigma}$

$S'_2 = S'_3 = \tilde{S}_{pp\Pi}$

i and j are z,x,y coordinates which define the p orbitals with respect to the molecular coordinate system.

d with d $\quad S_{d_i(a)d_j(b)} = \sum_{m=1,5} TD_{im}TD_{jm}S'_m$ $\quad S'_4 = S'_5 = \tilde{S}dd\delta$, $\quad S'_1 = \tilde{S}dd\sigma$, $\quad S'_2 = S'_3 = -\tilde{S}dd\Pi$

i and j define d orbitals z^2, xz, yz, x^2-y^2,xy from 1 to 5, respectively.

s with p $\quad S_{s(a)p_i(b)} = -TP_{i1}\tilde{S}_{sp\sigma}$ $\quad i = 1$ to 3

$S_{p_i(a)s(b)} = TP_{i1}\tilde{S}_{ps\sigma}$

s with d $\quad S_{s(a)d_i(b)} = TD_{i1}\tilde{S}_{sd\sigma}$

$S_{d_i(a)s(b)} = TD_{i1}\tilde{S}ds\sigma$

p with d $\quad S_{p_i(a)d_j(b)} = \sum_{m=1,3} TP_{im}TD_{jm}S'_m$ $\quad S'_1 = \tilde{S}pd\sigma$, $\quad S'_2 = S'_3 = -\tilde{S}pd\Pi$

$S_{d_i(a)p_j(b)} = \sum_{m=1,3} TD_{im}TP_{jm}S'_m$ $\quad S'_1 = -\tilde{S}dp\sigma$, $\quad S'_2 = S'_3 = \tilde{S}dp\Pi$

The primitive overlap values refer to the sign convention where $\check{z}(a)$ is directed to $\check{z}(b)$ and vice versa.

Two other associated subroutines are required; ABCALC and BOFFEN. The first calculates, from recursion formulae, the A and B values (functions of orbital exponents) required for the determination of primitive overlap values[198]. The second is used to generate B's when the standard recursion formula with double precision is not accurate enough ($pt \leqslant 0.2$). This is accomplished by a series expansion for the highest B value required and a reverse recursion formula to generate the lower B values[201].

The subroutines OVERLP, SPRING, BOFFEN, and ABCALC are listed below. Important storage location names are defined in the listings. A main program to calculate overlap values when d orbital exponents of a central atom are varied in a molecular fragment was used with these subroutines, and is on file with Dr. M.A.Whitehead, Department of Chemistry, McGill University.

The rotational transformation matrix, T_d;

$$\left(\begin{matrix}
\frac{1}{2}(3\cos^2\Theta-1) & \sqrt{3}\cos\Theta\sin\Theta & 0 & \frac{\sqrt{3}}{2}\sin^2\Theta & 0 \\
\sqrt{3}\sin\Theta\cos\Theta\cos\Omega & \cos\Omega(\sin^2\Theta-\cos^2\Theta) & -\cos\Theta\sin\Omega & -\sin\Theta\cos\Theta\cos\Omega & -\sin\Theta\sin\Omega \\
\sqrt{3}\sin\Theta\cos\Theta\sin\Omega & \sin\Omega(\sin^2\Theta-\cos^2\Theta) & \cos\Theta\cos\Omega & -\sin\Theta\cos\Theta\sin\Omega & \sin\Theta\cos\Omega \\
\frac{\sqrt{3}}{2}\sin^2\Theta(\cos^2\Omega-\sin^2\Omega) & \cos\Theta\sin\Theta(\sin^2\Omega-\cos^2\Omega) & -2\sin\Omega\cos\Omega\sin\Theta & \frac{1}{2}(\cos^2\Omega-\sin^2\Omega)(1+\cos^2\Theta) & 2\cos\Theta\sin\Omega\cos\Omega \\
\sqrt{3}\sin^2\Theta\cos\Omega\sin\Omega & -2\cos\Theta\sin\Theta\cos\Omega\sin\Omega & \sin\Theta(\cos^2\Omega-\sin^2\Omega) & \cos\Omega\sin\Omega(1+\cos^2\Theta) & \cos\Theta(\sin^2\Omega-\cos^2\Omega)
\end{matrix}\right]$$

where

$$\begin{pmatrix} d_{z^2} \\ d_{xz} \\ d_{yz} \\ d_{x^2-y^2} \\ d_{xy} \end{pmatrix} = T_d \begin{pmatrix} d_{\tilde{z}^2} \\ d_{\tilde{x}\tilde{z}} \\ d_{\tilde{y}\tilde{z}} \\ d_{\tilde{x}^2-\tilde{y}^2} \\ d_{\tilde{x}\tilde{y}} \end{pmatrix}$$

and coordinate systems and rotational angles are defined in the text, Appendix A.

```
      SUBROUTINE OVERLP(KAT,X,NM3,NM2,NMH,NOR,NUMX,NUMY,S,FS)
C     KAT=ATOMIC NO;NM3,NM2,NMH=NO.ATOMS WITH SPD,SP,S ORBITALS IN
C     VALENCE SHELL;X=COORDINATES;NOR=NO.ORBITALS;NUMY=DIMENSION OF
C     MATRICES S,FS; NUMX=DIMENSION OF ATOMIC NOS. AND COORDINATES
      DIMENSION KAT(NUMX),X(3,NUMX),S(NUMY,NUMY),FS(NUMY,NUMY)
      DIMENSION NQ(18),ZED(51),C(5,5),ST(14),FST(14)
      DIMENSION TP(3,3),TD(5,5)
      DOUBLE PRECISION A(7),B(7)
C     NQ=PRINCIPAL QUANTUM NUMBER, ZED=ORBITAL EXPONENT FOR SLATER
C     TYPE ORBITAL
C     ST,FST = TEMPORARY STORAGE LOCATIONS FOR OVERLAP AND CUSACH'S
C     FACTORS IN LOCAL COORDINATE SYSTEM PER ATOM PAIR.
      COMMON MA,MB,KATI,KATJ,FACTOR,R
      COMMON ZZ,XX,YY,MA1,MB1
      COMMON ZED
      COMMON NN
      DATA NQ/2*1,8*2,8*3/
      WRITE(6,29)ZED(NN)
   29 FORMAT(1H1,35H EXPONENT OF 3D SET FOR ATOM ONE IS,F6.3)
      WRITE(6,30)
   30 FORMAT(1H0,58H PRIMITIVE OVERLAP VALUES FROM TEMPORARY STORAGE LOC
     1ATIONS)
      DO 5 I=1,NUMY
      DO 5 J=1,NUMY
      S(I,J)=0.0
    5 FS(I,J)=0.0
C     CALCULATE OVERLAPS FOR LOCAL COORDINATE SYSTEM
      NAT=NM3+NM2+NMH
      DO 500 I=2,NAT
      KATI=KAT(I)
      NQA=NQ(KATI)
      ZA1=ZED(KATI)
      ZA2=ZED(KATI+17)
      ZA3=ZED(KATI+34)
      IF(I-NM3)60,60,61
   60 MA1=5
      GO TO 68
   61 IF(I-(NM3+NM2))63,63,62
   63 MA1=3
      GO TO 68
   62 MA1=1
C     ASSIGN EXPONENTS FOR  OVERLAPS
   68 JJJ=I-1
      DO 500 J=1,JJJ
      KATJ=KAT(J)
      NQB=NQ(KATJ)
      ZB1=ZED(KATJ)
      ZB2=ZED(KATJ+17)
      ZB3=ZED(KATJ+34)
      IF(J-NM3)65,65,66
   65 MB1=5
      GO TO 69
   66 IF(J-(NM3+NM2))67,67,64
   67 MB1=3
      GO TO 69
```

```
   64 MB1=1
C     COMPUTE INTERATOMIC DISTANCE,R, IN ANGSTROMS
   69 ZZ=X(1,J)-X(1,I)
      XX=X(2,J)-X(2,I)
      YY=X(3,J)-X(3,I)
      R=SQRT(ZZ**2+XX**2+YY**2)
C     AXES ARE ORDERED Z,X,Y, ORBITALS ARE ORDERED PZ,PX,PY AND DZ**2,DXZ,
C     DX**2-Y**2,DXY                                                  DYZ,
C     COMPUTE MULLIKEN PARAMETERS
C     ASSIGN EFFECTIVE PRINCIPAL QUANTUM NOS.
      MA=NQA
      MB=NQB
C     COMPUTE C MATRIX FOR S,P OVERLAPS
      MO=MA+MB
      M1=MO-1
      M2=MO-2
      DO 40 K=1,M1
      DO 40 L=1,M1
   40 C(K,L)=0.
      C(1,1)=1.
      IF(KATJ.EQ.1)GO TO 70
      SGN=1.
      DO 45 N=1,M2
      IF(N.EQ.MA)SGN=-1.
      DO 45 K=1,N
      L=N+1-K
      C(K+1,L)=C(K,L)
   45 C(K,L+1)=C(K,L+1)+C(K,L)*SGN
C     SET TEMPORARY STORAGE LOCATIONS EQUAL TO ZERO
   70 DO 75 K=1,14
      ST(K)=0.
   75 FST(K)=0.
C     COMPUTE OVERLAP BETWEEN S ORBITALS
      CALL ABCALC(ZA1,ZB1,A,B)
      DO 76 K=1,M1
      L=MO-K
   76 ST(1)=ST(1)+C(K,L)*(A(K+2)*B(L)-A(K)*B(L+2))
      ST(1)=0.5*ST(1)*FACTOR
C     IF BOTH ATOMS H COMPUTE ONLY THIS INTEGRAL
      IF(MB1.EQ.1) GO TO 300
C     COMPUTE INTEGRALS FOR WHICH FIRST IS S,SECOND P
      CALL ABCALC(ZA1,ZB2,A,B)
      DO 77 K=1,M1
      L=MO-K
   77 ST(2)=ST(2)+C(K,L)*(A(K+1)*(B(L)-B(L+2))+B(L+1)*(A(K)-A(K+2)))
      ST(2)=0.866025404*ST(2)*FACTOR
C     NOW COMPUTE P WITH S,P
      IF(MA1.EQ.1)GO TO 250
      CALL ABCALC(ZA2,ZB1,A,B)
      DO 78 K=1,M1
      L=MO-K
   78 ST(3)=ST(3)+C(K,L)*(A(K+1)*(B(L)-B(L+2))+B(L+1)*(A(K+2)-A(K)))
      ST(3)=0.866025404*ST(3)*FACTOR
C     COMPUTE P WITH P
```

```
      CALL ABCALC(ZA2,ZB2,A,B)
      DO 79 K=1,M1
      L=MO-K
      ST(4)=ST(4)+C(K,L)*(A(K)*B(L)-A(K+2)*B(L+2))
   79 ST(5)=ST(5)+C(K,L)*(A(K+2)-A(K))*(B(L)-B(L+2))
      ST(4)=1.5*ST(4)*FACTOR
      ST(5)=0.75*ST(5)*FACTOR
C     FOR INTEGRALS INVOLVING D ORBITALS MUST REDEFINE Z'S AND USE
C     NEW C MATRIX
  250 IF(MB1.LT.5)GO TO 300
      CALL ABCALC(ZA1,ZB3,A,B)
C    COMPUTE NEW C MATRIX
  100 IF (MA1.EQ.1)GO TO 105
      MO=MA+MB
      M1=MO-3
      M2=MO-4
      DO 101 K=1,M1
      DO 101 L=1,M1
  101 C(K,L)=0.
      C(1,1)=1.
      SGN=1.
      DO 102 N=1,M2
      IF(N+1.EQ.MA)SGN=-1.
      DO 102 K=1,N
      L=N+1-K
      C(K+1,L)=C(K,L)
  102 C(K,L+1)=C(K,L+1)+C(K,L)*SGN
C      COMPUTE INTEGRALS INVOLVING D ORBITALS FIRST IS,3D SIGMA SPECIAL CAS
      IF(MA1.NE.1)GO TO 107
  105 ST(6)=A(5)*(3.*B(3)-B(1))-A(3)*(3.*B(5)-3.*B(1))-4.*A(4)*B(2)
     1+4.*A(2)*B(4)-A(1)*(3.*B(3)-B(5))
      ST(6)=0.559016994*ST(6)*FACTOR
      GO TO 300
  107 DO 110 K=1,M1
      L=MO-2-K
  110 ST(6)=ST(6)+C(K,L)*(A(K+4)*(3.*B(L+2)-B(L))+6.*(A(K+3)-A(K+1))*
     1(B(L+3)-B(L+1))+A(K+2)*(3.*B(L+4)-10.*B(L+2)+3.*B(L))+A(K)*(3.*
     2B(L+2)-B(L+4)))
      ST(6)=0.559016994*ST(6)*FACTOR
      CALL ABCALC(ZA2,ZB3,A,B)
      DO 50 K=1,M1
      L=MO-2-K
      ST(7)=ST(7)+C(K,L)*(B(L+1)*(3.*A(K)-A(K+4)-2.*A(K+2))+B(L+3)*(3.*
     1A(K+4)-2.*A(K+2)-A(K))+A(K+3)*(-2.*B(L+2)+3.*B(L+4)-B(L))+A(K+1)*
     2(-2.*B(L+2)-B(L+4)+3.*B(L)))
   50 ST(10)=ST(10)+C(K,L)*((A(K+4)-2.*A(K+2)+A(K))*(B(L+3)-B(L+1))+(
     1B(L+4)-2.*B(L+2)+B(L))*(A(K+3)-A(K+1)))
      ST(7)=0.968245837*ST(7)*FACTOR
      ST(10)=1.677050983*ST(10)*FACTOR
C     IF ONLY ONE ATOM WITH D ORBITALS NEED ONLY THESE INTEGRALS
      IF(MA1.LT.5)GO TO 300
C     COMPUTE REMAINING INTEGRALS
      CALL ABCALC(ZA3,ZB1,A,B)
      DO 111 K=1,M1
      L=MO-2-K
```

```
  111 ST(8)=ST(8)+C(K,L)*(A(K+4)*(3.*B(L+2)-B(L))+6.*(A(K+3)-A(K+1))*(
     1B(L+1)-B(L+3))+A(K+2)*(3.*B(L+4)-10.*B(L+2)+3.*B(L))+A(K)*(3.*
     2B(L+2)-B(L+4)))
      ST(8)=0.559016994*ST(8)*FACTOR
      CALL ABCALC(ZA3,ZB2,A,B)
      DO 112 K=1,M1
      L=MO-2-K
      ST(9)=ST(9)+C(K,L)*(B(L+1)*(A(K+4)+2.*A(K+2)-3.*A(K))+B(L+3)*(-3.*
     1A(K+4)+2.*A(K+2)+A(K))+A(K+3)*(3.*B(L+4)-2.*B(L+2)-B(L))+A(K+1)*(
     23.*B(L)-2.*B(L+2)-B(L+4)))
  112 ST(11)=ST(11)+C(K,L)*((A(K+4)-2.*A(K+2)+A(K))*(B(L+1)-B(L+3))+(
     1B(L+4)-2.*B(L+2)+B(L))*(A(K+3)-A(K+1)))
      ST(9)=0.968245837*ST(9)*FACTOR
      ST(11)=1.677050983*ST(11)*FACTOR
      CALL ABCALC(ZA3,ZB3,A,B)
      DO 113 K=1,M1
      L=MO-2-K
      ST(12)=ST(12)+C(K,L)*(A(K+4)*(B(L)-6.*B(L+2)+9.*B(L+4))+A(<+2)*
     1(-6.*B(L)+4.*B(L+2)-6.*B(L+4))+A(K)*(9.*B(L)-6.*B(L+2)+B(L+4)))
      ST(13)=ST(13)+C(K,L)*(A(K+4)*(B(L+4)-B(L+2))+A(K+2)*(B(L)-B(L+4))
     1+A(K)*(B(L+2)-B(L)))
  113 ST(14)=ST(14)+C(K,L)*(A(K+4)-2.*A(K+2)+A(K))*(B(L)-2.*B(L+2)+
     1B(L+4))
      ST(12)=0.625*ST(12)*FACTOR
      ST(13)=3.75*ST(13)*FACTOR
      ST(14)=0.9375*ST(14)*FACTOR
C     COMPUTE FST INGEGRALS FOR CUSACHS MODIFICATION
  300 DO 305 K=1,14
  305 FST(K)=(2.0-ABS(ST(K)))*ST(K)
      WRITE(6,31)(ST(K),K=1,14)
   31 FORMAT(1H ,14F9.5)
      CONTINUE
C     NOW COMPUTE OVERLAP INTEGRALS AND CUSACHS FACTORS IN MOLECULAR SYSTEM
      IF(MB1.EQ.1)GO TO 340
      CALL SPRING(TP,TD)
  340 IF(MA1-3)350,351,352
  350 II=NM3*8+NM2*3+I
      GO TO 360
  351 II=NM3*5+4*I-3
      GO TO 360
  352 II=9*I-8
  360 IF(MB1-3)361,362,363
  361 JJ=8*NM3+3*NM2+J
      GO TO 365
  362 JJ=5*NM3+4*J-3
      GO TO 365
  363 JJ=9*J-8
  365 TWINK=MA1+MB1
      S(II,JJ)=ST(1)
      FS(II,JJ)=FST(1)
      IF(TWINK.EQ.2)GO TO 500
      DO 370 K=1,3
      JJK=JJ+K
      S(II,JJK)=-TP(K,1)*ST(2)
```

```
  370 FS(II,JJK)=-TP(K,1)*FST(2)
      IF(TWINK.EQ.4)GO TO 500
      IF(MA1.EQ.1)GO TO 380
C     NOW FIND P WITH S AND P WITH P INTEGRALS
      DO 371 K=1,3
      IIK=II+K
      S(IIK,JJ)=TP(K,1)*ST(3)
      FS(IIK,JJ)=TP(K,1)*FST(3)
      DO 371 L=1,3
      JJL=JJ+L
      S(IIK,JJL)=-TP(K,1)*TP(L,1)*ST(4)+(TP(K,2)*TP(L,2)+TP(K,3)*TP(L,3)
     1)*ST(5)
  371 FS(IIK,JJL)=-TP(K,1)*TP(L,1)*FST(4)+(TP(K,2)*TP(L,2)+TP(K,3)*
     1TP(L,3))*FST(5)
      IF(MB1.EQ.3)GO TO 500
C     NOW FIND S WITH D INTEGRALS
  380 DO 381 K=1,5
      JJK=JJ+3+K
      S(II,JJK)=TD(K,1)*ST(6)
  381 FS(II,JJK)=TD(K,1)*FST(6)
      IF(TWINK.EQ.6)GO TO 500
C     NOW FIND P WITH D INTEGRALS
      DO 382 K=1,3
      IIK=II+K
      DO 382 L=1,5
      JJL=JJ+3+L
      S(IIK,JJL)=TP(K,1)*TD(L,1)*ST(7)-(TP(K,2)*TD(L,2)+TP(K,3)*TD(L,3))
     1*ST(10)
  382 FS(IIK,JJL)=TP(K,1)*TD(L,1)*FST(7)-(TP(K,2)*TD(L,2)+TP(K,3)*
     1TD(L,3))*FST(10)
      IF(TWINK.EQ.8)GO TO 500
C     NOW FIND D WITH S,P,D INTEGRALS
      DO 385 K=1,5
      IIK=II+3+K
      S(IIK,JJ)=TD(K,1)*ST(8)
      FS(IIK,JJ)=TD(K,1)*FST(8)
      DO 384 L=1,3
      JJL=JJ+L
      S(IIK,JJL)=-TD(K,1)*TP(L,1)*ST(9)+(TD(K,2)*TP(L,2)+TD(K,3)*TP(L,3)
     1)*ST(11)
  384 FS(IIK,JJL)=-TD(K,1)*TP(L,1)*FST(9)+(TD(K,2)*TP(L,2)+TD(K,3)*
     1TP(L,3))*FST(11)
      DO 385 M=1,5
      JJM=JJ+3+M
      S(IIK,JJM)=TD(K,1)*TD(M,1)*ST(12)-(TD(K,2)*TD(M,2)+TD(K,3)*TD(M,3)
     1)*ST(13)+(TD(K,4)*TD(M,4)+TD(K,5)*TD(M,5))*ST(14)
  385 FS(IIK,JJM)=TD(K,1)*TD(M,1)*FST(12)-(TD(K,2)*TD(M,2)+TD(K,3)*
     1TD(M,3))*FST(13)+(TD(K,4)*TD(M,4)+TD(K,5)*TD(M,5))*FST(14)
  500 CONTINUE
C     ASSIGN DIAGONAL ELEMENTS AND SYMMETRIZE
      DO 510 K=1,NOR
      S(K,K)=1.
  510 FS(K,K)=1.
      DO 515 K=2,NOR
```

```
      LL=K-1
      DO 515 L=1,LL
      S(L,K)=S(K,L)
  515 FS(L,K )=FS(K,L)
      WRITE(6,33)
   33 FORMAT(1H1,15H OVERLAP MATRIX/1H0)
      CALL PRINT(S,50,NOR)
      CONTINUE
      RETURN
      END
```

```
      SUBROUTINE SPRING(TP,TD)
C     COMPUTES TRANSFORMATION MATRICES FOR ROTATION OF ORBITAL SET
C     IN MOLECULAR COORDINATE SYSTEM TO ONE IN LOCAL COORDINATE
C     SYSTEM DEFINED BY INTERNUCLEAR AXIS BETWEEN ATOM PAIR USING
C     EULER ANGLES AS IN GOLDSTEIN WITH PSI=0, THETA=THETA, PHI=
C     GAMMA + PI/2 ; RIGHT HANDED SYSTEMS
      DIMENSION DUMMY(6)
      COMMON DUMMY
      COMMON ZZ,XX,YY,LINDA,LINDB
      SEP=SQRT(ZZ**2+XX**2+YY**2)
      SXY=SQRT(XX**2+YY**2)
      IF(SXY-0.000001)10,10,15
   10 CGAMMA=1.0
      SGAMMA=0.0
      CTHETA=SIGN(1.0,ZZ)
      STHETA=0.0
      GO TO 20
   15 CTHETA=ZZ/SEP
      STHETA=SXY/SEP
      CGAMMA=XX/SXY
      SGAMMA=YY/SXY
   20 TP(1,1)=CTHETA
      TP(1,2)=STHETA
      TP(1,3)=0.0
      TP(2,1)=STHETA*CGAMMA
      TP(2,2)=-CTHETA*CGAMMA
      TP(2,3)=-SGAMMA
      TP(3,1)=STHETA*SGAMMA
      TP(3,2)=-CTHETA*SGAMMA
      TP(3,3)=CGAMMA
      IF(LINDB.EQ.3)GO TO 25
      TWIG=CGAMMA**2-SGAMMA**2
```

```
      TD(1,1)=1.5*CTHETA**2-0.5
      TD(1,2)=1.7320508*CTHETA*STHETA
      TD(2,1)=TD(1,2)*CGAMMA
      TD(3,1)=TD(1,2)*SGAMMA
      TD(4,1)=0.86602540*STHETA**2*TWIG
      TD(5,1)=1.7320508*STHETA**2*CGAMMA*SGAMMA
      IF(LINDA.EQ.1)GO TO 25
      TD(1,3)=0.0
      TD(2,2)=CGAMMA*(STHETA**2-CTHETA**2)
      TD(2,3)=-CTHETA*SGAMMA
      TD(3,2)=SGAMMA*(STHETA**2-CTHETA**2)
      TD(3,3)=CTHETA*CGAMMA
      TD(4,2)=-CTHETA*STHETA*TWIG
      TD(4,3)=-2.*STHETA*SGAMMA*CGAMMA
      TD(5,2)=TD(4,3)*CTHETA
      TD(5,3)=STHETA*TWIG
      IF(LINDA.LE.3)GO TO 25
      TD(1,4)=0.8660254*STHETA**2
      TD(1,5)=0.0
      TD(2,5)=-STHETA*SGAMMA
      TD(3,5)=STHETA*CGAMMA
      TD(2,4)=-CTHETA*TD(3,5)
      TD(3,4)=TD(2,5)*CTHETA
      TD(4,4)=0.5*TWIG*(1.+CTHETA**2)
      TD(4,5)=-TD(2,3)*2.*CGAMMA
      TD(5,4)=CGAMMA*SGAMMA*(1.+CTHETA**2)
      TD(5,5)=-CTHETA*TWIG
   25 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE ABCALC(ZA,ZB,A,B)
C     USES RECURSION FORMULAE TO GENERATE A'S AND B'S AS FUNCTIONS
C     OF ORBITAL EXPONENTS ZA,ZB
      DIMENSION DENOM(3)
      DIMENSION DUMB(5)
      DOUBLE PRECISION A(7),B(7),P,T,PT,BPLUS,BMINUS,ABPT
      COMMON MA,MB,KI,KJ,FACT,DIST
      COMMON DUMB
      DATA DENOM/2.,24.,720./
C     CLEARS A AND B ARRAY FOR ADDITION TO ABCALC
      DO 100 K=1,7
      A(K)=0.0
  100 B(K)=0.0
      P=(ZA+ZB)*DIST/1.058342
      T=(ZA-ZB)/(ZA+ZB)
C     COMPUTE A-S AND B-S WITH SUBSCRIPT INCREASED BY ONE FROM LOFTHUS
                                                                 FORMULAE
      A(1)=DEXP(-P)/P
      SGN=1.
      B(1)=2.
      M=MA+MB+1
      IF(ZA.EQ.ZB)GO TO 24
      PT=P*T
      BPLUS=DEXP(PT)
      BMINUS=DEXP(-PT)
      B(1)=(BPLUS-BMINUS)/PT
      ABPT=DABS(PT)
      IF(ABPT.GT.0.2)GO TO 24
      CALL BOFFEN(B,PT,BPLUS,BMINUS,ABPT,M)
      GO TO 20
   24 DO 25 K=2,M
      XK=K-1
      SGN=-SGN
      IF(ZA.EQ.ZB)GO TO 21
      B(K)=(SGN*BPLUS-BMINUS+XK*B(K-1))/PT
      GO TO 25
   21 B(K)=(1.+SGN)/(XK+1.)
   25 CONTINUE
   20 DO 26 K=2,M
      XK=K-1
   26 A(K)=A(1)+XK*A(K-1)/P
C     COMPUTE FACTOR MULTIPLYING SUMMATION FOR INTEGRALS
      FACT=P*(P*(1.+T))**MA*(P*(1.-T))**MB*
     1DSQRT((1.-T*T)/(DENOM(MA)*DENOM(MB)))
      RETURN
      END
```

```
      SUBROUTINE BOFFEN(BO,BETA,BPL,BMI,ABBETA,NDIM)
C     COMPUTES B S FOR CASE WHERE ORDINARY RECURSION FORMULA WITH DOUBLE
C     PRECISION NOT ACCURATE ENOUGH - USES SERIES EXPANSION FOR HIGHEST
C     REQUIRED, THEN REVERSE RECURSION FORMULA AS OUTLINED BY OFFENHARTZ
      DIMENSION DUMMY(11)
      DOUBLE PRECISION BO(7),BETA,BPL,BMI,ABBETA,BX,T1,T2,S1,S2,S3,S4,FN
      COMMON DUMMY
      N=NDIM-1
      BX=-ABBETA
      T1=1.0D0
      T2=1.0D0
      S1=1.0D0
      S2=1.0D0
      DO 12 I=1,N
      T1=T1*ABBETA/I
      T2=T2*BX/I
      S1=S1+T1
   12 S2=S2+T2
      T1=T1*ABBETA/(I+1)
      FN=T1
      S3=T1
      T2=T2*BX/(I+1)
      S4=T2
      MN=NDIM+1
      DO 13 K=MN,500
      T1=T1*ABBETA/K
      S3=S3+T1
      IF(T1/S3-(1.0D-12))20,13,13
   13 CONTINUE
   20 DO 14 L=MN,500
      T2=T2*BX/L
      S4=S4+T2
      IF(DABS(T2/S4)-(1.0D-12))21,14,14
   14 CONTINUE
   21 BO(NDIM)=(S3*S2-S1*S4)/(FN*NDIM)
      IF(BETA)22,22,23
   22 BO(NDIM)=DABS(BO(NDIM))
   23 SGN=1.0
      DO 25 J=1,N
      JJ=NDIM-J
      SGN=-SGN
   25 BO(JJ)=(SGN*BPL+BMI+BETA*BO(JJ+1))/JJ
      RETURN
      END
```

APPENDIX B. RESULTS FOR TYPICAL MOLECULES

B.1 Overlap Variation With d Orbital Exponent:

Results of the calculation described in III.1 are included for $(NPF_2)_3$ in the following. All overlap values have been multiplied by 10^5. Nomenclature is that of section III.1 (Figure and Table III-1). The signs of overlap values are noted below each column; upper and lower signs refer to overlap with N(1) and N(2) or F(1) and F(2), respectively. Results of calculations for all molecules studied are on file with Dr.M.A.Whitehead, Department of Chemistry, McGill University.

B.2 Bonded Overlap Calculation:

Calculation figures are included for the planar molecule, $(NPCl_2)_3$, and non-planar molecules, $(NPCl_2)_4$ $\bar{1}$ and $\bar{4}$, for crystallographic configurations. Overlap values were determined according to III.2 for optimized exponents; (1) EOV, (2) EOVП. The values shown are sums over fragment bond contributions multiplied by the appropriate factor for bonded overlap calculation, III.2.4, = 1 if bonding or -1/2 if non-bonding. Overlaps with N_{σ_A} orbitals are not included since they were neglected as bonding-oriented for these molecules (see III.1.3.2). All overlap values have been multiplied by 10^5.

B.1 d Orbital overlap variation with ξ, $(NPF_2)_3$:

Ring Π $\Pi_a(PN), \Pi_s(PN)$; sum over two bonds; $(PN(1), PN(2))$ Exocyclic Π $\Pi_e(PF), \Pi_e'(PF)$; 1/2 sum over two bonds.

	$\Sigma\lvert S_{A_d\Pi_a}\rvert$ or $\Sigma\lvert S_{A_d\Pi_s}\rvert$					$1/2\Sigma\lvert S_{A_dE_\Pi}\rvert$ or $1/2\Sigma\lvert S_{A_dE_{\Pi'}}\rvert$				
ξ_d	z^2, Π_s	xz, Π_a	yz, Π_a	x^2-y^2, Π_s	xy, Π_s	z^2, Π_e	xz, Π_e'	yz, Π_e	x^2-y^2, Π_e	xy, Π_e'
0.05	00042	00060	00034	00078	00040	00014	00013	00004	00008	00011
0.10	00382	00542	00316	00714	00358	00135	00121	00032	00078	00101
0.15	01256	01822	01064	02374	01160	00465	00419	00112	00269	00350
0.20	02740	04070	02378	05246	02492	04067	00959	00258	00616	00803
0.25	04782	07280	04254	09284	04273	01952	01756	00471	01127	01470
0.30	07258	11324	06618	14288	06376	03102	02789	00749	01791	02336
0.35	10002	16010	09356	19980	08626	04475	04024	01081	02584	03370
0.40	12858	21120	12342	26070	10872	06018	05412	01453	03475	04532
0.65	24668	46414	27122	54240	18420	14351	12906	03466	08286	10807
0.90	28338	61816	36122	68400	17796	20323	18277	04908	11734	15304
1.00	27772	64510	37696	69850	15856	21635	19456	05225	12491	16291
1.10	26426	65508	38280	69420	13422	22358	20106	05399	12908	16836
1.20	24552	65106	38044	67540	10756	22564	20292	05449	13027	16991
1.30	22366	63604	37168	64606	08064	22340	20090	05395	12898	16822
1.40	20044	61286	35812	60968	05496	21774	19582	05258	12572	16397
1.50	17712	58392	34122	56912	03144	20950	18840	05059	12096	15776
1.60	15462	55132	32216	52662	01066	19942	17934	04816	11514	14168
1.70	13356	51668	30194	48388	00714	18814	16920	04544	10862	14168
2.10	06800	37916	22158	32958	05050	13999	12589	03381	08082	10542
2.20	05630	34812	20342	29740	05562	12862	11567	03106	07246	09685
	- -	+ +	- +	+ +	- +	+ +	+ - + or -	- -	+ +	+ - + or -

B.1 (continued)

	With exocyclic orbitals, E_σ			With ring nitrogen orbitals, $N_{\sigma A}$ and $N_{\sigma A'}$					
	$1/2\Sigma\|S_{A_d E\sigma}\|$			$1/2\Sigma\|S_{A_d N\sigma_A}\|$			$1/2\Sigma\|S_{A_d N\sigma_{A'}}\|$		
ξ_d	z^2	yz	x^2-y^2	z^2	x^2-y^2	xy	z^2	x^2-y^2	xy
0.05	00003	00008	00004	00001	00001	00002	00022	00003	00022
0.10	00032	00074	00032	00007	00006	00011	00193	00028	00197
0.15	00120	00275	00117	00000	00000	00001	00634	00100	00680
0.20	00293	00674	00286	00050	00043	00076	01383	00270	01552
0.25	00571	01313	00558	00180	00153	00272	02418	00534	02838
0.30	00962	02215	00940	00420	00358	00634	03662	00908	04511
0.35	01467	03379	01435	00794	00675	01198	05046	01395	06515
0.40	02082	04792	02036	01310	01114	01977	06487	01985	08775
0.65	06254	14398	06116	05766	04903	08702	12446	05901	21308
0.90	10687	24607	10452	11492	09771	17341	14298	09796	31106
1.00	12155	27985	11888	13565	11534	20469	14012	10996	33601
1.10	13363	30768	13070	15336	13039	23141	13328	11931	35244
1.20	14292	32907	13979	16815	14297	25374	12388	12588	36191
1.30	14943	34406	14615	17924	15240	27047	11287	12992	36476
1.40	15333	35302	14996	18691	15893	28207	10113	13166	36207
1.50	15486	35655	15146	19142	16275	28884	08936	13139	35488
1.60	15432	35531	15093	19306	16415	29133	07802	12947	34448
1.70	15204	35006	14870	19226	16347	29012	06738	12621	33145
2.10	13165	30312	12876	17236	14655	26010	03431	10549	26736
2.20	12503	28788	12229	16494	14024	24889	02841	09948	25375
	$\substack{+\\+}$	$\substack{+\\+}$ or $\substack{-\\-}$	$\substack{-\\-}$	$\substack{-\\-}$	$\substack{+\\+}$	$\substack{-\\+}$	$\substack{-\\-}$	$\substack{-\\-}$	$\substack{-\\+}$

B.1 (continued)

Primitive overlap value variation for d orbitals:

ξ_d	$\tilde{S}d(P)s(N)\sigma$	$\tilde{S}d(P)p(N)\sigma$	$\tilde{S}d(P)p(N)\Pi$	$\tilde{S}d(P)s(F)\sigma$	$\tilde{S}d(P)p(F)\sigma$	$\tilde{S}d(P)p(F)\Pi$
0.05	00048	-00037	00034	00030	-00018	00017
0.10	00435	-00326	00314	00286	-00163	00158
0.15	01455	-01033	01055	00982	-00526	00546
0.20	03232	-02172	02357	02240	-01124	01251
0.25	05748	-03641	04216	04084	-01911	02289
0.30	08892	-05284	06558	06470	-02806	03638
0.35	12504	-06934	09272	09306	-03714	05249
0.40	16409	-08441	12231	12476	-04546	07059
0.65	35249	-10891	26878	29365	-05540	16833
0.90	46131	-04575	35798	41191	-00473	23838
1.00	47877	-00730	37358	43924	+02585	25376
1.10	48322	+03297	37936	45083	05829	26224
1.20	47911	07218	37703	45421	09031	26466
1.30	46665	10825	36834	44917	12016	26203
1.40	44864	13989	35491	43751	14666	25540
1.50	42683	16640	33816	42090	16910	24573
1.60	40269	18759	31928	40079	18715	23391
1.70	37735	20362	29922	37844	20082	22068
2.10	27839	22510	21958	28366	21793	16420
2.20	25624	22261	20160	26133	21504	15086

B.2 Bonded overlaps for optimized exponents; fragment totals for d orbital overlaps:

$(NPCl_2)_3$

Orbital and exponent	Value of overlap with neighbor atom orbital; m N_{Π_a}	N_{Π_s}	$N_{\sigma_{P'}}$	Cl_σ	Cl_Π or $Cl_{\Pi'}$	Net value; bonded overlap $\Pi_a(PN)$	$\Pi_s(PN)$	$\Pi_e(PCl)$
z^2								
(1) —	—	—	—	—	—	—	—	
(2) —	—	—	—	—	—	—	—	—
xz								
(1) 1.11	53643	01132	-02781			50919	01074	
(2) 1.02	53148	01131	-02754		46696	51698	01100	45422
yz								
(1) 0.18	01508	00034	-00096	-00669	-00597	00176	00004	
(2) 0.18	01508	00034	-00096	-00669	-00597	00969	00022	-00810
x^2-y^2								
(1) 0.83	-01288	63931	-07967	-17032		-01782	39426	
(2) 0.89	-01645	67156	-08845	-18558	36681	-02072	49710	27152
xy								
(1) —	—	—	—		—	—	—	
(2) —	—	—	—		—	—	—	—
					Sum over d orbital contributions:	(1) 49313	40504	
						(2) 50595	50832	71764

B.2 (continued) $(NPCl_2)_4$ $\bar{I}$

Orbital and exponent	Value of overlap with neighbor atom orbital; N_{Π_a}	N_{Π_s}	$N_{\sigma_{p'}}$	Cl_{σ}	Cl_{Π} or $Cl_{\Pi'}$	Net value; bonded overlap $\Pi_a(PN)$	$\Pi_s(PN)$	$\Pi_e(PCl)$
z^2								
(1) —	—	—	—	—	—	—	—	
(2) —	—	—	—	—	—	—	—	—
xz								
(1) 1.13	54688	29466	-09269			48665	26220	
(2) 1.09	54700	29470	-09198		53745	51052	27505	50161
yz								
(1) 0.40	12301	05249	-01644	-07891	-03237	03349	01429	
(2) 0.40	12301	05249	-01644	-07891	-03237	05618	02397	-03237
x^2-y^2								
(1) 0.96	-32628	61810	-03102	-13769		-38455	50866	
(2) 0.92	-32607	61291	-03485	-13372	36354	-36234	53326	31631
xy								
(1) —	—	—	—		—	—	—	
(2) —	—	—	—		—	—	—	—
					Sum over d orbital contributions:	(1) 13559	78515	
						(2) 20436	83228	78555

B.2 (continued)

$(NPCl_2)_4$ $\bar{4}$

Orbital and exponent	Value of overlap with neighbor atom orbital;					Net value; bonded overlap		
	$N_{\Pi a}$	$N_{\Pi s}$	$N_{\sigma p'}$	Cl_{σ}	Cl_{Π} or $Cl_{\Pi'}$	$\Pi_a(PN)$	$\Pi_s(PN)$	$\Pi_e(PN)$
z^2								
(1) —	—	—	—	—	—	—	—	
(2) —	—	—	—	—	—	—	—	—
xz								
(1) 1.11	49294	-29555	-10602			42667	-33530	
(2) 0.97	48040	-28805	-10332		56841	46778	-29561	46509
yz								
(1) —	—	—	—	—	—	—	—	
(2) —	—	—	—	—	—	—	—	—
x^2-y^2								
(1) 1.01	35313	55303	-00412	-14210		29616	46378	
(2) 0.98	34976	58164	-00117	-13951	36130	31171	51835	32199
xy								
(1) —	—	—	—		—	—	—	
(2) —	—	—	—		—	—	—	—
			Sum over d orbital contributions:			(1) 72283	12848	
						(2) 77949	22274	78708

Table III-1 Nomenclature of Localized Bonds for Sulfonitrile and Phosphonitrile Fragments, N(1)N(2)AE(1)E(2), With Orientation Specified in Figure III-1.

Bond system	Localized bond type	Localized atomic orbitals at A or A'	at N or E
Ring Π			
Π(AN)	Π_a(AN)	$A_d \equiv A_{d_{z^2}}, A_{d_{xz}}, A_{d_{yz}}, A_{d_{x^2-y^2}}, A_{d_{xy}}$	$N_{\Pi_a} \equiv h_P$
	Π_s(AN)	A_d as for Π_a(AN)	$N_{\Pi_s} \equiv h_L$
Ring σ			
σ(AN)	σ_A(AN)	$A_\sigma \equiv h_{N(1)}, h_{N(2)}$	$N_{\sigma_A} \equiv h_A$
	$\sigma_{A'}$(AN)	$A'_\sigma \equiv h'_{N(1)}, h'_{N(3)}$	$N_{\sigma_{A'}} \equiv h_{A'}$
Exocyclic Π			
Π(AE)	Π_e(AE)	$A_d \equiv A_{d_{z^2}}, A_{d_{yz}}, A_{d_{x^2-y^2}}$	$E_\Pi(1), E_\Pi(2)$
	Π'_e(AE)	$A_d \equiv A_{d_{xz}}, A_{d_{xy}}$	$E_{\Pi'}(1), E_{\Pi'}(2)$
Exocyclic σ			
σ(AE)	σ_E(AE)	$A_{\sigma E} \equiv h_{E(1)}, h_{E(2)}$	$E_\sigma \equiv h_{E\sigma}$

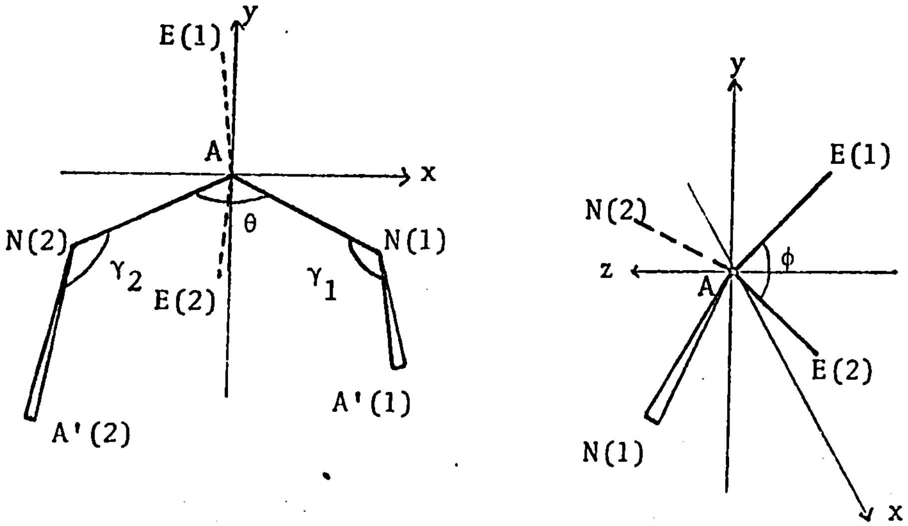

Figure III-1 Fragment N(1)N(2)AE(1)E(2) and Next-bonded Neighbors, A'(1) and A'(2).

Chlorine-35 Nuclear Quadrupole Resonance in Inorganic Molecules containing Phosphorus and Sulphur

By **M. Kaplansky, R. Clipsham, and M. A. Whitehead,*** Radiofrequency Spectroscopy Laboratory, Department of Chemistry, McGill University, Montreal 2, Canada

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Chlorine-35 Nuclear Quadrupole Resonance in Inorganic Molecules containing Phosphorus and Sulphur

By **M. Kaplansky, R. Clipsham, and M. A. Whitehead,*** Radiofrequency Spectroscopy Laboratory, Department of Chemistry, McGill University, Montreal 2, Canada

The ^{35}Cl n.q.r. frequencies of $Cl_3PNPOCl_2$, Cl_3PNSO_2Cl, $(SNOCl)_3$, $S_2PN_3O_2Cl_4$, and $C_6H_5PCl_4$, are reported. The frequencies are related to the chemical bonding of the ^{35}Cl, by *qualitative* comparison with previously reported ^{35}Cl frequencies in similar molecules. Where possible, the frequencies are related to the crystal structure of the molecule.

THE synthesis of inorganic heterocyclic mixed ring systems [1] led to a number of intermediates which were amenable to n.q.r. The frequencies are of interest as they permit the testing of some new theories of *d*-orbitals.[2] This preliminary report of frequencies and their *qualitative* interpretation continues previous work on the n.q.r. of ^{35}Cl bound to phosphorus and sulphur.[3]

The compounds which gave ^{35}Cl frequencies were $Cl_3PNPOCl_2$, Cl_3PNSO_2Cl, α-$(SNOCl)_3$, and $C_6H_5PCl_4$. The molecules which did not give n.q.r. spectra were $[Cl_3PNPCl_3]^+[PCl_6]^-$, $[Cl_3PNPCl_2NPCl_3]^+[PCl_6]^-$, and $Cl_3PNPSCl_2$. A preliminary result for the $S_2PN_3O_2Cl_4$ ring is given.

EXPERIMENTAL

Trichlorophosphazosulphuryl chloride was prepared by Kirsanov's procedure.[4] P_3NCl_{12} was prepared [5] and from it $P_4N_2Cl_{14}$, $Cl_3PNPSCl_2$, and $Cl_3PNPOCl_2$.[6] $C_6H_5PCl_4$ and $(C_6H_5)_2PCl_3$ were made by the addition, under dry nitrogen, of the required amount of chlorine gas (1 : 1 molar ratio) to the $PhPCl_2$ and Ph_2PCl respectively in solution in dry CCl_4. The solids precipitated were recrystallized from dry benzene in the absence of moisture.

The α-$(SNOCl)_3$ ring was prepared by pyrolysis [7] of Cl_3PNSO_2Cl while the $S_2PN_3O_2Cl$ ring was prepared by a modification of this procedure.[1]

The spectra were run [8] at 77°K. The frequencies were fixed as described [9] for ^{14}N n.q.r. and are shown in the Table, with relative line intensities where significant.

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[1] R. Clipsham, R. Hart, and M. A. Whitehead, in the press.

[2] R. Clipsham and M. A. Whitehead, in the press.

[3] E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 1961, 2459; M. A. Whitehead, *Canad. J. Chem.*, 1964, **42**, 1212.

[4] A. V. Kirsanov, *J. Gen. Chem. U.S.S.R.*, 1952, **22**, 101.

[5] M. Becke-Goehring and W. Lehr, *Chem. Ber.*, 1961, **94**, 1591.

[6] W. Lehr and M. Becke-Goehring, *Z. anorg. Chem.*, 1963, **325**, 287.

[7] A. Vandi, T. Moeller, and T. L. Brown, *Inorg. Chem.*, 1963, **5**, 899.

[8] M. Kaplansky and M. A. Whitehead, *Canad. J. Chem.*, 1967, **45**, 1669.

[9] C. T. Yim, M. A. Whitehead, and D. H. Lo, *Canad. J. Chem.*, 1968, **46**, 3595.

units of both types and this has been confirmed in the X-ray study.[2] The work discussed in this article was performed during the course of an investigation into the preparation and characterization of such mixed rings in an attempt to gain further insight into the bonding involved in inorganic compounds containing phosphorus and/or sulfur atoms.

The preparation reported by van de Grampel and Vos is based on a pyrolytic decomposition of trichlorophosphazosulfonyl chloride (Cl_3PNSO_2Cl, mp 32–36°, purified). This decomposition has been reported originally to yield a mixture of cyclic trimeric sulfanuric chlorides[3] and a subsequent report has confirmed this.[4] All of our attempts to prepare the mixed ring, as reported by van de Grampel and Vos, were unsuccessful. However, pyrolytic decomposition of unpurified trichlorophosphazosulfonyl chloride (slush at room temperature) produced a mixture of α-sulfanuric chloride, α-$(NSOCl)_3$ (crude yield, 25%), and the mixed ring $NPCl_2(NSOCl)_2$ (crude yield, 10%). Separation of the mixed ring could be achieved only after a long process of fractional crystallization with considerable loss.

An alternative method of preparation was discovered which yields the mixed ring without the concurrent production of cyclic trimeric sulfanuric chlorides. The product of a Kirsanov reaction between trichloro[(trichlorophosphoranylidene)amino]phosphorus(V) hexachlorophosphate, $[Cl_3PNPCl_3^+][PCl_6^-]$, and sulfamic acid, NH_2SO_2OH, is a liquid consisting of phosphorus oxytrichloride, an impure substance which may be a linear compound, $Cl_3PNPCl_2NSO_2Cl$, by analogy with the preparation of trichlorophosphazosulfonyl chloride.[5] The reaction proceeds in a manner similar to that preparation. Attempts to purify this product failed as it decomposes with further polymerization on distillation. However, if the decomposition is carried out at low pressures (1 mm) and temperatures of about 150°, $POCl_3$ is liberated and $NPCl_2(NSOCl)_2$ can be isolated from the polymeric residue remaining. Similarly, it is possible to obtain the mixed ring by starting with[6] $[Cl_3PNPCl_2NPCl_3^+][PCl_6^-]$. $NPCl_2(NSOCl)_2$ can be obtained in crude form by extraction from the residue with carbon tetrachloride and purified by recrystallization of the crude material from nonpolar solvents or by vacuum sublimation (50–60°, 1 mm). It is stable to hydrolysis by atmospheric moisture in the solid state. In solution, however, particularly in polar solvents, it is susceptible to hydrolysis.

Experimental Section

Materials.—All chemicals used were reagent grade. Carbon tetrachloride used for extraction was dried over calcium hydride at room temperature. Spectrograde solvents were used for recrystallizations and solution infrared measurements. Sulfamic acid was dried over phosphorus pentoxide prior to use. Ammonium chloride was dried at 120° and then stored over silica gel. Phosphorus pentachloride and ammonium chloride used in the initial reaction step were pulverized and weighed in a glove bag under dry N_2 atmosphere. Sulfamic acid when required was weighed in the glove bag and then transferred to a drybox for pulverization and addition to the linear phosphonitrilic chloride product. All reactions and manipulations of products were carried out under moisture-free conditions until the crude mixed-ring product was obtained.

$[Cl_3PNPCl_3^+][PCl_6^-]$ and $[Cl_3PNPCl_2NPCl_3^+][PCl_6^-]$.—These linear phosphonitrilic chlorides were prepared from the controlled reaction of PCl_5 with NH_4Cl according to the methods outlined by Becke-Goehring and Lehr.[6,7] Without further purification of reagent grade solvents, *sym*-tetrachloroethane and nitrobenzene, yields of 85% $[Cl_3PNPCl_3^+][PCl_6^-]$ and 25% $[Cl_3PNPCl_2NPCl_3^+][PCl_6^-]$ were obtained from the appropriate preparations.

$NPCl_2(NSOCl)_2$.—The mixed ring was prepared by a series of reactions starting with $[Cl_3PNPCl_3^+][PCl_6^-]$ or $[Cl_3PNPCl_2NPCl_3^+][PCl_6^-]$. The linear phosphonitrilic chloride was subjected to a Kirsanov reaction in a 1:1 molar ratio with sulfamic acid. The resulting product was pyrolyzed for many hours, after which $NPCl_2(NSOCl)_2$ was isolated from the polymeric reaction product. For example, 120 g of $[Cl_3PNPCl_3^+][PCl_6^-]$ and 21.8 g of NH_2SO_2OH were heated at 100° in a 500-ml round-bottomed flask fitted with a condenser until the reaction mixture had liquefied and most bubbling from the production of HCl had ceased. Total reaction time was approximately 6 hr. The product, a pale yellow viscous liquid containing granules of unreacted NH_2SO_2OH, was filtered under dry N_2. Using dried carbon tetrachloride for washing, the filtrate was transferred to a single-necked, round-bottomed 500-ml flask fitted with a Vigreux column, distillation head, and condenser. This was connected to a Dry Ice–ethanol slush trap leading to a vacuum pump. The contents of the flask were heated slowly at approximately 1 mm pressure until all the carbon tetrachloride and most of the $POCl_3$ from the Kirsanov reaction had been collected in the slush trap. Then the temperature was raised to about 155° (oil bath temperature) and pyrolysis begun. The liquid gradually became more brown and viscous as decomposition proceeded until, after a total heating time of approximately 32 hr, the polymeric residue began to foam. When the flask was cooled and brought to atmospheric pressure with dry N_2, treelike crystal formations appeared on the upper portions of the flask. During the pyrolysis, the liquid which refluxed in the column was first colorless and then gradually became bright yellow. $POCl_3$ from the decomposition was collected in the slush trap with a small amount of yellow-orange material which was not characterized.

The crystalline material was scraped from the column or extracted with the flask contents in warm carbon tetrachloride. After evaporation of the solvent in the atmosphere, needlelike crystals of $NPCl_2(NSOCl)_2$ were obtained contaminated with a colorless liquid and a white solid from hydrolysis of that portion of the polymeric residue which was soluble in the carbon tetrachloride. This crude product was recrystallized from *n*-hexane, cyclohexane, or *n*-heptane. The purified product had a melting point of 96.5° (uncor) without decomposition. A single crystal examined with a Weissenberg camera employing Cu Kα radiation was found to have the lattice parameters of the reported structural determination,[2] and the space group $P2_1/n$ was confirmed; yield, 15% of the theoretical value, based on reacted NH_2SO_2OH.

Anal. Calcd for $NPCl_2(NSOCl)_2$: S, 20.62; P, 9.96; N, 13.51; Cl, 45.60; O, 10.30; mol wt, 310.9. Found: S, 20.67; P, 9.79; N, 13.25; Cl, 45.59; mol wt, 311 (mass spectrometry).

α-$(NSOCl)_3$ and β-$(NSOCl)_3$.—Samples of these sulfanuric chlorides for nqr measurements were prepared, as described by Vandi, Moeller, and Brown,[4] from pyrolysis of trichlorophosphazosulfonyl chloride and each was identified by comparison of its ir spectrum reported therein. A sample of the β form obtained from a separation by vacuum sublimation was used

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[2] J. C. van de Grampel and A. Vos, *Acta Cryst.*, in press.

[3] A. V. Kirsanov, *J. Gen. Chem. USSR*, **22**, 93 (1952).

[4] A. Vandi, T. Moeller, and T. L. Brown, *Inorg. Chem.*, **2**, 899 (1963).

[5] A. V. Kirsanov, *J. Gen. Chem. USSR*, **22**, 101 (1952).

[6] W. Lehr and M. Becke-Goehring, *Z. Anorg. Allgem. Chem.*, **325**, 287 (1963).

[7] M. Becke-Goehring and W. Lehr, *Chem. Ber.*, **94**, 1591 (1961).

without recrystallization. Samples of the α form were purified by recrystallization from *n*-hexane.

Infrared Measurements.—Solution spectra were recorded for the region 4000–420 cm^{-1} on a Perkin-Elmer 337 grating infrared spectrometer using matched KBr cells of 0.1-mm path length. Solid-state spectra were recorded on this instrument and also on a Perkin-Elmer 521 grating infrared spectrometer for the range 4000–244 cm^{-1} using KBr or CsBr pellets or Nujol mulls between KBr or CsBr disks where appropriate. All spectra were obtained using polystyrene film bands for calibration of the wave number scale. Values listed for positions of maximum absorption were reproducible to within 2 cm^{-1}.

Nuclear Quadrupole Interaction Measurements.—A modified Dean-type externally quenched superregenerative oscillator[8] was employed with phase-sensitive detection and strip chart recording. The frequencies of the interactions were determined by observation of zero beat of the oscillator fundamental with a very loosely coupled BC 221 frequency meter precalibrated against WWV. The interactions have a recorded line width of about 6 kHz at half-height, so with a low level of frequency modulation and by operation in the quasi-incoherent mode it was simple to tune to the line center thereby obtaining the frequency with a reproducibility of ±0.0005 MHz. In this manner the interaction frequencies reproduced the reported Cl quadrupole moment ratio to better than ±0.001%. However, due to the limitation imposed by temperature fluctuations, the reported interactions are presumed to have an accuracy of only ±0.002 MHz. Samples of 0.9–1.9 g sealed under vacuum in glass ampoules were used.

Variation with temperature of the interactions was followed by allowing the sample, in a copper container, to warm. This method is simpler than employing stepwise slush measurements but imprecision in the measured temperature is greater. Temperatures were determined using a copper–constantan thermocouple and a Honeywell portable potentiometer.

Results and Discussion

The X-ray structural analysis[2] showed that molecules of $NPCl_2(NSOCl)_2$ are in a distorted chair configuration with both sulfur chlorine substituents axial. The most striking feature is the considerable distortion from C_s molecular symmetry resulting from intermolecular interactions between exocyclic atoms. If a mixed-ring molecule possessed C_s symmetry, the chlorines bonded to the sulfur atoms would be chemically equivalent, whereas those bonded to the phosphorus atom would not.

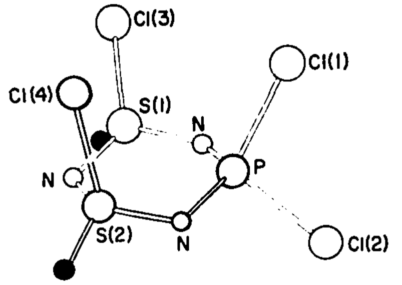

Figure 1.—Molecule of $NPCl_2(NSOCl)_2$. The black solid circles designate oxygen atoms.

Infrared Data.—The main bands in the infrared spectra of the mixed ring in the solid state and in solution in polar and nonpolar solvents are listed in Table I. The compound is appreciably soluble in Nujol, the resulting spectrum being that obtained from solution in a nonpolar solvent. Since the spectra obtained from Nujol mulls are thus concentration dependent, this must be taken into account when using the Nujol mull technique to obtain spectra of solid samples. The spectrum in the solid state is very similar to that in polar solvents. However, relative intensities and positions of maximum absorption for certain bands in the solution infrared spectra change gradually with solvent polarity. This variation can be followed from spectra of solutions in mixtures of carbon tetrachloride and acetonitrile as solvent; the over-all change can be seen from a comparison of the solution spectra for nonpolar and polar solvents in Table I.

Table I

Infrared Spectra of $NPCl_2(NSOCl)_2$[a]

	Soln	
Solid	Cyclohexane	Acetonitrile
1348 w, sh[b]	1348 s	1340 sh
1336 s	1335 s	1328 s
1312 w, sh		1280 w
1179 vs, br	1177 vs	1182 vs
1138 s, br	1142 s	1139 s
1028 ms	1035 m	1029 s
855 sh		915 m
840 m	840 mw	841 mw
722 s	720 ms	724 ms
666 w	666 w	668 w
		650 w, sh
640 s	624 s	635 s
562 s	558 s	564 s
548 m	537 s	540 m
488 mw	484 mw	487 mw
442 w	437 w	435 w
410 w		
348 w		
310 w		

[a] Values (in cm^{-1}) of maximum absorption for main bands observed. [b] Abbreviations: vw, very weak; w, weak; mw, medium weak; m, medium; ms, medium strong; s, strong; vs, very strong; sh, shoulder; br, broad. Relative intensities were estimated from absorbance scale.

Nqr Data.—The ^{35}Cl nuclear quadrupole resonance (nqr) spectra reported in Table II are those observed at room temperature in order to approach the temperatures of the available X-ray structural analysis. The spectrum of the mixed ring consists of four intense interactions of equal magnitude. Four further weaker interactions are attributable to ^{37}Cl. Considering the ^{35}Cl room-temperature nqr spectra of cyclic trimeric phosphonitrilic chloride, $(NPCl_2)_3$, and the α form of sulfanuric chloride, α-$(NSOCl)_3$, enables the interactions observed for the mixed ring to be identified with the phosphorus and sulfur chlorine atoms of the molecule. The frequency of the weighted average of the nuclear quadrupole interactions of $(NPCl_2)_3$ is 27.745 MHz. The weighted average of the interactions of α-$(NSOCl)_3$ is 36.243 MHz. Thus the lower frequency pair of interactions results from chlorines bonded to the phosphorus atom, and the higher frequency pair of interactions, from chlorines bonded to the two sulfur atoms of the mixed-ring molecules.

The observation of two separate phosphorus chlorine frequencies and also two separate frequencies from the

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(8) C. Dean and M. Pollack, *Rev. Sci. Instr.*, **29**, 630 (1958).

Table II

Frequencies (in MHz) of the ^{35}Cl Nuclear Quadrupole Interactions of Some Cyclic Inorganic Compounds at 294°K[a]

$NPCl_2(NSOCl)_2$	α-$(NSOCl)_3$	β-$(NSOCl)_3$[b]	$(NPCl_2)_3$[c]
28.660	36.138*	36.134	27.880*
29.836	36.454	36.445	27.812
34.521		37.55	27.684
35.472			27.608*

[a] All interactions for each compound are of equal intensity except those marked with an asterisk which are of twice the intensity of the others for that compound. [b] As the temperature of observation approaches the melting point (320°K), the interactions become less sharp and lose intensity. The highest frequency interaction is particularly affected. [c] M. Kaplansky, Ph.D. Thesis, McGill University, 1967.

chemically equivalent sulfur chlorines is in agreement with the solid-state structural determination.[2] The multiplicity of the sulfur chlorine frequencies results from intermolecular interaction reflected in molecular distortion from C_s symmetry.

The frequencies of the respective interactions appear to vary smoothly and exhibit the usual diminution with increasing temperature, implying that no phase transition nor major molecular reorientation occurs within the temperature range studied.

In the process of structural refinement[2] it was found that considerably larger corrections for thermal motion were required for two of the chlorine atoms, Cl(1) and Cl(4), than the corrections calculated using the rigid-body approximation. The temperature dependence of frequencies for molecular crystals has been considered by various authors.[9] At a given temperature, nuclear quadrupole interactions for two chlorine atoms in equivalent bonding situations but otherwise inequivalent environments (*i.e.*, inequivalent nonbonding situations) should be separated by a frequency difference proportional to the relative amount of thermal averaging of the electric field gradient at each nucleus. Contributions to the field gradient, either direct or indirect, from the nonbonded environment, become important only in ionic crystals.[10] The decrease in frequency of interaction with increasing temperature can be accounted for qualitatively by an increase in the amplitude of thermal motion which effects a greater averaging of the electric field gradient at the interacting nucleus. Considering the relative slopes and positions of the plots of nqr frequencies *vs.* temperature for the mixed ring (Figure 2) for the two pairs of interactions, it is possible to relate the higher frequency sulfur–chlorine interaction to Cl(4) and the lower frequency phosphorus–chlorine interaction to Cl(1).

These assignments will now be discussed in terms of current chemical concepts. The Townes–Dailey theory of nuclear quadrupole coupling considers the major contributions to the electric field gradient within the framework of the LCAO–VB approximation. An increase in chlorine s character and an increase in ionic character of the σ bond to a chlorine atom results in a reduction of the frequency of the quadrupolar interaction. Any π bonding involving the doubly filled chlorine valence atomic orbitals would reduce the field gradient at the chlorine nucleus thus further reducing the frequency.

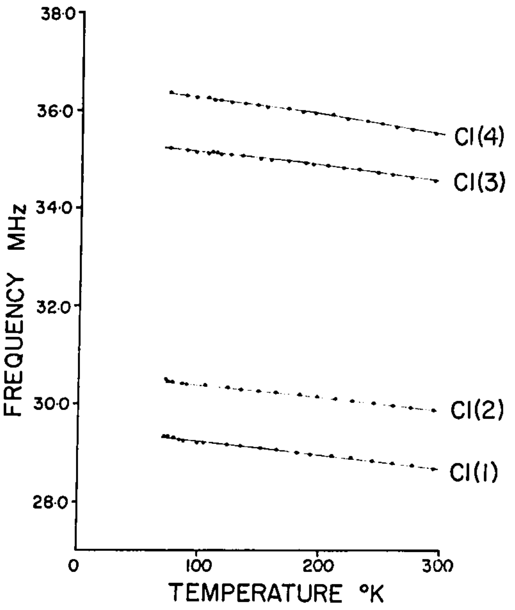

Figure 2.—Temperature dependence of ^{35}Cl nuclear quadrupole interactions of $NPCl_2(NSOCl)_2$ between the temperature of liquid nitrogen and 294°K.

To a first approximation the σ-bond hybrids at either a phosphorus or a sulfur atom in a ring system such as $NPCl_2(NSOCl)_2$ are tetrahedral. The electronegativity of a phosphorus tetrahedral hybrid is lower than that of a sulfur tetrahedral hybrid;[11] hence a phosphorus–chlorine bond would be more ionic than a sulfur–chlorine bond, and the frequency of interaction for phosphorus chlorines would be lower than that of sulfur chlorines. An estimation of the departure from sp^3 hybridization at the central atom can be made from a consideration of the determined bond angles. Reduction of the exocyclic angle from 109.4° at a ring phosphorus or sulfur atom reflects a decrease in s character of the central atom exocyclic hybrids. The electronegativity of a hybrid of s and p orbitals decreases with decreasing s character;[11] thus reduction of the exocyclic angle leads to lower ^{35}Cl nqr frequency. A comparison of the exocyclic angles for $NPCl(NSOCl)_2$, $(NPCl_2)_3$, and α-$(NSOCl)_3$ indicates that there are slight differences which may account for the difference in average frequencies for the s and p chlorines. The average ClPCl angle in $(NPCl_2)_3$ is 102°[12] while the ClPCl angle in $NPCl_2(NSOCl)_2$ is 104.4°. The OSCl angles in α-$(NSOCl)_3$ and in $NPCl_2(NSOCl)_2$ are 108[13] and 106°, respectively. Thus the interactions for the mixed-

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[9] (a) H. Bayer, *Z. Physik*, **130**, 227 (1951); (b) T. Kushida, G. B. Benedek, and N. Bloembergen, *Phys. Rev.*, **104**, 1364 (1956); (c) H. D. Stidham, *J. Chem. Phys.*, **49**, 2041 (1968).

[10] R. Ikeda, A. Sasane, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, **70**, 2926 (1966).

[11] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

[12] A. Wilson and D. F. Carroll, *J. Chem. Soc.*, 2548 (1960).

[13] A. C. Hazell, G. A. Wiegers, and A. Vos, *Acta Cryst.* **20**, 186 (1966).

ring phosphorus chlorines should occur at a higher average frequency than those observed for $(NPCl_2)_3$ and the interactions for the sulfur chlorines should occur at a lower average frequency than those for α-$(NSOCl)_3$; this is observed. It is therefore apparent that a σ bond inductive effect is present.

The endocyclic bonding in such cyclic inorganic compounds is complex and has recently been described by Mitchell.[14,15] It is characterized by π and π' systems in addition to the σ bonding. Exocyclic π bonding (discussed subsequently) will be in competition with the π and π' systems. Evaluation of the magnitude of the asymmetry parameter at the Cl atom is unlikely to yield further information on the bonding as both the Cl lone-pair orbitals can become involved in the exocyclic π bonding according to symmetry considerations.

The ^{35}Cl nqr spectrum of α-$(NSOCl)_3$ shows a single interaction and another half as intense separated by 0.316 MHz. This is in agreement with the solid-state structural determination[13] which places two-thirds of the chlorine atoms per unit cell in different crystallographic sites from the remaining third although all chlorine atoms are chemically equivalent. The ^{35}Cl nqr spectrum of β-$(NSOCl)_3$, Table II, shows three interactions of equal intensity; two are closely spaced and the third is much further removed. It is thus consistent with the suggestion of Vandi, Moeller, and Brown,[4] inferred from dipole moment studies, that the molecular configuration is chair with two chlorines axial and one chlorine equatorial.

The frequency separations of both pairs of interactions in the mixed ring are large compared with those of α-$(NSOCl)_3$ and $(NPCl_2)_3$ or $(NPCl_2)_4$.[16,17] In solid-state $NPCl_2(NSOCl)_2$ there is a significant difference in the sulfur–chlorine interatomic distances (S(1)–Cl(3), 2.007 Å; S(2)–Cl(4), 2.028 Å) due to a distorted C_s symmetry. The ^{35}Cl coupling constant increases with increasing bond length for covalent bonds due to a decrease in the chlorine σ-bond s and ionic characters.[18] This effect is considerable for a carbon–chlorine bond and can account for the separation observed between the sulfur–chlorine interactions.

The phosphorus–chlorine interatomic distances are identical within the limits of error. Dixon, *et al.*,[17] have assigned the interactions observed for the two known forms of $(NPCl_2)_4$ on the basis of varying amounts of exocyclic π bonding estimated from the "polar" angle between the exocyclic bond and the direction perpendicular to the plane of the ring segment NPN. The angle determines the amount of overlap between occupied chlorine p orbitals and suitably oriented unoccupied phosphorus d orbitals. For example, "polar" angles calculated for the chair form[19] of $(NPCl_2)_4$ are: Cl(1), 43.9°; Cl(2), 32.8°; Cl(3), 40.4°; Cl(4), 37.0°. The room-temperature interaction frequencies (in MHz) can be assigned as 27.224, 28.597, 28.093, and 28.150, respectively.[16] The "polar" angles for the mixed-ring phosphorus chlorines are: Cl(1), 39.0°; Cl(2), 36.0°. The assigned frequencies are 28.660 and 29.836 MHz, respectively. Any π effect is thus in the correct direction to explain the separation. However, in $(NPCl_2)_4$ for example, separations of 1.373 and 0.057 MHz are related to "polar" angle differences of 11.0 and 3.1°, while the separation of 1.786 MHz must be related to an angle difference of 3.0°. The relative positions of the interactions for α-$(NSOCl)_3$ cannot be accounted for by invoking similar π bonding involving the chlorine atoms. As has been noted, these interactions can be assigned unambiguously from the intensity ratios. The "polar" angles calculated for α-$(NSOCl)_3$ (Cl(1), 30.1°; Cl(2), 31.4°) would place the interactions in the reverse order to that observed. Therefore the effect, if it occurs, must be masked by some opposing effect.

Such chemically equivalent groups of chlorines would have differences in thermal averaging of their electric field gradients reflecting crystal-packing effects. A measure of mean-square amplitude of vibration, $\overline{u^2}$, in a given direction for an atom can be determined from the anisotropic thermal parameters, U_{ij}, found from a structural refinement according to Cruickshank[20]

$$\overline{u^2} = \sum_i \sum_j U_{ij} l_i l_j$$

$l = l_i, l_j, l_k$ is a unit vector defining the direction of vibration. Choosing directions of vibration along the bond to a particular chlorine atom, perpendicular to the plane defined by the exocyclic substituents and the atom to which they are bonded and perpendicular to the bond to the chlorine in this plane, values of $\overline{u^2}$ for each chlorine atom were determined. A qualitative comparison of the "net motion" of each chlorine atom with respect to that of the atom to which it is bonded in the same directions leads to the conclusion that the thermal motion of Cl(1) is greater than that of Cl(2) for $NPCl_2(NSOCl)_2$. From similar calculations for $(NPCl_2)_4$ and α-$(NSOCl)_3$ based on the U_{ij} values reported for the structural refinements,[12,19] the observed nqr interactions can be assigned to particular chlorine atoms. For $(NPCl_2)_4$, the assignment and relative separations fall in the same pattern as that based on the π effect.[17] In addition, the separation and relative position of the two interactions observed for the crystallographically inequivalent chlorines of α-$(NSOCl)_3$ can be explained on this basis.

Thus, both a π effect and consideration of relative thermal averaging fit the assignment of phosphorus–chlorine interactions, while the π effect alone cannot explain the assignment for the sulfur chlorines in these ring compounds.

It must be noted that relative thermal averaging calculated for Cl(3) and Cl(4) of $NPCl_2(NSOCl)_2$

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(14) K. A. R. Mitchell, *J. Chem. Soc., A*, 2683 (1968).

(15) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

(16) M. Kaplansky, Ph.D. Thesis, McGill University, 1967.

(17) M. Dixon, H. D. E. Jenkins, J. A. S. Smith, and D. A. Tong, *Trans. Faraday Soc.*, **63**, 2853 (1967).

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would position the interactions assigned to these chlorines in the reverse order, implying that the difference in bond lengths in this case is of much greater importance in determining interaction frequencies.[21,22]

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[21] An alternative approach to the assignment of the lower frequency pair of interactions was suggested by a referee: Cl(1) and Cl(2), having different crystallographic environments, have different average moments of inertia with respect to the principal direction of their field gradient tensors and hence different temperature dependences of their electric field gradients and nqr frequencies. Using the moments of inertia and a detailed calculation on an assembly of quantum mechanical harmonic oscillators the zero-point vibrational contribution to the electric field gradient could be separated out. This was attempted by Ragle[22] using a value for the restoring force constant for 1,2-dichloroethane, a simple and relatively well-understood molecule, and found to be about 1.2% of the value of the coupling constant. For Cl(1) and Cl(2) the splitting amounts to about 3.6% of the average of the estimated coupling constants and it is unlikely that the difference in their respective zero-point vibrational contributions could even approach 3.6%; thus this alternative approach would not reverse the assignments. Further calculation is not possible without knowledge of the restoring forces in the molecule.

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