THE PHOSPHONITRILIC HALIDES AND THEIR DERIVATIVES

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I. Introduction

The existence and stability of homologous series of compounds lie at the foundations of organic chemistry. The systematic variation of properties within the saturated and unsaturated series, both linear and cyclic, provides a firm basis for the development and criticism of stereochemical and thermochemical concepts, and for theories of chemical reactivity.

In the development of inorganic chemistry, on the other hand, homologous series have played a less important part. The only well-defined series which have been studied are the siloxanes $(R_2SiO)_n$ and the phosphonitrilic chlorides $(PNCl_2)_n$, based respectively on the isoelectronic repeating units SiO and PN. They each form extensive series of both cyclic and related linear polymers. Each includes an element of principal quantum number 3, a feature which accounts for some resemblances between the two groups, and which requires an extension of the ideas derived from the organic field.

The siloxanes have been dealt with in detail elsewhere (*15, 65*); this review is concerned almost exclusively with the phosphonitrilic halides. The chlorides were first recognized as a homologous series by Stokes (*85, 89*), who isolated and investigated the lower members, from trimer to heptamer. This, and more recent work, was reviewed in 1943 by Audrieth *et al.* (*3*).

The object of the present review is to correlate and interpret a growing body of chemical and physical information, to show how the more recent developments provide a context in which the older work can be understood, and to relate the chemistry of the phosphonitrilic series to other groups of organic and inorganic compounds.

II. Preparation of the Phosphonitrilic Halides

A. GENERAL

Of the various preparative methods described by Audrieth *et al.* (*3*), that originally developed by Schenk and Römer (*71*) has proved most generally useful. It involves the ammonolysis of phosphorus pentachloride according to the equation

$$PCl_5 + NH_4Cl \rightarrow PNCl_2 + 4HCl \qquad (1)$$

The reaction is carried out by heating phosphorus pentachloride with a small excess of finely divided ammonium chloride in refluxing *s*-tetrachloroethane, a solvent which boils at a suitable temperature (146°) and which is comparatively inert to chlorination. The initially vigorous reaction slowly subsides, until after 6-8 hr the evolution of hydrogen chloride is barely noticeable. The excess of ammonium chloride is filtered off, and the solution concentrated under reduced pressure at as low a temperature as possible. The residue is a mixture of oil and crystals, the bulk of which, typically 75-90%, is soluble in low-boiling petroleum ether, and consists of a mixture of polymers $(PNCl_2)_n$. The insoluble portion, a product of incomplete reaction, has the composition $(PNCl_2)_n \cdot PCl_5$, and depending on reaction conditions may vary in texture from a light oil to a plastic rubber.

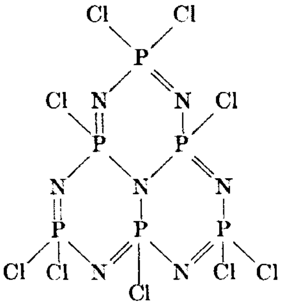
The reaction may also be carried out in monochlorobenzene or *o*-dichlorobenzene (*18*), though complete reaction in the former solvent may require more than 24 hr. High yields of the lower polymers may also be obtained from the dry reaction of ammonium chloride and phosphorus pentachloride (*84*).

The question of whether the phosphonitrilic chlorides have cyclic or linear structures has been frequently discussed in the literature. The structural evidence will be considered in Section IV, where it will be seen that the cyclic formulation is established beyond doubt for the trimer and tetramer, and is highly probable for the higher soluble polymers; it will meanwhile be assumed for all compounds of formula $(PNX_2)_n$. For reasons considered in Section II, C the petrol-insoluble fraction $(PNCl_2)_n \cdot PCl_5$ is believed to consist of a mixture of linear polymers. The two series are related, in that the linear compounds of low molecular weight are intermediates in the formation of the cyclics by the ammonolysis of phosphorus pentachloride.

B. Cyclic Polymers

Most attention will be paid here to the well-defined series $(PNCl_2)_n$ and related halides. The relative proportions of the individual chloride polymers in the soluble fraction vary with reaction conditions, but are, typically, trimer 40-45%, tetramer 15-20%, pentamer 15-20%, hexamer 1-3%, heptamer and upwards 25% (average). They may be separated by a combination of fractional crystallization and fractional distillation in vacuo. This method was first used by Stokes (*89*), who isolated the trimer to hexamer as crystalline solids, and the heptamer as an oil. The undistillable residue obtained after removal of the heptamer consists of a mixture of polymers, approximately $(PNCl_2)_{10\text{-}11}$. This has similar properties to the pure compounds of lower molecular weight, and is probably composed of molecules with similar structures.

One other related compound was isolated by Stokes (*89*), of formula $P_6N_7Cl_9$, almost certainly polycyclic and with the structure shown in formula I. It occurs with the hexameric chloride, which is approximately twenty times as abundant. Its low polarity has been demonstrated by Krause (*46*).



(I)

A comparable preparative method can be used for the phosphonitrilic bromides and chlorobromides. The trimeric and tetrameric bromides $(PNBr_2)_{3,4}$ may be prepared by the action of ammonia (*6*) or of ammonium bromide (*8*) on phosphorus pentabromide, though the dissociation of the latter at any convenient reaction temperature reduces the yield considerably, and the two polymers are difficult to separate. The mono-bromo-compound $P_3N_3Cl_5Br$, from ammonium bromide and phosphorus pentachloride, is the first derivative in which the chlorine atoms are substituted other than in pairs (*64*). The dibromo and tetrabromo derivatives were obtained in the same investigation, by the use of phosphorus chlorobromides.

The phosphonitrilic fluorides do not result from the interaction of ammonium fluoride with phosphorus pentachloride; ammonium hexafluorophosphate is formed instead (*47*). They may be prepared indirectly by the reaction of potassium fluorosulfite with the chlorides at 100°-120° (*75*),

$$(PNCl_2)_4 + 8KSO_2F \rightarrow (PNF_2)_4 + 8KCl + 8SO_2 \qquad (2)$$

Yields are good, and the method can be extended to the higher polymers. The pentameric fluoride, for instance, has been obtained by D. H. Paine (*2*).

Fluorination of the trimeric chloride with lead fluoride yields mixed derivatives of the tetramer, $P_4N_4F_6Cl_2$ (*74*) and $P_4N_4F_4Cl_4$ (*73*). Both compounds polymerize under pressure at 300° to rubbers; pyrolysis of the high polymer at atmospheric pressure gives the mixed chlorofluorides $P_3N_3F_2Cl_4$ and $P_3N_3F_4Cl_2$ (*73*).

No iodides have been reported. From a solution of triphosphonitrilic chloride in acetone, sodium iodide precipitates, in the course of months, all the chlorine as sodium chloride (*76*). The color of iodine is, however, seen in the solution almost from the beginning, and the phosphonitrilic iodides are evidently unstable, possibly for steric reasons.

C. LINEAR POLYMERS

Incomplete ammonolysis of phosphorus pentachloride gives a high yield of the petrol-insoluble oil of empirical composition $(PNCl_2)_n \cdot PCl_5$ referred to in Section II, A. A similar mixture of linear polymers may be prepared by the action of phosphorus pentachloride on the cyclic polymers at 350° (*1*). The reaction proceeds at a comparable rate to the polymerization which would occur in the absence of the pentachloride, and presumably depends in the same way on thermal opening of the ring. The product is a pasty solid for $n = 4$ or less; higher members are oils increasing in viscosity with n, until rubbery solids are eventually formed (H. T. Searle, *2*). The individual members of the series have not yet been obtained pure, since their thermal stability is not high, and phosphorus pentachloride easily splits off in even slightly polar solvents.

They are, however, distinguished as a class from the cyclic polymers by a high polarity, by a reactivity to water of the same order as that of phosphorus pentachloride itself, and by the appearance of two extra peaks in their ultraviolet absorption spectra (Fig. 1). These peaks vary

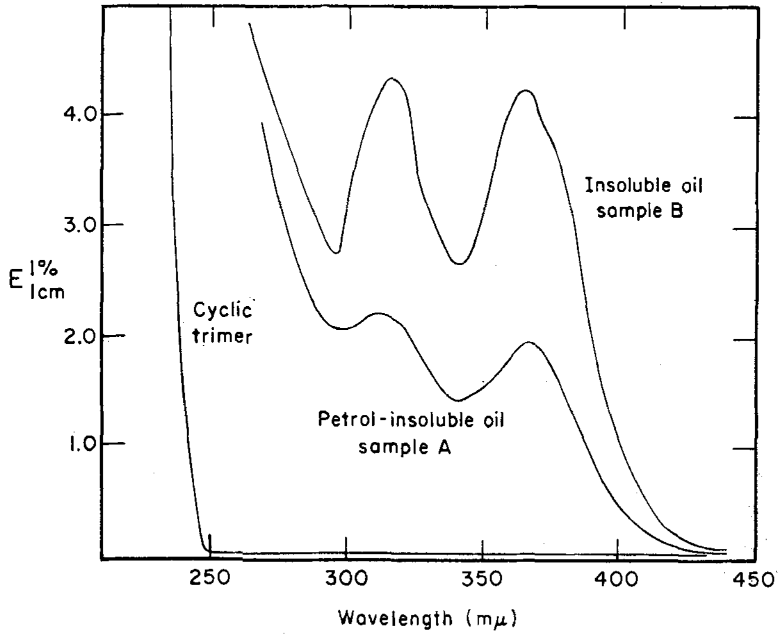


FIG. 1. The ultraviolet absorption spectra of two samples of insoluble oil, of composition $PCl_4(NPCl_2)_nCl$, (of different molecular weights), compared with the spectra of $(PNCl_2)_3$.

in intensity for samples of different molecular weights, but their position remains constant.

The linear structure of these polymers is strongly suggested by the conditions required for their formation from the cyclic compounds and phosphorus pentachloride. That the ring is actually broken in the reaction is shown by the fact that a mixture of polymers, not the original cyclic compound, is obtained by the ammonolysis of the reaction product. It is natural, therefore, to formulate these compounds as $PCl_4(NPCl_2)_n \cdot Cl$, the chlorides of the polyimidophosphoric acids.

They may be regarded as the prototypes of other linear phosphonitrilic derivatives. For instance, the cyclic trimeric chloride reacts with damp lead fluoride (*74*) to give the compound $P_3N_3F_6 \cdot 2HF \cdot 2H_2O$ which is probably linear, as are some of the phenylated products (*10*). The linear derivatives are usually highly reactive, and are therefore difficult to isolate and characterize. It is probable that they play a much more important part in phosphonitrilic chemistry than would be suggested by the small number which have been accurately described.

D. The Course of the Reaction

The manner in which the linear and cyclic polymers are formed in the ammonolysis of phosphorus pentachloride is not known in detail, but seems likely to involve a series of condensation reactions. The first stage is thought to be the formation of the unstable ammonium hexachlorophosphate:

$$NH_4Cl + PCl_5 \rightarrow NH_4PCl_6 \qquad (3)$$

This then breaks down, possibly to NH_2PCl_4 or more probably to $NH{:}PCl_3$, the true nitrogen analogue of $POCl_3$. This may react either with itself, or with more PCl_5 to give $PCl_4 \cdot N{:}PCl_3$. These two compounds are the first members of the two series $H(NPCl_2)_nCl$ and $PCl_4(NPCl_2)_nCl$; higher members can result from more than one condensation process involving the original reactants and the intermediates. No members of the first series have been obtained, although they are presumably the immediate precursors of the cyclic polymers, formed from them by intramolecular elimination of hydrogen chloride. The second series has been dealt with in Section II, C.

There is both direct and indirect evidence for parts of this proposed reaction path. Tetramethylammonium chloride dissolves in a solution of phosphorus pentachloride in acetonitrile to give tetramethylammonium hexachlorophosphate (*33*). As stated in Section II, B the reaction of ammonium fluoride with phosphorus pentachloride yields the very stable ammonium hexafluorophosphate. Ammonium chloride, though virtually insoluble in nitrobenzene, dissolves if phosphorus pentachloride is present, to give a conducting solution (*60*). The suggestion that ammonium hexachlorophosphate is formed as a first step in the reaction therefore appears to be reasonable.

Although no members of the linear series $H(NPCl_2)_nCl$ end-stopped with the elements of hydrogen chloride have been isolated, the methyl analogue $CH_3N{:}PCl_3$ of the lowest member has been obtained in high yield, from the reaction of methylammonium chloride and phosphorus pentachloride, as a hygroscopic crystalline compound resembling phosphorus pentachloride in reactivity (W. S. Holmes, *2*). The corresponding phenyl derivative was prepared by Gilpin (*35*).

Mixtures of the lower members of the second series, $PCl_4(NPCl_2)_nCl$, in which a phosphonitrilic chain is terminated by the elements of phosphorus pentachloride, can be isolated from a solution in which reaction between ammonium chloride and phosphorus pentachloride has not been allowed to go to completion. They are identical in type with those made by the direct reaction of the cyclic polymers with phosphorus pentachloride at high temperatures (Section II, C). Both products are converted to mixtures of cyclic polymers on treatment with ammonium chloride, provided n is small enough. If $n > 2$, chain growth predominates over ring closure.

General support for this type of reaction scheme is afforded by investigations on the effect of reactant concentrations. An excess of phosphorus pentachloride gives a high yield of the linear end-stopped bodies; the proportion of these petrol-insoluble compounds can be reduced almost to zero by extracting the phosphorus pentachloride slowly into a refluxing suspension of ammonium chloride in tetrachloroethane (*1*).

The hydrolysis of, for example, dimethyl dichlorosilane to cyclic dimethylsiloxanes and linear diols can be regarded as following a similar pattern, if $OH_3^+Cl^-$ is taken as the analogue of $NH_4^+Cl^-$. Increase of acid concentration, or the use of a mutual solvent, increases the proportion of cyclic polymers; their proportion is decreased by the use of insufficient, alkaline or "scarce" water in the form of hydrated salts (see pp. 80 ff. in ref. *65*).

III. Properties

A. GENERAL

The main features of the chlorides are comparative chemical inertness and thermal stability. Many derivatives have been obtained, but reaction is often slow and incomplete, and the products have not always been completely characterized. Although they are acid chlorides, the phosphonitrilic chlorides are not hydrolyzed rapidly; the trimer in particular can be steam-distilled without serious loss. As will be seen in more detail in Section III, C, 1, polymerization takes place near 350° to a rubberlike high polymer.

The patent literature on the phosphonitrilic chlorides is extensive; no attempt will be made to deal with it here. Most proposed applications have been to the high-polymer field, particularly where resistance to high temperatures is required. Phosphonitrilic compounds have proved valuable in flame-proofing treatments for fabrics and have been suggested as plasticizers, as oil additives, and as catalysts in silicone manufacture.

The lower polymers are beautifully crystalline solids, the trimer having a faint camphorlike smell. It has marked irritant properties. Inflammation of the eyes and difficulty in breathing is experienced some hours after exposure to the vapor; the symptoms may take a day or two to disappear. Great care should be taken in the manipulation of these compounds, particularly the trimer. They are dangerous in that the irritant effect is not immediate; it is also easy to become sensitized to their action, so that small doses may eventually have large effects. The effect is mainly one of discomfort; no permanent injury appears to result.

B. PHYSICAL PROPERTIES

The physical properties of the phosphonitrilic halides are presented in the three groups, general physical properties, crystallographic data, and solubility data. The general physical properties are summarized below. Each literature reference refers to all values following the preceding reference.[1]

Trimeric Phosphonitrilic Halides

$P_3N_3F_6$ (c) $d_{20} = 2.21$ (F. R. Tromans, *2*), mp (triple point) 27.1°, vp (27.1°) 293 mm Hg (*75*), vp (c) $\log_{10} p_{(mm)} = 11.252 - 2630.9\ (1/T)$ (from −50° to 27°), ΔH_{subl} 12.0 kcal/mole (W. S. Holmes, *2*), bp 51.8° (*75*).

$P_3N_3F_4Cl_2$ (l) bp 115-117° (*73*).

$P_3N_3F_2Cl_4$ (l) bp 140-142° (*73*).

$P_3N_3Cl_6$ (c) $d_{20} = 1.99$ (*85*) (A. Wilson, *2*), mp 114° (*85*), vp (c) $\log_{10} p_{(mm)} = 11.187 - 3978\ (1/T)$ (from 75.2° to 114.9°), ΔH_{fus} 5.0 kcal/mole (*84*), bp 256.5° (*85, 55* but see *84*), vp (l) $\log_{10} p_{(mm)} = 8.357 - 2880\ (1/T)$ (from 114.9° to 189.3°), ΔH_{vap} 13.2 kcal/mole (*84*), $\mu = 0.51$ D (*46*).

$P_3N_3Cl_5Br$ (c) $d_{20} = 2.27$, mp 123.5° (*64*).

$P_3N_3Cl_4Br_2$ (c) $d_{20} = 2.44$, mp 136.5° (*64*).

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[1] A list of symbols appears on p. 380.

$P_3N_3Cl_2Br_4$ (c) $d_{20} = 2.84$, mp 167° (*64*).

$P_3N_3Br_6$ (c) $d_{20} = 3.18$ (calc.) (*8*), mp 191° (*6, 8*).

Tetrameric Phosphonitrilic Halides

$P_4N_4F_8$ (c) $d_{20} = 2.22$ (F. R. Tromans, *2*), mp (triple point) 30.4°, vp (30.4°) 67.7 mm Hg, bp 89.7° (*75*).

$P_4N_4F_6Cl_2$ (l) $d_{13.5} = 1.8742$, mp −12.1°, bp 105.8°, vp (l) $\log_{10} p_{(\mathrm{mm})} = 7.923 - 1911\ (1/T)$, ΔH_{vap} 8.7 kcal/mole (*74*).

$P_4N_4F_4Cl_4$ (l) $d_0 = 1.9568$, coef. cu. exp. 0.71×10^{-3} deg^{-1} (calc), mp −24.9°, bp 130.5°, vp (l) $\log_{10} p_{(\mathrm{mm})} = 7.615 - 1911\ (1/T)$, ΔH_{vap} 8.7 kcal/mole (*73*).

$P_4N_4Cl_8$ (c) $d_{20} = 2.18$ (*85*), mp 123.5°, bp 188°/13 mm Hg, 328.5° (*89,* but see *55*), vp (l) (from published graph) $\log_{10} p_{(\mathrm{mm})} = 8.51 - 3360\ (1/T)$, ΔH_{vap} 15.5 kcal/mole (*55*), $\mu = 0.39$ D (*46*).

$P_4N_4Br_8$ (c) $d_{20} = 3.44$ (calc), mp 202° (*8*).

Pentameric Phosphonitrilic Halides

$P_5N_5F_{10}$ (l) bp 122°/751 mm Hg (D. H. Paine, *2*).

$P_5N_5Cl_{10}$ (c) $d_{20} = 2.02$ (H. McD. McGeachin, *2*), mp 41°, bp 223-224°/13 mm Hg (*89*), $\mu = 0.47$ D (*46*).

Hexameric Phosphonitrilic Halides

$P_6N_6F_{12}$ (l) bp 147° (D. H. Paine, *2*).

$P_6N_6Cl_{12}$ (c) $d_{20} = 2.05$ (A. Wilson, *2*), mp 91°, bp 261-263°/13 mm Hg (*89*), $\mu = 0.48$ D (*46*).

Heptameric Phosphonitrilic Halide

$P_7N_7Cl_{14}$ (l) mp reported (*89*) to be below −18°, but almost certainly at least 10° higher, bp 289-294°/13 mm Hg (*89*), $\mu = 0.54$ D (*46*).

Polycyclic Phosphonitrilic Halide

$P_6N_7Cl_9$ (c) mp 237.5°, bp 251-261°/13 mm Hg (*89*), $\mu = 0.72$ D (*46*).

The crystallographic data for the phosphonitrilic halides are summarized in Table I.

The solubilities of the phosphonitrilic chlorides in various solvents have been determined by de Ficquelmont (*29*) and L. G. Lund (*2*). The results for 20°, expressed in gm solute/100 gm solvent, are given in Table II.

The solubilities of the trimeric chloride over a range of temperature correspond, within a few percent, to those expected by the theory of regular solutions (*38*). They therefore depend on the relative internal

TABLE I

CRYSTALLOGRAPHIC DATA FOR THE PHOSPHONITRILIC HALIDES

Compound	Unit cell dimensions (Å) a	b	c	Z	Crystal system and space group	Optical constants (J. K. Leary, *2*)	Other references
$P_3N_3F_6$					Probably orthorhombic	$\alpha = 1.395$	
						$\beta = 1.440$	
						$\gamma = 1.47$	
						$2V = 75\text{-}80°$	
$P_3N_3Cl_6$	14.00	6.16	12.94	4	Orthorhombic	$\alpha(/\!/a) = 1.619$	*44*
	14.30	6.25	13.03	4	P_{nam}	$\beta(/\!/c) = 1.621$	*63*
	14.15	6.20	13.07	4		$\gamma(/\!/b) = 1.631$	A. Wilson, *2*
						$2V = 26°$	
$P_3N_3Cl_5Br$	14.24	6.28	13.00	4	Orthorhombic		*64*
$P_3N_3Cl_4Br_2$	14.27	6.34	13.02	4	Orthorhombic P_{na2_1}, or P_{nam}		*64*
$P_3N_3Cl_2Br_4$	14.29	6.48	13.33	4	Orthorhombic		*64*
$P_3N_3Br_6$	14.38	6.64	13.35	4	Orthorhombic	$\alpha(/\!/c) = 1.720$	*8*
					P_{nam}	$\beta(/\!/a) = 1.742$	
						$\gamma(/\!/b) = 1.812$	
						$2V = 54°$	
$P_4N_4F_8$	7.48	13.83	5.16	2	Monoclinic	$\alpha = 1.379$	F. R. Tromans, *2*
					$P2_1/n$	$\beta(/\!/b) = 1.428$	
	($\beta = 112°$)					$\gamma = 1.463$	
						$\gamma^\wedge c = 62°$	
						$2V = 80°$	
$P_4N_4Cl_8$	10.79		5.93	2	Tetragonal	$\epsilon = 1.675$	*44*
					$P4_2/n$	$\omega = 1.678$	
	10.82		5.95	2			*45*
$P_4N_4Br_8$	11.18		6.29	2	Tetragonal $P4_2/n$		*8*
$P_5N_5Cl_{10}$	19.37	15.42	6.23	4	Orthorhombic	$\alpha = 1.629$	D. E. C. Corbridge, *2*
					$P2_12_12_1$	$\beta = 1.644$	
						γ undetermined	
						(optically $-ve$)	
$P_6N_6Cl_{12}$	see footnote[a]						

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[a] Hexameric phosphonitrilic chloride exists in at least two, and probably three, crystalline forms. An orthorhombic modification was described by Stokes (*89*) and examined by Tassin (*92*), who found axial ratios $a{:}b{:}c{::}0.5482{:}1{:}1.757$; the crystals were optically positive, the plane of the optic axes being (100). The cell size of a triclinic form has been determined by A. Wilson (*2*); $a = 10.6$Å, $b = 10.7$Å, $c = 11.4$Å, $\alpha = 93.5°$, $\beta = 90°$, $\gamma = 117°$; its optical constants are $\alpha = 1.628$, $\beta = 1.649$, $\gamma = 1.650$, $2V = 34°$. A second, less stable, triclinic form has appreciably higher refractive indices.

TABLE II

SOLUBILITIES OF THE PHOSPHONITRILIC CHLORIDES IN VARIOUS SOLVENTS AT 20° EXPRESSED AS GM SOLUTE/100 GM SOLVENT

	$(PNCl_2)_3$		$(PNCl_2)_4$		$(PNCl_2)_5$	$(PNCl_2)_6$
Solvent	Ref. *29*	Ref. *2*	Ref. *29*	Ref. *2*	Ref. *2*	Ref. *2*
n-Pentane		25.5		6.1	~2000	27.8
n-Hexane		25.5		7.0		34.0
n-Heptane	27.9 (80-90°C petrol)		8.4 (80-90°C petrol)		1030	
Carbon disulphide	52.1		22.0			
Carbon tetrachloride	38.9	38.3	16.6	15.5		98
Sym-tetrachloroethane		33.4		7.9		
Benzene	55.0	56.5	21.4	23.5		145
Toluene	47.3		17.8			
Xylene	38.8		13.9			
Diethyl ether	46.4		12.4			
Dioxane	29.6		8.2			

pressures of solvent and solute, and show the comparative unimportance of chemical interaction between them. In particular, the solution in *sym*-tetrachloroethane is almost ideal; the temperature coefficient of solubility corresponds to a latent heat of fusion of the trimeric chloride of 4.8 kcal/mole, slightly lower than the figure, 5.0 kcal/mole, determined from the vapor pressure curves (*84*).

C. CHEMICAL PROPERTIES

The reactions of phosphonitrilic compounds may be conveniently considered in four groups: polymerization, reactions with donor molecules, alkyl and aryl derivatives, and reactions with acceptor molecules. The relation between structure and reactions will be considered in Section V.

1. Polymerization

All the lower phosphonitrilic chlorides polymerize on heating to 250°-350°C (*89*), though if the materials are carefully purified the reaction is slow. As normally prepared, the product retains small amounts of the lower cyclic polymers, which may be removed by extraction with a solvent (*27*). The high polymer, having a molecular weight of at least 20,000 (*78, 79*), is stable at room temperature, swells in benzene and other organic solvents, and gives a characteristic X-ray fiber diagram on stretching (*53*), see Section IV, B, 4. It also resembles natural rubber in its mechanical properties (*51, 52, 53*), though it hardens and breaks up in damp air. Depolymerization begins above 350°, with the formation of a mixture of lower polymers; quantities of a black, insoluble, infusible material are obtained on slow heating of the polymer to about 500°.

The equilibrium has been studied in a preliminary way by Schmitz-Dumont (*72*), who heated the trimeric chloride in the vapor phase at 600°. The mixture of polymers obtained included trimer, tetramer, and higher crystalline and liquid polymers. The existence of equilibrium was established by showing the same mixture of polymers to be obtained, whether the starting material was trimer, tetramer, or high polymer. The proportion of higher polymers was decreased by increasing the temperature; polymerization is therefore exothermic. The interconversion of the lower polymers has also been studied by de Ficquelmont (*28*).

The phosphonitrilic fluorides and chlorofluorides behave similarly, though the latter compounds are less thermally stable than the chlorides. Since tetrameric chlorofluorides are formed by fluorination of the trimeric chloride with lead fluoride, the eight-membered ring is evidently the more stable. Dissociation of the chlorofluoride $P_4N_4F_6Cl_2$ was observed in the range 207-302°. At the higher temperature the vapor density corresponded nearly to the dimer $P_2N_2F_3Cl$, and Schmitz-Dumont and Külkens (*74*) interpreted their results in terms of simple dissociation of the tetrameric molecule into two equal parts. $P_4N_4F_4Cl_4$ also dissociates in the same temperature range, but to a smaller extent (*73*). The chlorofluoride high polymers are stable at room temperature, but depolymerization at atmospheric pressure occurs at lower temperatures than with the chlorides.

Qualitatively, the results taken together indicate the increase of stability with polymer size in the series dimer, trimer, tetramer, and high polymer. They are, however, suggestive rather than exhaustive, and detailed determinations of heats of formation of the separate members would be valuable.

The kinetics of the polymerization of tri- and tetraphosphonitrilic chlorides in solution and in bulk have been studied by Patat and Kollinsky (*58*) and Patat and Frömbling (*57*). Hydrocarbons are unsuitable solvents, since they react to give hydrogen chloride; successful results were obtained in carbon tetrachloride. The proposed mechanism involves unimolecular initiation, either by oxygen (in solution) or another phosphonitrilic molecule (in bulk). A bimolecular propagation step is followed by unimolecular termination. Traces of water were found by Renaud to have a significant effect on the polymerization process (*62, 63*).

2. Reactions with Donor Molecules

The phosphonitrilic chlorides react with many donor molecules, particularly those carrying an active hydrogen atom, though the products are not always well-defined. (For references to work on mercaptans and thiophenols, see Audrieth *et al.* (*3*).) Attention will be directed here mainly to hydrolysis, esterification, and reactions with amines.

a. Hydrolysis. The hydrolysis of the chlorides to the cyclic imidophosphoric (phosphonitrilic) acids is slow. From the trimer the intermediate product $P_3N_3Cl_4(OH)_2$ has been obtained (*85, 86*). The acid $P_3N_3O_6H_6$ is normally tribasic, though a hexasilver salt has been obtained (*87*), and the structure is therefore usually written $(NH \cdot P(O)OH)_3$. (The tetrasodium salt obtained by Stokes (*87*) is probably a derivative of the linear acid $HO[PO(OH)NH]_3H$). Further hydrolysis of the acid to the imidophosphoric acids and finally to ammonia and phosphoric acid takes place easily (*7, 86, 87*). Narath *et al.* (*56*) have found that replacement of the NH groups in the sodium salt of triphosphonitrilic acid by oxygen atoms takes place without the formation of large amounts of chain imidophosphates. It may be that the ready interconversion of ring and chain forms suggested by Stokes for the pentameric and hexameric acids occurs also with the trimer.

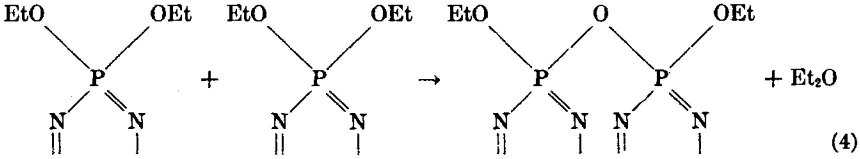
The tetrameric chloride is more readily hydrolyzed to the very stable acid $(NH \cdot P(O)OH)_4 \cdot 2H_2O$ (*85, 86, 88*). Two octasilver salts were obtained by Stokes (*88*); the cyclic acid is otherwise tetrabasic. The unit cell sizes of the dihydrate, the dipotassium and dirubidium salts have have been obtained by Corbridge (*19*). The tetrameric acid is also formed by decomposition of the pentameric acid (*90*). There is little definite information on the higher acids (*90, 91*).

The phosphonitrilic fluorides $(PNF_2)_{3,4}$ may also be hydrolyzed to the corresponding acids (*75*), apparently more readily than the chlorides (D. R. Smith, *2*), the trimer in each case being more resistant to attack.

The infrared absorption spectra of the tetraphosphonitrilates (*19*) show that hydrogen bonding in the solid is extensive, so that the distinction between the tautomeric forms $—NH \cdot PO(OH)—$ and $—N = P(OH)_2—$ is not as great as these formulas would suggest. Nevertheless, the alkali-metal salts of tri- and tetraphosphonitrilic acid react with sodium hypochlorite to give *N*-chloro derivatives (*93*).

b. Esterification. The chlorides react smoothly with alcohols and alkoxides, though side reactions giving hydrogen chloride and alkyl chlorides also occur. These may in part be avoided by working at a low temperature. The hexamethoxy derivative of the trimer (bp 127°/0.1

mm) was prepared by Dishon (*31*), though most of the product was converted into a water-soluble polymer. The hexaethoxy compound $(NP(OEt)_2)_3$ was prepared by Rätz and Hess (*61*), by the action of sodium ethoxide on the chloride, as a clear viscous oil, changing to a jelly on standing. On heating this ester to 125°, diethyl ether was eliminated irreversibly.


(4)

Goldschmidt and Dishon (*36*) were able to replace all the chlorine in the rubberlike high polymer, though the product was deficient in alkoxy groups, probably on account of a similar condensation process.

By the action of ethyl iodide on the tri- and tetrasilver salts of the appropriate phosphonitrilic acids, Rätz and Hess (*61*) have prepared the ethyl esters of the *N*-ethyl phosphonitrilates $(EtN \cdot PO(OEt))_{3,4}$. The trimeric ester is a crystalline compound which forms a dihydrochloride.

Trimeric phosphonitrilic azide has been prepared (*37*) from the trimeric chloride and sodium azide in solution in acetone.

Esterification, hydrolysis, and other reactions of the phosphonitrilic series may often be catalyzed by pyridine and other donor molecules; this effect will be considered in more detail in Section III, C, 2, d.

c. *Ammonia and Primary and Secondary Amines.* The chlorides also react with ammonia, and with primary and secondary amines, though complete elimination of the chlorine is difficult. Tri(phosphonitrile) diamidotetrachloride $P_3N_3(NH_2)_2Cl_4$ has been repeatedly investigated (*29, 54, 85, 86*); it melts at 162° with decomposition, and is much more soluble in ether and dioxane than in nonpolar solvents (*29*). The completely ammonated $(PN(NH_2)_2)_3$ can be obtained by prolonged action of liquid ammonia on the trimer (see p. 126 in ref. *3*). On heating, it loses ammonia to give, eventually, a product with the composition of phospham $(PN{:}NH)_n$. A less pure form of phospham has also been obtained by passing ammonia gas over the molten trimeric chloride (*20*).

Ammonolysis of the tetrameric chloride yields the diamidohexachloride and the tetraamidotetrachloride (*26*). Again, deammonation of the completely substituted tetramer gives phospham (see p. 127 in ref. *3*).

The reactions of primary and secondary amines with the phosphonitrilic chlorides have been studied by several investigators. Complete aminolysis is difficult to attain (see p. 127 in ref. *3*), though fully substituted derivatives of the trimer and tetramer have been reported.

The reactions of aliphatic and aromatic amines with the trimeric chloride have been studied by Schenk (*70*) and by Bode, *et al.* (*14*), who give details of the preparation of the dichlorotetraanilide, the hexa-*p*-toluidide, the hexapiperidide, the tetrachloro-bis-dimethylamide and the corresponding compound with ethylenediamine. The tetrachloro-*o*-phenylene diamide may possess a spiran structure. A number of amido derivatives of diphenyltriphosphonitrilic chloride were also prepared, such as the diphenyldiamide and diphenyldianilide and the diphenyl tetraanilide. Melting points of the amine derivatives are given in Table III. Many of these compounds are basic to perchloric and hydrochloric acids. Although attention has been concentrated on the trimer, there

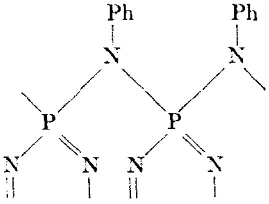
TABLE III

AMINE DERIVATIVES OF PHOSPHONITRILIC CHLORIDE TRIMER AND TETRAMER

	Derivative	Melting points and references
Fully substituted derivatives of trimer	hexaanilide $P_3N_3(NH \cdot C_6H_5)_6$	264° (*11*), 267° (*70*), 268° (*40*)
	hexa-*o*-toluidide $P_3N_3(NH \cdot C_6H_4 \cdot CH_3)_6$	241-242° (*20*)
	hexa-*p*-toluidide $P_3N_3(NH \cdot C_6H_4 \cdot CH_3)_6$	242° (*14*), 243° (*40*)
	hexapiperidide $P_3N_3(NC_5H_{10})_6$	266° (*14*), sinter point 231° (*70*), decomposes below mp (*20*)
	hexaphenylhydrazide $P_3N_3(NH \cdot NH \cdot C_6H_5)_6$	199-200° (*70*), 200° (*20*)
	diphenyltetraanilide $P_3N_3(C_6H_5)_2(NH \cdot C_6H_5)_4$	198-199° (*14*)
	diphenyldianilidediamide $P_3N_3(C_6H_5)_2(NH \cdot C_6H_5)_2(NH_2)_2$	218° (*14*)
	tetraanilidediamide $P_3N_3(NH \cdot C_6H_5)_4(NH_2)_2$	256-257° (*14*)
Tetra substituted derivatives of trimer	tetraanilide $P_3N_3(NH \cdot C_6H_5)_4Cl_2$	191° (*14*)
	tetra-*p*-toluidide $P_3N_3(NH \cdot C_6H_4 \cdot CH_3)_4Cl_2$	174° (*14*)
	diphenyldiamide $P_3N_3(C_6H_5)_2(NH_2)_2Cl_2$	162-163° (*14*)
	diphenyldianilide $P_3N_3(C_6H_5)_2(NH \cdot C_6H_5)_2Cl_2$	193° (*14*)
Fully substituted derivative of tetramer	octaanilide $P_4N_4(NH \cdot C_6H_5)_8$	244° (*70*)

seems little doubt that similarly detailed work could be carried out with the tetrameric chloride.

Bode and Clausen (*11*) have repeated earlier work on the anilide $(NP(NHPh)_2)_3$ (*40*). On heating, this compound loses aniline reversibly. (Compare the behavior of the ethyl esters, Section III, C, 2, b.) The products are soluble in nitromethane and nitrobenzene, and possibly contain the grouping $\geqslant P = N \cdot Ph$. On further heating, insoluble phenylphosphams $(NP{:}NPh)_n$ are formed without further loss in weight; for these the structure shown in formula II is suggested.



(II)

Indirect support is given to this formulation by an infrared study (*82*) of phospham $(NP{:}NH)_n$, which retains the strong absorption near 1300 cm^{-1} characteristic of the phosphonitrilic P-N bond, and shows other features which also occur in the spectra of the imidophosphates.

d. Tertiary Amines and Donor Solvents. Tertiary amines such as pyridine, quinoline, and tribenzylamine also react with the phosphonitrilic chlorides (H. Schäperkötter, quoted in ref. *3*); weak complexes are probably formed. One important consequence of the effect is that hydrolysis and esterification are accelerated in the presence of pyridine. The products of hydrolysis are pyridinium salts of polymeric acids, from which the pyridine can be removed by keeping in vacuo over sulfuric acid (*71*). Disruption of the ring need not occur, however. For instance, the butyl ester of the trimer [$P_3N_3(OBu)_6$, bp 170-171°/0.3 mm] was prepared by Dishon (*31*) by the interaction of the chloride and butanol in pyridine at 0°.

Other donor molecules react with phosphonitrilic compounds. Dioxane is said to facilitate the depolymerization of the high polymer (*53*) and of the phenyl derivatives (*13*). Acetone forms complexes with the amino acid derivatives of the tetramer (see p. 128 in ref. *3*). It is possible that ether acts as a catalyst for the hydrolysis of the trimeric chloride. The effect of these solvents is subtle, since the solubilities of the trimeric chloride in ether, in pyridine, and in dioxane show no sign of any specific chemical interaction.

The elucidation of the effect of donor solvents, and its extension to the preparation of new types of derivative, may be expected to become increasingly important in phosphonitrilic chemistry.

3. Alkyl and Aryl Derivatives

No phosphonitrilic alkyls have been obtained. Stokes (*85*) continued the work of Couldridge (*20*) on the reaction of zinc ethyl with the trimeric chloride; at high temperatures a violent reaction took place, but no identifiable products could be isolated. It is probable that alkyl phosphines were formed. W. Philpott (*2*) found the trimeric chloride in ethereal solution to be unreactive to methyl Grignard reagents and to aluminum alkyls. Unsuccessful attempts have been made by H. T. Searle (*2*) to prepare the methyl derivatives by reaction of Me_2PCl_3 with ammonium chloride, either dry or in tetrachloroethane. Most of the expected hydrogen chloride is evolved, but ring closure does not take place.

In the aromatic series, Bode and Bach (*10*) were able to isolate only linear products from the reaction of $PhPCl_4$ with NH_4Cl. Treatment of the trimeric chloride in ethereal solution with bromobenzene and sodium gave no isolable product. Partially and fully phenylated compounds have, however, been obtained in other ways.

Thus, Rosset (*66*) prepared the hexaphenyl derivative of the trimer ($P_3N_3Ph_6$) by the action of phenylmagnesium bromide on the trimeric chloride in boiling toluene. Bode and Bach (*10*) were unable to repeat this work, but obtained a small yield of the hexaphenyl compound (mp 185-187°C) by using anisole as a solvent. Its constitution was proved by the quantitative yield of diphenylphosphinic acid obtained on hydrolysis. The main product contained halogen, which reacted with silver perchlorate in alcohol to give the linear compound $Ph(PPh_2N)_3H \cdot HClO_4$. The trimeric chloride also undergoes the Friedel and Crafts reaction (*10*) to give the diphenyl derivative $P_3N_3Cl_4Ph_2$, mp ~ 92.5°C.

The tetrameric chloride also reacts with phenylmagnesium bromide to give partially and completely phenylated products (*13*). These include two octaphenyl derivatives (which may be boat and chair forms) and two tetraphenyl derivatives. Some of these compounds when hydrolyzed in the presence of dioxane gave $P_3N_3Ph_6$, suggesting that the formation of monomer is facilitated by this solvent. Two (probably linear) phenylated cleavage products containing halogen were also isolated.

Ultraviolet light has no effect on the phosphonitrilic chlorides themselves. Dishon and Hirshberg (*32*) found that solutions of the trimeric and tetrameric chlorides in hydrocarbon solvents became brown on irradiation with light from a mercury arc, and were able to isolate from the product distillable phenyl and decahydronaphthyl derivatives, the formation of which suggests radical attack.

4. Reactions with Acceptor Molecules

In many of the reactions referred to above, the phosphonitrilic compounds have behaved as acceptors; hydrolysis, esterification, aminolysis, and fluorination can all be understood in terms of nucleophilic attack at the phosphorus atom. Phosphonitrilic compounds also possess marked donor properties, though these have not been studied systematically until recently.

Besson and Rosset (*7*) found that nitrogen dioxide formed an unstable complex with the trimeric chloride, one molecule of which took up between two and three molecules of the oxide. Sulfur trioxide reacts with the trimeric chloride at 40° to give an addition compound $(PNCl_2 \cdot SO_3)_3$, a hygroscopic solid which yields sulfuric and sulfamic acids on hydrolysis (*34*). Bode *et al.* (*14*) prepared $(PNCl_2)_3 \cdot HClO_4$ and $(PNCl_2)_4 \cdot 2HClO_4$ by the action of perchloric acid on solutions of the chlorides in acetic acid; Stokes noted the solubility of the trimeric chloride in sulfuric acid (*85*).

By the use of cryoscopic measurements in 100% sulfuric acid, D. R. Smith (*2*) has found that the trimeric chloride takes up one proton, and the tetramer, pentamer and hexamer two each, thus confirming and extending the preparative work on perchlorates. Although the base strengths of all the polymers are of the same order as that of anthraquinone, they may be shown in various ways to differ significantly among themselves.

The principal way in which the acid-base equilibrium has been studied is the partition of the chlorides between sulfuric acid and *n*-hexane. A plot of the partition coefficient against acid concentration is shown in Fig. 2. It will be seen that the trimer is an appreciably stronger base than the others; as might be expected, the bromides are stronger and the fluorides weaker bases. A similar method has been used in the study of the azulenes (*59*).

The calculation of the numerical values of the base constants from the partition results is difficult for two reasons. First, no method has been found for the determination of the concentration of neutral base in the acid layer, and second, the partition coefficient is strongly dependent on polymer concentration even in dilute solutions. Nevertheless, by the use of simplifying assumptions the value $pK_a = -8.2$ may be obtained for the strength of the conjugate acid of the trimer (D. R. Smith, *2*). This is closely confirmed by indicator studies, and is consistent with the shift of the H-Cl stretching frequency at 3.46 μ observed in solutions of hydrogen chloride in the trimer (A. C. Chapman, *2*).

The difference in base strengths, and consequent difference in partition coefficients between sulfuric acid of a chosen concentration and an

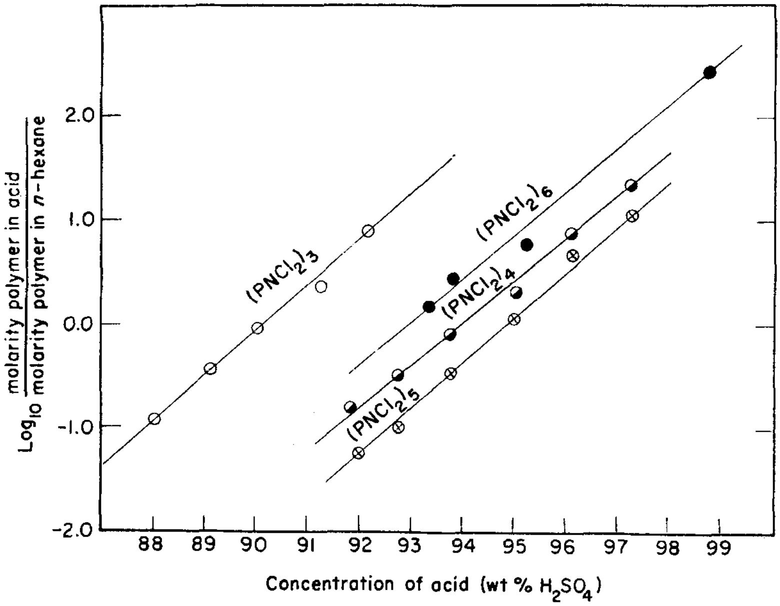


FIG. 2. The partition coefficients of the phosphonitrilic chlorides between sulfuric acid and *n*-hexane. The initial concentration of each polymer in the *n*-hexane was 3.5×10^{-3} m.

inert solvent, forms the basis of a useful method of separating the phosphonitrilic chlorides (*1*). In a comparable way, McCauley *et al.* (*50*) have separated the isomeric xylenes by utilizing their different basicities to an HF/BF_3 mixture. Although the phosphonitrilic chlorides are, like hydrocarbons, stable toward most cold concentrated acids, they are decomposed by hydrogen fluoride to ammonium hexafluorophosphate (*12*).

IV. Structure

A. GENERAL

The foregoing chemical reactions have shown the retention of the ring structure of the phosphonitrilic compounds through a variety of reactions in which the chlorine atoms are replaced by other electronegative substituents. They have chiefly concerned the trimeric and tetrameric chlorides, because these are more abundant than the higher polymers. It is known, however, that the pentameric chloride, for instance, is both thermally stable and resistant to hydrolysis. The higher polymers have not yet been separated but the mixture of approximate composition $(PNCl_2)_{8\text{-}9}$ is also comparatively inert. The individual members of which it is composed may therefore be expected to exhibit similar chemical behavior to the trimer and tetramer. As a class, the phosphonitrilic chlorides react much less readily than acid chlorides normally do.

There are two general points of interest: first, the interpretation of the stability of the polymers in terms of their known structural characteristics, and second, whether or not the cyclic structures proved for the trimeric and tetrameric chlorides are found in the higher members. The structural evidence relating to these two points will be detailed in Section IV, B.

B. EXPERIMENTAL

1. *Trimeric Compounds*

The structure of the trimeric chloride was investigated by Brockway and Bright by electron diffraction (*16*). The structure they proposed, in which each phosphorus atom carries two chlorine atoms in a plane perpendicular to the P_3N_3 ring, has been confirmed by the crystallographic work of A. Wilson (*2*). The results are given in Table IV, in which those of Ketelaar and de Vries (*45*) for the tetrameric chloride are also included for convenience. Some apparent inequalities in P-Cl bond lengths in the trimer may disappear after three-dimensional refinement of the crystal structure. The main point here is the shortness of the P-N bond lengths compared with 1.78 Å, the value obtained for the length of the single P-N bond in sodium phosphoramidate (*39*).

TABLE IV

THE MOLECULAR DIMENSIONS OF THE TRIMERIC AND TETRAMERIC PHOSPHONITRILIC CHLORIDES

Compound and method	P-N bond length (Å)	P-Cl bond length (Å)	Cl-P-Cl angle (degrees)	N-P-N angle (degrees)	P-N-P angle (degrees)
$(PNCl_2)_3$ E.D.[a]	1.65 ± 0.03	1.97 ± 0.03	107-110	assumed to be 120	
$(PNCl_2)_3$ X-ray	1.61 ± 0.04	1.99 ± 0.03	101 ± 2	121 ± 3	119 ± 3
$(PNCl_2)_4$ X-ray	1.67 ± 0.04	1.99 ± 0.03	105.5	117	123

[a] E.D. denotes electron diffraction.

The infrared absorption spectrum of the trimeric chloride has been determined by Daasch and others (*24*, *25*, *46*), and is shown, for the sodium chloride region, in Fig. 3. It is dominated by the absorption band at 1218 cm^{-1}, which is due principally to the P-N stretching mode and occurs at slightly different positions in the spectra of the other polymers.

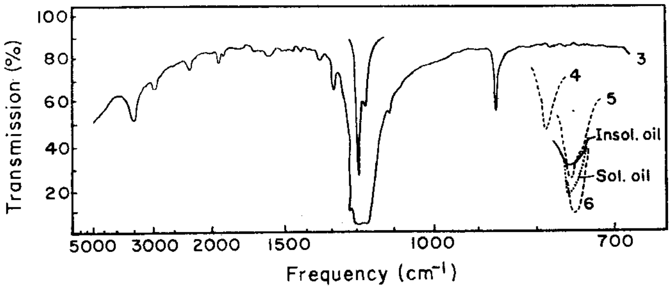


FIG. 3. The infrared absorption spectrum of the trimeric chloride, together with portions of the spectra of higher polymers (Section V, C.) The numbers denote n in $(PNCl_2)_n$.

If the P-N bond were single, absorption would be expected in the region 700-800 cm^{-1} (*41*). Such absorption is absent from the spectrum of the trimeric chloride.

The detailed structure of the infrared absorption and Raman spectra (*24, 30*) has been shown by Daasch to be in complete agreement with the planar structure of D_{3h} symmetry. From the Raman frequencies Iribarne and de Kowalewski (*43*) calculated the P-N stretching frequency of trimer to be 4.0 millidynes/Å. This value depends on the assignment of a line at 100 cm^{-1} to Cl-P-Cl angular deformation. Both the assignment and the numerical value of the stretching constant seem reasonable, but since the line was not observed by Daasch the conclusion should be accepted cautiously.

A partial analysis of the crystal structure of the trimeric bromide has been carried out (*9*), and is consistent with a planar molecule. The mixed chlorobromides $P_3N_3Cl_5Br$, $P_3N_3Cl_4Br_2$, $P_3N_3Cl_2Br_4$ have the same or nearly related crystallographic symmetry and cell dimensions, and presumably similar structures (Section III, B). Their infrared absorption spectra (*64*) also show that the order of the P-N bond exceeds unity.

There is some thermochemical evidence of bond-strengthening. S. B. Hartley (*2*) has found the heat of formation of crystalline triphosphonitrilic chloride to be $\Delta H_f = -196.3 \pm 3$ kcal/mole. By making some reasonable assumptions, the P-N bond energy is found to be 75-80 kcal/mole, appreciably greater than that expected for a single bond.

2. Tetrameric Compounds

In the tetrameric chloride crystal, the ring is puckered, with S_4 symmetry, though with equal bond lengths round the ring (*45*). This may be contrasted with the most recent data for cyclooctatetraene, which has been proved (*5*) to have the D_{2d} configuration in the vapor phase, with the unequal bond lengths C=C = 1.334 ± 0.001 Å, C—C = 1.462 ± 0.001 Å.

The spectroscopic data on the tetrameric chloride (*24*) conflict with the crystal structure determination. A larger number of fundamentals in both Raman and infrared, and of coincidences between them, would be expected than are in fact observed. The molecule must therefore have a higher symmetry in solution than in the crystal, and the data are most nearly in accord with a planar model of symmetry C_{4h}, though D_{2d} symmetry is not excluded.

The crystal structure of the tetrameric fluoride is at present being determined (F. R. Tromans, *2*). No detail is at present available, but the space-group determination shows that the molecule is centrosymmetrical.

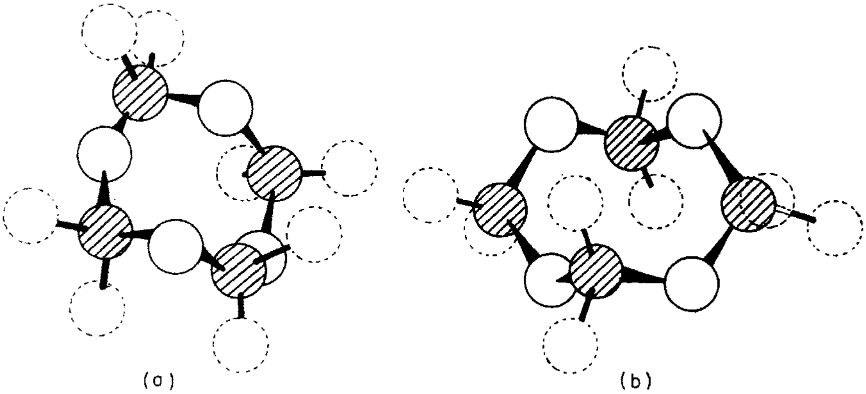


FIG. 4. The structure of (a) tetraphosphonitrilic chloride and (b) tetraphosphonitrilic fluoride. The phosphorus atoms are shaded and the halogen atoms dotted.

The phosphorus atoms must therefore lie in a plane, and the nitrogen atoms in another intersecting it, the configuration being similar to the eight-membered ring in octamethyl tetrasiloxane (*83*). It is unlikely that these planes coincide. The resulting ring, of C_{2h} symmetry, is, however, more nearly planar than that in the chloride. The two rings, which may be regarded as boat and chair forms, are illustrated in Fig. 4. The ends of the boat or chair are formed from two atoms each, rather than one as in the cyclohexane series.

3. Medium Polymers

a. General. There is no certain knowledge of the structure of the higher polymers, until the rubberlike high polymer is reached. Cyclic structures for the pentamer upwards have been accepted only reluctantly, involving as they do rings of ten members or more. It is, however, difficult to write a linear structure for $(PNCl_2)_n$ except as a di-radical or a highly polar entity.

There is no sign of behavior as a radical; the thermal stability of the carefully purified pentamer and hexamer is of the same order as that of the trimer and tetramer. The second possibility can be ruled out, since the dipole moments are all small, being of the order of 0.5 D (*46*) (Section III, B), and show no large differences as the series is ascended. The mixture of composition $(PNCl_2)_{8\text{-}9}$ has a comparably low polarity (H. T. Searle, *2*).

The evidence is strengthened by the preparation from the cyclic trimer or tetramer of the related linear compounds $(PNCl_2)_n \cdot PCl_5$ (Section II, C), which have quite different properties. The stable existence of such large rings has in any case seemed less unreasonable since the isolation of the separate members of the cyclic dimethylsiloxane series $(Me_2SiO)_n$ up to the nonamer, which has a 18-membered ring (see p. 80 in ref. *65*).

While the balance of evidence is therefore in favor of a cyclic formulation for all compounds $(PNCl_2)_n$ except the elastomer, a direct crystal structure determination of the pentamer or higher polymer would be of great value.

b. Spectroscopic Data. The ultraviolet absorption spectra of several members of the series have been published (*46*). Figure 5 includes the spectra of the trimeric to hexameric chlorides obtained by D. R. Smith (*2*) (cf. Krause, *46*), and of a phosphonitrilic oil, approximately $(PNCl_2)_8$. They differ characteristically from those of the end-stopped polymers (Fig. 1).

Since the spectra show little change in position or intensity as the series is ascended, π-π^* transitions are excluded. Figure 6 shows that the spectra are comparatively slightly affected by solution of the chlorides in sulfuric acid; absorption cannot, therefore, be due to an n-π^* transition from the nitrogen atom. It may be a result of excitation of the unshared electrons on the halogen atoms, consistent with the effect of bromine substitution on the position and intensity of the absorption band. The ultraviolet spectra therefore give no direct information on the structure of the ring.

The infrared spectra of trimer to heptamer have been published (*46*) though so far complete interpretation is restricted to the two lowest members (*24*). There is a common feature, however, in the very strong absorption in the 1200-1350 cm^{-1} region, principally contributed by the P-N stretching vibration. Daasch and Smith (*25*) examined the infrared absorption spectra of the phosphonitrilic esters, and showed that the

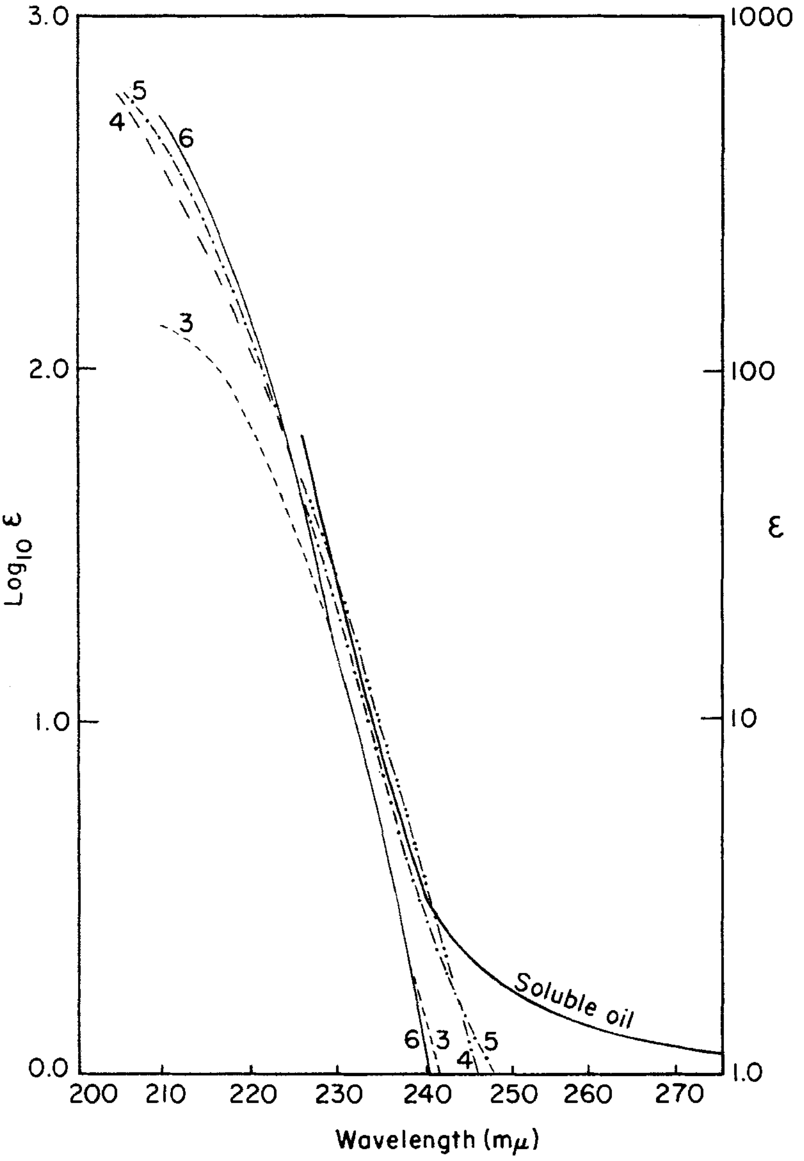


FIG. 5. The ultraviolet absorption spectra of the phosphonitrilic chlorides. Molar extinction coefficient ε calculated on a $PNCl_2$ monomer basis. KEY: — — — trimer; —·—·— tetramer; —··—··— pentamer; ——— hexamer; ——— soluble oil (approximately octamer); numbers denote n in $(PNCl_2)_n$. The molar extinction coefficient is calculated on a $PNCl_2$ monomer basis.

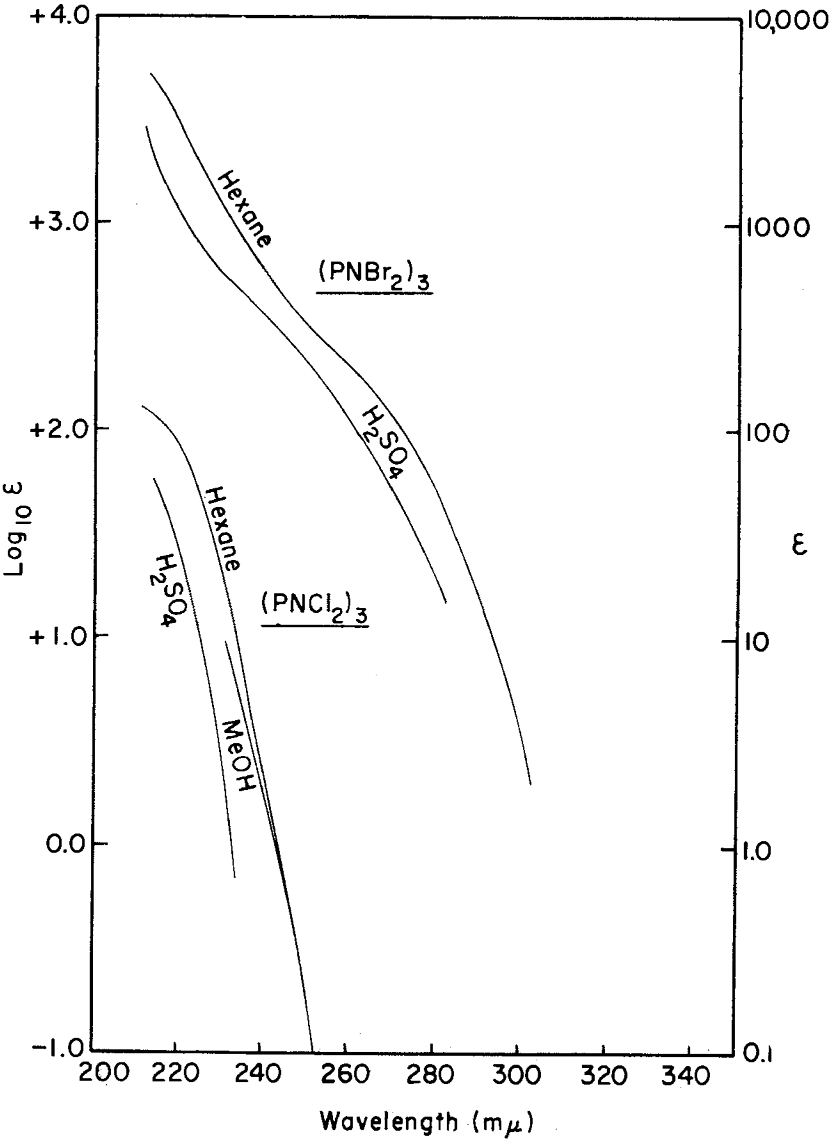


FIG. 6. The effect of solvents on the ultraviolet absorption spectra of $(PNCl_2)_3$ and $(PNBr_2)_3$. The molar extinction coefficient is calculated on a $PNCl_2$ or $PNBr_2$ monomer basis.

P-N stretching frequency was only slightly affected by the mass of the substituent over the range CH_3O to $C_8H_{17}O$. This frequency is therefore characteristic of the ring itself, and, provided due account is taken of other contributing factors, may be used as a measure of its stability.

It is principally dependent on the electronegativity of the atom attached to the ring, frequency increasing steadily with electronegativity, as shown in Table V.

TABLE V

THE P-N STRETCHING FREQUENCIES OF THE PHOSPHONITRILIC HALIDES

Compound	P-N stretching frequency (cm^{-1})	Reference[a]
$(PNBr_2)_3$	1170	*2*
$(PNCl_2)_3$	1218	*24*
$(PN(OMe)_2)_3$	1242	*25*
$(PNF_2)_3$	1287	*2*
$(PNF_2)_4$	1322	*2*
$(PNCl_2)_4$	1305	*24*
$(PNCl_2)_5$	1325	*2*
$(PNCl_2)_6$	1324	*2*
$(PNCl_2)_{8-9}$	1291	*2*
$(PNCl_2)_{8-9} \cdot PCl_5$	1240	*2*
$(PNCl_2)_n$ (rubber)	1365-1380	*2*

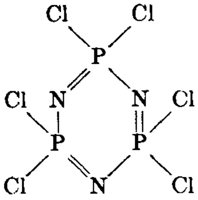
[a] Reference *2* identifies work carried out by A. C. Chapman.

4. High Polymer

Meyer *et al.* (*53*) examined the X-ray fiber pattern of the stretched high polymer, and with some assumptions based on a consideration of other phosphorus compounds, calculated the form of the chain. It has the helical configuration common in polymers, the set of chlorine atoms forming a screw of opposite hand to that of the phosphonitrilic skeleton. The principles of construction seem to be the maintenance of P-N-P and N-P-N angles close to those found in the lower polymers, and a dihedral angle which minimizes the repulsion of nonbonded atoms.

C. STRUCTURAL THEORY

The evidence from X-ray, spectroscopic, and thermochemical investigations considered in the previous sections shows clearly that the lower phosphonitrilic chlorides possess cyclic structures which exhibit a high degree of stability, suggestive of aromatic character. Such a view of their structure is compatible with their low reactivity compared with other acid chlorides, and with the maintenance of the ring structure in a variety of derivatives. It is easy to write Kekulé-type structures for the trimeric chloride (III); such structures have also been suggested



(III)

for the tetrameric chloride (*45*). The way in which aromatic character can arise in these compounds will be considered in the present section; it will be seen that there are important differences from aromatic series which involve only boron, carbon, or nitrogen.

In benzene the situation is clear and well-known. Three of the four valency electrons of each carbon atom may be regarded as occupying sp^2 hybrid orbitals, mutually spaced at angles of 120° in a plane; overlap of the orbitals of adjacent carbon atoms provide for a hexagonal ring firmly held together by σ-bonds at their natural angle. A hydrogen atom is attached to each carbon atom in the plane of the hexagon, and in the direction of the third sp^2 orbital. The fourth electron occupies a p_z orbital perpendicular to the plane; overlap between these orbitals round the ring gives rise to the characteristic delocalization and its consequences of short and strong bonds.

The lowest state has full circular symmetry and is nondegenerate; it can therefore accommodate two electrons. The next higher state is doubly degenerate, the two orbitals having each a nodal plane perpendicular to the ring and to each other, the combination having full circular symmetry and therefore exhibiting the characteristics of a closed shell. Six electrons complete the two lowest shells, accounting for the special stability of benzene. The next highest level is also doubly degenerate, so that a set of eight electrons (e.g., in cyclooctatetraene) corresponds to a half-filled uppermost shell and no special stability; aromaticity would be expected to occur next in the ten-electron system of cyclodecapentaene (*42*).

There are, however, significant differences when silicon, phosphorus or sulfur is included in the ring, since the possibility arises of using d-orbitals for π-bonding (*21*). These differences show up particularly clearly in the phosphonitrilic halides. In these compounds the electrons of the nitrogen atom may, to a first approximation, be regarded as occupying sp^2 hybrid orbitals, one in each bond to a phosphorus atom, two in a lone pair. The fifth electron can use a p_z orbital for the formation of a π-bond, as in pyridine. The phosphorus atom has five electrons for four bonds, arranged tetrahedrally. Again to a first approximation, we may think of these bonds as formed from sp^3 hybrid orbitals, leaving a d-orbital for π-bonding. The important difference is that a d-orbital has g-symmetry with respect to inversion at its center, whereas the adjacent p-orbitals have u-symmetry, and for maximum overlap must alternate in sign, as shown in Fig. 7. The repeating unit therefore consists of two PN units, and there is inevitably a mismatch of sign in the trimer, which has three such units. The trimer may therefore be expected to have a lower energy per π-electron than the tetramer, in which the signs can be matched all round the ring.

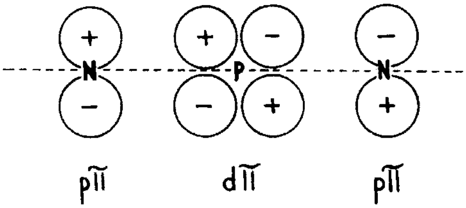


FIG. 7. The system of overlapping orbitals responsible for $d\pi$-$p\pi$ bonding.

A simplest possible molecular orbital treatment of the π-electrons (*23*) shows that the symmetry properties have a deeper significance, in that they require the highest filled orbital to be nondegenerate, so that any even number form a closed shell. By contrast, if the aromatic system is formed solely from p-orbitals, the lowest filled orbital only is nondegenerate, leading to Hückel's rule, that closed shells are formed only from $4n + 2$ electrons. Benzene is aromatic, cyclooctatetraene is not, corresponding to the calculated difference of π-electron energies and the alternating bond-lengths in cyclooctatetraene.

On the other hand, all the phosphonitrilic chlorides display comparable aromaticity. The assumption of a particular difference in electronegativity between phosphorus and nitrogen allows the calculation of π-electron energies in terms of the appropriate resonance integrals. Table VI compares the aromatic hydrocarbons and the phosphonitrilic chlorides. The calculated energies per electron relative to the Coulomb parameters α_C and α_P are expressed in terms of the appropriate resonance

TABLE VI

CALCULATED ENERGIES PER ELECTRON, IN TERMS OF THE APPROPRIATE RESONANCE INTEGRALS

No. of electrons		4	6	8	10	12
Aromatic hydrocarbons	$\alpha_c +$	1.0β	1.33β	1.20β	1.30β	1.24β
$(NPCl_2)_n$	$\alpha_p +$	1.78δ	1.87δ	1.89δ	1.90δ	1.90δ

integrals β and δ. It must be emphasised that the steady increase in π-electron energy in the phosphonitrilic series is a result of the symmetry, not of any particular arithmetical assumptions. Any even number of electrons forms a closed shell, and therefore has aromatic properties associated with it.

V. Discussion

A. FURTHER ASPECTS OF THE THEORY

There are two further aspects of the theory which are important in its application to the phosphonitrilic series. The first is that a $3d$ orbital is normally too diffuse to overlap effectively with a $2p$ orbital (*22*); it becomes sufficiently compact to do so in the present instance only if a partial positive charge is induced on the phosphorus atom by electronegative substituents attached to it.

The second aspect concerns the geometry of the system. It is assumed in the theory that the ring is planar, though since the *d*-orbitals have considerable lateral extension, this requirement is of smaller importance than in the series of aromatic hydrocarbons. The phosphonitrilic halides may therefore be expected to exhibit some flexibility without appreciable loss of aromatic character. At some stage, however, a limit will be reached. As the ring continues to increase in size, the steady increase in π-electron energies will be increasingly offset by folding of the ring and consequent partial uncoupling of the π-electrons, so that the observed energies should pass through a maximum.

The existence and main properties of the series of phosphonitrilic halides can be accounted for in these terms, even though only a small proportion of the valency electrons is considered by the theory, and in spite of the neglect of σ-π interaction, which must be more important here than in the hydrocarbon series. Other factors which influence stability will become apparent in Section V, C.

B. CHARGE DISTRIBUTION EFFECTS

The shortness and equality of the P-N bonds in the trimeric and in the tetrameric chloride have been demonstrated in Section IV,B. The thermochemical evidence for a bond order greater than unity in the trimeric chloride is confirmed by the high value of the observed P-N stretching frequency, which is maintained or even increased as the series is ascended. The effect of mass on ring vibration frequencies is not large (*24*, *25*), so that the higher and lower infra-red absorption frequencies characteristic of the phosphonitrilic fluorides and bromides, respectively, are indications of their relative bond strengths, and are consistent with the aromatic theory.

The phosphonitrilic halides are weaker bases than are some related nonaromatic compounds, just as pyridine is a weaker base than piperidine. The bond type in the phosphonitrilic series is probably the same as in the phosphine-imines $R_3P{:}NR$ (*80, 81*); the stability of these compounds, too, increases with the electronegativity of the substituents on the phosphorus. Tetraphenylphosphine-imine is one of the most stable of these compounds, and forms a hydrochloride. Its base strength is therefore greater than those of the phosphonitrilic halides, presumably because the opportunities for electronic delocalization are less. The *N*-ethyl ester of the trimeric phosphonitrilic acid, which has a cyclic structure, but in which resonance of the same type as in the phosphonitrilic halides cannot occur, also forms a hydrochloride (*61*). It is, therefore, a comparatively strong base, in spite of the inductive effect of the two oxygen atoms on the phosphorus. The extreme weakness of the phosphonitrilic halides as bases cannot therefore be wholly due to the inductive effect of the halogens.

The connection between aromatic character and base strength is confirmed by comparisons between members of the phosphonitrilic chloride series. The calculated difference in π-electron energy between the trimer and tetramer (Table VI) is greater than between successive higher members. The P-N bond stretching frequency (Table V) in the trimer is appreciably less than in the tetramer; correspondingly, the base strength of the trimer (Fig. 2) is the greater. As the series is ascended, successive differences between frequencies and between base constants become smaller, as expected, though it would be unwise to draw too detailed conclusions from their numerical values.

The trimeric bromide is a stronger base than the chloride; the fluoride is weaker again, since it is by far the least soluble in sulfuric acid. Qualitative observations show that ease of attack by nucleophilic reagents decreases with increasing base strength. In the absence of aromaticity, different effects occur. Skrowaczewska and Mastalerz (*77*) investigated the action of hydrogen chloride on compounds of the type $R_2N \cdot PO(OR)_2$, where the substituents *R* may be the same or different. The P-N bond is presumably single. The products of the reaction are the amine hydrochloride and the chloro-ester. Substituents which increase the base strength increase susceptibility to attack, the proposed mechanism involving the intermediate formation of a salt

$$R_2N{\cdot}PO(OR)_2 + HCl \rightleftharpoons [R_2\overset{+}{N}H{\cdot}PO(OR)_2]Cl^- \qquad (5)$$

the positive charge facilitating attack on the phosphorus by the chlorine atom of another hydrogen chloride molecule.

This possibility is not open to the phosphonitrilic halides, which are, by reason of their aromatic character, too weakly basic to form hydrochlorides. The partial positive charge on the phosphorus atom and its reactivity to nucleophilic reagents therefore increases with the electronegativity of the attached groups. The basicity of the nitrogen is thereby diminished as a secondary effect.

The charge separation which has been mentioned in Section V, A. as being one of the characteristics of $d\pi$-$p\pi$ aromaticity can cause stabilization in its own right, by electrostatic interaction in the sense P^+N^-. One would certainly expect structures of this type to be very flexible, and the larger rings to be stable. A similar polar bond Si^+O^- has been suggested to account for the high internal mobility observed in the siloxane series (*67*). This effect cannot, however, be a major factor in the phosphonitrilic series, because it would require the strongest base to exhibit the highest P-N stretching frequency, contrary to observation.

C. GEOMETRICAL EFFECTS

More detailed consideration of the tetrameric halides brings out some of the other factors which affect stability. On the simple theory, the tetramer should be more aromatic than the trimer, and should be planar. The evidence on both points is conflicting. The relative magnitudes of the P-N stretching frequency and the relative base strengths of the trimeric and tetrameric chlorides suggest the greater aromaticity of the tetramer; the relative bond lengths and the puckered structure of the tetrameric ring suggest the contrary.

As noted above, coplanarity is not likely to be such an important requirement for $d\pi$-$p\pi$ as for $p\pi$-$p\pi$ bonding. Hybridization of the sp^2 type at the nitrogen would require an N-P-N angle of 150° for a flat ring. Steric requirements for strong σ- and π-bonding may well, therefore, conflict to some extent with resultant puckering to a boat form and lengthening of the P-N bond from 1.61 Å in the trimeric chloride to 1.67 Å in the tetrameric chloride. This figure is still well below the 1.78 Å determined for a single P-N bond (*39*).

Inter- and intramolecular forces between the large nonbonded chlorine atoms are also likely to be important, as shown by the structural change which takes place on dissolution and which may account in part for the discrepancies noted above. In the tetrameric fluoride, however, not only is the aromaticity accentuated by the electronegative substituent, but, since the halogen atoms are smaller, they interact less strongly The more nearly planar chair form is therefore adopted.

There is no detailed structural knowledge of the medium polymers, though the infrared spectra do allow a comparison of the P-N stretching frequencies of the individual members. As an indication of aromatic character, however, the observed frequency must be used cautiously. This is because molecular vibrations are not independent of one another, and even if it were possible to isolate a pure bond-stretching constant, it would be a measure of the total bond strength, not merely of the contribution of the π-electrons. Nevertheless, it is consistent with the present theory that the P-N frequency (Table V) should increase to a maximum with increasing ring size, decrease with increasing folding of the ring, and increase again to its highest value in the rubber-like high polymer, in which steric inhibition of mesomerism should be least.

Tentative confirmation of this view is provided by another general feature of the infra-red spectra. As the chloride series is ascended, absorption near 750 cm^{-1}, which is absent in the trimer, increases in intensity, as shown in Fig. 3. Although an aromatic phosphonitrilic ring should be fairly flexible, a high degree of folding, which must occur in the pentamer upwards, would be expected to lead to uncoupling of the π-electrons and the formation of single bonds, with a characteristic absorption in the region observed. The assignment of the frequency must be regarded at present, however, only as a working hypothesis.

A further feature of the theory (*23*) is that, because the highest filled orbital is nondegenerate, a phosphonitrilic dimer would be expected to be less unstable relative to the trimer than is cyclobutadiene to benzene. The dissociation of $P_4N_4F_2Cl_6$ and $P_4N_4F_4Cl_4$ (Section III, C, 1), probably to dimeric forms, is suggestive but not conclusive; $P_3N_3F_6$ and $P_4N_4F_8$ are reported to be stable to 300° (*75*) and $P_4N_4Cl_8$ to 445° (*73*).

D. A GENERAL ELIMINATION REACTION

The formation of phosphonitrilic chlorides by ammonolysis of phosphorus pentachloride is considered (Section II, D) to proceed by formation of ammonium hexachlorophosphate, followed by elimination of hydrogen chloride and a series of related condensation processes. Similar reactions are quite common in inorganic chemistry, as will be seen below.

Their common feature is that the transfer of charge characteristic of intermediate salt or complex formation between donor and acceptor molecules facilitates simultaneously the release of positive and negative groups from adjacent atoms. In ammonium hexachlorophosphate, for example, the formation of the salt reduces electrostatic interaction, making easier the removal of the hydrogen atoms as protons. A chloride ion would be easily detached from a hexachlorophosphate ion.

There are many examples involving ammonium ions; for instance, the decomposition of ammonium nitrate to nitrous oxide. Ammonium tetraphenylborate on heating yields benzene, ammonia, and triphenyl boron (*94*).

$$NH_4BPh_4 \rightarrow NH_3 + C_6H_6 + Ph_3B \qquad (6)$$

From tetramethylammonium chloride and lithium borohydride the thermally stable tetramethylammonium borohydride is produced (*4*), supporting the hypothesis that a comparable salt is formed intermediately in the reactions of borohydrides with ammonium chloride to give borazole (*69*),

$$NH_4Cl + LiBH_4 \rightarrow [NH_4BH_4] \rightarrow \tfrac{1}{3}(BH \cdot NH)_3 + 3H_2 \qquad (7)$$

or with methylammonium chloride to give *N*-trimethyl borazole (*68*).

$$Me_3NH_3Cl + LiBH_4 \rightarrow [NH_3Me \cdot BH_4] \rightarrow \tfrac{1}{3}(BH \cdot NMe)_3 + 3H_2 \qquad (8)$$

The reaction of boron trichloride with ammonium chloride is even more nearly analogous to that of phosphorus pentachloride (*48*),

$$NH_4Cl + BCl_3 \rightarrow [NH_4BCl_4] \rightarrow \tfrac{1}{3}(NH \cdot BCl)_3 + 3HCl \qquad (9)$$

The corresponding ammonium tetrafluoroborate, like ammonium hexafluorophosphate, is stable to heat, and does not give the *B*-trifluoroborazole.

The reaction is not restricted to phosphorus, silicon, and boron compounds; the tetrameric $(NSEt)_4$ is, for instance, formed from ethylamine hydrochloride and sulfur dichloride (*49*). Nor is it restricted to nitrogen compounds; the very stable cyclic phosphinoborines are formed by elimination of hydrogen from the dimethyl-phosphine borine complex (*17*).

The initial charge separation makes the reaction possible; its completion clearly requires stability of the products, which may be attained in different ways. In the borazoles and the phosphonitrilics, aromatic character is postulated, and if conditions do not allow its development cyclization is discouraged. In the phosphonitrilic series, the strength of the π-system increases with the electronegativity of the substituents on the phosphorus, so that it is perhaps not surprising that derivatives of phosphorus pentachloride carrying groups of low electronegativity like methyl do not easily give cyclic polymers on treatment with ammonium chloride.

VI. Conclusion

The phosphonitrilic chlorides have normally occupied a somewhat uncomfortable place in textbooks of inorganic chemistry, in that although they contain no carbon, in their properties they resemble organic rather than inorganic compounds. This review will have succeeded in its purpose if it has demonstrated their systematic relation to other groups of compounds, both organic and inorganic, through the mode of their formation and their properties. Their theoretical treatment as π-electron systems extends the conventional modes of thought, applicable particularly to aromatic hydrocarbons, and can act as a guide to further experimental work.

The range of experimental methods employed has not so far been very wide; further work on the spectroscopic, thermochemical, and magnetic properties and on the kinetics of the formation and substitution reactions can be expected to be illuminating. Most work has been done on the trimeric chloride, the lowest stable member of the series, and the most abundant. As in the boron hydride series, significant advances are likely to result from investigations of the higher polymers.

List of Symbols

a, b, c	Unit cell dimension (Ångstrom units, Å)
α, β, γ	Angles between triclinic cell axes; in monoclinic systems $\beta =$ angle between a and c axes (degrees) *Or:* Refractive indices of biaxial crystal in increasing order of magnitude (numbers)
ϵ, ω	Extraordinary, ordinary, refractive indices of uniaxial crystal
$2V$	Optic axial angle (degrees)
T	Absolute temperature
mp, bp	Melting point, boiling point
vp	Vapor pressure; following letter denotes the condensed phase
d	Density; measured except where otherwise stated. The subscript denotes the temperature in degrees Centigrade
(c), (l)	Crystal, liquid
coef. cu. exp.	Coefficient of cubical expansion
ΔH_f	Standard heat of formation
ΔH_{subl}	Latent heat of sublimation
ΔH_{fus}	Latent heat of fusion
ΔH_{vap}	Latent heat of vaporization
μ	Dipole moment (Debye units, D) *Or:* 10^{-4} cm; m$\mu = 10^{-7}$ cm
n-π^*	Electronic transition of nonbonded electrons to a higher antibonding level
π-π^*	Electronic transition from a π-ground state to a higher antibonding level
ε	Molar extinction coefficient
$E^{1\%}_{1\text{cm}}$	Extinction coefficient, path length 1 cm, concentration 1% (^{w}/v)
Z	Number of molecules per unit cell.
Pnam	This and other space-group symbols are explained in "International Tables for X-ray Crystallography," Kynoch Press, 1952.

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* Other references to early work may be found in Audrieth *et al.* (*3*). Ref. *2* identifies work done by members of the Research Department of Albright & Wilson (Mfg.) Ltd. Full publication may be expected during 1958-59, particular contributions being traceable through the name quoted in the text.

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