Contribution from the Department of Chemistry,
University of Nottingham, Nottingham, United Kingdom

Cyclic Inorganic Compounds. V.* Chlorobromotriphosphonitriles

G. E. Coxon and D. B. Sowerby

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Mixed chlorobromotriphosphonitriles have been prepared both by partial ammonolysis of mixed phosphorus(V) halides and by the reaction between mercury(II) chloride and trimeric bromophosphonitrile. In each case mixtures result which can be separated by gas-liquid chromatography. Phosphorus-31 nuclear magnetic resonance and infrared spectroscopy indicate that the compounds obtained by the mercury(II) chloride reaction are the non-geminally substituted compounds.

Introduction

The preparation of three members, i.e. $P_3N_3Cl_5Br$, $P_3N_3Cl_4Br_2$ and $P_3N_3Cl_2Br_4$, of the series of mixed chlorobromotriphosphonitriles by an adaptation of Schenck and Römer's chlorophosphonitrile synthesis[1] was reported by Rice *et al.*;[2] no tetrameric species were isolated from the reaction products. Steger and Rost[3] however, on the basis of changes in melting point and infrared spectra on fractional crystallization of these products from benzene, showed them to be mixtures. Both Rotzsche *et al.*[4] and the present authors[5] showed that it was not possible to obtain pure compounds from these systems by fractional crystallization, but that all members of the series, $P_3N_3Cl_xBr_{6-x}$ (where x=0-6), could be separated by gas-liquid chromatography. We now report details of the separation of mixed chlorobromophosphonitriles, their characterization and an alternative method for their preparation.

Experimental Section

Reaction of phosphorus pentachloride and ammonium bromide in 1,1,2,2-tetrachloroethane. The method was that described previously[2] using phosphorus pentachloride (157 g, 0.76 mole) and ammonium bromide (150 g, 1.53 mole). The residue after evaporation of the tetrachloroethane was crystallized from light petroleum and yielded 20 g of white solid, m.p. 129-131°. Attempts to obtain pure compounds from this solid by an extended series of fractional crystallizations from light petroleum were unsuccessful. Fractions with sharp melting points and increasing molecular weights were obtained; those with molecular weights of 418, 437, 467 and 504 had melting points 122°, 128°, 137° and 149° respectively. Examination by mass spectrometry however showed that all were mixtures of various trimeric chloride bromides. A fraction (m.p. 133-5°) was obtained which had an intense infrared absorption at 1285 cm^{-1} and a molecular weight of 489. This was thought to be $P_4N_4Cl_7Br$ (M, 494) but the mass spectrum (see Figure 1) showed the sample contained not only the tetrameric compounds $P_4N_4Cl_xBr_{8-x}$ (where x=2-8) but most of the possible trimeric chloride bromides also.

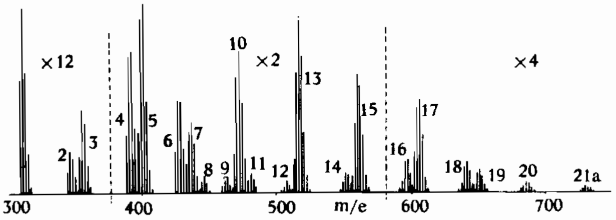


Figure 1. Partial Mass Spectrum of «Tetrameric Fraction».
1, $P_3N_3Cl_5^+$; 2, $P_3N_3Cl_6^{+\cdot}$; 3, $P_3N_3Cl_4Br^+$;
4, $P_3N_3Cl_5Br^{+\cdot}$; 5, $P_3N_3Cl_3Br_2^+$; 6, $P_4N_4Cl_7^+$;
7, $P_3N_3Cl_4Br_2^{+\cdot}$; 8, $P_3N_3Cl_2Br_3^+$; 9, $P_4N_4Cl_8^{+\cdot}$;
10, $P_4N_4Cl_6Br^+$; 11, $P_3N_3Cl_3Br_3^{+\cdot}$; 12, $P_4N_4Cl_7Br^{+\cdot}$;
13, $P_4N_4Cl_5Br_2^+$; 14, $P_4N_4Cl_6Br_2^{+\cdot}$; 15, $P_4N_4Cl_4Br_3^+$;
16, $P_4N_4Cl_5Br_3^{+\cdot}$; 17, $P_4N_4Cl_3Br_4^+$; 18, $P_4N_4Cl_4Br_4^{+\cdot}$;
19, $P_4N_4Cl_2Br_5^+$; 20, $P_4N_4Cl_3Br_5^{+\cdot}$; 21, $P_4N_4Cl_2Br_6^{+\cdot}$.

Reaction of phosphorus trichloride, bromine and ammonium bromide. The reaction between a 1:1 molar mixture of phosphorus trichloride and bromine and ammonium bromide in tetrachloroethane was carried out as described previously.[2] The product in this case was also a mixture of both trimeric and tetrameric chlorobromophosphonitriles.

Reaction of hexabromotriphosphonitrile with mercury(II) chloride. Preliminary experiments showed that the rate of halogen exchange between the phosphonitrile and excess of mercury(II) chloride in boiling p-xylene was very low but that extensive exchange occurred on heating the components in the absence of solvent. With a large excess of mercury(II) chloride (20:1 mole ratio) only hexachlorotriphosphonitrile was isolated. With smaller amounts, however, mixed chloride-bromides could be obtained.

(*) Part IV. G. E. Coxon, T. F. Palmer and D. B. Sowerby, *J. Chem. Soc.*, A, 1568 (1967).
(1) R. Schenck and G. Römer, *Ber.*, *57B*, 1343 (1924).
(2) R. G. Rice, L. W. Daasch, J. R. Holden and E. J. Kohn, *J. Inorg. Nuclear Chem.*, 5, 190 (1958).
(3) E. Steger and J. Rost, *J. Inorg. Nuclear Chem.*, *25*, 732 (1963).
(4) H. Rotzsche, R. Stahlberg and E. Steger, *J. Inorg. Nuclear Chem.*, *28*, 687 (1966).
(5) G. E. Coxon, T. F. Palmer and D. B. Sowerby, *Inorg. Nuclear Chem. Letters*, *2*, 215 (1966).

An intimate mixture of hexabromotriphosphonitrile (10 g, 0.016 mole) and mercury(II) chloride (13.2 g, 0.049 mole) was heated in a flask fitted with a short air condenser on a sand bath. The mixture melted at ~145° and the temperature of the melt then rose rapidly to ~240°. Heating was discontinued and the reaction was allowed to proceed spontaneously. After cooling, the product was extracted with light petroleum and yielded 5.6 g of white crystals (71% yield calculated as $P_3N_3Cl_3Br_3$). This material was a mixture of trimeric chlorobromophosphonitriles rather than a single product. The residue contained mixed mercury(II) halides together with a small amount of polymerized phosphonitrile.

In an experiment in which a 2:1 mixture of the trimeric bromide and mercury(II) chloride was heated only insoluble, highly polymerized halophosphonitriles were obtained. Attempts to moderate the reaction by using silica as an inert diluent were not successful. On the other hand, bromine was liberated, but no detectable halogen exchange occurred when the trimeric chloride was heated with mercury(II) bromide.

Separation of chlorobromophosphonitriles. The mixtures of chlorobromophosphonitriles from both the reaction of phosphorus and ammonium halides and by substitution of the trimeric bromophosphonitrile with mercury(II) chloride were separated into their components using an Autoprep, model 705 Gas Chromatograph. Aliquots of a benzene solution were injected directly on to a glass column (10ft by 3/8 inch) packed with 30% silicone oil (DC200) on silanized Chromosorb W at 200°. Very low recoveries were obtained when aluminium columns were used. The carrier gas was nitrogen at 65 p.s.i. and a flow rate of 200 ml/min.; a cross section detector was generally used. In some experiments, the detector was a flame ionization detector, modified by allowing the flame to burn through sodium sulphate.[6] Phosphorus is detected with this arrangement and the relative yields of the pure compounds from different preparations can be assessed. Mass spectrometry confirmed the identity of each of the separated compounds and showed that they were free from contaminants.

Infrared spectra. Spectra were measured on KBr pressed discs, Nujol mulls and CS_2 solutions between 4000 and 250 cm^{-1} using a Perkin-Elmer 521 spectrometer.

Nuclear magnetic resonance spectra. Phosphorus-31 resonances were obtained on benzene solutions on a Varian HA100 spectrometer.

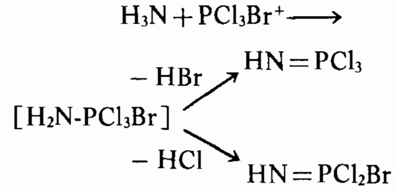
Mass spectra. A single focussing Atlas CH4 mass spectrometer with a high temperature inlet system was used in conjunction with a AN4 electron bombardment source.

Results and Discussion

The preparation of mixed chlorobromophosphonitriles can be approached by two routes. Modification of the method of Schenck and Römer[1] by using a phosphorus chloride-bromide mixture with an ammonium halide is one method. Such a system might be expected to be labile toward halogen exchange, and a variety of both trimeric and tetrameric products would then result. Rapid halogen exchange does occur, for example, between mixtures of various phosphorus halides[7] and between phosphorus bromides and 1,1,2,2-tetrachloroethane.[8,9]

The preparation of all members of the series $P_3N_3Cl_xBr_{6-x}$ by the reaction of phosphorus pentachloride and ammonium bromide implies that extensive halogen exchange processes occur in this system. During the reaction there is also evolution of a considerable amount of bromine.

In general, the preparation of halophosphonitriles is considered to proceed by Kirsanov reactions on halophosphonium cations and phosphinimine-type intermediates.[10] Mixed cations, i.e. $PCl_xBr_{4-x}^+$, must then be formed which react with ammonia liberating hydrogen halide, *e.g.*;



$$H_3N + PCl_3Br^+ \longrightarrow [H_2N\text{-}PCl_3Br] \begin{cases} \xrightarrow{-HBr} HN{=}PCl_3 \\ \xrightarrow{-HCl} HN{=}PCl_2Br \end{cases}$$

In this reaction preferential evolution of hydrogen chloride apparently occurs as bromine containing products predominate. Hydrogen chloride loss is favoured statistically in the case above but is also expected on the grounds of its higher volatility. This reaction and similar ones starting with mixed phosphorus halides are thus expected to yield not only the geminally and non-geminally substituted trimeric chlorobromophosphonitriles but also similar derivatives of higher homologues.

An inherently simpler alternative is *via* the exchange of the halogen atoms in either the hexachloro- or the hexabromotriphosphonitrile. Heavy metal compounds are used for these metatheses and extensive conversion series have been drawn up.[11] With organo-silicon or -tin compounds, it is usually possible to convert bromides into the corresponding chlorides by heating the compound with silver, mercury or lead chlorides. A similar reaction has now been shown to occur when hexabromotriphosphonitrile is treated with mercury(II) chloride. In refluxing p-xylene very slow exchange only occurred but heating an intimate mixture of the compounds allowed the preparation of the mixed halides. Gas-liquid chromatography showed that the product obtained when, for example, three moles of mercury(II) chloride were used consisted of all the trimeric chlorobromophosphonitriles, $P_3N_3Cl_xBr_{6-x}$, together with some of the completely chlorinated compound and the unchanged hexabromide. It did not seem possible to design experiments that would yield even predominantly one compound. It was not

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[6] C. H. Hartmann, Research Notes, Varian Aerograph, Summer (1966).

[7] J. C. Lockhart, *Chem. Rev.*, *65*, 131 (1965).

[8] T. Moeller and P. Nanelli, *Inorg. Chem.*, *1*, 721 (1962).

[9] G. E. Coxon and D. B. Sowerby, *J. Chem. Soc.*, *A*, 1566 (1967).

[10] M. Becke-Goehring and E. Fluck, *Angew Chem. Int. Ed.*, *1*, 281 (1962).

[11] C. Eaborn, *J. Chem. Soc.*, 3077 (1950).

possible to brominate the trimeric chloride by reaction with mercury(II) bromide and it has recently been shown that no exchange occurs with boron tribromide.[12]

The relative retention times together with the melting points of products separated from the mercury chloride reaction are listed in Table I. Corresponding data for compounds separated from the PCl_5-NH_4Br and PCl_3Br_2-NH_4Br reactions are very similar. The linear relationship between log (retention time) and bromine content of these compounds is confirmed,[4] and it has been shown that the pure compounds do not rearrange while passing through the column.

Table I. Melting Points and Retention Times of $P_3N_3Cl_{6-x}Br_x$

Compound	Retention Time, R_f (min)	Relative R_f	$\log_{10} R_f$	m.p. (°C) (PCl_5-NH_4Br method)	m.p. (°C) ($P_3N_3Br_6$-$HgCl_2$ method)
$P_3N_3Cl_6$	3.0	1	0.48	112	112
$P_3N_3Cl_5Br$	3.8	1.26	0.58	119	120
$P_3N_3Cl_4Br_2$	5.4	1.80	0.73	129	131
$P_3N_3Cl_3Br_3$	7.2	2.40	0.86	142	143
$P_3N_3Cl_2Br_4$	10.2	3.40	1.01	159	157
$P_3N_3ClBr_5$	14.4	4.80	1.16	175	175
$P_3N_3Br_6$	20.7	6.90	1.32	192	192

An attempt to separate the crude product from the reaction between PCl_3Br_2 and NH_4Br by gas-liquid chromatography was not completely successful. Mass spectrometric examination showed that pure trimeric compounds containing up to four bromine atoms were obtained but the fraction with a retention time corresponding to $P_3N_3ClBr_5$ was extensively contaminated with $P_4N_4Cl_4Br_4$. Although tetrameric compounds are found in much smaller amounts than trimers, it is desirable that they should be separated by preliminary fractional crystallizations. We have previously reported that pure $P_3N_3ClBr_5$ can be separated from the crude trimeric bromide prepared from phosphorus pentabromide and ammonium bromide in tetrachloroethane as solvent.[9]

An attempt has been made to assess the relative yields of the chloride bromides from the areas of the peaks on chromatograph traces obtained using the modified flame ionization detector. These figures are included in Table II and indicate the relative yields of the possible compounds from a mercury(II) chloride reaction and from that between PCl_3Br_2 and NH_4Br. The former reaction gives predominantly unchanged $P_3N_3Br_6$, while the latter gives mainly $P_3N_3Cl_3Br_3$ and $P_3N_3Cl_2Br_4$.

Table II. Percentage Yield of Products from PCl_3Br_2-NH_4Br and $P_3N_3Br_6$-$HgCl_2$ Reactions

Compound	PCl_3Br_2-NH_4Br method	$P_3N_3Br_6$-$HgCl_2$ method
$P_3N_3Cl_6$	2.3	9.0
$P_3N_3Cl_5Br$	7.2	8.9
$P_3N_3Cl_4Br_2$	15.0	12.1
$P_3N_3Cl_3Br_3$	25.0	12.5
$P_3N_3Cl_2Br_4$	23.5	6.8
$P_3N_3ClBr_5$	16.9	5.6
$P_3N_3Br_6$	10.0	45.2

Although apparently single gas chromatograph peaks were obtained for each component of the separated mixtures, this does not rule out the presence of mixtures of isomers. Isomerism in substituted trimeric phosphonitriles has been discussed by Audrieth[13] and by Shaw, Fitzsimmons and Smith.[14] If optical isomers are neglected, there are three possible forms for both di- and tri-substituted triphosphonitriles. A disubstituted compound, $P_3N_3X_2Y_4$, may occur in a form in which the two X groups are attached to the same phosphorus atom (the 1,1- or geminal form) and in two forms, i.e. the *cis* and *trans* isomers, in which the substituents are on different phosphorus atoms (the 1,3- or non-geminal forms). One 1,1,3- (geminal) and two 1,3,5- (non-geminal) trisubstituted forms are similarly possible for a compound $P_3N_3X_3Y_3$.

Nuclear magnetic resonance spectra. Phosphorus-31 nuclear magnetic resonance spectroscopy would distinguish between the geminally and non-geminally substituted compounds and the expected spectra for all the possible isomers are shown in Figure 2. Engelhardt *et al.*[15] have shown that the products from the ammonolysis of mixed phosphorus halides contain both the geminal and non-geminal isomers. These measurements have been confirmed and the chemical shifts associated with PCl_2, PClBr and PBr_2 units have been confirmed.

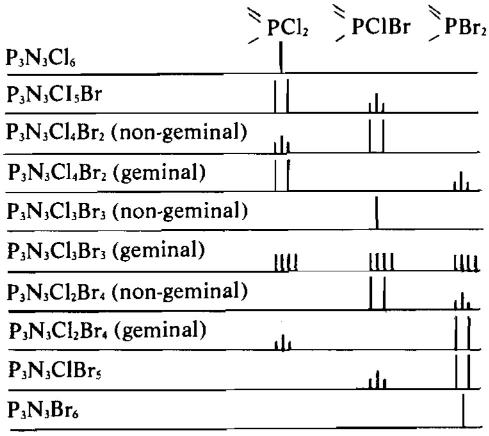

Figure 2. Predicted ^{31}P n.m.r. spectra for $P_3N_3Cl_{6-x}Br_x$ (x = 0-6).

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[12] P. M. Bruce, M. F. Lappert and P. N. K. Riley, *Chem. Comm.*, 486 (1967).

[13] L. F. Audrieth, *Rec. Chem. Progr.*, 20, 57 (1959).

[14] R. A. Shaw, B. W. Fitzsimmons and B. C. Smith, *Chem. Rev.*, 62, 247 (1962).

[15] G. Engelhardt, E. Steger and R. Stahlberg, *Z. Naturforsch.*, *21b*, 1231 (1966).

The products obtained from the chlorination of the trimeric bromide on the other hand show different n.m.r. spectra in agreement with the predictions in Figure 2. These indicate that, within the limits of detection, the compounds $P_3N_3Cl_4Br_2$ and $P_3N_3Cl_3Br_3$ are the pure non-geminally substituted isomers. The spectrum of $P_3N_3Cl_3Br_3$ shows a single signal at +9.8 p.p.m. with respect to 85% phosphoric acid rather than the pattern of three multiplets superimposed on a single signal observed for the mixture from the PCl_5-NH_4Br reaction. That for $P_3N_3Cl_4Br_2$ shows a triplet with a doublet of twice the intensity at higher field; this spectrum can only arise from a non-geminal arrangement of the bromine atoms.

It is not possible solely on the basis of the single ^{31}P signal to assign a *cis* configuration to the non-geminally substituted $P_3N_3Cl_3Br_3$. Although similar spectra arise from the *cis* isomers of $P_3N_3Br_3Ph_3$[16] and $P_3N_3Cl_3Ph_3$[17] (the corresponding *trans* compounds each show two distinct signals), the spectrum of $P_3N_3Cl_3(NMe_2)_3$ known to be the *trans* isomer also shows one signal only.[18] Infrared evidence, in fact, points to a *trans* configuration for the halogens in $P_3N_3Cl_3Br_3$.

Infrared spectra. There are definite differences, particularly between 400 and 700 cm^{-1} in the infrared spectra of samples of the di-, tri- and tetra-bromides obtained by the alternative preparative routes. Figures 3-7 contain this portion of the spectrum for each sample and for comparison purposes, similar sections of the spectra of $P_3N_3Cl_5Br$, $P_3N_3ClBr_5$, $P_3N_3Cl_6$ and $P_3N_3Br_6$ are included.

All the possible isomeric chlorobromophosphonitriles are of lower symmetry than the trimeric chloride and bromide; the point groups to which they belong are given in Table III. The assignments are made assuming that the P_3N_3 ring remains planar. For each compound, there will be thirty fundamental vibrations distributed as shown in Table III. Also included in the table are the numbers of infrared and Raman active vibrations for each possible compound.

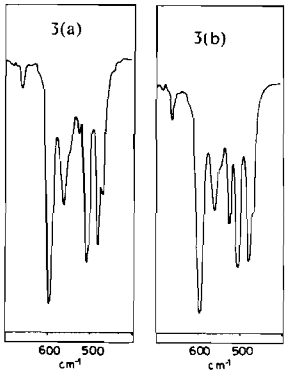

Figure 3. Infrared Spectrum of $P_3N_3Cl_4Br_2$. (a) Non-geminal isomer, (b) mixture of isomers.

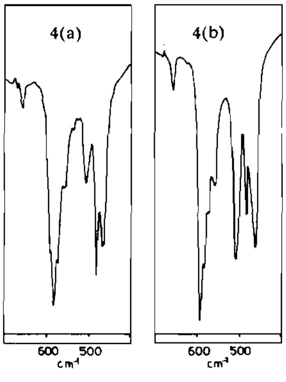

Figure 4. Infrared Spectrum of $P_3N_3Cl_3Br_3$. (a) Non-geminal isomer, (b) Mixture of isomers.

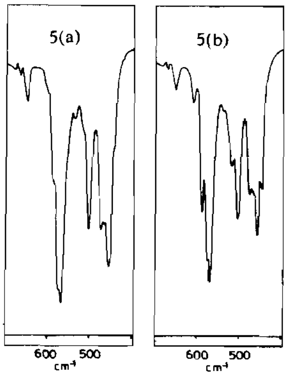

Figure 5. Infrared Spectrum of $P_3N_3Cl_2Br_4$. (a) Non-geminal isomer, (b) Mixture of isomers.

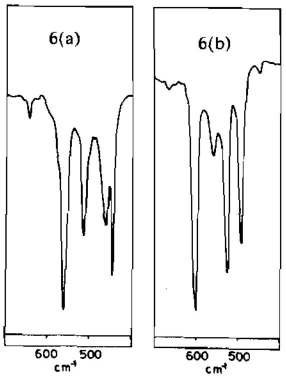

Figure 6. Infrared Spectra of (a) $P_3N_3ClBr_5$, (b) $P_3N_3Cl_5Br$.

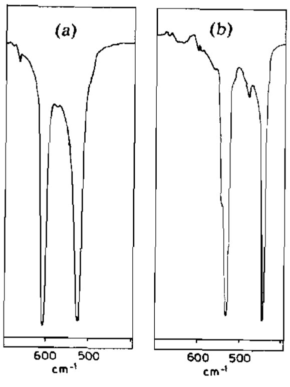

Figure 7. Infrared Spectra of (a) $P_3N_3Cl_6$, (b) $P_3N_3Br_6$.

Most of the ring vibrations and phosphorus-halogen stretching vibrations are expected in the region covered in the present investigation. The highest energy phosphorus-halogen deformation is however on the limit of the instrument and these are not considered in the following assignment of the spectra. The major absorption bands from carbon disulphide solution spectra are listed in Tables IV and V and tentative assignments of the ring vibrations and the phosphorus-halogen vibrations are given.

Ring Vibrations. These are listed in Table IV. A major feature of all the spectra is the highly intense absorption in the 1200 cm^{-1} region. This includes the (degenerate) in-plane ring stretching vibration, ν_{11} in Califano's notation[19] for $P_3N_3Cl_6$, and a lower energy combination band, $\nu_2+\nu_{12}$. The degeneracy of both the ring elongation, ν_{12}, at ~860 cm^{-1} and the in-plane ring bend, ν_{13}, at ~520 cm^{-1} should be lifted in the chloride bromides but there is little evidence of this. There are no added absorption bands similar to those found in the spectra of metal halide adducts of the phosphonitriles.[20,21] The absorption between 850 and 875 cm^{-1} is of medium intensity in all the compounds, but that at ~520 cm^{-1} decreases in intensity as bromine atoms are substituted by chlorine until $P_3N_3Cl_3Br_3$ is reached. As further chlorine atoms are introduced, the intensity rises again.

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(16) T. Moeller and P. Nanelli, *Inorg. Chem.*, *2*, 659 (1963).
(17) B. Grushkin, M. G. Sanchez and R. G. Rice, *Inorg. Chem.*, 3, 623 (1964).
(18) M. Becke-Goehring, K. John and E. Fluck, *Z. anorg. Chem.*, *302*, 103 (1959).

(19) S. Califano, *J. Inorg. Nuclear Chem.*, *24*, 483 (1962).
(20) M. F. Lappert and G. Srivastava, *J. Chem. Soc.*, 210 (1966).
(21) G. E. Coxon and D. B. Sowerby, unpublished results.

Table III. Distribution of Vibrational Modes of $P_3N_3X_{6-x}Y_x$ (x=0-3)

Vibrational Mode	$P_3N_3X_6$ D_{3h}	$P_3N_3X_5Y$ C_s	$P_3N_3X_4Y_2$ C_s (*cis*-non-geminal)	$P_3N_3X_4Y_2$ C_2 (*trans*-non-geminal)	$P_3N_3X_4Y_2$ C_{2v} (geminal)	$P_3N_3X_3Y_3$ C_{3v} (*cis*-non-geminal)	$P_3N_3X_3Y_3$ C_s (*trans*-non-geminal)	$P_3N_3X_3Y_3$ C_1 (geminal)
Ring stretch	$A_1'+A_2'+2E'$ (I2, R3) [a]	$3A'+3A''$ (I6, R6)	$3A'+3A''$ (I6, R6)	$3A+3B$ (I6, R6)	$3A_1+3B_2$ (I6, R6)	A_1+A_2+2E (I3, R3)	$3A'+3A''$ (I6, R6)	(I6, R6)
Ring deformation	$A_1'+A_2''+E'+E''$ (I2, R3)	$4A'+2A''$ (I6, R6)	$4A'+2A''$ (I6, R6)	$3A+3B$ (I6, R6)	$2A_1+A_2+2B_1+B_2$ (I5, R6)	$2A_1+2E$ (I4, R4)	$4A'+2A''$ (I6, R6)	(I6, R6)
PX_2 stretch	$A_1'+A_2''+E'+E''$ (I2, R3)	$2A'+2A''$ (I4, R4)	$2A'$ (I2, R2)	$A+B$ (I2, R2)	$A_1+A_2+B_1+B_2$ (I3, R4)	—	—	(I2, R2)
PX_2 deformation	$A_1'+A_1''+A_2'$ $+A_2''+2E'+2E''$ (I3, R5)	$4A'+4A''$ (I8, R8)	$2A'+2A''$ (I4, R4)	$2A+2B$ (I4, R4)	$2A_1+2A_2+2B_1+2B_2$ (I6, R8)	—	—	(I4, R4)
PY_2 stretch	—	—	—	—	A_1+B_1 (I2, R2)	—	—	(I2, R2)
PY_2 deformation	—	—	—	—	$A_1+A_2+B_1+B_2$ (I3, R4)	—	—	(I4, R4)
PX stretch	—	A' (I1, R1)	$A'+A''$ (I2, R2)	$A+B$ (I2, R2)	—	A_1+E (I2, R2)	$2A'+A''$ (I3, R3)	(I1, R1)
PY stretch	—	A' (I1, R1)	$A'+A''$ (I2, R2)	$A+B$ (I2, R2)	—	A_1+E (I2, R2)	$2A'+A''$ (I3, R3)	(I1, R1)
PX deformation	—	$2A'+2A''$ (I4, R4)	$4A'+4A''$ (I8, R8)	$4A+4B$ (I8, R8)	—	$2A_1+2A_2+4E$ (I6, R6)	$6A'+6A''$ (I12, R12)	(I4, R4)

[a] I is the number of infrared active vibrations, R the number of Raman active.

Table IV. Infrared Assignments of Ring Vibrational Modes

Assignment [a]	$P_3N_3Cl_6$	$P_3N_3Cl_5Br$	$P_3N_3Cl_4Br_2$	$P_3N_3Cl_3Br_3$	$P_3N_3Cl_2Br_4$	$P_3N_3ClBr_5$	$P_3N_3Br_6$
Trigonal P-N stretch (ν_9)	1370 [b]	1350 w sh	1330 w sh	1325 w sh [b]	1300 w	1285 w sh	1273 w [b]
Ring stretch in-plane (ν_{11})	1213 vs	1205 vs	1200 vs	1193 vs	1185 vs	1180 vs	1175 vs
Ring elongation (ν_{12})	875 m	870 m	865 m	863 m	858 wm	855 wm	852 w
Ring breathing [b] (ν_1)	783 w	779 w	773 w	770 w	760 w	758 w	750 w
Trigonal ring deformation (ν_2)	668 vw	665 vw	660 w	658 w	650 w	645 w	640 vw
Ring deformation out-of-plane (ν_5)	610 vs	603 vs	595 vs	583 vs	569 vs	562 s	543 m sh
Ring bending in-plane (ν_{13})	528 vs	525 s	508 s	508 m	502 ms	515 ms	532 vs
Ring deformation out-of-plane (ν_{18}) [c]							

[a] Notation for D_{3h} used. [b] From KBr disc spectra. [c] Not observed, outside range studied.

Table V. Infrared Assignments of Phosphorus-Halogen Stretching Modes of the Non-geminal Chlorobromotriphosphonitriles

		$P_3N_3Cl_6$	$P_3N_3Cl_5Br$	$P_3N_3Cl_4Br_2$	$P_3N_3Cl_3Br_3$	$P_3N_3Cl_2Br_4$	$P_3N_3ClBr_5$	$P_3N_3Br_6$
ν_{sym} PCl_2	i.p. [a]	365 w [b]	350 vw	340 vw				
	o.p.	334 m	333 w					
ν_{asym} PCl_2	i.p.	540 m sh	540 w sh	561 m				
	o.p.	580 w [b]	558 m					
νPCl	i.p.		(525 s) [c]	548 m	590 m sh	575 s	575 m sh	
	o.p.			525 w	570 s sh	538 w		
	o.p.				558 m sh			
νPBr	i.p.		490 s	480 s	535 w (?)	465 m sh	(445 s)	
	o.p.			470 m	482 s	455 s		
	o.p.				468 s			
ν_{sym} PBr_2	i.p.					350 w	340 w	320 vw [b]
	o.p.						[d]	257 vw
ν_{asym} PBr_2	i.p.					475 m sh	445 s	443 vs
	o.p.						463 m	478 w [b]

[a] i.p. and o.p. are in-phase and out-of-phase respectively. [b] Vibration formally forbidden. [c] Vibration obscured by ring bending mode. [d] Outside range studied.

The ring vibrations, designated in Table IV as ν_1 and ν_2, are of A_1' species in D_{3h} and are Raman allowed and infrared forbidden. Both vibrations become allowed when the symmetry is lowered in the mixed compounds. It is significant that the ring breathing vibration, ν_1, is not observed for any member of the series in the solution spectra but appears as a sharp, low intensity band in the spectra of KBr pressed discs. The ring deformation, ν_2, does appear in the spectra of both solutions and solids but only as a weak or very weak absorption.

Chapman and Paddock[22] have calculated that the trigonal ring stretch ν_9, which is forbidden in both the infrared and Raman in D_{3h}, would occur at ~ 1450 cm^{-1}. This vibration becomes allowed in all the chloride bromides except in $P_3N_3Cl_3Br_3$ with C_{3v} symmetry. In no case however is there a strong absorption in the region between 1300 and 1550 cm^{-1}, but a shoulder does occur on the high frequency side of the ν_{11} band at ~ 1200 cm^{-1} in the spectra of KBr discs. This absorption, which decreases in energy from 1330 cm^{-1} in the hexachloride to 1273 cm^{-1} in the corresponding bromide, is assigned to the trigonal ring stretch. The out-of-plane ring deformation ν_{18}, which occurs at 204 cm^{-1}[23] in $P_3N_3Cl_6$, has not been observed for any compound in the present study.

The absence of splitting of the degenerate ring vibrations together with the low intensity of those which become infrared allowed, indicate that ring vibrations are not sensitive to the lowering of symmetry from D_{3h} in $P_3N_3X_6$.

Phosphorus-Halogen Vibrations. These are assigned in Table V following previous analyses of the spectra of $P_3N_3Cl_6$[19,23] and $P_3N_3Br_6$.[24] In the non-geminally substituted chlorobromotriphosphonitriles, the positions of the various types of phosphorus-halogen stretching vibrations are found in fairly well defined regions of the spectrum. For example, asymmetric PCl_2 stretches occur between 540 and 580 cm^{-1} while the symmetric components lie between 330 and 365 cm^{-1}. The corresponding asymmetric PBr_2 stretches are found between 440 and 480 cm^{-1}; the highest energy component of the symmetric vibration is observed as a weak band at 340 cm^{-1} while the out-of-phase component occurs at the instrument limit (257 cm^{-1} in $P_3N_3Br_6$[24]).

Chlorine and bromine atoms on the same phosphorus atom give rise to absorptions between 525 and 590 cm^{-1} (PCl stretches) and 445 and 490 cm^{-1} (PBr stretches). In the non-geminally substituted $P_3N_3Cl_4Br_2$ and $P_3N_3Cl_2Br_4$ isomers, coupling of the vibrations of the two PClBr units occurs giving in-phase and out-of-phase components for both the PCl and PBr vibrations. Assignments of bands to these modes are given in Table V. The two configurations for the non-geminally substituted $P_3N_3Cl_3Br_3$ isomer each require three PCl and three PBr vibrations. In the *cis* isomer (C_{3v}), the two out-of-phase vibrations are however degenerate while three independent vibrations are expected for the *trans* form (C_s). Three absorptions bands for both thc PCl and PBr vibrations are observed and a *trans* form is most likely.

The fact that differences occur in the spectra of different samples of the di- and tri- substituted compounds has been mentioned above. Products from the ammonolysis of phosphorus halides contain absorption bands which do not appear in the spectra of the corresponding compounds obtained by the mercury(II) chloride methods (see Table VI and Figures 3-5). On the basis of the ^{31}P n.m.r. spectra, these must be ascribed to the geminally substituted isomers. The extra infrared absorptions expected for the trisubstituted compound will be due to asymmetric and symmetric PCl_2 and PBr_2 stretching vibrations. The dibromoderivative will lead to one further asymmetric and one symmetric PCl_2 vibration as well as to an asymmetric and a symmetric PBr_2 vibration. Tentative assignments of some of the extra absorption are given in Table VI.

Table VI. Bands due to Geminal Isomers (cm^{-1})

	$P_3N_3Cl_4Br_2$	$P_3N_3Cl_3Br_3$	$P_3N_3Cl_2Br_4$
ν_{asym} PCl_2	525 ms	592 s	590 m
ν_{sym} PCl_2			
ν_{asym} PBr_2		460 ms	447 m sh
ν_{sym} PBr_2		340 w	
			610 w
			518 m

Recently, Stahlberg and Steger[25,26] have assigned the spectra of the mixtures of isomers obtained from the PCl_5-NH_4Br reaction. In general, we agree with the assignments of the P_3N_3 ring vibrations but we prefer to follow Califano[19] in assigning the out-of-plane ring deformation (ν_5) to absorption in the range 560 to 603 cm^{-1} and the in-plane ring bend (ν_{13}) to that between 500 and 525 cm^{-1}. The latter absorptions have been attributed[26] to the symmetric PCl_2 stretch in $P_3N_3Cl_5Br$, and to asymmetric PBr_2 vibrations in the other mixed chloride bromides. These bands, however, are present in the spectra of the pure, non-geminal, di- and tribromo compounds in which there are no PBr_2 units. Assignment as ring vibrations thus seems more likely. In $P_3N_3ClBr_5$, the assignment of the medium-strong band at 516 cm^{-1} as a PBr_2 vibration is perhaps unreasonable as the highest value for $P_3N_3Br_6$ itself is considered to occur at 488 cm^{-1}.[24] Similarly, the strong band at 528 cm^{-1} in the $P_3N_3Cl_5Br$ spectrum is at too high energy for a symmetric PCl_2 vibration[19] and is better assigned as a ring vibration.

The out-of-plane ring deformation (ν_5) which is strongly infrared active in both $P_3N_3Cl_6$ (610 cm^{-1}) and $P_3N_3Br_6$ (543 cm^{-1}) is assigned to weak absorptions at 465 and 492 cm^{-1} respectively for $P_3N_3Cl_2Br_4$ and $P_3N_3ClBr_5$ only.[26] This absorption is expected to be strong in all the chloride bromides and for this reason our assignments of ν_5 have been made to strong absorptions falling between the limits set by the values in the hexachloride and hexabromide. These strong bands are assigned alternatively[26] as PCl vibrations.

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(22) A. C. Chapman and N. L. Paddock, *J. Chem. Soc.*, 635 (1962).
(23) I. C. Hisatsune, *Spectrochim. Acta, 21*, 1899 (1965).
(24) T. R. Manley and D. A. Williams, *Spectrochim. Acta, 23A*, 149 (1967).
(25) R. Stahlberg and E. Steger, *J. Inorg. Nuclear Chem., 28*, 688 (1966).
(26) R. Stahlberg and E. Steger, *Spectrochim. Acta, 23A*, 2057 (1967).