119. *Phosphonitrilic Derivatives. Part VIII.*[1] *The Vibrational Spectra of Phosphonitrilic Halides.*

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Band systems similar to that previously reported for the phosphonitrilic fluorides lead, with other new information, to revised assignments for both fluorides and chlorides. The symmetries of individual molecules are discussed, and the fluorides other than the trimer are shown to be more flexible than the chlorides.

IN Part III,[2] a system of bands in the infrared and Raman spectra of the phosphonitrilic fluorides $[PNF_2]_n$ was shown to be governed by a standing-wave condition, and to arise from the symmetrical PF_2 stretching vibrations. We now report the Raman and infrared spectra, in the condensed and the vapour phase, of the trimeric, tetrameric, and pentameric fluorides and chlorides, parts of the spectra of the higher polymers, parts of the low-temperature spectra of the lower fluorides, and the polarized infrared spectra of

[1] Part VII, McGeachin and Tromans, *J.*, 1961, 4777.
[2] Chapman, Paddock, Paine, Searle, and Smith, *J.*, 1960, 3608.

the two forms of tetrameric chloride. The standing-wave treatment, applied to both ring and exocyclic vibrations, leads, with the other new data, to some revised assignments, without changing earlier conclusions [3,4] on the symmetry of the trimeric molecules. The evidence for tetraphosphonitrilic chloride is conflicting, but the ring is not planar in the vapour phase. The tetrameric and the pentameric fluoride are both flexible; the pentameric chloride is less so and has a low symmetry. Some assignments and group-frequency correlations are presented for the triphosphonitrilic fluoride chlorides.[5]

Ring Stretching Vibrations.—The standing-wave condition [2] applied to the ring stretching frequencies gives a series of modes in which the phase difference between the displacements of adjacent atoms is given by $\delta = 2\pi n/N$, where N is the number of atoms in the ring, and $n = 0, 1 \ldots N$. In the trimeric molecules this series consists of a ring breathing vibration I of species A_1' ($\delta = 0$), two degenerate vibrations II and III ($\delta = \pi/3$ and $2\pi/3$), and a trigonal vibration IV of species A'_2 ($\delta = \pi$).

(I) (IIa) (IIb) (IIIa) (IIIb) (IV)
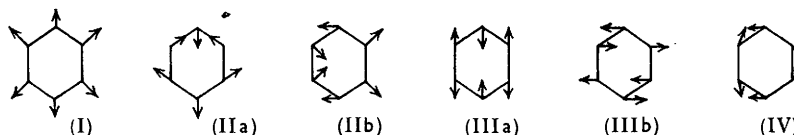
Vibrations I—IV are expected to occur in order of increasing frequency, II, III, and IV lying close together and much higher than I, as in other cyclic molecules. For example, the corresponding frequencies in benzene are [6] 991, 1485, 1596, and 1648 cm.$^{-1}$, and in borazole [7] 851, 1466, 1610 cm.$^{-1}$ (and 1650 cm.$^{-1}$ calc.). In the phosphonitrilics, the large ratio of the masses of phosphorus and nitrogen must influence the distribution of frequencies, and we have therefore calculated the frequencies and normal co-ordinates of two hypothetical six-membered rings, the first with alternate phosphorus and nitrogen atoms (D_{3h}), the second with equivalent atoms having an inverse mass midway between those of nitrogen and phosphorus (D_{6h}). The frequencies (Table 1) were calculated by

TABLE 1.

Calculated [a] frequencies of in-plane vibrations of six-membered rings.

P$_3$N$_3$ ring (D_{3h})			Equivalent atom ring (D_{6h})		
Frequency (cm.$^{-1}$)	Symmetry Species	Normal co-ordinate [b]	Frequency (cm.$^{-1}$)	Symmetry species	Normal co-ordinate
1450	A_2'	IV	1450	B_{2u}	IV
1391	E'	-0.81 III $- 0.20$ II $+ 0.55$ E	1374	E_{2g}	-0.80 III $+ 0.60$ E
1053	E'	-0.16 III $+ 0.83$ II $+ 0.58$ E	1062	E_{1u}	II
934	A_1'	0.64 I $- 0.77$ T	845	B_{1u}	T
608	A_1'	0.36 I $- 0.93$ T	726	A_{1g}	I
406	E'	0.13 III $- 0.07$ II $+ 0.99$ E	441	E_{2g}	0.12 III $+ 0.99$ E

[a] See text for details. [b] See diagram for details; E = degenerate ring elongation; T = trigonal ring deformation.

Wilson's FG matrix method,[8] by using a simple valency force field with a stretching force constant of 8·0 md/Å and a single bending constant of 0·5 md/Å. Detailed agreement would not be expected from such an idealized force-field; nevertheless, (1) the frequencies

[3] Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403.

[4] Becher and Seel, *Z. anorg. Chem.*, 1960, **305**, 148.

[5] Chapman, Paine, Searle, Smith, and White, *J.*, 1961, 1768.

[6] Bailey, Hale, Herzfeld, Ingold, Leckie, and Poole, *J.*, 1946, 255; Herzfeld, Ingold, and Poole, *J.*, 1946, 316.

[7] Crawford and Edsall, *J. Chem. Phys.*, 1939, **7**, 223; Price, Fraser, Robinson, and Longuet-Higgins, *Discuss. Faraday Soc.*, 1950, **9**, 131.

[8] Wilson, Decius, and Cross, " Molecular Vibrations," McGraw-Hill, New York, 1955.

occur in the expected order, (2) the totally symmetric vibration is widely separated from the others for equivalent atoms, and (3) it remains separate for non-equivalent atoms. Furthermore, II is infrared-active in both D_{6h} and D_{3h}, while III relies on the reduction of symmetry for its activity in D_{3h}. In the rings with 3-fold symmetry, therefore, II is expected to be stronger in infrared than III, as in borazole. The trigonal ring stretching band IV is theoretically inactive.

In triphosphonitrilic chloride (Table 2) we therefore assign the breathing vibration I

TABLE 2.

Spectra and assignments of triphosphonitrilic chloride.

Raman (cm.$^{-1}$)	Infrared (cm.$^{-1}$) Vapour	Condensed phases [a]	Assignment
76?			A_1' PCl$_2$ deformation, in phase
162 (4,dp)			E'' PCl$_2$ rock, degenerate
173 (3,dp)			E'' Ring deformation, out of plane
210 (3,dp)			E'' PCl$_2$ torsion, degenerate
		315w [b]	
340 (1,dp)		336s [b]	E' ring elongation
365 (10,p)			A_1' sym. PCl$_2$ stretch, in phase
523vw	523vs	527vs	E' sym. PCl$_2$ stretch, degenerate
	554ms [c]		See text
582 (1,dp)			See text
	620vs	612vs	A_2'' antisym. PCl$_2$ stretch, in phase
	638ms [c]		See text
671 (4,p)		672m	(and/or 785) A_1' trigonal ring deformn.
	702vw	695w	
	741vw	740w	
	754vw		
785 (2,p)		782m	(and/or 671) A_1' ring breathing (I)
	845w		
	875vw		
885vw [d]		875s	E'' antisym. PCl$_2$ stretch, degenerate
	912w	915vw	
	995w	985m	
		1040vw	
		1060w	
	1072w		
		1092w	
	1121w	1119m	
	1148w		
	1202s	1200s	527 + 672 = 1199?
	1218vs	1218vs	E' ring stretching, degenerate (II)
	1295m	1310m	E' ring stretching, degenerate (III)
	1365w	1368m	A_2' trigonal ring stretching? (IV)

[a] Solutions in CS$_2$ and CCl$_4$, and (above 650 cm.$^{-1}$ only) liquid and solid films and KCl discs. [b] Beyond the range of the instrument used; reported by Daasch.[3] [c] Intensity shows apparent positive temperature-dependence. [d] Not detected in the present work but reported by de Ficquelmont, Magat, and Ochs (*Compt. rend.*, 1939, **208**, 1900).

to one of the polarized Raman bands (672 or 785 cm.$^{-1}$) (the infrared bands at these frequencies, attributed by Daasch[3] to accidental coincidences, are absent in the spectrum of the vapour), the degenerate vibration II to the intense band at 1218 cm.$^{-1}$, and the degenerate vibration III to the medium-strength band at 1295 cm.$^{-1}$. The three corresponding bands in the fluoride (Table 3) are at 570 or 689 cm.$^{-1}$ (I), 1297 cm.$^{-1}$ (II), and 1343 cm.$^{-1}$ (III).

In the higher polymers the totally symmetric vibration does not follow a smooth sequence, and is not assigned. The degenerate vibrations are expected to form a system in which an extra sequence of bands is added at each successive polymer. The first sequence is formed by vibrations in which one wavelength is fitted round the ring and will be strongly infrared-active. The last degenerate vibration in each molecule, corresponding to the fitting of $n-1$ wavelengths round the ring of n PN units, will be weakly active, as in the trimeric molecules. The intermediate degenerate or pseudo-degenerate

vibrations will become active only as the symmetry departs from D_{nh}; moreover, since the bands are close together in the trimeric molecules, the additional bands are unlikely to be resolved. Accordingly, we find that a broad shoulder appears on the high-frequency side of the main absorption, and gains in intensity throughout the fluoride series (Fig. 1).

TABLE 3.

Spectra and assignments of triphosphonitrilic fluoride.

Raman	Infrared			Assignments
		Condensed phases		
	Vapour	Room temp.[a]	Low temp.[b]	
282 (4,dp)				E''
311 (4½,p)				A_1' PF$_2$ deformation, in phase
342 (¾,dp)				E' ring elongation?
469 (1½,dp)	468s	465s		E' PF$_2$ wag or deformation, degen.
	516s	510s		A_2'' PF$_2$ rocking, in phase
	534ms	537vw		
570 (2½,p)				(and/or 689) A_1' trigonal ring deformn.
	589m			
	621m			
	635m			
	678w [d]			
689 (½,p)				(and/or 570) A_1' ring breathing (I)
	733w			
743 (10,p)				A_1' sym. PF$_2$ stretching, in phase
	803vw	795w		
	862s	862vs	850vs	E' sym. PF$_2$ stretching, degen.
	888ms	890ms		See text
	931vw			
951 (¾,p)				
			929m	See text
	973s	963vs	940s	A_2'' antisym. PF$_2$ stretch, in phase
			962s	}E'' antisym. PF$_2$ stretch, degen.
			975s	
1012 (¾,p)	1008m	1000m	1006m	See text
	1030wm	1025vw		
	1202w	1200w		
	1235vw			
	1270m	1270m		
	1297vs	1287vs	1286vs	E' ring stretching, degen. (II)
	1343m	·1338m		E' ring stretching, degen. (III)
	1367wm	1373wm		A_2' trigonal ring stretching? (IV)
	1422vw	1422vw		
	1456wm	1456wm		

[a] See Table 1.   [b] Crystalline film and matrix in solid carbon dioxide (which gave very similar spectra), above 650 cm.⁻¹ only.   [c] Intensity shows strong positive temperature-dependence.   [d] Intensity shows strong negative temperature-dependence.

A similar effect is shown by a mixture of higher cyclic chlorides (Fig. 1) and by the cyclic polydimethylsiloxanes.[9]

PCl$_2$ *Stretching Vibrations.*—The number and activities of a system of infrared and Raman bands of the phosphonitrilic chlorides (Fig. 2) are as required [2] for s-PCl$_2$ stretching vibrations, except that in the pentamer the degeneracy of the two higher-frequency vibrations is resolved, indicating a low symmetry, and that in the heptamer and octamer the expected increase in the number of bands does not take place, probably because band width prevents resolution. That the series of strong polarized Raman bands belongs to the system is shown by comparing the intensities of the bands, and their position relative to the rest of the system, with the corresponding series in the fluorides.[2] In the trimeric chloride, we therefore assign the infrared band at 520 cm.⁻¹ to the degenerate symmetrical PCl$_2$ stretching vibration (E'), and the polarized Raman band at 365 cm.⁻¹ to symmetrical in-phase stretching (A_1').

[9] Wright and Hunter, *J. Amer. Chem. Soc.*, 1947, **69**, 803.

The antisymmetrical PCl_2 stretching vibrations are expected to form a system of modes in which one limit, the in-phase vibration, is strongly infrared-active, the other vibrations being inactive if the symmetry is high enough. The other limit would be present only in the even-numbered polymers, an extra sequence of degenerate vibrations
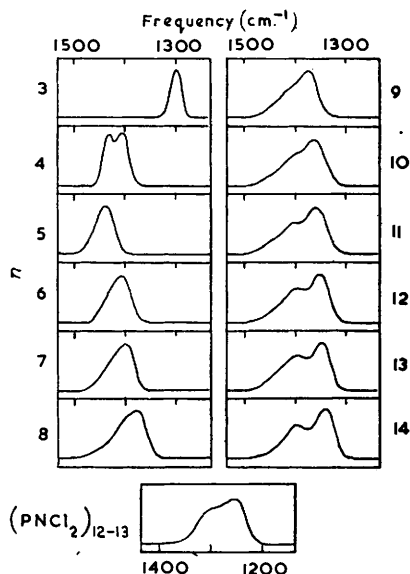

FIG. 1. The " P⚌N absorption bands " of the phosphonitrilic fluorides $[PNF_2]_n$ from $n = 3$ to $n = 14$, and of a phosphonitrilic chloride $[PNCl_2]_{12-13}$, showing the high-frequency shoulder arising from unresolved degenerate vibrations.
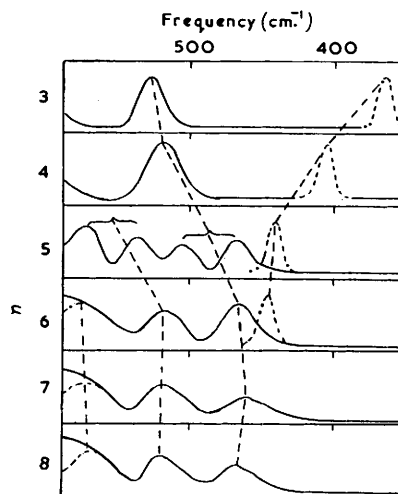

FIG. 2. The infrared spectra from 350 to 580 cm.$^{-1}$ of the phosphonitrilic chlorides $[PNCl_2]_n$ from $n = 3$ to $n = 8$ showing the system of symmetrical PCl_2 stretching vibrations. Broken peaks represent polarized Raman bands; series of bands having the same number of standing wavelengths in the ring are indicated by broken lines.
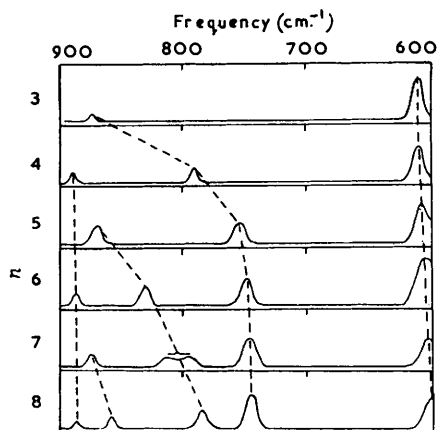

FIG. 3. The infrared spectra from 600 to 900 cm.$^{-1}$ of the phosphonitrilic chlorides $[PNCl_2]_n$ from $n = 3$ to $n = 8$, showing the system of unsymmetrical PCl_2 stretching vibrations. Series of bands having the same number of standing wavelengths in the ring are indicated by broken lines.

being added at each odd-numbered polymer.[2] The first degenerate vibration, corresponding to the fitting of one wavelength round the ring, should be Raman-active, and this vibration is also likely to show stronger infrared activity than the others if the symmetry is low.

The observed system of bands (Fig. 3) agrees with these requirements. Other systems, such as that arising from ring deformation, have different requirements for numbers

of bands and activity, and are expected elsewhere. Furthermore, the polarized infrared spectra of the tetramer (Table 4) show that the bands at 620, 790, and 885 cm.⁻¹ are out-of-plane vibrations. We therefore assign the strongly infrared-active band at 612 cm.⁻¹ in the trimer to the in-phase mode (A_2''), and the band at 875 cm.⁻¹ to the degenerate band

TABLE 4.

Spectra and assignments of tetraphosphonitrilic chloride.

No.[b]	Raman		Infrared					
	S_4 form (cm.⁻¹)	C_4 form (cm.⁻¹)	Vapour (from 650 cm.⁻¹ only)	Solution (cm.⁻¹)	S_4 form (cm.⁻¹)	polarn.	C form (cm.⁻¹)	polarn.
	143 (12)	129 (30)						
		170 (40)						
	178 (48)	185 (37)						
	190 (37)	193 (39)						
		201 (33)						
	248 (31)	256 (14)						
	280 (10)	309 (4)						
	336 (19)	328 (83)						
1	387 (100)	413 (100)						
	421?							
2	512 (6)	515 (11)		516vs	515vs	?	515vs	?
3	557 (30)	537 (41)		567m?	570m	?		
	572?	580 (7)		585m?				
4	601 (32)	596 (25)		607vs	590vs out of plane		615vs out of plane	
5		726 (5)	726m	726m			{ 735m? in plane? / 741m? out of plane?	
6		788 (2)	790s	790s	{ 772m out of plane / 790m	?	{ 775s out of plane / 793s out of plane	
7	904 (3)	892 (7)	890s	890s	885s out of plane			
8			1305vs	1305vs	1262vs in plane ⌉ further		1280vs in plane	
9		1350? (4)	1375s	1355s	1355s in plane ⌋ structure[a]		1355s in plane	

[a] When the plane of vibration is perpendicular to the tetrad axis, medium-strength peaks appear at 1250 and 1275 cm.⁻¹, and these also appear in unoriented films. [b] Assignments: 1, In-phase sym. PCl₂ stretching. 2, Degenerate sym. PCl₂ stretching. 3, Out-of-phase sym. PCl₂ stretching and ring vibrn.? 4, In-phase antisym. PCl₂ stretching. 5, Ring vibrn. 6, Degenerate antisym. PCl₂ stretching. 7, Antisym. out-of-phase PCl₂ stretching. 8, 1st degenerate ring stretching. 9, 2nd degenerate ring stretching.

(E''). An earlier assignment [3] of this frequency to an E' mode is disproved by its infrared inactivity in the vapour phase. The first degenerate band increases strongly in intensity with increasing ring size, indicating departures from D_{nh} symmetry; the high-frequency limit is present in the tetramer, hexamer, and octamer at 885 cm.⁻¹. The Raman bands are weak; the degenerate band of the trimer reported earlier [10] was not detected. The wide range of the P–Cl stretching vibrations shows that the coupling between the P–Cl bonds is exceptionally strong; the coupling between the P–F bonds in the fluorides, though weaker, is also strong. Such strong coupling must be related to the delocalized nature of the bonding.[11]

PF₂ *Stretching Vibrations* (Tables 3, 5, and 7).—The symmetrical PF₂ stretching vibrations have already been assigned [2] to a band system lying below 885 cm.⁻¹, and the antisymmetrical vibrations are therefore expected above 900 cm.⁻¹. The band at 973 cm.⁻¹ in the spectrum of the trimeric fluoride changes only slightly in frequency in the higher polymers, but is split into two in the tetramer in solution and in pressed disc spectra, and into three in the pentamer. The higher polymers all show two partially resolved broad bands, which are probably the envelope of a series of bands.

At 77° K, the band in the spectrum of the trimer is split into a strong singlet and a

[10] de Ficquelmont, Magat, and Ochs, *Compt. rend.*, 1939, **208**, 1900.
[11] Craig and Paddock, *Nature*, 1958, **181**, 1052; Craig, *J.*, 1959, 997; Dewar, Lucken, and Whitehead, *J.*, 1960, 2423.

TABLE 5.

Spectra and assignments of pentaphosphonitrilic fluoride.

Raman	Infrared					Assignments
	Vapour	Liquid	Solution [a]	CO_2 matrix at 77° [b]	Cryst. film at 77° [b]	
200 (2,dp)						
293 (4,p)						
388 ($\frac{1}{4}$,dp)						
440 ($\frac{3}{4}$,p)	480—550s (complex unresolved structure?)	As in vapour	490—520s (complex unresolved structure)			$\{$PF$_2$ deformation, wagging, rocking, etc.
615 (10,p)	609w	610w				Sym. PF$_2$ stretch, in phase
	725vs	715vs	717vs	710vs	708s $\}$ 717s	$\{$1st degenerate sym. PF$_2$ stretching
798 ($\frac{1}{2}$,p)						
946 (1,dp)						
866 ($\frac{1}{4}$,dp)	875s	863s	866s	870s	873s	2nd degen. sym. PF$_2$ stretching
946 (1,dp)	941s	948vs	937s	935s	918s $\}$ 934s	$\}$Degenerate antisymmetrical PF$_2$
	967vs	970sh?	956vs	953vs	945ms $\}$ 950ms	stretching vibrns.
	982vs		970s–vs	972vs		
				982vs	967s	Antisym. PF$_2$ stretching in phase
1010 (2,p)				1008m	998m	
	1450vs (unresolved structure)	1425vs	1440vs	1430vs (unresolved structure)	1405vs $\}$ 1467vs	$\{$Degenerate ring stretching
1905vw						
2010vw						

[a] Solution in CS$_2$ from 400 cm.$^{-1}$, in CCl$_4$ from 650 cm.$^{-1}$. [b] Above 650 cm.$^{-1}$ only.

TABLE 6.

Characteristic frequencies for phosphorus–halogen stretching vibrations in triphosphonitrilic rings.

Group	Type of vibration	Individual frequencies						Frequency range (cm.$^{-1}$)
		a	b	c	d	e	f	
PF$_2$	Symmetrical (single group or 2/3 in phase)	—	746	744	735	741	743	735—746
	Symmetrical (two groups out of phase or 3 degenerate)	—	—	—	835	—	862	835—862
	Antisymmetrical	—	943	943	952	957	973	942—973
PCl$_2$	Symmetrical (single group of 2/3 in phase)	365	362	350—360	359			350—365 (Raman)
	Antisymmetrical (single group or 2/3 in phase)	620	602	591	595			595—620
	Antisymmetrical (two groups out of phase or 3 degenerate)	875	866					866—875
PFCl (single group)	PF			846				
	PCl			564				
a	triphosphonitrilic chloride							
b	,,	1,1,3,3-tetrachloride-5,5-difluoride						
c	,,	1,1,3-trichloride-3,5,5-trifluoride						
d	,,	1,1-dichloride-3,3,5,5-tetrafluoride						
e	,,	1,3-dichloride-1,3,5,5-tetrafluoride						
f	,,	fluoride						

strong doublet. These are the in-phase (A_2'') and the resolved-degenerate vibration, respectively, the activity and resolution of an E'' mode being due to the low site symmetry in the crystal [12] and matrix. The in-phase and near-degenerate vibrations belong to the

[12] Jagodzinski and Oppermann, *Z. Krist.*, 1960, **113**, 241.

same species of the site group, and as the frequencies are close together they interact strongly, equalizing the intensities. The similar spectrum of the tetramer was determined only in the matrix and is interpreted in the same way, the out-of-phase vibration not being observed. The low-temperature spectrum of the pentamer consists of the in-phase vibration and the two split degenerate frequencies, which appear single at room temperature. The band systems of all three molecules are accompanied by weaker bands at their edges. These may be overtones or combinations which gain intensity in low site symmetries by interaction with neighbouring fundamentals.

The assignment of the bands near 970 cm.$^{-1}$ to PF_2 vibrations is confirmed by the spectra of the trimeric chloride fluorides (Table 6). A band appears at 943 cm.$^{-1}$ in the tetrachloride 5,5-difluoride and shifts only slightly, without splitting, with further increase of fluorine content. The band at 973 cm.$^{-1}$ in the trimeric fluoride cannot therefore be one of the ring vibrations, which behave differently: such an assignment [4] would also be inconsistent with the behaviour of the band at low temperatures, where site splitting could give at most a doublet structure, and correlation field splitting could not explain the structures observed in either the matrices or the trimer crystal.

Assignments and Symmetry of Individual Molecules.—(a) *Triphosphonitrilic, chloride, fluoride, and chloride fluorides* (Tables 2, 3, 6).—Of the doubtful features [3,10] of the Raman spectrum of the chloride, it has been confirmed that the band at 582 cm.$^{-1}$ is depolarized, and that the 785 cm.$^{-1}$ band is polarized. The band at 100 cm.$^{-1}$ reported by de Ficquelmont *et al.*,[10] and doubtfully by Daasch,[3] was not detected even by the use of interference filters to reduce the background from the mercury exciting line.

The doubling of the strong ring stretching band at 1218 cm.$^{-1}$ in the chloride is attributed to a Fermi resonance, possibly with the combination band from 527 cm.$^{-1}$ (E') and 627 (A'). The degenerate ring elongation vibration, expected at a lower frequency than the trigonal ring deformation vibration, is assigned at 336 cm.$^{-1}$ in the chloride and 342 cm.$^{-1}$ in the fluoride.

The Raman bands at 582 cm.$^{-1}$ in the chloride, and 951 and 1012 cm.$^{-1}$ in the fluoride cannot be satisfactorily assigned as fundamentals. Their nearness to A_2'' anti-symmetrical PX_2 stretching fundamentals suggests that they may arise from upper-stage transitions.[13] Such transitions may also account for the weak bands which appear in the vapour-phase infrared spectrum of the chloride at 554 and 638 cm.$^{-1}$, and for the weak infrared bands at 1008, 929 (low temperature only), and 888 cm.$^{-1}$ in the fluoride. Although several assignments have here been revised, previous conclusions [3,4] that both molecules exhibit D_{3h} symmetry are unaffected. The deformation found in the crystal [14] indicates that the molecule is slightly flexible.

The effect of substitution on the main ring stretching frequencies of four trimeric chloride fluorides has been previously determined;[5] we limit discussion here to the PX_2 frequencies, which occur in the ranges shown in Table 6. The out-of-phase vibrations of two identical PX_2 groups evidently occur close to the corresponding degenerate frequencies of the fully substituted molecule, while the in-phase vibration of either two or three identical groups occurs close to the corresponding vibration of a single group. The unsymmetrical PF_2 group vibrations are little affected by ring size, and their correlated frequencies are probably also applicable to larger rings.

(b) *Tetraphosphonitrilic chloride and fluoride.* The spectra and assignments of tetra-phosphonitrilic chloride are shown in Table 4. All the major bands are still active in the vapour phase, and the activity of the out-of-phase antisymmetrical PCl_2 vibration at 890 cm.$^{-1}$ shows that the symmetry is not D_{4h}, as has been suggested,[3] or S_4, as in one crystal form.[15] The highest symmetry consistent with the appearance of this peak is

[13] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, p. 267; Dennison, *Rev. Mod. Phys.*, 1940, **12**, 175.
[14] Wilson and Carroll, *J.*, 1960, 2548; Pompa and Ripamonti, *Ric. Sci.*, 1959, **29**, 1516
[15] Ketelaar and de Vries, *Rec. Trav. chim.*, 1939, **58**, 1081.

C_{2h}. In solution, some Raman–infrared coincidences, particularly that at 890 cm.$^{-1}$, are evidence against C_{2h} symmetry, and six polarized Raman bands are further evidence against D_{4h} symmetry. The appearance, but not the depolarization, of the Raman band at 890 cm.$^{-1}$ would be consistent with S_4 symmetry if the appearance of the infrared band were due to a violation of selection rules as in the trimer. In the crystalline form of known structure,[15] neither the infrared activity of the out-of-phase unsymmetrical PCl_2 stretching vibration at 890 cm.$^{-1}$, nor the splitting of the degenerate vibrations at 1315 and 790 cm.$^{-1}$, can be accounted for in terms of the site group (S_4) or factor group (C_{4h}). In the other form the absence of the 890 cm.$^{-1}$ band is not explained by the site group (C_i) [16] or factor group (C_{4h}).[17] Whatever the explanation of the anomalies, the behaviour of the band at 890 cm.$^{-1}$ indicates a change in molecular configuration and a flexible molecule.

TABLE 7.

Spectra and assignments of tetraphosphonitrilic fluoride.

Raman	Infrared				Assignment
	Vapour	Liquid [a]	Solution KCl	CO$_2$ matrix at 77° [a]	
175 (2,dp)					
295 (5,dp)					
425 (1,dp)					
	493s		490s		} PF$_2$ deformation, rocking, wagging,
	515s		515ms		} etc.
	532s				
552 (1½,p)					Ring vibration (breathing?)
605 (10,p)					Sym. PF$_2$ stretch, in phase
	770vs	770vs	760vs	Masked	Sym. PF$_2$ stretch, degen.
	795vw				
	858vw	862vw			
	887vw	895w	895w	895m	Sym. PF$_2$ stretch, out of phase
	913vw	920w			
940 (1½,dp)		945w		930m	
	979vs	979vs	962s	957vs	Antisym. PF$_2$ stretch, in phase
			979s	975vs	} Antisym. PF$_2$ stretch, degen.
				985vs	
1005 (2,p?)					
	1216vw				
	1419vs	1423vs	1410vs	1410vs	} First degen. ring stretching vibrn.
	1438vs	1443vs	1435vs	1445vs	
	1505m	1510s			Second degen. ring stretching vibrn.
	1580w	1590m			

[a] Above 650 cm.$^{-1}$ only. [b] Possibly a doublet.

The spectra and assignments of tetraphosphonitrilic fluoride are given in Table 7. The band at 1430 cm.$^{-1}$ is split, the components remaining comparable in intensity although the splitting varies with the state of aggregation. The splitting is therefore due to resolution of the degeneracy, and indicates C_{2h} or lower symmetry, as proposed on the same grounds by Becher and Seel.[4] Also, the out-of-phase symmetrical PF_2 stretching vibration at 895 cm.$^{-1}$ is weakly active, suggesting S_4, C_4, or lower symmetry. The appearance, in solutions and in disc and matrix samples, of an additional strong band or bands due to antisymmetrical PF_2 stretching vibrations is a further indication of low symmetry. Since the strength of these extra bands is dependent on the mixing of different vibrations of the same symmetry species, the appearance of these bands and their variability indicate that the symmetry is both low and variable, the molecule being very flexible. This is confirmed by the contrast between the D_{4h} symmetry of the molecule in the crystal [1] and the low symmetry in other phases.

(c) *Pentaphosphonitrilic chloride and fluoride* (Tables 5 and 8). For the chloride, the symmetry groups D_{5h} and C_{5v} are both ruled out by the large number of polarized Raman

[16] Wilson, unpublished work.

TABLE 8.

Spectra and assignments of pentaphosphonitrilic chloride.

Raman	Infrared		Assignment
	Vapour [a]	Condensed phases [b]	
135 (6p?)			
167 (8p?)			
203 (0·3dp)			
230 (0·3p)			
253 (0·2p)			
308 (4·2p)			
380 (0·7p)			
420 (0·2dp)			
439 (10p)			Sym. PCl$_2$ stretch, in phase
		464s	⎫
485 (1·6p)			⎬ 1st degen. sym. PCl$_2$ stretching
		503m	⎭
522 (1·0p)			Ring vibration
		535s	⎫ 2nd degen. sym. PCl$_2$ stretching
		569s	⎭
584 (1·6p)			Ring vibrn.?
		601vs	Antisym. in phase PCl$_2$ stretching
739 (0·7p)			
	750s [c]	752 [c]	1st degen. antisym. PCl$_2$ stretching
870 (0·9p)	865s	866s	2nd degen. antisym. PCl$_2$ stretching
	1285vs	1298vs	⎫ 1st degen. P=N ring vibrn.
	1345vs	1354vs	⎭
	1520m		

[a] Above 650 cm.[-1] only. [b] Solutions in CS$_2$ and CCl$_4$, liquid films, and KCl discs. [c] There is a suggestion of unresolved splitting of this band in some of the spectra.

bands (10—12) (particularly the polarization of the second degenerate symmetrical PCl$_2$ stretching band at 870 cm.[-1]), the number of infrared bands (9), the splitting of the first degenerate P=N stretching band and of the degenerate symmetrical PCl$_2$ stretching bands, and the strong infrared activity of the degenerate antisymmetrical PCl$_2$ stretching bands and of the second degenerate symmetrical PCl$_2$ stretching band. The molecular symmetry is therefore low.

For the fluoride, the number of polarized Raman bands (5), infrared bands (8—12), and coincidences (1—3) indicate that the symmetry is lower than D_{5h}, but that the average deviation from it is small. The appearance of the symmetrical in-phase PF$_2$ stretching vibration as a weak band in the infrared region at 609 cm.[-1], and of the second degenerate symmetrical PF$_2$ stretching vibration at 875 cm.[-1] also show that the molecule passes through configurations in which 5-fold symmetry is absent. The low-temperature spectra exhibit the maximum number of five antisymmetrical PF$_2$ stretching vibrations, and, in some cases, splitting of the degenerate symmetrical PF$_2$ vibrations, showing that the molecule is frozen in a configuration of low symmetry. A high flexibility, especially if compared with that of the pentameric chloride, is indicated by the variability of the antisymmetric PF$_2$ stretching vibrations, the variation in the splitting of degenerate vibrations, and the breadth of the complex band system around 500 cm.[-1].

Experimental.—The preparation and purification of the polymers have already been described.[2,5,17] Infrared spectra were taken on a Perkin-Elmer model 21 infrared spectrometer with sodium chloride and potassium bromide optics. Vapour-phase spectra of phosphonitrilic chlorides were taken in a heated 10 cm. gas cell. Low-temperature spectra were obtained either by passing a stream of dry carbon dioxide over the polymer and spraying on to a rock-salt plate maintained at 77° K *in vacuo*, or by sealing a thin film of polymer between two sodium chloride plates with a Polythene gasket and cooling the resulting " sandwich."

The polarized infrared spectra of oriented samples of tetraphosphonitrilic chloride were obtained with a Perkin-Elmer polarizer. Samples of the form of known crystal structure [15]

[17] Lund, Paddock, Proctor, and Searle, *J.,* 1960, 2542.

were prepared by withdrawing a potassium bromide plate from a solution of the tetramer in carbon disulphide and selecting an oriented region from the resulting crystalline film by examination under a polarizing microscope. The region selected showed oriented fibrous crystals which are known to grow along the tetrad axis; this axis is normal [15] to the " planes " of the phosphonitrilic rings. Samples of the other form were prepared by allowing a thin film of the molten tetramer to solidify between two potassium bromide plates, one of which was given a reciprocating motion. A suitable region was selected with a polarizing microscope, and the orientation of the tetrad axis (again normal to the ring " planes ") [16] confirmed by a study of the interference figure.

Raman spectra were taken on a Hilger recording Raman spectrometer. Depolarization factors were determined by the Edsall–Wilson method.[18] The spectra of the solids were taken with well-crystallized samples and a re-entrant conical tube window.[19]

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[18] Edsall and Wilson, *J. Chem. Phys.*, 1939, **6**, 124.
[19] Woodward and Roberts, *Trans. Faraday Soc.*, 1956, **52**, 1458.