The Reactions of *N*,*N*′-Dimethylethylenediamine with Cyclic Phosphonitrilic Halides[1]

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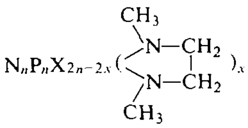
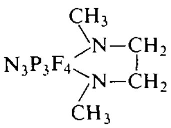
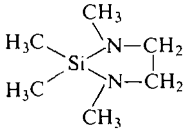
The reactions of *N*,*N*′-dimethylethylenediamine with the cyclic phosphonitrilic halides $N_3P_3F_6$, $N_4P_4F_8$, $N_3P_3Cl_6$, and $N_4P_4Cl_8$ lead to spiro halogenophosphonitrilic imidazolidines of the type



($n = 3, 4$; $x = 1, 2$; X = Cl, F) together with polymeric materials. Structure

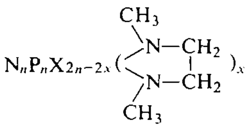


has also been prepared by fluorination of the corresponding chloride with KSO_2F and from $N_3P_3F_6$ and

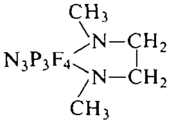


The ^1H and ^{19}F n.m.r., i.r., and mass spectra of the phosphonitrilic imidazolidines are discussed.

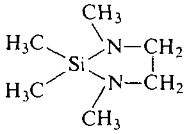
Les réactions entre la *N*,*N*′-diméthyléthylènediamine et les halogénures phosphonitriliques cycliques, $N_3P_3F_6$, $N_4P_4F_8$, $N_3P_3Cl_6$, et $N_4P_4Cl_8$, conduisent à des imidazolidines halogénophosphonitriliques spiro du type



($n = 3, 4$; $x = 1, 2$; X = Cl, F), et à des produits polymériques. Le composé



a également été préparé par fluoration des chlorures correspondant avec KSO_2F et à partir de $N_3P_3F_6$ et



Les spectres r.m.n. (^1H et ^{19}F), de masse, et i.r. des imidazolidines phosphonitriliques sont discutés.

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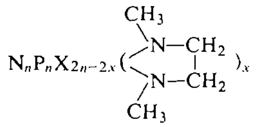
[1] For a preliminary account see Chivers and Hedgeland (24).

Introduction

The reactions of cyclic phosphonitrilic chlorides (chlorocyclophosphazenes) with monofunctional amines have been investigated in considerable detail and different substitution pathways have been recognized (1). Geminally substituted spirocyclic derivatives of $N_3P_3Cl_6$ have been prepared from the difunctional amine, *o*-phenylenediamine (2). More recently the reactions of cyclic phosphonitrilic fluorides with amines, *e.g.* Me_2NH (3–5), $MeNH_2$ (4, 5), or Me_3SiNMe_2(3), have been shown to follow a non-geminal substitution pathway and, under appropriate conditions, good yields of the monoamino derivatives can be obtained. Deamination by hydrogen chloride or bromide provides an expeditious route to the corresponding monohalogeno or non-geminally substituted halogeno derivates of cyclic phosphonitrilic fluorides (3–7) which are otherwise difficult to purify (8, 9). In an attempt to extend this synthetic route to the preparation of *gem*-dihalogenophosphonitrilic fluorides we have investigated the reactions of *N*,*N*′-dimethylethylenediamine with the cyclic phosphonitrilic halides $N_nP_nX_{2n}$ ($n = 3, 4$; X = Cl, F). Geminal substitution occurs to give spiro halogenophosphonitrilic imidazolidines of the type



$$N_nP_nX_{2n-2x}\Big(\begin{array}{l} \overset{CH_3}{>N}-CH_2 \\ \qquad\quad | \\ \underset{CH_3}{>N}-CH_2\end{array}\Big)_x$$

($n = 3, x = 1, 2; n = 4, x = 1$)

Particularly in the case of $N_4P_4F_8$ oily, presumably polymeric, products were also formed. The reactions of the spiro compounds with hydrogen chloride or bromide gave adducts which could not be converted to the corresponding *gem*-dihalogenophosphonitrilic fluorides.

Experimental

General

The preparations of the phosphonitrilic imidazolines were carried out under an atmosphere of nitrogen, which was replaced by air in the work-up procedure. Hydrocarbon solvents were redistilled from calcium hydride before use. The following chemicals were obtained commercially and used without further purification: anhydrous diethyl ether (Mallinckrodt), hydrogen chloride, hydrogen bromide, dimethylamine (Matheson), *N*,*N*′-dimethylethylenediamine (Columbia Organic), dichlorodimethylsilane (Peninsular Chem Research), and potassium fluorosulfite (Ozark-Mahoning). $N_3P_3Cl_6$ and $N_4P_4Cl_8$ were purchased from Alfa Inorganics and recrystallized from petrol (30–60°) before use. $N_3P_3F_6$ and $N_4P_4F_8$ were prepared from the corresponding chlorides by the reaction with potassium fluorosulfite in paraffin oil at *ca.* 110° (10). 1,2,2,3-Tetramethyl-1,3-diaza-2-silacyclopentane was prepared by the method of Abel and Bush (11).

The following instruments were used for spectroscopic studies: ^{1}H n.m.r. spectra (Varian A60 and HA100), ^{19}F n.m.r. spectra (Varian HA100 operating at 94.1 MHz), i.r. spectra (Perkin–Elmer 337 and 621), mass spectra (Varian Atlas CH-5 operating at 70 eV and an accelerating voltage of 3 kV). The ^{19}F n.m.r. spectra were obtained for saturated solutions in benzene with CCl_3F as internal standard.

Carbon, hydrogen, and nitrogen analyses were carried out in this department by Mrs. S. Swaddle and Mr. R. Davidson, and by Organic Microanalyses, Montreal, Quebec who also performed the halogen analyses.

Preparation of gem-N,N′-Dimethylethylenediaminotetrafluorocyclotriphosphonitrile

(a) From N,N′-Dimethylethylenediamine

Hexafluorocyclotriphosphonitrile (27.0 g, 0.108 mol) in diethyl ether (250 ml) was cooled to −15° and *N*,*N*′-dimethylethylenediamine (19.1 g, 0.216 mol) in ether (100 ml) was added dropwise with continual stirring. After the addition was complete, the reaction mixture was allowed to come to room temperature and the insoluble *N*,*N*′-dimethylethylenediamine hydrofluoride was filtered off. Removal of solvent from the filtrate yielded white crystals of *gem*-N,N′-dimethylethylenediaminotetrafluorocyclotriphosphonitrile (13.6 g, 0.046 mol) which, after recrystallization from petroleum ether (30–60°), had m.p. 97°.

Anal. Calcd. for $C_4H_{10}F_4N_5P_3$: C, 16.2; H, 3.4; N, 23.6. Found: C, 16.1; H, 3.7; N, 23.9.

(b) From 1,2,2,3-Tetramethyl-1,3-diaza-2-silacyclopentane

Hexafluorocyclotriphosphonitrile (5.4 g, 0.024 mol) and 1,2,2,3-tetramethyl-1,3-diaza-2-silacyclopentane (3.5 g, 0.024 mol) were heated at 80° for 2 h in a sealed Carius tube under vacuum. Vacuum transfer gave difluorodimethylsilane (2.3 g, 0.024 mol) and a white solid which, after recrystallization from ether, was identified as *gem*-N,N′-dimethylethylenediaminotetrafluorocyclotriphosphonitrile (4.5 g, 0.015 mol) from its m.p. 93–95°, ^{1}H n.m.r. spectrum, and analysis.

Anal. Found: C, 16.4; H, 4.0; N, 22.9.

(c) From gem-N,N′-Dimethylethylenediaminotetrachlorocyclotriphosphonitrile

gem-*N*,*N*′-Dimethylethylenediaminotetrachlorocyclotriphosphonitrile (1.9 g, 0.005 mol) and an excess of potassium fluorosulfite (9.6 g) were heated to 105° for 4 h in paraffin oil (20 ml). White crystals were collected by sublimation (25°/0.01 mm) and identified as *gem*-*N*,*N*′-dimethylethylenediaminotetrafluorocyclotriphosphonitrile (0.25 g, 0.0007 mol) from the ^{1}H n.m.r. spectrum and m.p. 95°.

Preparation of gem-Bis(N,N′-dimethylethylenediamino)-difluorocyclotriphosphonitrile

In one preparation of *gem*-*N*,*N*′-dimethylethylenediaminotetrafluorophosphonitrile the insoluble white precipitate (mainly dimethylethylenediamine hydrofluoride) was heated under reflux with diethyl ether for 15 min. After filtration of the solution, white crystals began to precipitate which were identified as *gem*-bis(*N*,*N*′-dimethylethylenediamino)difluorocyclotriphosphonitrile (0.41 g, 0.0016 mol), m.p. 174°.

Anal. Calcd. for $C_8H_{10}F_2N_7P_3$: C, 27.8; H, 5.8; N, 28.4. Found: C, 27.2; H, 5.8; N, 27.8.

Preparation of gem-N,N′-Dimethylethylenediaminohexafluorocyclotetraphosphonitrile

Octafluorocyclotetraphosphonitrile (4.3 g, 0.013 mol) in toluene (150 ml) was cooled to − 78° and *N,N′*-dimethylethylenediamine (2.3 g, 0.026 mol) in toluene (50 ml) was added dropwise to the cooled solution with continual stirring. After the addition was complete, the solution was allowed to stir for a further 30 min at − 78°, and then the insoluble amine hydrofluoride was filtered off before the solution was allowed to come to room temperature. Solvent was removed rapidly on a rotary evaporator and finally on the vacuum line in a sublimation apparatus. The solid residue sublimed (25°/0.01 mm.) to give white crystals of *gem-N,N′*-dimethylethylenediaminohexafluorocyclotetraphosphonitrile (0.5 g, 0.0014 mol), m.p. 40° (dec.).

Anal. Calcd. for $C_4H_{10}F_6N_6P_4$: C, 12.6; H, 2.6; N, 22.1. Found: C, 12.8; H, 2.7; N, 22.2.

The residue from the sublimation, a brown oil containing some crystals, was chromatographed on a florisil column using petroleum ether (30–60°) as eluant to give impure *gem-N,N′*-dimethylethylenediaminohexafluorocyclotetraphosphonitrile.

Anal. Found: C, 13.2; H, 2.7; N, 20.4.

Preparation of gem-N,N′-Dimethylethylenediaminotetrachlorocyclotriphosphonitrile

Hexachlorocyclotriphosphonitrile (5.3 g, 0.015 mol) in ether (700 ml) was cooled to − 78°. *N,N′*-Dimethylethylenediamine (2.7 g, 0.031 mol) in ether (150 ml) was added dropwise over a period of 3 h to the cooled solution with continual stirring. The solution was allowed to reach room temperature overnight and then the insoluble amine hydrochloride was filtered off (1.9 g, 0.012 mol). Solvent was removed on the rotary evaporator, and the residue dissolved in hot hexane (150 ml). Insoluble material (0.13 g) was filtered off, and solvent was removed from the filtrate which deposited white crystals of *gem-N,N′*-dimethylethylenediaminotetrachlorocyclotriphosphonitrile (2.5 g, 0.007 mol), m.p. 114–116°.

Anal. Calcd. for $C_4H_{10}Cl_4N_5P_3$: C, 13.2; H, 2.8; N, 19.3; Cl, 39.1. Found: C, 13.1; H, 3.1; N, 19.2; Cl, 38.7.

Preparation of gem-Bis(N,N′-dimethylethylenediamino)dichlorocyclotriphosphonitrile

Hexachlorocyclotriphosphonitrile (1.5 g, 0.0043 mol) and *N,N′*-dimethylethylenediamine (2.4 g, 0.028 mol) were heated at reflux in ether solution for 2 h. The insoluble amine hydrochloride (1.3 g, 0.0081 mol) was filtered off, and removal of solvent gave a white solid which, after recrystallization from toluene, was identified as *gem*-bis(*N,N′*-dimethylethylenediamino)dichlorocyclotriphosphonitrile (1.3 g, 0.0035 mol), m.p. 208° (dec.).

Anal. Calcd. for $C_8H_{20}Cl_2N_7P_3$: C, 25.4; H, 5.3; N, 25.6. Found: C, 24.7; H, 6.0; N, 24.4.

Preparation of gem-N,N′-Dimethylethylenediaminohexachlorocyclotetraphosphonitrile

Octachlorocyclotetraphosphonitrile (4.8 g, 0.010 mol) in ether (600 ml) was cooled to 0° and *N,N′*-dimethylethylenediamine (1.8 g, 0.020 mol) in ether (150 ml) was added dropwise during 3 h with continual stirring. The solution was allowed to come to room temperature overnight. The insoluble amine hydrochloride (1.5 g, 0.009 mol) was filtered off and solvent was removed to give a solid residue which was treated with boiling hexane. Insoluble material (0.28 g) was filtered off and removal of some solvent from the filtrate caused the precipitation of white crystals of *gem-N,N′*-dimethylethylenediaminohexachlorocyclotetraphosphonitrile (1.5 g, 0.003 mol), m.p. 91–92°.

Anal. Calcd. for $C_4H_{10}Cl_6N_6P_4$: C, 10.0; H, 2.1; N, 17.5; Cl, 44.7. Found: C, 9.6; H, 2.3; N, 17.2; Cl, 44.8.

Reaction of gem-N,N′-Dimethylethylenediaminotetrafluorocyclotriphosphonitrile with Anhydrous Hydrogen Chloride

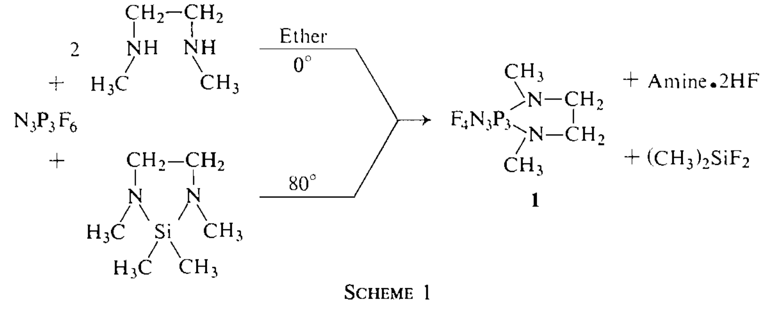
gem-N,N′-Dimethylethylenediaminotetrafluorocyclotriphosphonitrile (0.87 g, 0.0029 mol) and an excess of anhydrous hydrogen chloride were heated in a sealed Carius tube under vacuum for 16 h at 130°. Vacuum transfer of the volatile products gave only unreacted hydrogen chloride. The white solid residue, which was stable at 160°, was tentatively identified as an adduct $N_3P_3F_4\ (CH_3NCH_2CH_2NCH_3)xHCl$ ($x = 1$ or 2).

Anal. Calcd. for the mono-adduct: C, 14.5; H, 3.3; N, 21.1. Calcd. for the di-adduct: C, 13.0; H, 3.2; N, 18.9. Found: C, 13.9; H, 4.1; N, 20.0.

The i.r. spectrum (Nujol mull) 1280s, 1140w, 1115w, 1060s, 920s, 840sh, 810s, 727m, 670w, 505s cm^{-1}.

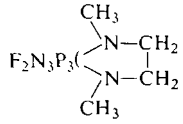
Discussion

The trimeric phosphonitrilic fluoride, $N_3P_3F_6$, reacts with either *N,N′*-dimethylethylenediamine in ether or, preferably, 1,2,2,3-tetramethyl-1,3-diaza-2-silacyclopentane in a sealed tube to



SCHEME 1

give *gem-N,N′*-dimethylethylenediaminotetrafluorocyclotriphosphonitrile (**1**) (see Scheme 1). Some of the disubstituted compound **2** was also isolated in the reaction with *N,N′*-dimethylethylenediamine.



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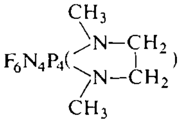

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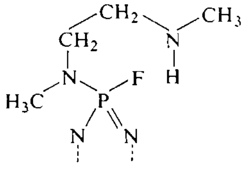
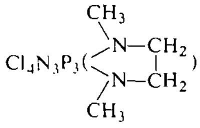


A

Similar reactions using the tetrameric fluoride, $N_4P_4F_8$, were mostly unsuccessful, yielding only a colorless oil which on standing turned brown, became more viscous, and after several days solidified. However, low yields of **3** were obtained from *N,N′*-dimethylethylenediamine using *dilute* solutions of the reactants in toluene at − 78° followed by a rapid work-up procedure. Apparently in the case of the tetramer the formation of a linear polymer is favored over the formation of the spiro derivative. Nucleophilic substitution by a difunctional amine will likely be a stepwise process, with the substitution of a fluorine by one of the amino groups as the first step. There are now two substitution processes that the monoamino derivative, **A**, can undergo. (*a*) The second amino group can substitute at the same phosphorus atom yielding a spiro derivative, or (*b*) the second amino group can substitute at a phosphorus atom on another phosphonitrilic molecule leading to the formation of linear polymers.[2] Consideration of cyclization kinetics shows that dilute solutions will favor the formation of the spiro derivative over the linear polymers as found experimentally.

It has previously been observed that other imidazolidines show a tendency to polymerize. For example, 1,2,2,3-tetramethyl-1,3-diaza-2-silacyclopentane polymerizes to a highly viscous liquid on standing, particularly in the presence of ammonium sulfate (11). The polymerization is reversible on heating. Similar behavior has been reported for the corresponding germanium imidazolidine, but attempts to prepare the tin analog gave a viscous liquid, apparently polymeric (12).



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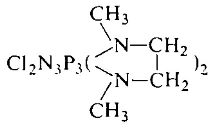

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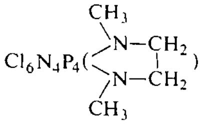

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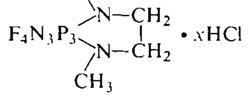
Both $N_3P_3Cl_6$ and $N_4P_4Cl_8$ react with *N,N′*-dimethylethylenediamine in a large volume of ether at − 10° to give good yields of the corresponding monosubstituted spiro compounds, **4** and **6**. The disubstituted derivative **5**, was obtained from $N_3P_3Cl_6$ and an excess of *N,N′*-dimethylethylenediamine under reflux in ether. More vigorous reaction conditions are apparently necessary to prepare the trisubstituted spiro compound.

Fluorination of the chloride **4** with potassium fluorosulfite in paraffin oil gave the corresponding fluoride **1**. Fluorination of the corresponding chlorides has also been used to prepare *cis*- and *trans*-1,3-$N_3P_3F_4(NMe_2)_2$ (6), $N_4P_4F_5(NMe_2)_3$, and $N_4P_4F_4(NMe_2)_4$ (from SbF_3) (7), and 1,2-$N_3P_3F_4(NH_2)_2$ (from CsF in acetonitrile) (13).

The reaction of an excess of anhydrous hydrogen chloride with **1** yielded an adduct tentatively identified as



(x = 1 or 2)

which was thermally very stable. An adduct is also formed initially in the reaction of $N_3P_3F_5$-NMe_2 with hydrogen halides, but in this case heating effects decomposition (3–5).

$$N_3P_3F_5NMe_2.HX \xrightarrow[>70^\circ]{HX} N_3P_3F_5X + Me_2NH.HX$$

(X = Cl, Br)

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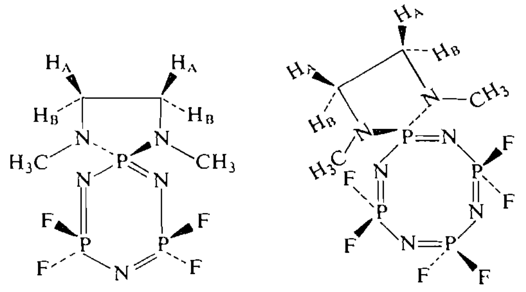
[2] Non-geminal substitution on the same phosphonitrilic molecule is considered to be unlikely for steric reasons.

The greater stability of the adduct in the case of the spiro compound may indicate a more basic exocyclic nitrogen than in $N_3P_3F_5NMe_2$. Some evidence to support this suggestion comes from measurements of the shifts in ν(C—D) of deuteriochloroform solutions of the compounds relative to ν(C—D) for pure deuteriochloroform. For $N_3P_3F_5NMe_2$, $\Delta\nu = 65\ \mathrm{cm}^{-1}$ compared to $\Delta\nu = 77\ \mathrm{cm}^{-1}$ for the spiro compound **1**. However, reservations have been expressed concerning this method of measuring base strengths (14).

The geminal structure of **1** (see Fig. 1) is indicated by its ^{19}F n.m.r. spectrum which shows only one doublet ($\delta = 68.4$ p.p.m., $J'_{\mathrm{PF}} = 930$ Hz) corresponding to the $\equiv PF_2$ fluorines. The disubstituted compound **2** also shows a $\equiv PF_2$ doublet ($\delta = 65.5$ p.p.m., $J'_{\mathrm{PF}} = 800$ Hz) and is thus assigned a geminal structure. The ^{19}F n.m.r. spectrum of **3** shows two doublets of relative intensity (2:1) ($\delta = 67.6$ p.p.m., $J'_{\mathrm{PF}} = 840$ Hz; $\delta = 68.7$ p.p.m., $J'_{\mathrm{PF}} = 835$ Hz) which have chemical shifts which are similar to those of *gem*-$N_4P_4F_6Cl_2$ (8) rather than those of non-geminal-$N_4P_4F_6(NMe_2)_2$ (3). The two doublets can therefore be assigned to nearest neighbor and antipodal $\equiv PF_2$ groups, respectively.



1 3

FIG. 1. Spiro fluorophosphonitrilic imidazolidines: *gem*-(*N*,*N*′-dimethylethylenediamino)tetrafluorocyclotriphosphonitrile (**1**) and *gem*-(*N*,*N*′-dimethylethylenediamino)hexafluorocyclotetraphosphonitrile (**3**).

The ^{1}H n.m.r. spectra of the phosphonitrilic imidazolidines are shown in Figs. 2 and 3. The spectra of both **1** and **3** show two doublets of relative intensities 3:2, the doublet to low field is therefore assigned to the methylene protons and the doublet to high field to the *N*-methyl

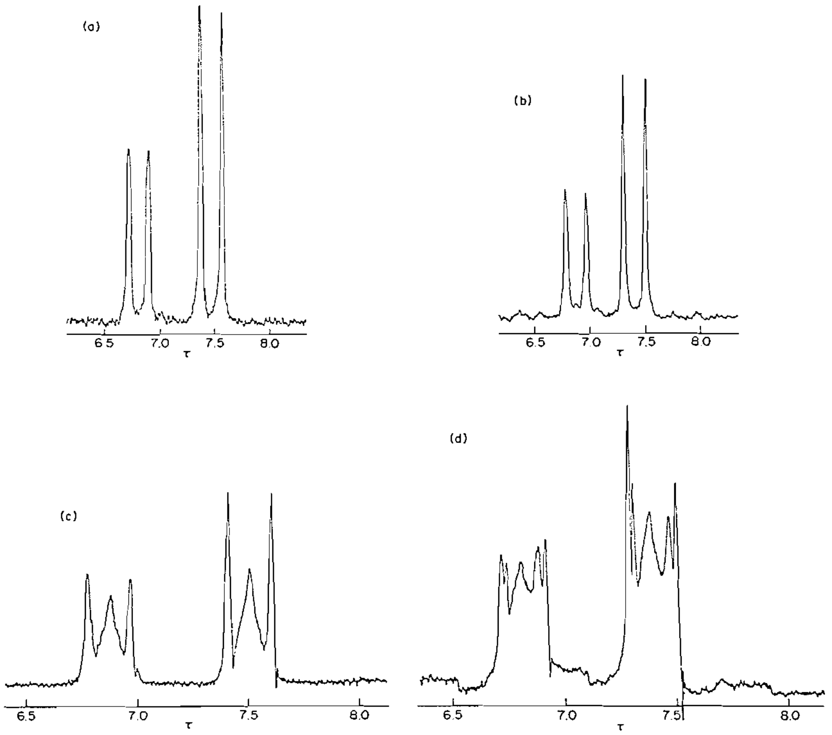


FIG. 2. The ^{1}H n.m.r. spectra of (*a*) *gem*-(*N*,*N*′-dimethylethylenediamino)tetrafluorocyclotriphosphonitrile (**1**); (*b*) *gem*-(*N*,*N*′-dimethylethylenediamino)hexafluorocyclotetraphosphonitrile (**3**); (*c*) *gem*-bis(*N*,*N*′-dimethylethylenediamino)difluorocyclotriphosphonitrile (**2**); (*d*) *gem*-bis(*N*,*N*′-dimethylethylenediamino)dichlorocyclotriphosphonitrile (**5**).

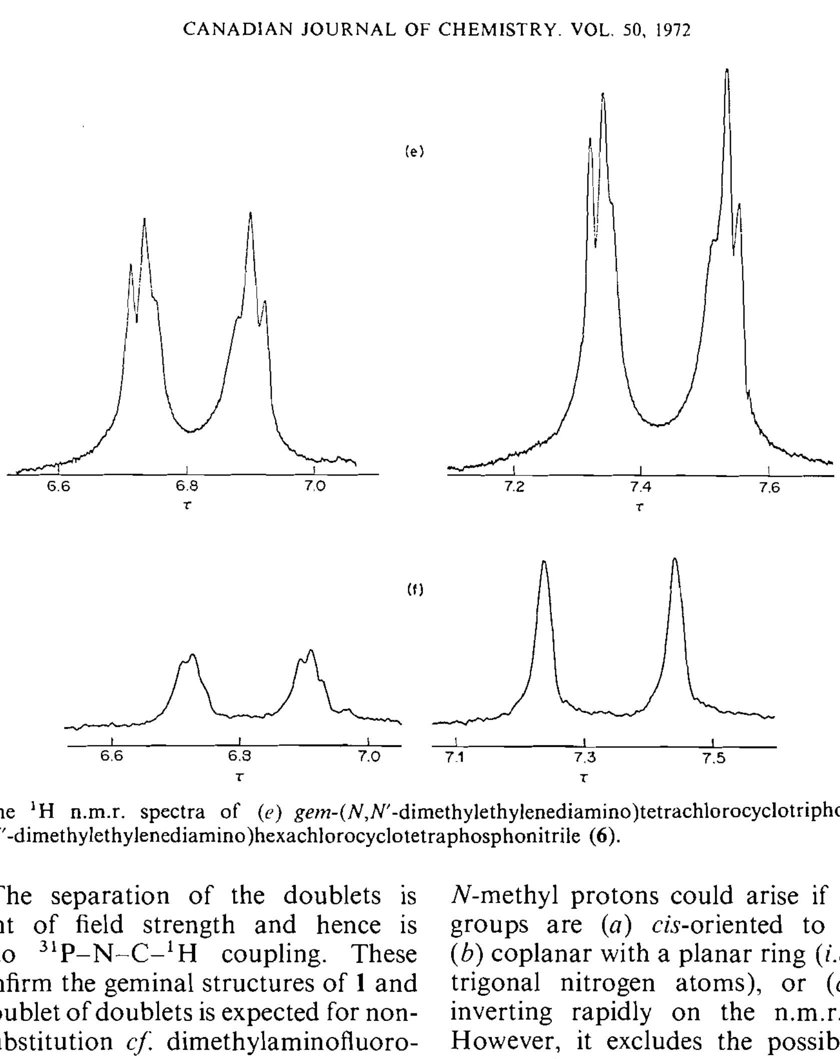


FIG. 3. The ^1H n.m.r. spectra of (*e*) *gem*-(*N*,*N*′-dimethylethylenediamino)tetrachlorocyclotriphosphonitrile (**4**); (*f*) *gem*-(*N*,*N*′-dimethylethylenediamino)hexachlorocyclotetraphosphonitrile (**6**).

protons. The separation of the doublets is independent of field strength and hence is assigned to $^{31}P–N–C–^1H$ coupling. These spectra confirm the geminal structures of **1** and **3** since a doublet of doublets is expected for nongeminal substitution *cf.* dimethylaminofluorophosphonitriles (3).

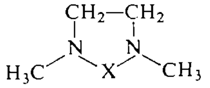
The apparent chemical equivalence of the methylene protons H_A and H_B in the ^1H n.m.r. spectra of the fluorophosphonitrilic imidazolidines **1** and **3** is perhaps unexpected and persists even at − 80°. It should be noted however that unexpectedly simple ^1H n.m.r. spectra have previously been observed for the methylene protons in both phosphorus (15, 16) and boron (11) imidazolidines.

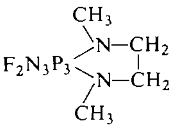
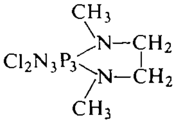
In the present examples a number of possible explanations can be given for this observation. Either (*a*) inversion, which is rapid with respect to *ca.* 0.01 s is occurring at the nitrogen atoms of the imidazolidine ring or, less likely (*b*) the imidazolidine ring is planar, or (*c*) protons H_A and H_B show accidental chemical shift equivalence. The sharp doublet observed for the *N*-methyl protons could arise if the *N*-methyl groups are (*a*) *cis*-oriented to the ring, or (*b*) coplanar with a planar ring (*i.e.* attached to trigonal nitrogen atoms), or (*c*) *trans* and inverting rapidly on the n.m.r. time scale. However, it excludes the possibility that the *N*-methyl groups are in a fixed *trans* position.

The ^1H n.m.r. spectra of the chlorides **4** and **6**, Fig. 3, are similar to those of the corresponding fluorides **1** and **3** except that splitting of the methylene proton doublets and of the *N*-methyl proton doublets (resolved for **4** only) into triplets is observed. This additional splitting (*ca.* 1 Hz) is probably due to long range coupling with the neighboring $\equiv PCl_2$ phosphorus atoms. Such interactions have previously been observed in the ^1H n.m.r. spectra of *cis*- and *trans*-1,3-$N_3P_3Cl_4(NMe_2)_2$ (6).

The ^1H n.m.r. spectra of the disubstituted compounds **2** and **5**, Fig. 2, are clearly not first-order and, in particular, a broad absorption is observed between the components of both the methylene proton doublet and the *N*-methyl proton doublet. This type of spectrum is

TABLE 1. ^1H n.m.r. data for some phosphorus imidazolidine derivatives



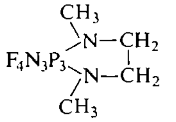
	N-CH$_2$			N-CH$_3$			
X*	τ	J'_{PH}(Hz)	M†	τ	J'_{PH}(Hz)	M†	Reference
P—C$_6$H$_5$	7.15	—	m	7.50	14.3	d	13
P—CH$_3$	6.95	—	m	7.45	14.7	d	13
	6.88	11.0	m	7.50	12.0	m	‡
F$_6$N$_4$P$_4$	6.87	11.5	d	7.42	12.0	d	‡
	6.82	12.0	m	7.41	12.8	m	‡
Cl$_6$N$_4$P$_4$	6.82	11.1	m	7.34	12.2	d	‡
Cl$_4$N$_3$P$_3$	6.82	10.0	m	7.42	11.6	m	‡
F$_4$N$_3$P$_3$	6.81	10.8	d	7.45	10.7	d	‡
O=P—C$_6$H$_5$	6.7	—	d of d	7.47	10.0	d	14

*Measured as saturated solutions in CCl$_4$ *vs.* tetramethylsilane as internal standard.
†Multiplicity: s, singlet; d, doublet; m, multiplet.
‡This work.

characteristic of an $X_nAA'X'_n$ system (17) and has been observed for a large number of dialkylaminophosphonitrilic derivatives (3, 6, 18). The separation of the two outer components of these signals is $|J_{AX} + J_{AX'}|$. The spectrum of the chloride **5** shows further splitting of the outer components into doublets, presumably due to long range coupling with the unique $\equiv PCl_2$ phosphorus atom.

Table 1 shows the relevant ^1H n.m.r. parameters for a series of heterosubstituted imidazolidines. The chemical shifts for the methylene protons indicate the following order of electron withdrawal by phosphorus substituents, $O{=}P{-}C_6H_5 > N_3P_3X_4 \sim N_4P_4X_6 > P{-}CH_3 > P{-}C_6H_5$ ($X = F, Cl$).

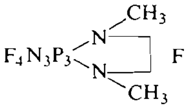
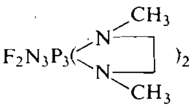
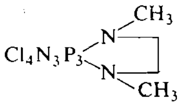
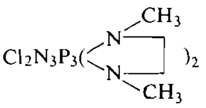
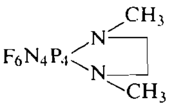
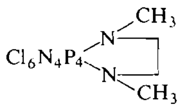
The i.r. spectra of the phosphonitrilic imidazolidines are reported in Table 2. The actual symmetry of



is at most C_{2V} (planar imidazolidine and phosphonitrilic rings) and is probably lower. The degeneracy of the ring vibration ν_{as}(PNP) and 1200–1300 cm^{-1} is therefore removed and peaks are observed at *ca.* 1250 cm^{-1} (**1**) and at 1240 and 1208 cm^{-1} (**2**). The decrease in ν_{as}(PNP) compared to $N_3P_3F_6$ (1290 cm^{-1}) (19) is consistent with weakening of the endocyclic π-bonding on replacement of fluorine by the less electronegative amino substituents, and is also observed for the tetrameric derivative (**3**)ν_{as}(PNP) 1385 cm^{-1} *cf.* ν_{as}(PNP) 1419 and 1438 cm^{-1} for $N_4P_4F_8$ (10). Other assignments can be made from a knowledge of the i.r. spectra of the phosphonitrilic fluorides (20) and chlorides (21) and their dialkylamino derivates (3). C—N antisym stretching 1160–1170 cm^{-1}; C_2NP sym. stretching 1030–1040 cm^{-1}; PF_2 asym. stretching 700–800 cm^{-1}; PCl_2 sym. and asym. stretching 500–600 cm^{-1}; and PF_2 deformation 480–500 cm^{-1}.

The partial mass spectra of the spiro compounds (**1**) and (**3**) and of $N_3P_3F_5NMe_2$, for

TABLE 2. The i.r. spectra of phosphonitrilic imidazolidines*

					
				1385 s	1325 s
					1310 m
1280 sh	1240 s	1250 s	1225 s	1262 m	
1245 sh	1208 s	1230 s	1205 sh	1250 sh	
1230 vs				1212 m	
1160 s	1162 s	1180 vs	1160 s	1160 s	1160 m
	1115 sh	1140 sh		1120 sh	
1040 m	1030 s	1035 m	1030 s	1040 s	1040 m
932 m	945 s	948 m	940 s	980 s	985 w
905 vs	930 sh			960 sh	945 m
				950 sh	
				935 vs	
				915 sh	
803 s	892 m	880 w	860 m	865 w	885 m
	868 m	865 m	810 m	820 m	825 w
	852 m	845 m			
		805 m			
747 vs	755 s	745 m	745 m	732 vs	745 m
	735 m			702 vs	725 w
695 w	690 s	690 w	690 s		620 m
		630 m			
		585 sh	580 m		590 s
		562 s	540 m		550 w
		525 s			510 s
487 s	490 s	492 m	490 s	495 sh	488 sh
462 m	472 s			488 vs	455 w
				445 sh	

*Nujol mull.

comparison, were obtained. Noteworthy features include the fact that the parent ions exhibit the strongest peak in the spectra of the spiro compounds, (*m/e* 297, **1**; *m/e* 389, **3**) whereas the ion $N_3P_3F_5^+$ (*m/e* 230) is predominant in the spectrum of $N_3P_3F_5NMe_2$. The P + 1 peaks are larger than expected on the basis of natural isotopic abundances, especially for the spiro compounds. This may be due to the formation of a protonated ion PH^+, which suggests that the exocyclic nitrogen atom is more basic in the spiro compound than in $N_3P_3F_5NMe_2$ (*cf.* adduct formation with hydrogen halides). Strong peaks corresponding to fluorophosphonitrilic hydride ions *e.g.* $N_3P_3F_4H_2^+$ (*m/e* 213) were observed in the spectra of all three compounds. Halogenophosphonitrilic hydrides are not known although extensive attempts have been made to prepare them[3] (22, 23).

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[3] For example, the reaction between $N_4P_4F_7Br$ and tri-*n*-butyltin hydride gives tri-*n*-butyltin bromide in almost quantitative yield, but the major phosphonitrilic product is $N_4P_4F_8$ (T. Chivers and N. L. Paddock, unpublished data).

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