514. *Phosphonitrilic Derivatives. Part I. The Preparation of Cyclic and Linear Phosphonitrilic Chlorides.*

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The reaction between phosphorus pentachloride and ammonium chloride in *sym.*-tetrachloroethane gives rise to two series of compounds, cyclic $(PNCl_2)_n$ and linear $(PNCl_2)_n,PCl_5$. The latter are distinguished by their high polarity and consequent insolubility in non-polar media. The conditions required for the preparation of each series in high yield are given. In the cyclic series, the octameric chloride is described for the first time; improved values for the physical properties of the other cyclic chlorides are presented.

THE phosphonitrilic chlorides $(PNCl_2)_n$ were first recognised as an homologous series by Stokes,[1] who separated the trimer to hexamer and an impure form of the heptamer from the products of the reaction of ammonium chloride with phosphorus pentachloride in sealed tubes at temperatures in the range 150—200°. The method of preparation was improved by Schenk and Römer,[2] who used *sym.*-tetrachloroethane as a solvent for the phosphorus pentachloride. We now show that, when carried out by the latter method, the reaction gives a mixture of two series of phosphonitrilic chlorides, linear and cyclic, and describe the conditions required for obtaining each type of product in high yield.

The ideal equation for the reaction is

$$PCl_5 + NH_4Cl \longrightarrow \frac{1}{n}(PNCl_2)_n + 4HCl$$

but reaction is never quite complete, even when ammonium chloride is used in excess. If the reaction is carried out as described by Schenk and Römer, the product is a pasty mass of oil and crystals; most of it, typically 75—80%, is a mixture of polymers soluble in light petroleum. The insoluble portion is a brown viscous oil having the composition $(PNCl_2)_n,PCl_5$, where n usually exceeds ten.

The yield of petrol-insoluble polymers can be reduced almost to zero [3] by adding the phosphorus pentachloride to a refluxing suspension of ammonium chloride during 7—8 hr. The yield of the trimer is greatly increased, mainly at the expense of the petrol-insoluble compounds. Conversely, if an excess of phosphorus pentachloride is used, the yield of petrol-insoluble compounds is increased, mainly at the expense of the higher cyclic polymers; as the excess is increased, the proportion of petrol-insoluble material increases.[4] This is equivalent to stopping the reaction before completion; if it is stopped when half the theoretical hydrogen chloride has been evolved, the product is almost wholly insoluble in petrol.

The petrol extract from the product of a normal reaction is an oily crystalline mass consisting exclusively of polymers $(PNCl_2)_n$. Individual polymers from the trimer to the octamer have been obtained from it by a combination of fractional extraction, fractional distillation *in vacuo*, and fractional crystallisation. The residue after removal of the octamer is a light yellow oil of average composition $(PNCl_2)_{12-13}$, which is not further separable by distillation. Fluorination of this mixture (to be described later) shows it to contain polymers up to at least $(PNCl_2)_{17}$. Physical properties of the polymers, differing in some cases from those described by Stokes, are given in Table 1.

We have found the ultraviolet spectra to be different from those reported in the literature.[6] Numerical values of the logarithm of the molar extinction coefficient,

[1] Stokes, *Amer. Chem. J.*, 1897, **19**, 782.
[2] Schenk and Römer, *Ber.*, 1924, **57**, 1343.
[3] Paddock, Proctor, and Searle, B.P. Appln. 13222/58.
[4] See also X. Bilger, Fr. P. 1,157,097

TABLE 1. *Some physical properties of the phosphonitrilic chlorides.*

Polymer	M. p.[e]	d_{20} (g. c.c.$^{-1}$)	Space group or crystal system	Unit cell dimensions (Å) *a*	*b*	*c*	*Z*	P–N stretching frequency [a] (cm.$^{-1}$)	NMR chemical shift [b] (p.p.m.)
$(PNCl_2)_3$	112·8°	1·99[f]	*Pnam*	14·15	6·20	13·07	4	1218	−20
$(PNCl_2)_4$[c]	122·8	2·18[f]	P_{4_2}/n	10·82	—	5·95	2	1310	+7
$(PNCl_2)_5$[d]	41·3	2·02	$P_{2_12_12_1}$	19·37	15·42	6·23	4	1355	+17
$(PNCl_2)_6$[d]	92·3	1·96	Triclinic	10·6	10·7	11·4	2	1325	+16
				$\alpha = 93·5°$	$\beta = 90°$	$\gamma = 117°$			
$(PNCl_2)_7$	8—12	1·890	—	—	—	—	—	1310	+18
$(PNCl_2)_8$	57—58	1·99	C_2/c or *Cc*	24·7	6·2 $\beta = 111°$	20·4	4	1305	+18

[a] This frequency corresponds to the E' and E_u modes in the trimer and tetramer respectively.[5] For the pentamer, hexamer, and an impure form of the heptamer, similar results have been obtained by Krause.[6] Detailed assignments will be given in another paper. [b] Relative to 85% phosphoric acid; a positive shift indicates greater shielding than in phosphoric acid. The shifts are estimated to be accurate to within ±1 p.p.m. [c] This form is obtained by crystallisation from solvents near room temperature and the crystallographic data are those of Ketelaar and de Vries:[8] Jaeger and Beintema[g] found $a = 10·79$, $c = 5·93$ Å. At temperatures above 60° it is transformed irreversibly into a second form (space group P_{4_2}/n, $a = 10·82 \times \sqrt{2}$, $c = 5·95$ Å), which may also be obtained by recrystallising from the melt. [d] A triclinic form of the pentamer and a second triclinic form of the hexamer have been obtained, but not the orthorhombic form described by Stokes[1] and Tassin.[i] [e] The m. p.s determined by Stokes[1,h] were, in order, 114°, 123·5°, 40·5—41°, 91°, and $< -18°$. The differences are small except for the heptamer. [f] These values were also obtained by Stokes.[h] [g] Jaeger and Beintema, *Proc. Acad. Sci. Amsterdam*, 1932, **35**, 756. [h] Stokes, *Amer. Chem. J.*, 1895, **17**, 275. [i] Tassin, *Z. Krist.*, 1899, **31**, 304.

calculated on a monomeric $PNCl_2$ basis, are given in Table 2. In each case the peak of the absorption band lies at an unattainably short wavelength. Nevertheless, it can be seen from the Table that the spectra are closely similar, and show no regular progression with increase of molecular weight. The absorption cannot therefore be due to a $\pi \longrightarrow \pi^*$ transition in the ring. The spectrum of the trimer is nearly the same, whether cyclohexane or methanol is used as a solvent, and is not greatly changed even in sulphuric acid. The absorption is therefore unlikely to be due to an $n \longrightarrow \pi^*$ transition on the nitrogen atoms; it is tentatively assigned to an excitation of the unshared electrons on the chlorine atoms.

TABLE 2. *Ultraviolet absorption spectra of the phosphonitrilic chlorides.*

	$\log_{10} \varepsilon$ (on a monomeric $PNCl_2$ basis) for wavelengths indicated (in mμ)						
Compound	210	215	220	225	230	235	240
$(PNCl_2)_3$[a]	—	1·76	1·48	1·06	0·50	0·00	—
$(PNCl_2)_3$[b]	2·12	2·05	1·82	1·53	1·16	0·66	0·13
$(PNCl_2)_4$	2·56	2·30	2·03	1·72	1·37	0·95	0·53
$(PNCl_2)_5$	2·63	2·37	2·07	1·70	1·30	0·86	0·44
$(PNCl_2)_6$	2·70	2·44	2·12	1·69	1·17	0·66	0·00
$(PNCl_2)_7$	—	—	2·10	1·72	1·30	0·94	0·61
$(PNCl_2)_8$	—	—	—	1·74	1·21	0·72	0·23
$(PNCl_2)_{12-13}$	—	—	—	1·72	1·28	0·88	0·36

[a] In 98·7% sulphuric acid. [b] This, and all other spectra, were obtained in n-hexane.

The cyclic nature of the trimer[7] and of the tetramer[8] has been proved directly by *X*-ray crystallography. If the higher polymers were linear they would be either highly polar entities, or diradicals; they do not show properties characteristic of either structure. Krause[6] has shown that the trimer to heptamer have small dipole moments. The dielectric constant of the mixture $(PNCl_2)_{12-13}$ is 3·63 at 20°, only slightly greater than

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

[6] Krause, *Z. Elektrochem.*, 1955, **59**, 1004.

[7] Wilson and Carroll, *Chem. and Ind.*, 1958, 1558; Part II, following paper.

[8] Ketelaar and de Vries, *Rec. Trav. chim.*, 1939, **58**, 1081.

that of the pentamer at 45° (3·48). The cyclic nature of all the polymers is demonstrated by their nuclear magnetic resonance spectra, which all exhibit a single peak, indicating that all the phosphorus atoms in a particular molecule are equivalent. The mixture $(PNCl_2)_{12-13}$ also shows only one resonance, because the chemical shift becomes independent of ring size above the pentamer (see Table 1).

The insolubility of the mixture of composition $(PNCl_2)_n,PCl_5$ in light petroleum shows that it cannot be merely a solution of phosphorus pentachloride in a mixture of cyclic polymers. Further proof is provided by its dielectric constant, 14·3, which is high compared with those of the cyclic polymers (see above) and that of phosphorus pentachloride itself (2·85 in the liquid at 160°, increasing to 4·23 in the solid at 22·8°).[10] Its nuclear magnetic resonance spectrum shows no resonance due to free phosphorus pentachloride.

Although they are closely related to the cyclic compounds in formula, the compounds $(PNCl_2)_n,PCl_5$ are much more reactive; they are hydrolysed, for instance, more readily than the cyclic chlorides. The elements of phosphorus pentachloride are slowly eliminated in boiling tetrachloroethane, with formation of a rubber-like high polymer. Reaction is more rapid in the presence of ammonium chloride, with the evolution of hydrogen chloride. When its amount reaches that corresponding to the conversion of the combined phosphorus pentachloride into $PNCl_2$, polymerisation takes place. The rubber-like high polymer is again the main product, showing that the phosphorus pentachloride is not loosely attached to a medium-sized cyclic polymer. At the same time, cyclic polymers are formed in greater yield than would be expected from the phosphorus pentachloride content; they consist mainly of cyclic polymers (heptamer and above) with a small amount of the trimeric chloride.

The most likely interpretation is that the polymers $(PNCl_2)_n,PCl_5$ are linear, some phosphorus pentachloride dissociating off the ends to give the trimeric chloride found on ammonolysis in tetrachloroethane solution. The composition of the remaining product would then depend upon a competition between cyclisation and chain extension, the latter predominating to an increasing extent with chain growth. The suggestion of linearity of the compounds $(PNCl_2)_n,PCl_5$ is supported by the fact that direct interaction of phosphorus pentachloride with the cyclic polymers requires temperatures [11] of the order of 300—350°, which, in the absence of the phosphorus pentachloride, lead to rupture of the ring bonds and polymerisation.[12]

The first member of the series was prepared by Groenveld *et al.*,[13] who suggested the constitution $PCl_4{}^+NPCl_3{}^-$. The second was isolated by Bilger [4] from the products of the reaction of phosphorus pentachloride with a deficit of ammonium chloride. He characterised it as its anilide $P_3N_2Cl_2(NHPh)_7$, and suggested the general formulation $Cl\cdot[PCl_2N]_n\cdot PCl_4$ (see also ref. 14). The covalent and generalised ionic structures are not necessarily incompatible; phosphorus pentachloride itself exists in both ionic and covalent forms, and Rydon [15] has demonstrated the ready interchange of groups in other derivatives of quinquevalent phosphorus. Both types of structure, however, contain phosphorus in three different environments, and should therefore exhibit three nuclear magnetic resonances. In fact, only two are observed, a major one at +18 p.p.m. and a minor one at −12 p.p.m. The first, in the same place as the phosphorus resonance in the cyclic polymers, must be due to the PCl_2 group, and may, of course, coincide with that for another type of environment. The other is not yet identified. Such a symmetrical structure as $\{Cl\cdot[PCl_2N]_n{:}PCl_3\}^+Cl^-$, from which two resonances would be expected, seems to be ruled

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[10] Lowry and Hofton, *J.*, 1932, 207.

[11] Paddock, B.P. Appln. 28,207/57.

[12] Meyer, Lotmar, and Pankow, *Helv. Chim. Acta*, 1936, **19**, 930.

[13] Groenveld, Visser, and Seuter, *J. Inorg. Nuclear Chem.*, 1958, **8**, 245.

[14] Paddock and Searle, " Advances in Inorganic Chemistry and Radiochemistry," Vol. 1, Academic Press Inc., New York, 1959, p. 347.

[15] Rydon, *Chem. Soc. Special Publ. No.* 8, 1957, p. 61.

out by their relative intensities. The ratio of peak areas should be $(n - 1) : 2$, whereas in fact it is nearer $n : 1$. The determination of the precise mode of termination of the phosphonitrilic chain clearly requires further work.

Other linear phosphonitrilic derivatives are known; Bode and Bach[16] described the compound $Ph{\cdot}[PPh_2N]_3{\cdot}H,HClO_4$, and Schmitz-Dumont and Külkens[17] have obtained a fluoride $P_3N_3F_6,2HF,2H_2O$ which can be formulated somewhat similarly. Phosphonitrilic chlorides in which the end-groups are formed from the elements of hydrogen chloride, rather than phosphorus pentachloride, as above, have been prepared by Becke-Goehring and Koch.[18]

EXPERIMENTAL

The following abbreviations have been found convenient. CPNC is used for the mixture of cyclic and linear polymers obtained on reaction of phosphorus pentachloride with ammonium chloride. LPNC refers to the linear component, insoluble in light petroleum, SPNC to the unfractionated mixture of cyclic, soluble polymers. From this mixture, trimeric to octameric phosphonitrilic chlorides were isolated, the residual mixture of higher cyclic phosphonitrilic chlorides being denoted by HPNC.

The phosphorus pentachloride was fresh commercial-grade material. The ammonium chloride was dried in air, ground, and sieved. Except where otherwise stated, its specific surface was approximately 850 $cm.^2$ $g.^{-1}$. The solvents used in the preparations were technical-grade reagents; for the infrared work they were analytical-grade chemicals further purified where necessary. The n-hexane used for the ultraviolet spectroscopy was purified chromatographically on silica-gel.

Analyses of mixtures of phosphonitrilic chlorides were carried out by infrared methods. The infrared spectra were obtained from potassium chloride discs or solutions in carbon disulphide or in carbon tetrachloride, a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics being used. The ultraviolet spectra were obtained by using a Unicam S.P. 500 spectrophotometer. The nuclear magnetic resonance spectra were obtained for the liquids or solutions in benzene in 12 mm. diameter tubes, the Varian Associates V4300B high-resolution nuclear magnetic resonance spectrometer being used at a frequency of 12 Mc./sec. and a field strength of approximately 7000 gauss.

M. p.s of polymers from the trimer to the hexamer were taken from cooling curves and are corrected; other m. p.s were measured by micro-methods. Molecular weights were measured cryoscopically in benzene or ebulliometrically in carbon tetrachloride. Dielectric constants were measured in a water-jacketed glass cell, the electrodes being concentrically-mounted gold-plated silver tubes, with a capacity (in air) of 34·5 $\mu\mu$F. The cell was calibrated with nitrobenzene which was redistilled *in vacuo* after prolonged drying (P_2O_5) at room temperature. Capacities were measured at 15 kc./sec. by comparison with a variable standard capacitance.

Preparation of Phosphonitrilic Chlorides.—Standard preparation. Phosphorus pentachloride (625·5 g., 3·0 moles) and ammonium chloride (176·5 g., 3·3 moles) were heated in refluxing *sym.*-tetrachloroethane (1·0 l.) for 7½ hr., during which time 12·0 moles hydrogen chloride (100%) were evolved. (A little of this was due to attack on the solvent.) The excess of ammonium chloride (20·0 g.) was filtered off from the resulting pale brown solution, and the solvent was removed by distillation under reduced pressure; 326·5 g. (93·9%) of a brown mixture of oil and crystals (CPNC) were recovered. From this mixture, 235·5 g. of a mixture of cyclic polymers (SPNC) were obtained by repeated extraction with light petroleum (b. p. 40—60°), leaving 88·0 g. (27%) of a brown oil (LPNC) consisting of a mixture of linear polymers. The SPNC was a mixture of polymers $(PNCl_2)_n$ (Found: P, 26·5; N, 11·9; Cl, 60·9. Calc. for $PNCl_2$: P, 26·7; N, 12·1; Cl, 61·2%). Infrared analysis showed it to contain 37% of trimer, 28% of tetramer, and 35% of higher cyclic polymers.

If the reaction is carried out as described, the molecular weight of the product insoluble in petrol is too great for chemical analysis to be a sensitive index of molecular composition. By reaction of ammonium chloride with 107 g. of another sample of LPNC prepared as above,

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[16] Bode and Bach, *Ber.*, 1942, **75**, 215.

[17] Schmitz-Dumont and Külkens, *Z. anorg. Chem.*, 1938, **238**, 189.

[18] Becke-Goehring and Koch, *Chem. Ber.*, 1959, **42**, 1188.

0·2 mole of hydrogen chloride was evolved, indicating an average of the elements of one phosphorus pentachloride molecule to 17 $PNCl_2$ units, or an average molecular weight of 2180, agreeing within experimental error with 2400 (ebulliometric) and 2100 (cryoscopic). The main product was a rubber-like solid insoluble in light petroleum.

The dielectric constant of another sample of LPNC was 14·3, implying a highly polar structure. The hydrolysis rates of this sample of LPNC and pure heptamer were compared by adding water to agitated solutions of the polymers in chloroform (1·13 g./100 ml.). After 7 hr., 4·3% of the chlorine in the LPNC was present as chloride ion. Even after 72 hr., however, the concentration of chloride ion from the hydrolysis of the heptamer was too small to be detected with silver nitrate solution.

The LPNC exhibited two peaks in its nuclear magnetic resonance spectrum, at +18 p.p.m. and −12 p.p.m. respectively, showing that it contains compounds of the same type as described below.

Effect of slow addition of phosphorus pentachloride. Phosphorus pentachloride (62·5 g., 0·3 mole) and ammonium chloride (176·5 g., 3·3 moles) were heated in refluxing *sym.*-tetrachloroethane (1·0 l.). The refluxing solvent was returned to the reaction vessel through a bed of phosphorus pentachloride (563 g., 2·7 moles) which was thereby slowly extracted into the reaction vessel during a period of 6 hr. After a total reaction time of 7½ hr., 11 moles (92%) of hydrogen chloride had been evolved and 21·7 g. excess of ammonium chloride remained; CPNC (322·3 g., 92·6%) was recovered from the solution. It contained 5% LPNC, 54% of trimer, 11·5% of tetramer, and 29% of higher cyclic polymers.

In another experiment, phosphorus pentachloride (563 g., 2·7 moles) was dissolved in hot *sym.*-tetrachloroethane (1·0 l.), and the solution added during 8 hr. to a mixture of phosphorus pentachloride (62·5 g., 0·3 mole) and ammonium chloride (176·5 g., 3·3 moles) in refluxing *sym.*-tetrachloroethane (1·0 l.). After a total reaction time of 10½ hr., 11·7 moles (98%) of hydrogen chloride had been evolved and 20·7 g. of excess of ammonium chloride remained. CPNC (328·0 g., 94·2%) was recovered, and contained 2% of LPNC, 63% of trimer, 13% of tetramer, and 22% of higher cyclic polymers.

Effect of an excess of phosphorus pentachloride. Ammonium chloride (321·0 g., 6·00 moles) and phosphorus pentachloride (1313·5 g., 6·30 moles), which had been heated *in vacuo* to drive off phosphorus oxychloride, were heated in *sym.*-tetrachloroethane (2·0 l.; dried over K_2CO_3 and fractionated) for 8 hr. under reflux; 736·8 g. of CPNC were obtained from which the SPNC was separated by solution in petrol (448·3 g., 60·9%). The analysis (P, 25·4; N, 10·5; Cl, 63·6%) of the residual LPNC (288·5 g., 39·1% yield) corresponded to $(PNCl_2)_{11}PCl_{4\cdot2}$. Its nuclear magnetic resonance spectrum exhibited two peaks, at +18 p.p.m. and −12 p.p.m., of relative areas 10·5 : 1. There was no peak at +80 p.p.m. corresponding to free phosphorus pentachloride.[19]

118·1 g. of this LPNC were heated with 14·0 g. of ammonium chloride in 340 ml. of *sym.*-tetrachloroethane under reflux. Polymerisation occurred after 5½ hr., at which time 0·328 mole of hydrogen chloride had been evolved, corresponding to the composition $(PNCl_2)_{10\cdot6}PCl_5$. The rubbery product was extracted with light petroleum, giving 18·65 g. of a dark oil, containing 10·5% of trimer. The remainder consisted of cyclic polymers higher than the heptamer. Another sample of LPNC was heated in tetrachloroethane solution, but without ammonium chloride; it polymerised after 29 hr.

In another experiment, ammonium chloride (160·5 g., 3·0 moles), having a specific surface of 2800 cm.^{2} g.$^{-1}$, and phosphorus pentachloride (688 g., 3·3 moles) were heated in refluxing *sym.*-tetrachloroethane (1·0 l.) for 3¼ hr. Hydrogen chloride (11·8 moles, 98%) was evolved and 2·0 g. of ammonium chloride remained; 444 g. of CPNC were recovered, containing 68% of LPNC, 23% of trimer, 6% of tetramer, and 3% of higher cyclic polymers.

Separation of Cyclic Polymers.—CPNC (7750 g.) was extracted with 16·5 l. of light petrol (b. p. 40—60°) to obtain 19·5 l. of a solution of cyclic polymers (5700 g.; containing 35% of trimer, 22% of tetramer) and insoluble LPNC (2050 g.). The petrol solution was extracted in batches with 98·7% sulphuric acid (2300 ml.) in a three-stage fractionation scheme. Trimer was dissolved preferentially by the acid and was recovered from it by diluting the acid solution to approximately 60% sulphuric acid and back-extracting the precipitated trimer with fresh petrol. Fractional crystallisation from this petrol solution then gave 1060 g. of trimer (m. p. 112°) and 690 g. of a mixed polymer fraction. After further recrystallisation from petrol and

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[19] Van Wazer, Callis, Shoolery, and Jones, *J. Amer. Chem. Soc.*, 1956, **78**, 5715.

from the melt the trimer had m. p. 112·8° (Found: P, 26·7; N, 12·1; Cl, 61·2%; *M*, 347. Calc. for $P_3N_3Cl_6$: P, 26·7; N, 12·1; Cl, 61·2%; *M*, 348).

The acid-insoluble SPNC was fractionally crystallised to give 712 g. of tetramer (m. p. 122°), 515 g. of a mixed polymer fraction (69% of trimer, 20% of tetramer), 808 g. of a mixture of oil and crystals, and 1915 g. of a light yellow oil. After recrystallisation from petrol and from the melt the tetramer had m. p. 122·8° (Found: P, 26·8; N, 12·1; Cl, 61·2%; *M*, 465. Calc. for $P_4N_4Cl_8$: *M*, 464).

Several samples of the residual pale yellow oil from different acid extractions were mixed to form the starting material (3930 g.) for the extraction of higher cyclic polymers. It was stripped of petrol at 100°/0·1 mm. and distilled. A crude pentameric fraction, b. p. 130—185°/0·1 mm. (1650 g.), some fairly pure hexamer crystals (40 g.), and an oily residue A (2240 g.) were obtained. The crude pentameric fraction (1650 g.) was redistilled to give a mixed trimer and tetramer fraction (250 g.), b. p. $<130°/0·1$ mm., a main pentamer fraction (1020 g.), m. p. 34—35°, b. p. 130—155°/0·1 mm., and an oil + crystal residue B (350 g.) containing pentamer, hexamer, and heptamer. Repeated crystallisation of the main pentamer fraction from petrol and from the melt gave 250 g. of pure pentamer, m. p. 41·3° (Found: P, 26·8; N, 12·0; Cl, 61·2%; *M*, 582. Calc. for $P_5N_5Cl_{10}$: *M*, 580). Its dielectric constant at 45° was 3·43.

Residue B was crystallised from light petroleum at 0° to give 180 g. of hexamer, m. p. 91°, and 170 g. of residue C. After recrystallisation from petrol the hexamer had m. p. 92·3° (Found: P, 26·8; N, 12·05; Cl, 61·2%; *M*, 697. Calc. for $P_6N_6Cl_{12}$: *M*, 696).

Some residue A (1780 g.) was redistilled to give a crude heptamer fraction (289 g.), b. p. 140—190°/10^{-3} mm., and 1472 g. of residue D. On cooling the crude heptamer fraction to $-10°$ overnight, 48 g. of crystals were deposited which, when recrystallised from light petrol, yielded 27 g. of *octamer*, m. p. 57—58° (Found: P, 26·8; N, 12·0; Cl, 61·25%; *M*, 915. $P_8N_8Cl_{16}$ requires *M*, 928).

The residual crude heptamer fraction (242 g.) was redistilled to give a mixed pentamer and hexamer fraction (41 g.), b. p. $<160°/10^{-3}$ mm., a 98% pure heptamer fraction (106 g.), b. p. 160—180°/10^{-3} mm., and an oily residue. The heptamer fraction was mixed with residue C, which had been stripped of pentamer and hexamer at 190°/0·1 mm., and redistilled to give pure heptamer (87 g.), m. p. 8—12° (Found: P, 26·7; N, 12·0; Cl, 61·2%; *M*, 805. Calc. for $P_7N_7Cl_{14}$: *M*, 812).

Finally, residue D was redissolved in light petroleum, separated from polymerised material, and recovered; it is referred to in the main text as HPNC (Found: P, 26·7; N, 12·1; Cl, 61·2%; *M*, 1420—1450). Its dielectric constant at 20° was 3·63.

Reaction of Phosphorus Pentachloride with Trimeric Phosphonitrilic Chloride.—The trimeric chloride and phosphorus pentachloride, in the proportions required for final average compositions $(PNCl_2)_n,PCl_5$, where $n = 2, 4, 6, 8, 10, 15$, and 20, were ground, intimately mixed, and heated in sealed glass tubes at 350° for 5 hr. The products were shown to be free from unchanged trimeric phosphonitrilic chloride. All were insoluble in low-boiling petrol and all absorbed at 1230—1246 cm.$^{-1}$, and at 1300—1305 cm.$^{-1}$; so did all the samples of LPNC described in the text. Similarly, all the compounds of composition $(PNCl_2)_n,PCl_5$, however prepared, exhibit two nuclear magnetic resonance peaks, at +18 p.p.m. and −12 p.p.m.

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