# **721.** *Phosphonitrilic Derivatives. Part III.*[1] *The Cyclic Phosphonitrilic Fluorides.*

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The phosphonitrilic fluorides ($[PNF_2]_n$, $n = 3$—11) have been prepared by reaction of a mixture of sulphur dioxide and potassium fluoride with the cyclic phosphonitrilic chlorides. Their main physical properties are tabulated, together with less detailed information on the higher polymers up to $[PNF_2]_{17}$; their infrared spectra show them all to be monocyclic. Intermolecular forces are weak, and the rings flexible.

VARIOUS investigators have shown that it is not possible to prepare the phosphonitrilic fluorides either by reaction of ammonium fluoride with phosphorus pentachloride,[2] or by fluorination of the corresponding phosphonitrilic chlorides with anhydrous hydrogen fluoride.[3] The chief product of the fluorination of the trimeric chloride with lead fluoride [4] is a mixture of tetrameric chlorofluorides, though traces of the trimeric fluoride may also be formed.[5] Seel and Langer have shown that the trimeric and tetrameric phosphonitrilic chlorides can be fluorinated completely by potassium fluorosulphite, either dry [6] or in nitrobenzene.[7]

The preparation of the higher members of the series is now described, and their cyclic nature proved. The main physical properties of the polymers $(PNF_2)_n$ are recorded, where $n = 3$—11 inclusive, together with less detailed information on polymers up to $(PNF_2)_{17}$. The preparative technique has been modified by using a mixture of potassium fluoride and sulphur dioxide instead of potassium fluorosulphite.* The trimeric–hexameric fluorides were prepared from the corresponding chlorides, the higher members by fluorination of a mixture of the higher cyclic chlorides followed by fractional distillation.

The retention times of the individual polymers on a vapour-phase chromatographic

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* After the preparative part of this work was complete, Haber and Uenishi [8] published details of their preparation of the trimeric and tetrameric fluorides by the same method.

[1] Part II, Wilson and Carroll, *J.*, 1960, 2548.

[2] Lange and von Krueger, *Ber.*, 1932, **65**, 1253.

[3] Bode and Clausen, *Z. anorg. Chem.*, 1951, **265**, 229.

[4] Schmitz-Dumont and Külkens, *Z. anorg. Chem.*, 1938, **238**, 189; Schmitz-Dumont and Braschos, *ibid.*, 1939, **243**, 113.

[5] Schmitz-Dumont and Walther, *Z. anorg. Chem.*, 1959, **298**, 193.

[6] Seel and Langer, *Angew. Chem.*, 1956, **68**, 461.

[7] Seel and Langer, *Z. anorg. Chem.*, 1958, **295**, 316.

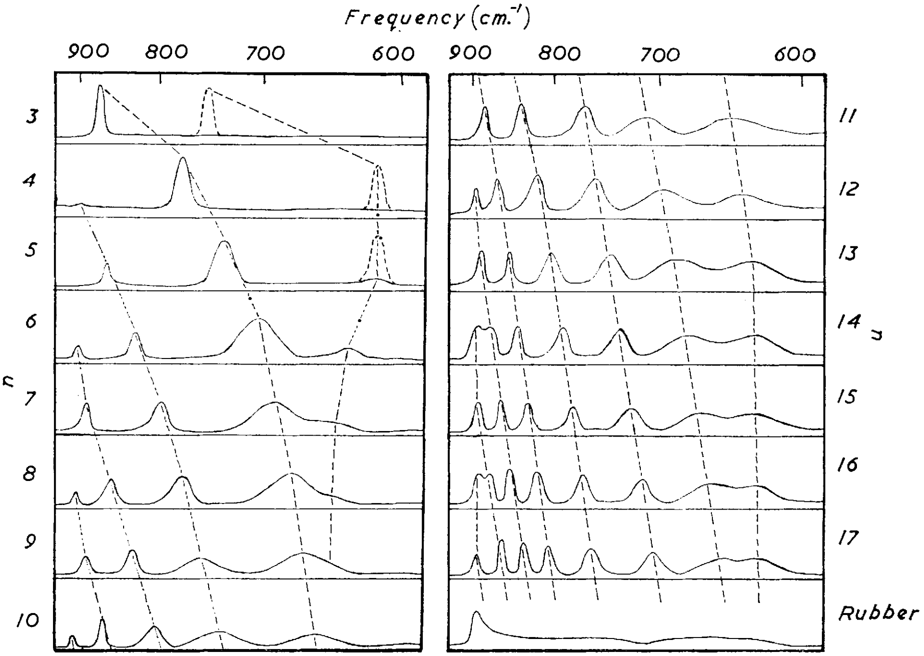
[8] Haber and Uenishi, *Ind. Eng. Chem., Chem. Eng. Data Ser.*, 1958, **3**, 323.

column increase with polymer size according to the equation $\log_{10} t_r = \text{A}n + \text{B}$, where $n$ is the degree of polymerisation, a relationship typical of homologous series.[9] By the use of this equation, the peaks observed in the chromatograms of the higher-boiling mixtures can be assigned to individual polymers $(PNF_2)_n$ up to $n = 17$, such assignments agreeing with those from infrared spectroscopy.

The infrared spectra of the phosphonitrilic fluorides show a system of bands due to $PF_2$ stretching vibrations which changes in a regular manner throughout the series (see Fig.) and can be interpreted in the following way.

The normal vibrations of a molecule of $n$ identical units can be regarded as a system of standing waves, the system differing according to whether the molecule is linear or cyclic. An open chain may accommodate up to $n$ half-wavelengths in its length;[10] the phase difference between adjacent groups[11] is $\delta = m\pi/(n-1)$, where $m = 0, 1, 2, \ldots (n-1)$. Ring closure increases the number of links by one, and strengthens the phase-difference condition; an integral number of complete wavelengths must be included in the ring, the phase difference between the vibrations of adjacent groups being now $\delta = 2\pi m/n$, where $m = 0, 1, 2, \ldots (n-1)$.

*The infrared spectra from* 900 *to* 600 *cm.*$^{-1}$ *of the phosphonitrilic fluorides* $(PNF_2)_n$ *from* $n = 3$ *to* $n = 17$, *and of the rubbery high polymer. Dotted peaks represent polarised Raman bands; series of bands arising from vibrations having the same number of standing wavelengths in the ring are indicated by dotted lines.*



The vibrations of adjacent units will be coupled to some extent, so that modes of different $\delta$ give rise to different frequencies. For a linear molecule, the values of $\delta$ are all distinct, giving the $n$ normal vibrations. For the cyclic molecule, the displacements are the same for the $m$th mode and the $(n-m)$th. If the symmetry is high enough, therefore, the vibrations occur in degenerate pairs except for $\delta = 0$ or $\pi$, all possible frequencies being accommodated by limiting $m$ to the range 0, 1,... $(n-1)/2$ for odd values of $n$, and to

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[9] Ray, *J. Appl. Chem.*, 1954, **4**, 21.

[10] Brown, Sheppard, and Simpson, *Phil. Trans.*, 1954, *A*, **247**, 35.

[11] Liang, Sutherland, and Krimm, *J. Chem. Phys.*, 1954, **22**, 1468.

0, 1,...$n/2$ for even values of $n$. The vibration corresponding to the maximum possible phase difference, of $\pi$, between the displacements of adjacent units, is only present for even values of $n$ and would be expected to give the highest frequency of the series.

Linear molecules can therefore show a system of up to $n$ peaks; if the chain is straight, the vibrations should alternate between infrared and Raman activity with increasing $m$. In the phosphonitrilic fluorides, there is no evidence for any alternation in activity or intensity, and too few peaks are observed to allow assignment on the basis of an open-chain structure, which can therefore be rejected.

The results are, however, in complete accord with the requirements of a cyclic structure. The high-frequency limit of the set, at 885 cm.$^{-1}$, is formed by the out-of-phase vibrations, which occur only in the even members. Each out-of-phase vibration forms the non-degenerate head of a series of degenerate vibrations having the same number of standing waves in the ring. Although in $(PNF_2)_{14}$ and $(PNF_2)_{16}$ the adjacent degenerate band is very close to the high-frequency limit, the difference from $(PNF_2)_{13,15,17}$ is clear. The other limiting frequency, corresponding to the in-phase modes (for which $\delta = 0$), is Raman-active. It is inactive in the infrared in the trimer and tetramer, but becomes weakly active in the pentamer. It is infrared-active in the higher polymers, but is more variable in position than the high-frequency limit, and merges into the first degenerate band above the nonamer. The number of bands observed is that required for the number of modes of a cyclic structure, being $(n + 1)/2$ for odd $n$ and $(n + 2)/2$ for even $n$, the number being the same for an even-numbered polymer and the next-higher odd polymer.

As will be shown later, the symmetry of the trimer is $D_{3h}$, and that of the tetramer is close to $D_{4h}$. If the $PF_2$ vibrations observed here were antisymmetric, the in-phase modes of both molecules would be infrared active and Raman inactive, while the degenerate modes would be Raman-active and infrared-inactive. For both types of mode, and for both molecules, these predictions are contrary to observation. On the other hand, if the bands arise from the symmetrical stretching vibrations, the in-phase modes should be Raman-active and infrared-inactive, while the degenerate modes should be Raman-inactive and infrared-active. The results are in complete accord with these requirements, and the bands must therefore be due to the symmetrical $PF_2$ vibrations.

As the series is ascended, assignment of the molecular symmetry to a particular point-group becomes more difficult. Deviations from $D_{nh}$ symmetry are shown by weak infrared activity of the in-phase modes, infrared activity of the highest degenerate modes (only the first degenerate mode should be active in $D_{nh}$), and activity of the out-of-phase modes. The degenerate vibrations are nevertheless not split. It is probable that the molecules are very flexible, a high symmetry being attained statistically. As shown above, the demonstration of the cyclic nature of the phosphonitrilic fluorides is independent of their precise symmetry. The rubber-like phosphonitrilic fluoride high polymer (prepared by heating any of the cyclic polymers to 300—350°) shows a sharp peak from the out-of-phase vibration; a series of unresolved degenerate vibrations is seen as a broad weak tail extending to about 600 cm.$^{-1}$. For all but the high polymer (which has not been examined), the nuclear magnetic resonance spectra[12] show that only one type of phosphorus atom is present in each of the phosphonitrilic fluorides, as expected for monocyclic molecules, and confirming the above analysis.

Fluorination of the trimeric–hexameric chlorides by the technique takes place without change in ring size. Since the higher members of the fluoride series have been prepared from a mixture of chlorides, no similar statement can be made about them with certainty. Since, however, they can be purified by distillation without disproportionation, the higher fluorides are evidently quite stable, and it seems most likely that they are formed from the corresponding chlorides in every case. If so, the two series are co-extensive up to at least $(PNX_2)_{17}$, the infrared spectra of the fluorides providing an indirect proof of the

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[12] Gillespie and White, to be published.

cyclic nature of the chlorides above the octamer, and supplementing the evidence from nuclear magnetic resonance quoted in Part I of this series.[13]

The physical properties of the phosphonitrilic fluorides are given in Table 1, in which the results obtained for the trimer and tetramer by other investigators are included for completeness.

TABLE 1. *Physical properties of the phosphonitrilic fluorides.*

| $n$ in $(PNF_2)_n$ | 3 [a] | 4 [a] | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|
| P–N stretching frequency (cm.$^{-1}$) | 1297 | 1419<br>1438 | 1439 | 1408 | 1400 | 1386 | 1375 | 1363 | 1357 |
| M. p. | 27·1° | 30·4° | −50° | —45·5° | −61° | −16·9° | < −78° | −51° | < −78° |
| B. p.[f] | 51·0° | 89·7° | 120·1° | 147·2° | 170·7° | 192·8° | 214·4° | 230·8° | 246·7° |
| $\Delta H$, vap. (kcal. mole$^{-1}$) | 7·65 | 8·91 | 9·8 | *e* | 11·6 | 12·0 | 12·7 | 13·5 | 14·6 |
| $\Delta S$, vap. (e.u.) | 23·6 | 24·6 | 24·9 | *e* | 26·2 | 25·8 | 26·1 | 26·9 | 28·0 |
| $d_4^{20}$ (g. ml.$^{-1}$) | 2·237 | 2·239 | 1·8259 [g] | 1·8410 | 1·8496 | 1·8567 | 1·8589 [h] | 1·8638 | 1·8644 |
| Molar vol. at 20° (ml.) | 112·7 | 149·6 | 227·40 | 270·63 | 314·22 | 357·78 | 402·03 | 445·54 | 489·92 |
| Solubility parameter (cal.$^{\frac{1}{2}}$ ml.$^{-\frac{1}{2}}$) | *b* | *b* | 6·4 | *e* | 5·9 | 5·6 | 5·5 | 5·4 | 5·4 |
| $n_{4358}^{20}$ | *c* | *c* | 1·3550 | 1·3604 | 1·3644 | 1·3677 | 1·3699 | 1·3710 | 1·3723 |
| $n_D^{20}$ | *c* | *d* | 1·3482 | 1·3533 | 1·3570 | 1·3602 | 1·3622 | 1·3633 | 1·3645 |
| $[M]$ (Na$_D$, ml.) ...... | 28·3 [d] | 38·1 [d] | 48·67 | 58·70 | 68·80 | 78·96 | 89·16 | 99·08 | 109·29 |

[a] The m. p.s, b. p.s, and densities quoted for the trimeric and tetrameric fluorides are those determined by Seel and Langer;[7] the heats and entropies of vaporisation of these two compounds are derived from the concordant vapour-pressure data of these authors and of Haber and Uenishi.[8] [b] Not calculated; volume changes on fusion unknown. [c] Not determined. [d] The monoclinic tetrameric fluoride has refractive indices (Na$_D$, 20°) 1·379, 1·428, 1·463; cf. Jagodzinski *et al.*,[i] who found 1·37, 1·43, 1·46 and for the orthorhombic trimeric fluoride 1·388, 1·419, 1·443. The molar refractivity quoted was calculated from these last figures. [e] Vapour-pressure data too inaccurate. [f] Other vapour-pressure data are quoted in the Experimental part. [g] Over the range 20—80°, the temperature coefficient of density was found to be $-2·76 \times 10^{-3}$ g. ml.$^{-1}$ deg.$^{-1}$. [h] Over the range 10—60°, the temperature coefficient of density was found to be $-2·10 \times 10^{-3}$ g. ml.$^{-1}$ deg.$^{-1}$. [i] Jagodzinski, Langer, Oppermann, and Seel, *Z. anorg. Chem.*, 1959, **302**, 81.

The term " P–N stretching frequency " in Table 1 corresponds to the most intense peak observed in the infrared spectrum; for $(PNF_2)_{12,13,14}$ and the high polymer it is 1351, 1346, 1340, and 1321 cm.$^{-1}$ respectively. Its order of magnitude shows that the phosphonitrilic fluorides have the same type of bond as the phosphonitrilic chlorides, but perhaps rather stronger. A simplified treatment of the ring vibrations, analogous to that given above for the $PF_2$ vibrations, suggests that the " P–N stretching frequency " for each polymer corresponds to the fitting-in of one whole wavelength round the ring. The phase difference between vibrations at adjacent atoms therefore decreases as the series is ascended. The lowering of frequency from the pentamer upwards is probably to be attributed largely to this phase effect, rather than to any weakening of the P–N bond. Further details will be published elsewhere.

The boiling points of the phosphonitrilic fluorides are close to those of saturated aliphatic fluorocarbons of comparable molecular weight. The hexameric phosphonitrilic fluoride (*M*, 498) boils 21·9° above perfluorononane[14] (*M*, 488), the difference decreasing with increasing molecular weight; the decameric phosphonitrilic fluoride (*M*, 830) boils only 1·2° below perfluorohexadecane[14] (*M*, 834). The entropies of vaporisation of the phosphonitrilic fluorides are high, and tend to increase with molecular weight. Though no great accuracy is claimed for the individual values, which for the heptamer and upwards are based on vapour pressures at only two temperatures, their order of magnitude seems established. They may contain a large component due to the freeing of the rotational movement of (or in) molecules of high moment of inertia.

The low boiling points of all the fluorides are a consequence of a low internal pressure,

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

[14] Haszeldine and Smith, *J.*, 1951, 603.

here expressed as the Hildebrand solubility parameter [15] $\delta = (\Delta E_{\text{vap}}/V_{\text{m}})^{\frac{1}{2}}$. The tabulated values can be compared with the typical value of 5·7 for perfluoroheptane.[16] The solubility parameter of the pentameric phosphonitrilic fluoride was determined approximately as 6·1, by measuring its critical solution temperature with toluene. As found for mixtures of fluorocarbons and hydrocarbons,[17] the experimental value is somewhat lower than that calculated from vapour-pressure data.

All the polymers investigated have low refractive indices and low dispersions. The calculated absorption maximum, based on a single Sellmeier dispersion term, lies in all cases below 100 mμ; experimentally, the molar extinction coefficients are less than unity down to 210 mμ. The molar refractivities may be expressed by the equation $[M]_{\text{D}} = 10{\cdot}103n - 1{\cdot}86$ ml., where $n$ is the degree of polymerisation, with an average deviation of 0·06 ml.

Unlike the fluorocarbons, the phosphonitrilic fluorides are flexible molecules. The infrared spectra show no evidence of the multiple peaks characteristic of the configurational isomerism observed in the hydrocarbon series.[18] The barriers to internal motion in the fluorides are therefore small. Further evidence that the molecules can be folded in upon themselves economically is provided by the molar volumes, which are expressible by the formula $V_{\text{m}} = (43{\cdot}753n + 8{\cdot}19)$ ml., within an average deviation of 0·27 ml. The constant term is a measure of the volume made unavailable by ring closure, and therefore, indirectly, of molecular rigidity. For the parallel series of cyclic dimethylsiloxanes [19] the constant term is 13·3 ml., and for the cycloparaffins it is approximately 20 ml. On this argument, therefore, the fluorides are the most flexible of the three series.

Molecular flexibility is demonstrated more directly by transport properties. The viscosity of the pentameric fluoride at 25° is 1·37 cp., and its activation energy for viscous flow is 2·54 kcal. mole.$^{-1}$. For decamethylpentasiloxane, which also has a ten-membered ring, the corresponding values [19] are 3·824 cp., and 3·71 kcal. mole.$^{-1}$, respectively. The ratio of this activation energy to the energy of vaporisation is also smaller for the fluoride (0·27) than for the siloxane (0·33), implying a smaller unit of flow in the former series, and therefore a greater flexibility.[20] This is even more marked in the nonameric fluoride, which has a viscosity of 3·22 cp., at 25°, and an activation energy for viscous flow of 2·75 kcal. mole$^{-1}$; in this case the ratio of this last value to the energy of vaporisation is even lower (0·23). How far the flexibility is due to torsional freedom about the P–N bonds, and how far to easy angular deformation, is not yet known. Any such movements permitted by the underlying electronic structure would, however, be expected to show up in such a series as this, in which the exocyclic atoms are only slightly polarisable and are well spread out.

## EXPERIMENTAL

The m. p.s of the phosphonitrilic fluorides liquid at room temperature were measured on large samples with a toluene thermometer; otherwise, m. p.s and b. p.s at atmospheric pressure were measured by micro-techniques, and, except where indicated, are corrected. Molecular weights were measured either by Victor Meyer's method (VM) or by cryoscopy in benzene (C). Vapour-phase chromatograms were obtained by using a Griffin and George Mark II VPC apparatus with a column packing of I.C.I. silicone (Series E301) on 60—80 mesh Celite; the column temperature was 174—175°. The densities of the liquids were measured pyknometrically at 20° ± 0·01°, and were reproducible to within ±0·0002 g. ml.$^{-1}$. Refractive indices were measured at 20° ± 0·2° with a Pulfrich refractometer, using either $\text{Na}_{\text{D}}$ or $\text{Hg}_{4358}$ radiation; their average estimated error is ±0·00015. Infrared spectra were taken with a

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[15] Hildebrand and Scott, "Solubility of Nonelectrolytes," 3rd Edn., Reinhold, New York, 1950, p. 129.

[16] Scott, *J. Amer. Chem. Soc.*, 1948, **70**, 4090.

[17] Neff and Hickman, *J. Phys. Chem.*, 1955, **59**, 42; Scott, *ibid.*, 1958, **62**, 136.

[18] Kohlrausch and Köppl, *Z. phys. Chem.*, 1934, **26**, *B*, 209; Billeter and Günthard, *Helv. Chim. Acta* 1958, **41**, 338.

[19] Hurd, *J. Amer. Chem. Soc.*, 1946, **68**, 364.

[20] Ewell and Eyring, *J. Chem. Phys.*, 1937, **5**, 726.

Perkin-Elmer Model 21 spectrophotometer with rock-salt and potassium bromide optics. Spectra were taken from the liquids, from potassium chloride discs, from solutions in carbon tetrachloride and, where necessary, from solutions in carbon disulphide. Raman spectra were obtained from the liquids by means of a Hilger photoelectric recording spectrometer; depolarisation factors were measured by Edsall and Wilson's technique.[21] Only those physical properties not already quoted in Table 1 are given below.

*Materials.*—A reagent grade of anhydrous potassium fluoride was used. It was dried and freed from hydrogen fluoride by prolonged heating at 400°. Sulphur dioxide was reagent grade liquid. Pure crystalline samples of the trimeric to hexameric chlorides were used; the higher fluorides were prepared from a mixture of chlorides from which the lower chlorides had been extracted by a method similar to that previously described.[13]

*Trimeric Phosphonitrilic Fluoride.*—Liquid sulphur dioxide (80 ml., approx. 1·8 moles) was condensed on to trimeric phosphonitrilic chloride (200 g., 0·575 mole) and anhydrous potassium fluoride (300 g., 5·16 moles) (previously ground together) in a stainless-steel, rocking autoclave, which was then kept at 98—100° for 22 days. The volatile products were then transferred to a low-temperature still and the excess of sulphur dioxide (65 ml.) was fractionated off. The residue was fractionally distilled in a spinning-band column, and 115·3 g. (80% of theory) of material boiling in the range 49—49·8°/747 mm. were collected; it was a slightly yellow, crystalline solid containing a little sulphur. After sublimation it was colourless and had m. p. 27·8°, b. p. 51·0° (reported[6] for $P_3N_3F_6$, m. p. 27·8°, b. p. 51·0°).

*Tetrameric Phosphonitrilic Fluoride.*—A similar experiment with tetrameric phosphonitrilic chloride (200 g., 0·431 mole) yielded 103 g. of tetrameric phosphonitrilic fluoride (72% of theory); it had m. p. 30·5°, b. p. 89·0° (reported[6] for $P_4N_4F_8$, m. p. 30·5°, b. p. 89·7°).

*Pentameric Phosphonitrilic Fluoride.*—A similar experiment with pentameric phosphonitrilic chloride (203 g., 0·350 mole), yielded 113·8 g. (78% of theory) of slightly impure liquid product. The yellow impurity was removed with activated charcoal, and on redistillation *pentameric phosphonitrilic fluoride* was obtained [Found: P, 36·8; N, 16·5; F, 45·2%; *M*, 415 (C). $P_5N_5F_{10}$ requires P, 37·3; N, 16·9; F, 45·8%; *M*, 415]. Over the range 25—120°, the vapour pressure can be expressed by the equation $\log_{10} p = -2141{\cdot}7/T + 8{\cdot}3373$. Over the range 20—80°, the viscosity is given by $\log_{10} \eta$ (centipoises) $= 556/T - 1{\cdot}728$ kcal. mole$^{-1}$. The solubility parameter was determined by measuring the mutual solubility temperature of equal volumes of pentameric phosphonitrilic fluoride and toluene, and calculating from the approximate expression $4RT_c = (V_m' + V_m'')(\delta_1 - \delta_2)^2$, in which $T_c$ is the mutual solution temperature of the two components with molar volumes $V_m'$, $V_m''$ and solubility parameters $\delta_1$, $\delta_2$. The measured solution temperature was 49·0°; for toluene $V_m = 112$ ml. and $\delta = 8{\cdot}9$, leading to $\delta = 6{\cdot}1$ for the pentameric fluoride. This compound was miscible with n-hexane ($\delta = 7{\cdot}3$) but immiscible with ethyl iodide ($\delta = 9{\cdot}4$) up to at least 70°.

*Hexameric Phosphonitrilic Fluoride.*—This compound was prepared from the corresponding chloride (20 g., 28·8 millimoles) in the same way as the lower members of the series. A yield of 11 g. (77% of theory) of the *hexameric phosphonitrilic fluoride* was obtained [*M*, 506 (VM). $P_6N_6F_{12}$ requires *M*, 498].

*Higher Polymers.*—The higher phosphonitrilic fluorides were prepared from a mixture of chlorides from which the trimer, tetramer, and most of the pentamer had been removed. After fluorination of the chloride oil in the way described above, the products were obtained partly by fractional distillation of the more volatile part (carried over with the excess of sulphur dioxide) and partly by extracting the solid residue in the autoclave with light petroleum (b. p. 40—60°). From 611 g. of phosphonitrilic chloride oil in three experiments, 312 g. of mixed fluorides were obtained (71% of theory). The more volatile part (25·3 g.) contained: tetrameric, 4; pentameric, 77; hexameric, 17; higher phosphonitrilic fluorides, 2% (vapour-phase chromatographic analysis). The main product was a brown mobile liquid, which, on removal of the petroleum, deposited a small amount of a brown crystalline impurity, which was largely removed with activated charcoal. After purification, the product was found to consist of a mixture of phosphonitrilic fluorides contaminated with a little sulphur impurity (Found: P, 36·1; N, 16·7; F, 42·6; Cl, 0·5; S, 1·0%). A vapour-phase chromatogram showed the presence of polymers up to at least the duodecamer.

Part of this product was fractionally distilled under reduced pressure to give 18 fractions, which were recombined and redistilled to give the pure polymers from the heptamer to the

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[21] Edsall and Wilson, *J. Chem. Phys.*, 1938, **6**, 124.

undecamer. The progress of the fractionation was followed by vapour-phase chromatography, which showed that the polymers eventually obtained were better than 99% pure. Their retention times conformed to the equation $\log_{10} t_r$ (min.) = 0·1176*n* — 0·432 within ±0·1 min.; this relation was therefore used to determine the degree of polymerisation of the higher members of the series. Over the range 10—60°, the viscosity of the nonamer is given by the equation $\log_{10} \eta$ (cp.) = $602/T$ — 1·512. Further details of these higher polymers are given in Table 2.

TABLE 2.

| *n* in $(PNF_2)_n$ | 7 | 8 [a] | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|
| N (%) [b] | 16·9 | 16·8 | 16·8 | 16·8 | 16·8 | — | — | — |
| F (%) [b] | 45·7 | 45·3 | 45·5 | 45·4 | 45·3 | | | |
| B. p. (at mm. pressure) [c] | 60—60·2° | 80—81° | 96—97° | 91—91·5° | 103—105° | 143—148° | 154—159° | 166—170° |
| | (9·35) | (12·5) | (11·4) | (4·25) | (3·6) | (12·65) | (12·65) | (12·65) |
| V.P.C. retention time [d] (min.) | | | | | | | | |
| Obs. | 2·46 | 3·17 | 4·15 | 5·51 | 7·34 | 9·8 | 13·2 | 16·4 |
| Calc. | 2·46 | 3·23 | 4·23 | 5·55 | 7·28 | 9·53 | 13·40 | 16·37 |

[a] *M*, 661. $P_8N_8F_{16}$ requires *M*, 664. [b] $(PNF_2)_n$ requires N, 16·9; F, 45·8%. [c] The data for the three highest polymers are approximate only. [d] The observed retention times of the polymers up to the undecamer together with those for the pentamer (1·50 min.) and hexamer (1·97 min.) were used to determine the formula quoted in the Experimental part. This formula was used to calculate the values given in the last row of the table.

The purity of the three compounds $(PNF_2)_{12}$, $(PNF_2)_{13}$, and $(PNF_2)_{14}$ probably does not exceed 90%, and the only physical property quoted is therefore an approximate b. p. Their individuality is nevertheless established by the agreement of calculated and observed retention times, and by the details of the infrared spectra shown in the Figure. Three further fractions were obtained (b. p.s 136—142°/1·7 mm., 143—148°/1·85 mm., and 152—157°/1·85 mm.). Their infrared spectra, after correction for a small amount of irrelevant absorption (see Figure), showed their main constituents to be the cyclic fluorides $(PNF_2)_{15}$, $(PNF_2)_{16}$, and $(PNF_2)_{17}$ respectively. The observed retention times of these three fractions (22, 28, and 37 min., respectively) are consistent with this assignment but the peaks were too broad for accurate measurement.

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