

1053. Cyclic Inorganic Compounds. Part II.¹ Decabromopentaphosphonitrile

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The reaction between phosphorus pentabromide and ammonium bromide in *sym*-tetrachloroethane yields, together with the trimeric and tetrameric bromophosphonitriles, the previously unknown pentamer.

THE reaction between phosphorus pentachloride and an excess of ammonium chloride in *sym*-tetrachloroethane yields cyclic chlorophosphonitriles containing up to seventeen phosphorus–nitrogen units.^{2,3} The corresponding partial ammonolysis of phosphorus pentabromide^{4,5} yields the trimeric and tetrameric compounds, P₃N₃Br₆ and P₄N₄Br₈, but, thus far, no higher homologues in the bromide series have been reported. In general, species higher than tetramers have not yet been isolated from the products of ammonolysis of other phosphorus(v) halides.⁶ This Paper reports the isolation and characterisation of the third member of the bromide series, decabromopentaphosphonitrile.

RESULTS AND DISCUSSION

The method given by John and Moeller⁴ for the preparation of the trimeric and tetrameric bromides has been modified slightly in the present study. The mixture of crude bromophosphonitriles was not sublimed, as this causes polymerisation of the high homologues. Fractional crystallisation from light petroleum was used exclusively in the working-up procedure, and the pentamer was obtained from the concentrated mother-liquors after separation of the trimer–tetramer mixtures.

The solubilities of the trimeric and tetrameric bromophosphonitriles are similar to those of the corresponding chlorides, except that they are, in general, lower in a given solvent. The same relationship holds with the pentameric compounds; no quantitative data are available for the bromide, but qualitatively it parallels the chloride in its high solubility in benzene, light petroleum, carbon tetrachloride, chloroform, and carbon disulphide. It is also interesting that the variation in melting point of the bromophosphonitriles (192, 202, and 104.5° for trimer, tetramer, and pentamer, respectively) is similar to that found in the chloride series.

X-Ray powder diffraction patterns have been obtained for the three bromophosphonitriles; the data for the pentamer, and the *d* spacings for the strongest lines in the trimer and tetramer patterns, are listed in Table 1. The lines in the pattern for the tetramer have been indexed, and the dimensions of the tetragonal unit cell are calculated as *a* = 11.14, and *c* = 6.29 Å, confirming the values previously reported.⁷ Rotation and Weissenberg photographs of a single crystal of the pentameric bromide indicate that the unit cell is triclinic.

The absorption bands in the infrared spectrum of the pentameric bromide are listed in Table 2, together with the data for both the trimeric and tetrameric compounds. These latter compounds have been studied over a wider frequency range than previously, and there are some differences from the published data.⁸ The two intense absorptions at 1330 and 1265 cm.⁻¹ are due to vibrations associated with the pentameric ring system. Analogous bands occur at 1467 and 1405 cm.⁻¹ for the pentameric fluoride, and at 1354

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⁶ (a) N. L. Paddock, *Quart. Rev.*, 1964, 18, 168; (b) C. D. Schmulbach, *Prog. Inorg. Chem.*, 1963, 4, 275; (c) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, 62, 247.

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⁸ E. Steger and R. Stahlberg, *Z. anorg. Chem.*, 1964, 326, 243.

TABLE 1

X-Ray powder pattern data for the bromophosphonitriles

$P_3N_3Br_6$		$P_4N_4Br_8$		$P_5N_5Br_{10}$		$P_6N_6Br_{12}$	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
5.89 ^a	29	7.79	14	8.86	14	3.08	30
3.76	100	3.91	100	8.57	15	3.02	15
3.32	54	3.54	82	4.24	100	2.95	17
3.19	35	3.20	14	3.86	75	2.93	27
3.13	38	2.64	77	4.17	26	2.88	27
2.22	60			3.52	52	2.75	25
				3.41	55	1.96	21
				3.34	20	1.95	21
				3.28	57	1.85	15
				3.20	19	1.81 ^a	11

^a Doublet.

TABLE 2

Infrared spectra of the bromophosphonitriles

$P_3N_3Br_6$		$P_4N_4Br_8$		$P_5N_5Br_{10}$	
Nujol mull	CS ₂ soln.	Nujol mull	CS ₂ soln.	Nujol mull	CS ₂ soln.
2020w					
1964w					
1920w					
1270w, sh	1262w				
1225w, sh		1300vw, sh			
1170vs	1173vs	1250s	1270vs	1311s	1330s
	1128w-m	1160vw, sh		1252s	1265s
	1108vw				
	1080vw	868m	869m	840m	848w
	1020vw	760w	756m	728m	719m
	970vw		681m-w	699m	
846w	848w-m	519s		513s	
		497s		488w	
543sh		451s		468w	
523s		415m		449m	
480m-w		382vw		418w	
440vs				402vw	
		311w		388s	
318w				360vw	
				334w	

and 1298 cm⁻¹ for the corresponding chloride.⁹ There is the same general lowering in the frequency of these ring vibrations with decrease in electronegativity of the attached halogen atoms, as is observed with the halogeno-tri- and tetra-phosphonitriles.

Becke-Goehring and Lehr¹⁰ have recently shown that ionic species such as $[Cl_3P:N \cdot PCl_2 \cdot N \cdot PCl_3]^+ [PCl_6]^-$ are intermediates in the preparation of the chlorophosphonitriles. It seems likely that similar ionic intermediates will occur in the bromide system. There is, however, little evidence for the PBr_6^- anion; its existence in acetonitrile solutions has been postulated to account for the electrochemical behaviour,¹¹ but there is no evidence for its occurrence in the solid state. The compounds P_2NBr_7 and P_2NBr_9 are the only known intermediates in the bromide synthesis.⁴ By analogy with the chloride system, a likely constitution for P_2NBr_7 is $[Br_3P:N \cdot PBr_3]^+ Br^-$. The observed addition of bromine to give P_2NBr_9 , a product which loses bromine only slowly *in vacuo* at 85°, can then be formulated as the corresponding tribromide $[Br_3P:N \cdot PBr_3]^+ Br_3^-$. The stability is similar to that of other tribromides containing large cations, *e.g.*, rubidium and caesium, which also have low bromine dissociation pressures at room temperature.¹²

⁹ A. C. Chapman and N. L. Paddock, *J.*, 1962, 635.¹⁰ M. Becke-Goehring and W. Lehr, *Z. anorg. Chem.*, 1964, 327, 128.¹¹ G. S. Harris and D. S. Payne, *J.*, 1956, 4617.¹² F. Ephraim, *Ber.*, 1917, 50, 1069.

EXPERIMENTAL

Bromophosphonitriles.—The reaction mixture, heated on an oil-bath, consisted of 370 g. of phosphorus(III) bromide, 370 g. of ammonium bromide, 240 g. of bromine, and 700 ml. of *sym*-tetrachloroethane. The temperature was raised to 130° over 5 days and then held at 140–150° for a further 12 days. Periodically, small additions of bromine (total 200 g.) were made. The mixture was filtered, evaporated to dryness, and the residue extracted with hot benzene. The extracts were treated with charcoal, and evaporated to dryness. The solid was then extracted with 800 ml. of boiling light petroleum (b. p. 80–100°); the saturated solution was decanted from the undissolved solid, treated with charcoal, filtered, and allowed to crystallise. The mother-liquor was then returned to continue the extraction process. A total of 130 g. (47%) of trimer–tetramer mixture was obtained; this weight includes also the solid obtained by concentrating the final mother-liquor to a volume of ~100 ml. On further concentration, the *pentameric bromide* separated as diamond-shaped crystals. (The trimeric and tetrameric compounds crystallise from light petroleum in characteristic hexagonal plates and needles, respectively.) A further small amount (0.5 g.) of the pentamer was obtained from the mother-liquors in the separation of the trimeric and tetrameric compounds. After recrystallisation from light petroleum (b. p. 40–60°), the total yield was 5 g. (1.8%) (Found: Br, 78.5; N, 6.7%; *M*, 997, 1036. $\text{Br}_{10}\text{N}_5\text{P}_5$ requires Br, 78.0; N, 6.8%; *M*, 1024).

X-Ray Diffraction.—Powder data for the compounds were obtained with a Philips X-ray powder diffractometer using Cu-K_α radiation. Single-crystal analysis of the pentameric bromide gave the dimensions of the triclinic unit cell as $a = 10.58 \pm 0.04$, $b = 9.48 \pm 0.05$, $c = 14.02 \pm 0.05$ Å, $\alpha = 108^\circ \pm 1^\circ$; $\beta = 124.5^\circ \pm 1^\circ$; $\gamma = 99.5^\circ \pm 1^\circ$, $U = 1060 \pm 10$ Å³, $D_m = 3.08$ (flotation in methylene iodide–carbon tetrachloride), $Z = 2$, $D_c = 3.21$.

Infrared Spectra.—A Perkin-Elmer 521 infrared spectrometer was used. Measurements were made on Nujol mulls (CsI windows) and, in the range 4000–700 cm^{-1} , on solutions in CS_2 using a 0.2-mm. NaCl cell.

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