Cyclic Inorganic Compounds. Part XII.[1] Reaction between Octachlorotetraphosphonitrile and Dimethylamine

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Very slow addition of dimethylamine to octachlorotetraphosphonitrile in ether at −78° gives non-geminally substituted compounds with the general formula $P_4N_4Cl_n(NMe_2)_{8-n}$ (n = 2—6). Increasing the rate of amine addition gives both a greater spread of product stoicheiometries and an increasing proportion of geminally substituted compounds. Isomeric forms have been separated for n = 3 (three compounds), 4 (four compounds), and 5 (two compounds) and provisional structures have been assigned on the basis of i.r. and ^1H n.m.r. spectroscopy. Evidence has been obtained for the formation of $P_4N_4Cl(NMe_2)_7$.

REACTIONS leading to partial substitution of the chlorine atoms in hexachlorotriphosphonitrile have been systematically studied for a variety of nucleophiles, but similar data for the tetrameric chloride are not extensive. Shaw and his co-workers[2] have examined the reaction with dimethylamine in ether at room temperature and isolated one bis-, two tris-, three tetrakis-, three pentakis-, and two hexakis-derivatives. Provisional structures have been assigned on the basis of ^1H and ^{31}P n.m.r. spectroscopy and basicity measurements.[3] Stahlberg and Steger[4] have also examined this reaction under similar conditions and shown by t.l.c. that five isomeric bis-compounds can be obtained. One isomer was isolated and the mono-substituted compound was also obtained. Lehr[5] isolated all five of the possible bis-isomers and in a preliminary report assigned structures to them. Four tris-derivatives were shown to be present and structures have been assigned to two that were isolated.

In extension of experiments on the fluorination of aminochlorotriphosphonitriles,[1,6] similar tetrameric derivatives of known structure were required and aspects of the reaction between the tetrameric chlorophosphonitrile and dimethylamine have been examined and are reported here.

EXPERIMENTAL

Preparation of Chlorodimethylaminotetraphosphonitriles.— These compounds were prepared by adding dimethylamine to a well-stirred solution of octachlorotetraphosphonitrile in ether. In many cases it was found that, for a given ratio of amine to phosphonitrile, the distribution of products depended largely on the rate of addition of the amine and the temperature (volume of solvent was less important). Because of this a standard procedure was devised whereby the amine, initially at 0°, was allowed to distil into the $P_4N_4Cl_8$ solution held at −78°. Loss of amine was prevented by circulating alcohol at −20° through a condenser attached to the reaction flask. Ingress of moisture was prevented by attaching a calcium chloride drying tube to the top of the condenser.

Reactions were carried out with phosphonitrile solutions that were *ca.* 1% (w/v) at room temperature, but since cooling to −78° caused some of the compound to crystallize, the effective concentration was much lower. Addition of amine took between 1 and 1½ h. After addition, stirring was continued at −78° for 2 h after which the solution was allowed to warm slowly to room temperature. The dimethylamine hydrochloride was filtered off and extracted with boiling petroleum (b.p. 60—80°). The combined filtrate and petroleum extract was then evaporated to dryness and traces of amine hydrochloride were removed by re-extraction into hot petroleum. The crude product was then examined by g.l.c. In most cases, the components of the mixtures obtained were separated by a series of fractional crystallizations from light petroleum but sometimes preparative g.l.c. was necessary.

The results of experiments with 4, 6, 8, 10, and 12 moles of amine under these conditions are summarized in Table

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[1] Part XI, B. Green, D. B. Sowerby, and P. Clare, *J. Chem. Soc.* (*A*), 1971, 3487.

[2] S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1963, 3236.

[3] V. B. Desai, R. A. Shaw, B. C. Smith, and D. Taylor, *Chem. and Ind.*, 1969, 1177.

[4] R. Stahlberg and E. Steger, *J. Inorg. Nuclear Chem.*, 1968, **30**, 737.

[5] W. Lehr, *Naturwiss.*, 1969, **56**, 214.

[6] B. Green and D. B. Sowerby, *J. Chem. Soc.* (*A*), 1970, 987.

1. Also included in this table are results from reactions in which the amine was either distilled into the reaction flask *via* a cold finger at −78° or was added as a solution in ether. In all cases, however, the chlorophosphonitrile solution was held at −78°. Analytical data for the compounds isolated together with melting points are given in Table 2. Further points on individual reactions are summarized below.

TABLE 1

Distribution of products (%)

Compound	Reaction number [a] 4·1 [b]	6·1 [b]	6·2 [c]	6·3 [d]	8·1 [b]	8·2 [d]	8·3 [e]	10·1 [b]	10·2 [c]	12·1 [b]	12·2 [c]
$P_4N_4Cl_8$				8							
$P_4N_4Cl_7(NMe_2)$	Trace		2	3							
(I)	60	30	34	5	6						
(II)	40	49	28	14	18	2 [f]	14 [f]				
(III)		21	15	6	10						
(IV)			14	8	3						
(V)			8 [f]	32 [f]	17	15	21		4		
(VI) + (VII)					46	77	53	14	61		9
(VIII)						6	7				
(IX)							5	69	9	11	4
(X)											24
(XI)								14	11	89	63
$P_4N_4(NMe_2)_8$								3	15		

[a] First number gives approximate molar quantity of amine. [b] Amine at 0° distilled into solution at −78°. [c] Amine at room temperature added via cold finger at −78°. [d] Ether solution of amine. [e] 15% Excess amine in ether solution. [f] Isomer composition not known.

TABLE 2

Analytical data

	M.p. (°C)		C	H	N
$P_4N_4Cl_6(NMe_2)_2$ (I)	171 (170) [a]	Found	10·1	2·8	17·5
		Calc.	10·0	2·5	17·5
$P_4N_4Cl_5(NMe_2)_3$ (II)	107 (106—107)	Found	15·1	3·6	20·3
$P_4N_4Cl_5(NMe_2)_3$ (III)	Liquid	Found	[b]		
$P_4N_4Cl_5(NMe_2)_3$ (IV)	103 (103)	Found	14·5	3·6	19·5
		Calc.	14·7	3·7	20·0
$P_4N_4Cl_4(NMe_2)_4$ (V)	169	Found	19·2	4·6	22·5
$P_4N_4Cl_4(NMe_2)_4$ (VI)	200 (200)	Found	19·3	4·9	22·1
$P_4N_4Cl_4(NMe_2)_4$ (VII)	130	Found	19·5	4·7	22·3
$P_4N_4Cl_4(NMe_2)_4$ (VIII)	110 (110)	Found	19·7	4·9	22·3
		Calc.	19·3	4·8	22·5
$P_4N_4Cl_3(NMe_2)_5$ (IX)	154	Found	24·1	6·2	24·8
$P_4N_4Cl_3(NMe_2)_5$ (X)	51	Found	24·2	6·3	24·5
		Calc.	23·7	5·9	24·9
$P_4N_4Cl_2(NMe_2)_6$ (XI)	168 (168)	Found	28·0	6·9	26·8
		Calc.	28·0	7·0	27·2

[a] Literature values in parentheses. [b] See text.

Reactions with 4 *Mol of Dimethylamine.*—It was not possible to obtain convincing evidence by g.l.c. for more than one isomer in the reaction product but ^1H n.m.r. spectroscopy clearly indicated that more than one product was present. Compound (I) was obtained pure by crystallization from petroleum.

Reactions with 6 *Mol of Dimethylamine.*—A preliminary fractional crystallization from petroleum separated the crude product from reaction 6·1 into the bis-compound (I) and a mixture of the two tris-isomers, (II) and (III). The latter were separated by preparative g.l.c. (OV 225 column at 255°). It was, however, not possible to obtain the compound with the lower retention time (III) free from contamination with stationary phase but its identity was confirmed by observation of a parent ion peak in the mass spectrum at *m*/*e* 487 showing the correct distribution of isotopic peaks for a species containing five chlorine atoms. A third tris-isomer (IV) was found in reaction 6·2 and was separated from the bis (I) with which it crystallizes by preparative g.l.c. (OV 225 column at 240°).

Reactions with 8 *Mol of Dimethylamine.*—Separation of the products from reaction 8·1 by fractionation from petroleum was monitored by g.l.c. This is not completely satisfactory as it is not possible to distinguish between compounds (VI) and (VII). The two could be separated by fractional crystallization using melting point, ^1H n.m.r. and i.r. spectra as criteria of purity. Compound (VI) crystallized first from solution. Compound (VIII) was obtained by fractional crystallization from reactions 8·2 and 8·3.

Reactions with 10 *and* 12 *Mol of Dimethylamine.*—Only one compound (IX) with stoicheiometry $P_4N_4Cl_3(NMe_2)_5$ was obtained with 10 mol of amine. Similarly with slow addition (experiment 12·1) only a single hexakis-compound (XI) resulted. With more rapid addition of amine, however, g.l.c. showed the presence of a more volatile compound, $P_4N_4Cl_3(NMe_2)_5$ (X), which was obtained pure by fractional crystallization from petroleum.

Preparation of $P_4N_4Cl(NMe_2)_7$.—Dimethylamine (1·2 g) was added to a solution of $P_4N_4Cl_2(NMe_2)_6$ (2·8 g) in n-hexane (30 ml) and the mixture was refluxed overnight. Amine hydrochloride was filtered off and crystals were obtained from the solution after concentration and cooling. G.l.c. (gum rubber column) showed two peaks consistent with the presence of starting material and $P_4N_4(NMe_2)_8$ while three peaks were obtained with an OV 225 column. Observation of a parent ion with the required isotopic peaks confirmed the presence of $P_4N_4Cl_2(NMe_2)_6$, $P_4N_4Cl(NMe_2)_7$, and $P_4N_4(NMe_2)_8$ in the ratio 5 : 3 : 2.

Instruments.—G.l.c. apparatus has been described previously.[6,7] Glass columns (10 ft × 3/8 in) packed respectively with 10% gum rubber and 10% OV 225 were used. N.m.r. spectra were obtained on 5% (w/v) solutions in carbon tetrachloride and benzene using an HA 100 spectrometer; in addition four samples were examined at 220 MHz. I.r. spectra were measured on a Perkin-Elmer 521 using 5% (w/v) solutions in carbon tetrachloride and carbon disulphide.

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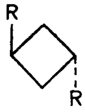
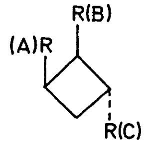
[7] B. Green and D. B. Sowerby, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3687.

DISCUSSION

Preparations.—Although replacement of the chlorine atoms in octachlorotetraphosphonitrile with dimethylamine groups is expected to follow a predominantly non-geminal path, it is clear that the products obtained are more markedly dependent on reaction conditions than those prepared in corresponding reactions with the trimer. This is in part a consequence of the greater number of replaceable groups and also of the known greater reactivity of the tetrameric compounds. There is a total of 32 possible mixed compounds, $P_4N_4Cl_n(NMe_2)_{8-n}$ where $n = 1$—7, of which 20 are the result of a non-geminal reaction scheme.[8] Sixteen compounds are known, ten of which (including four bis-isomers) are non-geminal compounds. In this work, eleven compounds (I)—(XI) have been isolated. Five of these are new and on the basis of ^1H n.m.r. and i.r. spectroscopy they have provisionally been assigned structures (III), (V), (VII), (IX), and (X). In the formulae shown, the corners of the square represent the phosphorus atoms of the P_4N_4 ring and the orientation of substituents is shown by lines above (*cis*) or below (*trans*) the ring.



(I)



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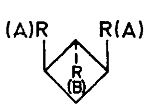

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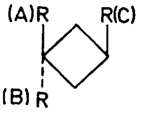

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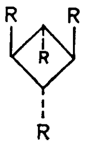

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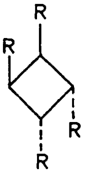

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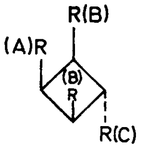
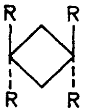
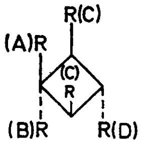


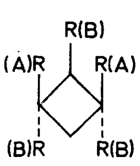
(VII)



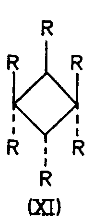
(VIII)



(IX)



(X)



(XI)

R = NMe_2
throughout

By carrying out reactions under the mildest conditions, *i.e.* slow distillation of amine into a well stirred, dilute solution of phosphonitrile in ether at —78°, it is possible to maximize the yield of non-geminal products with the stoicheiometry expected on the basis of the ratio of reactants. The course of the reaction is markedly affected by the rate of amine addition and the temperature at which the reaction is carried out.

Increasing the rate of amine addition causes (*a*) a greater spread in the product stoicheiometries with both more and less highly aminated compounds being formed and (*b*) an increased proportion of products containing geminal, $P(NMe_2)_2$, groups. Both observations probably result from the presence of high local concentrations of amine. It is also apparent that the difference in activation energies for the geminal and non-geminal reaction paths is much smaller than that for comparable reactions with the trimer.

Evidence has been obtained for the presence of $P_4N_4Cl(NMe_2)_7$ but the compound has not yet been obtained pure. This seems to parallel the situation with the trimer where the presumed non-formation of the monochloride was due to difficulty in detection and isolation.

Gas-liquid Chromatography.—The situation here is more complex than in the trimeric system because of both the greater number of compounds present and their lower volatility.

Column temperatures were generally in the region 220—260° greatly limiting the choice of stationary phases and often broad, asymmetric peaks were obtained. In cases where resolution was doubtful other criteria, *e.g.* n.m.r. or i.r. spectroscopy, had to be employed.

Table 3 contains the retention times under standardized conditions for $P_4N_4Cl_8$, $P_4N_4(NMe_2)_8$, and compounds (I)—(XI), together with log (retention time relative to $P_4N_4Cl_8$) on the gum rubber column at 240°. Retention times generally increase with degree of amination but there is a decrease for both the hexakis-derivative (XI) and $P_4N_4(NMe_2)_8$. For a given stoicheiometry, the presence of geminal, $P(NMe_2)_2$, groups greatly lowers the retention time while for non-geminal isomers the compound with the greatest number of pairs of *cis*-amine groups has the longest retention time. If log (relative retention time) is

TABLE 3

Retention times

Compound	Retention time (min)	log (Retention time relative to $P_4N_4Cl_8$)
$P_4N_4Cl_8$	2·8	0·00
(I)	6·6	0·38
(II)	9·5	0·53
(III)	8·6	0·49
(IV)	6·8	0·38
(V)	12·3	0·64
(VI)	13·1	0·67
(VII)	13·1	0·67
(VIII)	7·1	0·40
(IX)	16·8	0·78
(X)	9·0	0·51
(XI)	10·4	0·57
$P_4N_4(NMe_2)_8$	12·0	0·63

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[8] D. B. Sowerby, *Internat. Rev. Sci.*, *Inorg. Chem.*, Series 1, vol. 2.

plotted against degree of amination, the points fall close to two straight lines. That with the lower slope includes the geminal compounds, (IV), (VIII), (X), (XI), and $P_4N_4(NMe_2)_8$, while the line with the greater slope connects non-geminally substituted compounds. Similar results were obtained using a column packed with OV 225 but the effects due to the presence of geminal groups and pairs of *cis* amine groups (polarity effects) were more marked.

N.m.r. Spectroscopy.—^{1}H N.m.r. spectroscopy has played the most important part in assigning structures to the isolated compounds but in some cases the structure can only be considered as tentative. Spectra at 100 MHz have been obtained using both carbon tetrachloride and benzene solutions,[9] but measurements at 220 MHz greatly aided the assignments of structures to compounds (II), (VII), (IX), and (X).

Chemical shifts and apparent coupling constants (J^*_{HP}) for compounds (I) to (XI) and $P_4N_4(NMe_2)_8$ in carbon tetrachloride and benzene solutions are given in Table 4. The final column gives values of $\Delta\tau[\tau(\text{benzene}) - \tau(\text{carbon tetrachloride})]$.

TABLE 4

^{1}H n.m.r. spectra

Compound	$\tau(CCl_4)$	J^*_{HP} (CCl_4)	$\tau(C_6H_6)$	J^*_{HH} (C_6H_6)	$\Delta\tau$
(I)	7·25	15·8	7·70	16·0	+0·45
(II) [a]	7·281 (1) [b]	16·3	7·593 (1)	16·3	+0·31
	7·297 (1)	16·3	7·606 (1)	16·5	+0·31
	7·302 (1)	16·0	7·639 (1)	16·5	+0·34
(III)	7·28	15·8	7·52 (1)	15·8	+0·24
			$7{\cdot}57_5$ (2)	16·2	$+0{\cdot}29_5$
(IV)	7·27 (1)	16·9	7·61 (1)	17·0	+0·34
	7·34 (2)	11·8	7·55 (1)	11·4	+0·21
			$7{\cdot}58_5$ (1)	11·2	$+0{\cdot}23_5$
(V)	7·30	16·8	7·49	16·4	+0·19
(VI)	7·32	16·7	7·51	16·6	+0·19
(VII) [a]	7·298	16·0	7·502 (1)	16·0	+0·204
	7·326	15·7	7·563 (2)	15·5	+0·237
	7·336	15·4	7·586 (1)	15·8	+0·250
(VIII)	7·36	11·5	$7{\cdot}49_5$	11·4	+0·13
(IX) [a]	7·360	10·0	7·319 (1)	10·6	−0·04
	7·373 (1)	15·6	7·526 (1)	15·6	+0·15
	7·382 (2)	15·5	7·491 (2)	16·0	+0·11
	7·508 (1)	12·1	7·615 (1)	11·6	+0·11
(X) [a]	7·364	11·0	7·400	11·0	+0·04
	7·369	15·8	7·454	16·2	+0·08
	7·428	11·4	7·491	11·5	+0·06
(XI)	7·37 (1)	15·7	7·36 (1)	15·8	−0·01
	7·43 (2)	11·0	7·37 (2)	10·8	−0·06
$P_4N_4(NMe_2)_8$	7·44	10·1	7·31	10·0	−0·13

[a] Measurements at 220 MHz. [b] Relative intensity shown in parentheses.

Bis-compound.—The ^{1}H n.m.r. spectrum of compound (I), previously assigned the 1,5-*trans*-structure, consists of a doublet in both carbon tetrachloride and benzene solution. The solvent shift ($\Delta\tau$) is the largest observed for any tetrameric compound.

Tris-compounds.—Compound (II) previously[3,5] assigned the 1-*cis*-3-*trans*-5 structure, contains three non-equivalent amine groups but only two signals in the ratio 1 : 2 were observed at 100 MHz. In carbon tetrachloride at 220 MHz three doublets with coupling constants indicative of non-geminal amine groups are clearly seen (see Figure 1). The structure of compound (II) is therefore firmly established, as this is the only isomer which contains three non-equivalent non-geminal groups. In accordance with the '*cis*-effect,'[10] the doublet at lowest field is associated with the ***trans***-amine group C, and that at the highest field with amine B.

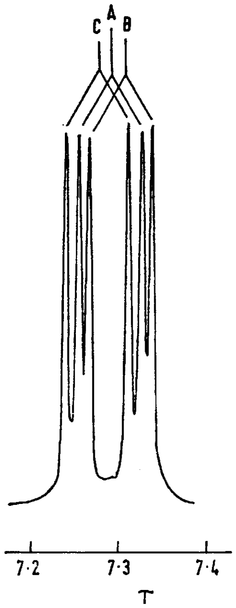

FIGURE 1 ^{1}H N.m.r. spectrum of $P_4N_4Cl_5(NMe_2)_3$ (II) at 220 MHz in CCl_4 solution

Compound (III) gives a spectrum in carbon tetrachloride at 100 MHz consisting of a broad doublet, which is resolved in benzene solution to give a high-field signal (intensity 2) and a lower-field signal (intensity 1). Coupling constants indicate the presence of non-geminal groups only. The specific interaction with benzene causes a greater shift in the signal due to the A groups and the two signals, expected from structure (III), are resolved.

The presence of a $P(NMe_2)_2$ group in compound (IV) is confirmed by a doublet of intensity 2 with $J^*_{\mathrm{HP}} =$ 11·8 Hz, while a second doublet at lower field arises from group C. The similarity between the chemical shift for group C here and both C in (II) and A and B in (III) indicates 1,5- rather than 1,3-substitution.

Tetrakis-compounds.—There are ten isomers with stoicheiometry $P_4N_4Cl_4(NMe_2)_4$, of which four contain only non-geminal groups. The spectra of compounds (V) and (VI) in both carbon tetrachloride and benzene consist of a single doublet with a broad central hump, and the coupling constants indicate the presence of only non-geminal amine groups. Such spectra could arise from three of the non-geminal compounds, *i.e.* (V), (VI), and the isomer with all amine groups in *cis*-positions. Structure (VI) has previously[3] been assigned to the compound melting at 200° and the chemical shift for the all-*cis*-isomer is expected at higher field. The

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[9] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1968, 703.

[10] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 908.

compound melting at 168° is thus assigned structure (V) as resonance occurs to low field of compound (VI).

100 MHz Spectra of the third isomer (VII) were not easily interpreted but clearly indicated an isomer of low symmetry. I.r. spectroscopy (see later) showed the presence of only non-geminal amine groups. The 220 MHz spectrum in carbon tetrachloride (see Figure 2) showed three types of non-equivalent amine groups confirming structure (VII). Doublets at high and low field can be assigned to groups A and C respectively.

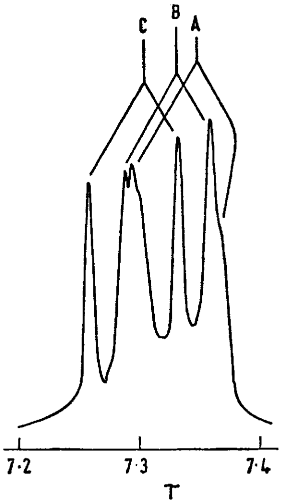


FIGURE 2 ^{1}H N.m.r. spectrum of $P_4N_4Cl_4(NMe_2)_4$ (VII) at 220 MHz in CCl_4 solution

Spectra of the fourth tetrakis-isomer (VIII) showed a single doublet which, from the coupling constant, can be associated with a compound containing only geminal amine groups. A 1,5-rather than 1,3-arrangement has been suggested previously.[3]

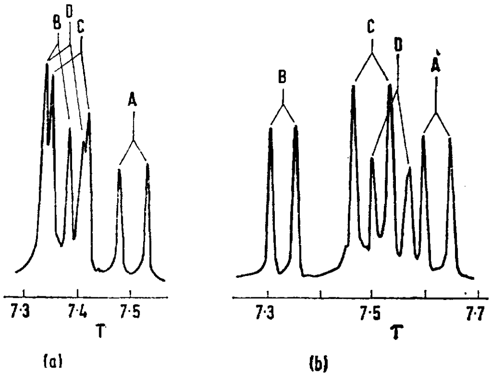
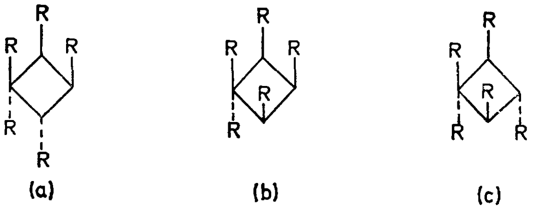


FIGURE 3 ^{1}H N.m.r. spectrum of $P_4N_4Cl_3(NMe_2)_5$ (IX) at 220 MHz in (a) CCl_4 and (b) C_6H_6 solution

Pentakis-compounds.—From the 220 MHz spectra of compound (IX) it is possible to discount structures which contain two geminally substituted phosphorus atoms. In the carbon tetrachloride spectrum (see Figure 3), doublets at τ 7·508 and 7·360 can be assigned to the non-equivalent geminal amine groups A and B respectively while the remainder of the spectrum consisting of two doublets in the ratio 2 : 1 is associated with the non-geminal groups C and D. The compound then has one of the three structures shown below.

Structure (a), with three non-equivalent non-geminal amine groups, has already been assigned[3] to a compound melting at 99·5°. The remaining two both contain two types of amine groups. However, for (c) the '*cis*-effect' would predict that in carbon tetrachloride solution the higher intensity doublet would occur upfield of the doublet of intensity 1. This is in fact observed and structure (IX) is assigned to the compound.



R = NMe$_2$ throughout

The pentakis-isomer melting at 51° gave spectra at 220 MHz showing two pairs of non-equivalent geminal amine groups and suggesting structure (X). The alternative arrangements, in which the geminal groups occupy 1,3-positions, is less likely as this would give further splitting of the geminal signals.

Hexakis-compound.—The spectra consisted of two doublets, the non-geminal groups being associated with that at low field. The higher intensity geminal signal is not split in benzene and, as suggested earlier,[3] the compound can be assigned structure (XI).

General trends.—In general, resonances for carbon tetrachloride solutions move to higher field with increasing amination paralleling the behaviour in the trimeric system.[11] This is probably a consequence of the greater difficulty of electron delocalization from the amine lone pairs leading to increased shielding.

The up-field shift is not constant and, for a given stoicheiometry, the presence of amine groups *cis* in 3- and 7-positions causes an increased up-field shift. A benzene-induced solvent shift to high field is observed with the aminochlorotetraphosphonitriles containing up to five dimethylamino-groups, but the magnitude is greatest for the least aminated compounds.

Vibrational Spectra.—Infrared spectra of the compounds are very similar above 750 cm^{-1}. The symmetric and asymmetric stretches of the NC_2 amine groups can be assigned for all compounds at *ca.* 990 and 1185 cm^{-1} respectively but, in contrast to the trimer case,[1,6] the former shows no change with isomer type. The latter, however, is clearly seen here while in analogous trimers it is obscured by a strong ring absorption.

Major differences occur in the 700 cm^{-1} region associated with P–N (amine) stretching modes,[12] and it is possible to determine the presence of geminal and/or non-geminal groups. Geminal amine groups give two

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[11] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 7193.

[12] R. Stahlberg and E. Steger, *Spectrochim. Acta*, 1967, **23A**, 2005.

fairly widely separated bands (ν_s and ν_a PN_2) while when only non-geminal groups are present either a single band or bands with a small splitting are observed. The spectra of compounds (IV), (VIII)—(XI), and $P_4N_4(NMe_2)_8$ all show a medium to strong band at *ca.* 740 cm^{-1} which is assigned to the asymmetric component of the PN_2 stretch. In those compounds containing only one $P(NMe_2)_2$ grouping, *i.e.* (IV) and (IX), the symmetric stretch occurs some 60 cm^{-1} to lower energy. When more than one geminal group is present, the separation is increased to *ca.* 100 cm^{-1} and the symmetric mode occurs at *ca.* 640 cm^{-1}.

Compounds containing equivalent non-geminal amine groups give one band in this region, *i.e.* at 718 cm^{-1} for (V) and at 703 cm^{-1} for (VI). However, when the amine arrangement is unsymmetrical as in (VII), two strong bands at 715 and 699 cm^{-1} are found.

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