1324. *Phosphorus–Nitrogen Compounds. Part XVII.*[1] *The* ^{1}H *and* ^{31}P *Nuclear Magnetic Resonance Spectra of Dimethylamino-derivatives of Hexachlorocyclotriphosphazatriene* *

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The ^{1}H nuclear magnetic resonance (n.m.r.) spectra of a series of dimethylamino-derivatives of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_{6-n}(NMe_2)_n$ (n = 1—4 or 6), have been measured at 60 and 100 Mc./sec. and used to assign structures to geometric and positional isomers when n = 2, 3, or 4. The origin of the broad humps between the sharp outside lines which are a feature of these spectra, is discussed. ^{31}P n.m.r. measurements were made at 40·5 Mc./sec., which confirm the assignments to positional isomers.

IN Part IX[2] of this Series we reported the isolation of a number of dimethylamino-derivatives of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_{6-n}(NMe_2)_n$ (n = 1—4 or 6). Reference was briefly made to their ^{1}H n.m.r. spectra as a means of making structural

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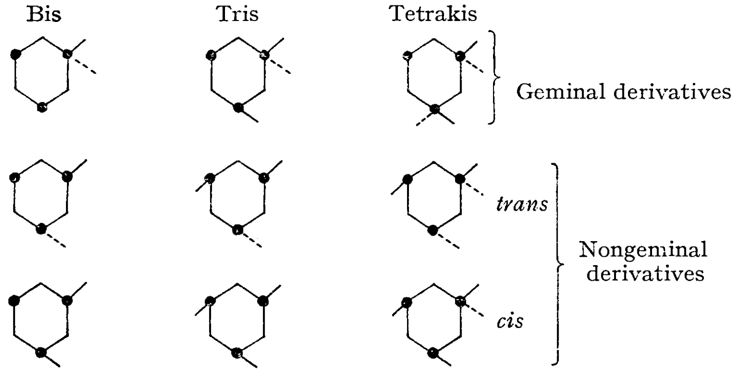
[1] Part XVI, S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J.*, 1965, 5032.

[2] R. Keat and R. A. Shaw, *J.*, 1965, 2215.

assignments. These are now reported in detail, together with their ^{31}P n.m.r. spectra. When $n = 2$, 3, or 4 in the above series, positional and geometrical isomerism is possible [3] (other forms of isomerism are neglected); the structures of these isomers are as shown.



The structures of isomeric bis-, tris-, and tetrakis-dimethylamino-derivatives of hexachlorocyclotriphosphazatriene

● = Phosphorus atom.
Unbroken lines at phosphorus atom represent dimethylamino-groups above the plane of the ring and broken lines the same groups below. Chlorine atoms are omitted.

A study of the ^{1}H n.m.r. spectra of mononuclear phosphorus(v) compounds containing the P–NMe$_2$ group was recently reported,[4] in which the signals from the dimethylamino-groups took the form of a simple doublet, the splitting of which was equal to the phosphorus–proton spin–spin coupling constant, $J_{\text{P–H}}$. Early studies,[5] however, of the ^{1}H n.m.r. spectra of five dimethylaminocyclotriphosphazatrienes, measured at 40 Mc./sec., showed these to be at their simplest a triplet. The chemical shift of the triplet was dependent on whether a $\equiv$PCl·NMe$_2$ or a $\equiv$P(NMe$_2$)$_2$ group was present. The tetrakisdimethylamino-derivative was shown to be nongeminal since its spectrum figured two such triplets, corresponding in chemical shifts to both of these groupings. Nongeminal structures were assigned to the bis- and tris-derivatives (III) and (VI) in Table 1. The 60 Mc./sec. ^{1}H n.m.r. spectra of these same derivatives together with an isomeric tris-derivative were recently reported by Ford, Dickson, and Bezman; [6] further fine structure was resolved and recognised to be a consequence of geometrical isomerism. Structures were directly assigned to two tris- and one tetrakis-dimethylamino-derivative which agree with our findings.

The results of our measurements at 60 and 100 Mc./sec. are shown in Table 1. A common feature of these spectra is a sharp doublet, between the extremities of which is a very broad peak whose shape is only centrosymmetric in compounds (V) and (IX). It has been suggested that this broad peak is due to coupling with the other two phosphorus atoms five bonds removed, and to quadrupole relaxation of the adjacent nitrogen atom.[6] The latter cause seemed unlikely in the light of the spectra of the mononuclear phosphorus(v) compound containing P–NMe$_2$ groupings,[4] and of trisdimethylamino-1,3,5-triazine (a sharp singlet at τ 6·94) which show no such broadening. This is confirmed by the fact that, on irradiation of the trisdimethylamino-derivative (VI) with a suitable radio-frequency source to decouple the nitrogen nuclear spin, no change in the ^{1}H n.m.r. spectrum is observed.

In the hexakisdimethylamino-derivative (IX), for example, the phosphorus nuclei are

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[3] R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.
[4] R. Keat and R. A. Shaw, *J.*, 1965, 4802.
[5] S. K. Ray and R. A. Shaw, *J.*, 1961, 872.
[6] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1964, **3**, 177.

TABLE 1

^{1}H n.m.r. data for dimethylamino-derivatives of hexachlorocyclotriphosphazatriene

Compound	M. p.	τ π§			J^{*}_{P-H} (c./sec.) π			J^{*}_{P-H} (c./sec.) †			Structural assignment ‡
$N_3P_3Cl_5{\cdot}NMe_2$ (I)	16°	7·25	—	—	17·6	—	—	17·6	—	—	ng
$N_3P_3Cl_4(NMe_2)_2$ (II) ...	86	7·29	—	—	17·3	—	—	17·3	—	—	ng, *cis*
$N_3P_3Cl_4(NMe_2)_2$ (III)...	103	7·27	—	—	17·3	—	—	17·0	—	—	ng, *trans*
$N_3P_3Cl_4(NMe_2)_2$ (IV) ...	62	7·36	—	—	13·9	—	—	—	—	—	g
$N_3P_3Cl_3(NMe_2)_3$ (V) ...	152	7·32	—	—	17·2	—	—	17·5	—	—	ng, *cis*
$N_3P_3Cl_3(NMe_2)_3$ (VI) ...	105	7·28^{1}	7·31^{2}	—	17·5	17·6	—	17·2	17·3	—	ng, *trans*
$N_3P_3Cl_3(NMe_2)_3$ (VII)	71	7·32^{1}	7·36^{1}	7·41^{1}	16·3	12·7	12·7	16·7	12·7	12·8	g
$N_3P_3Cl_2(NMe_2)_4$ (VIII)	104	7·35	7·36	7·48	16·6	11·6	11·5	16·8	11·7	11·4	ng, *cis*
$N_3P_3(NMe_2)_6$ (IX)	104	7·45	—	—	11·2	—	—	11·7	—	—	g

π Measured at 60 Mc./sec. † Measured at 100 Mc./sec. ‡ ng = nongeminal; g = geminal. § Superscripts represent relative intensity [these could not be reliably estimated for compound (VIII)].

chemically, but not magnetically, equivalent and so represent a cyclic $X_6AX'_6A'X_6''A''$ spin system. The calculation of transition energies and the relative intensities of each transition of the X (hydrogen) nuclei are very complex and have as yet not been solved, but some useful correlations can be made by consideration of the results of analyses of simpler spin systems. The characteristics of ABX [7] and ABX_3 [8] spin systems are well known in organic chemistry; when J_{AB} is comparable to or greater than J_{AX}, the X nucleus is effectively coupled to both A and B nuclei, even though J_{BX} may be zero. The general profile of the calculated X spectrum in the ABX_3 system is not unlike that observed for the dimethylamino-derivatives of hexachlorocyclotriphosphazatriene when the above condition is satisfied and the chemical shift between A and B nuclei is small or zero. Individual transitions should however still be resolvable in the ABX_3 spin system with high-resolution instruments. A similar treatment has recently been extended to account for the ^{1}H spectra of tetramethyldiphosphine derivatives,[9,10] the simplest of which (structurally), tetramethyldiphosphine, $Me_2P{-}PMe_2$, is an example of an $X_6AA'X'_6$ spin system. In this case the separation of the two most intense signals in the spectrum is equal to the sum of the short-range and long-range P–H coupling constants. The spectrum is complex, but again individual transitions are nearly all resolved. In contrast, the broadened peaks observed in the ^{1}H spectra of individual dimethylamino-derivatives must consist of a large number of transitions all with a separation of less than 0·5 c./sec., the limit of resolution of the spectrometer. In these spectra there are no transitions outside each of the doublets (which are arising from different proton environments), excluding ^{13}C satellites. This appears to be a consequence of the magnitudes of the coupling constants involved and their relative signs. In the related case of the ^{19}F n.m.r. spectrum of the difluoro-derivative, $N_3P_3Cl_4F_2$, an AB_2X_2 spin system, there were but few transitions situated between the two most intense lines in the spectrum.[11] The separation of these lines was very similar in magnitude to the coupling constant J_{AX}. Comparison of the separation of the doublets in the spectra of compounds (I)—(IX) with those of mononuclear phosphorus compounds [4] indicates that the actual value of J_{P-H} over three bonds must approximate to this separation which is referred to as J^{*}_{P-H} in Table 1.

The field invariant nature (within experimental error) of the J^{*}_{P-H} values in Table 1 confirms that the observed doublets are intimately connected with J_{P-H}. Unfortunately, chemical shifts are not available for the 100-Mc./sec. measurements, so that these cannot be compared with those determined at the lower frequency. The peaks in the spectra of the tris- (VII) and tetrakis-derivatives (VIII) show signs of further splitting at

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[7] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.
[8] F. A. L. Anet, *Canad. J. Chem.*, 1961, **39**, 2262.
[9] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.
[10] R. K. Harris and R. G. Hayter, *Canad. J. Chem.*, 1964, **42**, 2282.
[11] M. L. Heffernan and R. F. M. White, *J.*, 1961, 1382.

60 Mc./sec. which almost disappears at 100 Mc./sec. This is probably because at the latter frequency the spectra are a closer approach to first-order; the ratio of the chemical shifts between individual phosphorus nuclei to phosphorus–phosphorus coupling constant (J_{P-P}) will certainly increase at the higher frequency.

The signals from the dimethylamino-protons all occur in the region τ 7·2—7·5 and their mean positions move upfield with increasing degree of aminolysis, but the transition between $\equiv PCl \cdot NMe_2$ and $\equiv P(NMe_2)_2$ groups is not as clear cut as for the J^*_{P-H} values. In agreement with trends observed for mononuclear phosphorus(v) compounds,[4] J^*_{P-H} values decrease with increasing degree of aminolysis. In fact the magnitude of J^*_{P-H} is a much better criterion with which to distinguish between $\equiv PCl \cdot NMe_2$ and $\equiv P(NMe_2)_2$ groups. For the former J^*_{P-H} never falls below 16·3 c./sec. and for the latter is never greater than 13·9 c./sec.

The number of dimethylamino-proton environments (*i.e.*, number of doublets in the spectra of tris- and tetrakis-derivatives) can be used to make structural assignments.[2,6] For example, the geminal trisdimethylamino-derivative has a geminal dimethylamino-group with two chlorine atoms on the same side of the phosphazene ring, another geminal dimethylamino-group with a chlorine atom and a nongeminal dimethylamino-group on the same side of the ring, and a nongeminal dimethylamino-group. The trisdimethylamino-derivative (VII), m. p. 71°, has three such environments, and is thus assigned a geminal structure. The other two tris-isomers, m. p. 105 and 152° have two and one environments, respectively. A similar analysis leads to a *trans*-structure for the isomer of m. p. 105° and to a *cis*-structure for that of m. p. 152°. The sole tetrakis-derivative isolated, (VIII), has a spectrum consisting of three proton environments which is only consistent with a nongeminal *cis*-structure. In all cases the doublets, indicating the number of environments, overlap, and the presence of broad peaks between these doublets sometimes makes it difficult to estimate the relative numbers of protons in each environment. The above observations concerning the magnitude of J^*_{P-H} in geminal and nongeminal dimethylamino-groups is of considerable assistance in assigning a doublet to a given dimethylamino-group environment. It should be pointed out that the relative chemical shift between each dimethylamino-proton environment is strongly dependent on the nature of the other groups attached to phosphorus. For example, when piperidino- and dimethylamino-groups only are attached to the phosphazene ring the dimethylamino-proton environments cannot be resolved,[12] although some of them are chemically non-equivalent. When phenoxy- and dimethylamino-groups are present, however, the relative shifts, imposed on the dimethylamino-protons, are such as to separate their signals completely, *i.e.*, there is no overlap of the doublets.[13]

The assignment of structures to bisdimethylamino-derivatives represents a more difficult problem since each isomer can theoretically only have one proton environment. The isomer of m. p. 62° (IV) has a considerably smaller J^*_{P-H} value and the protons are more shielded than in the other two isomers. The trends observed in these parameters (cf. above) for mononuclear phosphorus(v) compounds allows this isomer to be assigned a geminal structure. This distinction between positional isomers is confirmed by the fact that the bis-isomers (II) and (III) undergo a *cis–trans* isomerisation in the presence of aluminium chloride[14] and amine hydrochlorides,[15] which can only be reconciled with their having nongeminal structures. Also, the preparation of a series of mixed amino-phosphazenes[12] provides evidence that the nongeminal bis-isomer (III) has a *trans*-configuration. Table 1 shows that the protons of the *cis*-trisdimethylamino-derivative are more shielded than those in the *trans*-isomer; further, the protons in the two dimethyl-amino-groups on the same side of the phosphazene ring in the *trans*-isomer are more

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[12] R. Keat and R. A. Shaw, unpublished results.

[13] D. Dell, B. W. Fitzsimmons, R. Keat, and R. A. Shaw, unpublished results.

[14] R. Keat, R. A. Shaw, and C. Stratton, *J.*, 1965, 2223.

[15] R. Keat and R. A. Shaw, *Chem. and Ind.*, 1964, 1232; *J.*, 1965, 4067.

shielded than those of the sole dimethylamino-group (flanked by two chlorine atoms) on the other side. These observations show that, at least when the other groups on the ring are chlorine atoms, the protons in dimethylamino-groups *cis* to each other are more shielded than those in which these groups are *trans* to one another. This observations permits the assignment of a *cis*-structure to the bis-isomer (II), and a *trans*-structure to (III) in agreement with the chemical evidence above and with the dipole-moment studies of Koopman.[16] The chemical-shift difference between these two isomers, although small, was repeatable.

Similar arguments allow spin–spin coupling constants and chemical shifts to be assigned to individual dimethylamino-groups in compounds (VII) and (VIII). In the former (VII), the geminal dimethylamino-group where $\tau = 7{\cdot}41$, $J^*_{\text{P-H}} = 12{\cdot}7$ c./sec. is that flanked by a chlorine atom and a dimethylamino-group, and the environment where $\tau = 7{\cdot}36$, $J^*_{\text{P-H}} = 12{\cdot}6$ c./sec., the geminal dimethylamino-group is flanked by two chlorine atoms. The environment where $\tau = 7{\cdot}48$, $J^*_{\text{P-H}} = 11{\cdot}5$ c./sec. in the tetrakis-derivative (VIII) corresponds to the one geminal dimethylamino-group on the same side of the ring as the two nongeminal dimethylamino-groups and that at $\tau = 7{\cdot}36$, $J^*_{\text{P-H}} = 11{\cdot}6$ c./sec. to the other flanked by two chlorine atoms.

The ^{31}P n.m.r. data for all the dimethylamino-derivatives except (IV) and (IX) are given in Table 2, there being insufficient sample available for a satisfactory spectrum of compound (IV). The spectrum of the monodimethylamino-derivative (I) was analysed as being an AB_2 type,[17] yielding a J_{AB} value of 34 c./sec. The bisdimethylamino-derivatives (II) and (III) provide spectra in which the shifts between the two types of phosphorus nuclei are increased and the spectrum approaches first-order, *i.e.*, AX_2 (X pertains to the phosphorus nucleus). Such a system should take the form of a triplet and a doublet in a first-order analysis, but the doublet is broadened in both cases by phosphorus–proton coupling. The broadening of the doublet and the fact that the ratio of the areas under this broad peak to that under the triplet (the middle component of which is just resolvable into a doublet) is 2 : 1, confirms that both are nongeminal. Only approximate values of J_{AB} are obtainable because of the broadening of the spectra. Structural assignments cannot be made to these geometrical isomers from the ^{31}P n.m.r. data available. A similar broadening of phosphorus resonance absorptions has been observed in a mono-(1-aziridinyl) derivative, $N_3P_3Cl_5\,(\overline{N-CH_2-CH_2})$;[18] irradiation of the protons at their resonance frequency revealed a perturbed triplet and doublet. It is noteworthy however that the AB_2 type spectrum of (I) is not broadened in this manner.

TABLE 2

^{31}P n.m.r. data for dimethylamino-derivatives of hexachlorocyclotriphosphazatriene

Compound	Spin system *	ν_A (p.p.m.)	ν_B (p.p.m.)	J_{AB} (c./sec.)
$N_3P_3Cl_5{\cdot}NMe$ (I)	AB_2	−22·0	−20·4 †	34
$N_3P_3Cl_4(NMe_2)_2$ (II)	AX_2–AB_2	−21·6 †	−24·9 ‡	~48
$N_3P_3Cl_4(NMe_2)_2$ (III)	AX_2–AB_2	−20·5 †	−24·5 ‡	~44
$N_3P_3Cl_3(NMe_2)_3$ (V)	A_3	−27·6 ‡	—	—
$N_3P_3Cl_3(NMe_2)_3$ (VI)	AB_2	−26·1 ‡	—	—
$N_3P_3Cl_3(NMe_2)_3$ (VII)	ABC	−21·6 ‡	—	—
$N_3P_3Cl_2(NMe_2)_4$ (VIII)	AB_2	−23·9 ‡	−30·5 ‡	—

* Neglecting protons. † Signal arising from $\equiv PCl_2$. ‡ Broadened by P–H coupling; only approximate values.

Both the trisdimethylamino-derivatives (V) and (VI) give rise to broadened singlet absorption, whilst the third isomer (VII) shows two broad peaks of unequal intensity.

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[16] H. Koopman, XIXth I.U.P.A.C. Congress, London, 1963, Abstracts AB4–36, p. 178; and personal communication.

[17] J. A. Pople, W. G. Schneider, and H. J. Bernstein, " High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 123.

[18] G. Ottmann, H. Agahigian, H. Hooks, G. D. Vickers, E. Kober, and R. Rätz, *Inorg. Chem.*, 1964, 3, 753.

The greatest shift between phosphorus nuclei would be expected from a geminal rather than a nongeminal structure so that structure (VII) is assigned the former. With sufficient resolution it should be theoretically possible to assign structures to the geometrical tris-isomers; the *cis*-isomer should exhibit only one phosphorus nuclear environment, whilst the *trans* would show two. The isomer (VI) has a greater linewidth at half-peak height (38 c./sec.) than the isomer (V) (28 c./sec.). This is an indication that, at this field strength, resolution for the former is not sufficient to separate the two phosphorus environments. On this basis the former isomer (VI) can be assigned a *trans*-structure, and the latter (V) a *cis*-structure. These conclusions are in agreement with those obtained from ^{1}H n.m.r. measurements. Becke-Goehring and co-workers [19] assigned earlier a nongeminal structure compound (VI) because of its single line ^{31}P n.m.r. spectrum. When phenyl groups are present as in the nongeminal *trans*-triphenyl derivatives, $N_3P_3Ph_3X_3$ ($X = Cl$ [20] or Br [21]), the neighbour anisotropy effect is sufficient to resolve the two phosphorus nuclear environments. The two very broad peaks obtained for the tetrakisdimethylamino-derivative (VIII) are a good indication that it has a nongeminal structure because, if only $\equiv P(NMe_2)_2$ and $\equiv PCl_2$ groups were present, as in a geminal isomer, a better-resolved spectrum would be expected.

If the magnitude of J_{P-P} values observed for the mono- and bis-dimethylamino-derivatives remains of the same order for the remaining dimethylaminocyclotriphosphazatrienes, then J_{P-P} will be greater than J_{P-H} in all cases, and one of the conditions for the observation of a complex proton spectrum will have been established. The second condition, that the chemical shift between the phosphorus nuclei comprising the phosphazene ring be small, is also complied with. For the nongeminal *cis*–tris- and the hexakis-dimethylamino-derivatives the shift is zero, and, in the light of the observed spectra, is likely to be small for the remaining compounds. It is interesting to note that when J_{P-P} is small, as in the tetrachlorobisethylmercapto-derivative $N_3P_3Cl_4(SEt)_2$ ($J_{P-P} = 4{\cdot}8$ c./sec.), no fine structure is observed in the methylene proton signal [22] other than that due to coupling with the methyl group and the phosphorus atom ($J_{P-H} = 18{\cdot}1$ c./sec.).

It can thus be seen that the agreement in the structural assignments made to positional and geometrical isomers on the basis of their ^{1}H and ^{31}P n.m.r. spectra, basicities,[2,23] dipole moments,[16] and chemical reactions [12,14,15] is excellent.

EXPERIMENTAL

Preparative methods for all the dimethylamino-derivatives used in this study have been described previously.[2] ^{1}H n.m.r. spectra at 60 Mc./sec. were obtained with a Varian A60 spectrometer. ^{1}H and ^{31}P n.m.r. spectra were recorded on a Varian HR 100 spectrometer at 100 and 40·5 Mc./sec., respectively. Calibration on the latter machine was by the side-band technique. Spectra were run on samples consisting of approximately 30% w./w. solutions in carbon tetrachloride. Tetramethylsilane was used as an internal reference for the ^{1}H spectra and 85% phosphoric acid as an external reference for the ^{31}P spectra.

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[19] M. Becke-Goehring, K. John, and E. Fluck, *Z. anorg. Chem.*, 1959, **302**, 103.
[20] B. Grushkin, M. G. Sanchez, and R. G. Rice, *Inorg. Chem.*, 1964, **3**, 623.
[21] T. Moeller and P. Nannelli, *Inorg. Chem.*, 1963, **2**, 896.
[22] N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Chem. and Ind.*, 1962, 1909.
[23] D. Feakins, W. A. Last, and R. A. Shaw, *J.*, 1964, 4464; *Chem. and Ind.*, 1961, 1173; and unpublished results.