Use of Chlorine-35 Nuclear Quadrupole Resonance Spectroscopy for Structural Assignments in Chlorocyclotriphosphazatrienes

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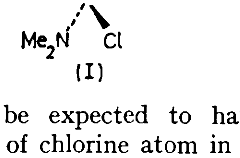
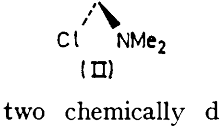
The ^{35}Cl nuclear quadrupole resonance spectra of a series of aminochlorocyclotriphosphazatrienes $N_3P_3Cl_{6-n}R_n$ ($R = NMe_2$, n = 1—4; $R = NC_5H_{10}$, n = 1—3) have been recorded at 77 and/or 273 K. These data show that positional isomers may be distinguished, but that unambiguous structural assignments to geometrical isomers are not generally possible. Similar conclusions may be drawn for other aminochloro- and phenylchloro-cyclotriphosphazatrienes. Resonance frequencies diagnostic of PCl_2, $PCl{\cdot}NR_2$, and PClPh groups fall in the ranges 26—29, 22—25, and 23—25 MHz respectively, but the last two groups cannot be distinguished by this technique.

NUCLEAR QUADRUPOLE RESONANCE (n.q.r.) spectroscopy can be used as a probe to obtain information about the environment of a given quadrupolar nucleus,[1] but its routine use in the identification of chemically distinct nuclei as an aid to structural assignments is often limited by problems of sensitivity to detection and by crystal-packing effects. These problems became apparent during our studies [2,3] of the ^{35}Cl n.q.r. spectra of phosphorus–chlorine compounds, although a linear relationship between n.q.r. frequencies and P–Cl bond lengths was established [2] for cyclophosphazenes. Related observations have since been reported by other workers.[4]

We have now studied the ^{35}Cl n.q.r. spectra of a series of derivatives of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, in order to assess the usefulness of this technique in obtaining structural information on the cyclophosphazenes. Most structural information in this area refers to the amino-derivatives [5] and our n.q.r. results for some of these are given in the Table. Previously reported data [2] for $N_3P_3Cl_6$ is also included for comparisons. Spectra were not always obtainable at both 77 and 273 K, and the signal strength was such that spectra could not generally be obtained from molecules containing fewer than three chlorine atoms. The spectra of the monoamino-derivatives show signals in two distinct regions, with those at higher frequency (26·8—28·6 MHz) clearly associated [2] with the PCl_2 groups, and those at lower frequency (24·3—25·0 MHz) with the $PClNR_2$ groups, with the latter group expected to have the longest P–Cl bonds.[6,7] The PClR frequencies were also characterised by a smaller temperature dependence than the PCl_2 frequencies. These differences indicate that positional isomers might readily be distinguished and this is found to be the case. For example, of the three trisdimethylamino-derivatives only that of m.p. 71 °C has a signal in the PCl_2 range and must therefore have a geminal structure. However, it is not clear which of the PCl_2 signals for the monoamino-derivatives are assignable to chlorine atoms in a *cis*- or *trans*-relationship to the amino-group. An ability to distinguish these signals is obviously important in making structural assignments to geometrical isomers. Thus the *cis*-bisdimethylamino-derivative (I) may be expected to have two chemically distinct types of chlorine atom in the PCl_2 group, whereas the *trans*-bisdimethylamino-derivative (II) should have only one. Two PCl_2 signals are indeed observed for the *cis*-isomers covering a range of 0·5 and 0·2 MHz for dimethylamino- and piperidino-derivatives respectively. There are also two PCl_2 signals for the *trans*-bisdimethylamino-derivative, but their separation is only about half that in the *cis*-isomer. A peculiarity of


(I)


(II)

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[1] E. A. C. Lucken, ' Nuclear Quadrupole Coupling Constants,' Academic Press, New York, 1969.

[2] R. Keat, A. L. Porte, D. A. Tong, and R. A. Shaw, *J.C.S. Dalton*, 1972, 1648.

[3] T. S. Cameron, C. Y. Cheng, T. Demir, K. D. Howlett, R. Keat, A. L. Porte, C. K. Prout, and R. A. Shaw, *Angew. Chem. Internat. Edn.*, 1972, **11**, 510.

[4] V. E. Belskii, V. A. Naumov, and I. A. Nuretdinov, *Doklady Akad. Nauk S.S.S.R.*, 1974, **215**, 355.

[5] R. Keat and R. A. Shaw, ' Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Interscience, New York, 1973, vol. 6, ch. 17.

[6] F. R. Ahmed and D. R. Pollard, *Acta Cryst.*, 1972, **B28**, 513.

[7] F. R. Ahmed and D. R. Pollard, *Acta Cryst.*, 1972, **B28**, 3530.

the *trans*-bispiperidino-derivative is that the difference between the mean PCl_2 and PClR frequencies is 3·9 MHz, but for all the other bisamino-derivatives it lies between 2·8 and 3·1 MHz at 293 K. This structural feature may also be related to an unusually large splitting[8] of the band corresponding to the P=N stretching vibration in the i.r. spectrum of this derivative, both in the solid state and in solution. It is even more difficult to distinguish *cis*- and *trans*-tris- than bis-dimethylamino-derivatives where the $PClNMe_2$ signals both cover a range of about 1 MHz. The large number of signals arising from the *cis*-isomer are a consequence of the fact that there are two molecules in the asymmetric unit and that the ring has a slight 'chair' conformation.[7] The dimethylamino- and piperidino-derivatives also show a trend for the PCl_2 and $PCl{\cdot}NR_2$ resonances to move to lower frequencies with increasing degree of aminolysis.

The PCl_2 signals for $N_3P_3Cl_5NHPr^i$ fall into a frequency range similar to those observed for $N_3P_3Cl_5NMe_2$, and the presence of signals between 24·1 and 25·8 MHz is indicative of a nongeminal structure for $N_3P_3Cl_4(NHEt)(NMe_2)$ and for $N_3P_3Cl_4(NHEt)_2$. It may also be noted that NH·Alkyl groups induce significantly higher resonance frequencies than $-N{\cdot}Alkyl_2$ groups.

^{35}Cl N.q.r. data for amino- and phenyl derivatives of $N_3P_3Cl_6$

Compound	M.p. (*t*/°C)	Structure[a]	N.q.r. frequency (MHz) at 77 K	N.q.r. frequency (MHz) at 293 K
$N_3P_3Cl_6$ [d]	113		28·3175, 28·3279 28·5982, 28·6842	27·608, 27·684 27·812, 27·880
$N_3P_3Cl_5NMe_2$	12—14	2,2,4,4,6 : 6	24·930, 24·976 27·463, 27·845 28·406, 28·550 28·116 [b]	liquid
$N_3P_3Cl_5NC_5H_{10}$	68	2,2,4,4,6 : 6	24·950, 25·000 24·749, 27·806 28·096, 28·154 38·355, 28·408	24·346 26·827, 26·902 27·162, 27·411
$N_3P_3Cl_4(NMe_2)_2$	103	2-*trans*-4,6,6 : 2,4	24·14, 24·67 27·45	23·50, 23·95 26·40, 26·64
$N_3P_3Cl_4(NC_5H_{10})_2$	104—105	2-*trans*-4,6,6 : 2,4	23·726, 23·770 24·176, 24·218 27·927	23·129,[b] 23·185 [b] 27·122 (all at 300 K)
$N_3P_3Cl_4(NMe_2)_2$	86	2-*cis*-4,6,6 : 2,4	24·073 27·388, 28·139	23·583 26·614, 27·067
$N_3P_3Cl_4(NC_5H_{10})_2$	129	2-*cis*-4,6,6 : 2,4	*c*	23·789, 23·964 26·947, 27·080
$N_3P_3Cl_3(NMe_2)_3$	105	2-*trans*-4,6 : 2,4,6	*c*	22·704, 23·760
$N_3P_3Cl_3(NMe_2)_3$	152	2-*cis*-4-*cis*-6 : 2,4,6	*c*	22·832, 23·159 23·291, 23·465 23·735
$N_3P_3Cl_3(NMe_2)_3$	71	2,2,4 : 4,6,6	23·974 26·84, 27·574	23·33 26·68
$N_3P_3Cl_2(NMe_2)_4$	104	2-*cis*-4 : 2,4,6,6	23·27 [b]	*c*
$N_3P_3Cl_4(NHEt)(NMe_2)$	73—74	2,2,4,6 : 4,6	24·183, 25·216 27·220, 28·231	*c*
$N_3P_3Cl_4(NHEt)_2$	35	2-*trans*-4,6,6 : 2,4	24·62, 25·75 27·95, 28·32	
$N_3P_3Cl_5NHPr^i$	54—55	2,2,4,4,6 : 6	25·745,[b] 25·963 [b] 28·140,[b] 28·182 [b] 28·340,[b]	24·586 26·075, 26·293 27·003, 27·104
$N_3P_3Cl_4(N{=}PPh_3)_2$	199—200	2,2,4,4 : 6,6	27·44, 27·75	
$N_3P_3Cl_3Ph_3$	158—159	2-*trans*-4,6 : 2,4,6	*c*	23·867, 24·331 24·787
$N_3P_3Cl_3Ph_3$	191—192	2-*cis*-4-*cis*-6 : 2,4,6	*c*	23·965, 24·126 24·341, 24·383 24·522
$N_3P_3Cl_3Ph_3,C_6H_6$		2-*cis*-4-*cis*-6 : 2,4,6	24·277, 24·320 24·668, 24·716 25·052, 25·092	23·893, 24·326 24·385

[a] For nomenclature see R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247. [b] Barely observable above the background electronic noise level. [c] No signals detectable; this was also the case for *cis*- and *trans*-$N_3P_3Cl_3(NC_5H_{10})_3$, and *cis*-$N_3P_3Cl_2(NC_5H_{10})_4$. [d] R. Clipsham, R. M. Hart, and M. A. Whitehead, *Inorg. Chem.*, 1969, **8**, 2431; M. Kaplansky and M. A. Whitehead, *Canad. J. Chem.*, 1957, **45**, 1669.

The geminal phenyl derivatives, $N_3P_3Cl_{6-n}Ph_n$ (n = 2 and 4), were shown[2] to give ^{35}Cl n.q.r. signals in the range 26·3—28·3 MHz at 77 K. Although the non-geminal *cis*- and *trans*-triphenyl derivatives, $N_3P_3Cl_3Ph_3$, gave no signals at this temperature, the results obtained at 293 K (Table) clearly show that PCl_2 and PClPh groups have characteristic frequency ranges, with the latter group covering 23·8—24·8 MHz. The resonance frequencies observed for *trans*-$N_3P_3Cl_3Ph_3$ are spread over a wider range (1 MHz) than for *cis*-$N_3P_3Cl_3Ph_3$ (0·6 MHz) as expected from the chemical inequivalence of the chlorine atoms in the former. The range for the *cis*-isomer may be extended by the presence of more than one molecule in the asymmetric unit, which is

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[8] R. Keat, R. A. Shaw, and M. Woods, unpublished results.

suggested by the five signals observed for this molecule. The presence of a benzene molecule within the crystal lattice has little effect on the frequency range observed for the *cis*-isomer.

Since the ^{35}Cl resonance frequencies for compounds of related structure containing NMe_2, Ph, or $N{=}PPh_3$ groups fall into similar frequency ranges, we assume [2] that the P–Cl bonds are of a similar length. This contention is already consistent with the observation that the P–Cl bond lengths are equal within experimental error in the nongeminal (2,4,6,8 : 2,4,6,8 structures) tetramer derivatives, $N_4P_4Cl_4R_4$ (R = Ph [9] and NMe_2 [10]). However, the electron-supplying properties of the NMe_2, Ph, and $N{=}PPh_3$ groups, as estimated by basicity measurements,[11] follow the order $Ph < NMe_2 \ll N{=}PPh_3$, where the electronic structures of the phosphazene molecules are perturbed by protonation.

Our results may be summarised in that n.q.r. frequencies characteristic of PCl_2, $PClNR_2$, and PClPh groups occur in the ranges 26—29, 22—25, and 23—25 MHz respectively at both 77 and 293 K. The characteristic frequency ranges of the last two groups overlap and therefore these functional groups cannot be distinguished by this technique. *cis*- and *trans*-Isomers may be distinguished by comparison of the range of frequencies observed, but only when results for both isomers are available.

EXPERIMENTAL

Aminochloro- and phenylchloro-cyclotriphosphazatrienes were prepared by literature methods.[5] The preparation of $N_3P_3Cl_4(NHEt)(NMe_2)$ by the dimethylaminolysis of $N_3P_3Cl_5NHEt$ will be reported later.[8] Nuclear quadrupole resonance spectra were recorded on a Decca n.q.r. spectrometer as before.[2] In some cases the number of lines changed on altering the temperature thereby implying a 'freezing out' of molecular motions or possibly signifying phase changes or both. However, we have not examined these effects further.

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[9] G. J. Bullen and P. A. Tucker, *Chem. Comm.*, 1970, 1185.

[10] G. J. Bullen and P. A. Tucker, *J.C.S. Dalton*, 1972, 2437.

[11] M. Biddlestone and R. A. Shaw, *J.C.S. Dalton*, 1973, 2740; M. Biddlestone, S. N. Nabi, and R. A. Shaw, unpublished results.