# A Correlation Between P–Cl Bond Lengths and $^{35}$Cl Nuclear Quadrupole Resonance Frequencies in Some Cyclophosphazenes; the Use of $^{35}$Cl Nuclear Quadrupole Resonance Spectroscopy for Structural Assignments in Cyclodiphosphazanes

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The $^{35}$Cl n.q.r. spectra of a series of chlorocyclophosphazenes have been obtained and are discussed in the light of their known crystal structures. An approximately linear relationship exists between $^{35}$Cl n.q.r. frequencies and P–Cl bond lengths in closely related structures. The $^{35}$Cl n.q.r. spectra of the cyclodiphosphazanes, $(Cl_3PNR)_2$ (R = Me, Et, or Ph), are reported. The axial and equatorial chlorine atoms in the trigonal bipyramidal distribution of atoms about phosphorus in the latter class of compound can be identified by their frequency ranges, and by relative changes in frequency with temperature.

SEVERAL studies[1-4] of the $^{35}$Cl n.q.r. spectra of compounds containing P–Cl bonds have been reported, but in general detailed structural information on these compounds in the solid state is lacking. It is only within the last few years that, by means of *X*-ray diffraction methods, a number of extremely accurate crystal-structure determinations have been carried out on compounds containing phosphorus–chlorine bonds. These have revealed significant differences in the P–Cl bond lengths in different structural environments. Most of this information pertains to the chlorocyclophosphazenes, $(NPCl_2)_n$ ($n$ = 3, 4, or 5), and their derivatives, where four-co-ordinated phosphorus atoms are present, and it is to this area that our n.q.r. studies have been mainly directed. We have also examined the $^{35}$Cl n.q.r. spectra of the cyclodiphosphazanes, $(Cl_3PNR)_2$ (R = Me, Et, or Ph), where five-co-ordinated phosphorus atoms are present, and where accurate P–Cl bond lengths are known for $(Cl_3PNMe)_2$.

TABLE 1

Crystal and $^{35}$Cl n.q.r. data for chlorocyclophosphazenes

| | Crystal structures | | | | $^{35}$Cl n.q.r. frequencies/MHz [b] | | |
|---|---|---|---|---|---|---|---|
| Compound | Type | Space group | P–Cl bond length/Å [a] | Ref. | at 77 K | at 273 K | Ref. |
| $N_3P_3Cl_6$ | Orthorhombic | *Pnma* | 1·995(5), 1·993(5), 1·992(4), 1·991(4) (mean 1·993) | 5 | 28·3175$^1$, 28·3279$^2$, 28·5982$^1$, 28·6842$^2$ (mean 28·4820) | 27·608$^2$, 27·684$^1$, 27·812$^1$, 27·880$^2$ (294 K) | 6 and 15 |
| $N_3P_3Cl_4Ph_2$ | Monoclinic | $P2_1/n$ | 1·989(2), 1·990(2), 2·002(2), 2·010(2) (mean 1·998) | 7 | 27·091$^1$, 27·619$^1$, 28·079$^1$, 28·248$^1$ (mean 27·759) | | *c* |
| $N_3P_3Cl_2Ph_4$ | Monoclinic | $C2/c$ | 2·005(5), 2·008(5), 2·024(5), 2·030(5) (mean 2·017) | 8 | 26·341$^1$, 26·436$^2$, 26·755$^3$ (mean 26·510) | | *c* |
| $N_3P_3Cl_3(NMe_2)_3$ geminal | Monoclinic | $P2_1/n$ | 1·992(2), 2·010(2), 2·049(2) | 9 | 23·974$^2$, 26·84$^1$, 27·574$^4$ | 23·33$^1$, 26·68$^2$ | *c* |
| $N_3P_3Cl_3(NMe_2)_3$ *cis*-non-geminal | Monoclinic | $P2_1/a$ | 2·050(4), 2·054(4), 2·055(4), 2·057(4), 2·063(4), 2·065(4) (mean 2·057) | 10 | | 22·832$^1$, 23·159$^1$, 23·291$^2$, 23·465$^1$, 23·735$^1$ (mean 23·296) (293 K) | *c* |
| $N_4P_4Cl_8$ (K-form) | Tetragonal | $P4_2/n$ | 1·985(4), 1·993(4) (mean 1·989) | 11 | 28·611$^1$, 28·634$^1$ (mean 28·623) | Given graphically | 14 |
| $N_4P_4Cl_8$ (T-form) | Tetragonal | $P4_2/n$ | 1·988(4), 1·989(4) 1·990(4), 2·002(4) (mean 1·992) | 12 | 27·815$^1$, 28·651$^1$ 28·691$^1$, 29·059$^1$ (mean 28·554) | Given graphically | 14 |
| $N_5P_5Cl_{10}$ | Orthorhombic | $P(2_12_12_1)$ | 1·948—1·987(10) (mean 1·969) | 13 | 27·6876, 27·8415, 27·9270, 27·9423, 28·2220, 28·2474, 28·4400, 28·4850 (mean 28·0991) | 26·8 to 27·4 (293 K) | 16 |
| $NPCl_2(NSOCl)_2$ | Monoclinic | $P2_1/n$ | 1·954(6), 1·960(6) (mean 1·958) | 16 | *ca.* 30 (given graphically, 1 : 1 doublet) | 28·660, 29·836 (294 K) | 6 |

[a] Standard deviations in parentheses. [b] Superscripts to frequencies represent relative intensities. [c] This work.

The P–Cl bond lengths in $N_3P_3Cl_6$ (Table 1) have

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[1] For references before 1968 see E. A. C. Lucken, 'Nuclear Quadrupole Coupling Constants', Academic Press, New York, 1969.

[2] R. M. Hart and M. A. Whitehead, *J. Chem. Soc.* (*A*), 1971, 738, and references therein.

[3] R. M. Hart and M. A. Whitehead, *Mol. Phys.*, 1970, **19**, 383.

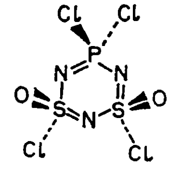
[4] M. Hashimoto, T. Morie, and Y. Kato, *Bull. Chem. Soc. Japan*, 1971, **44**, 1455.

recently been shown[5] to be equal within experimental error. The molecule is in a slight ' chair ' conformation and it is bisected by a mirror plane, so that although the P–Cl bond lengths are identical, there are four structurally different types of chlorine atom. The four n.q.r. signals from this compound[6] are in keeping with the ' chair ' conformation, and the relatively narrow range of frequencies (0·3667 MHz) are consistent with small packing differences in the crystal. However, in the geminal diphenyl derivative, $N_3P_3Cl_4Ph_2$, which also possesses a slight ' chair ' conformation (albeit slightly twisted), there are significant differences in P–Cl bond lengths within each of the $\equiv PCl_2$ groups.[7] These structural features give rise to the four observed $^{35}Cl$ n.q.r. signals, which are spread over a wider frequency range (1·157 MHz). The different P–Cl bond lengths in the geminal derivative $N_3P_3Cl_2Ph_4$ (which has a slight ' boat ' conformation) are on the borderline of being significant[8] (but are being quoted as their mean in the Figure). This, together with the fact that there are two molecules in the asymmetric unit, might give rise to four n.q.r. signals; only three are observed, probably owing to an accidental overlap of two signals.

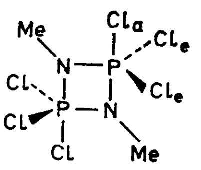
As expected on chemical grounds, there are three significantly different P–Cl bond lengths in the geminal trisdimethylamino-derivative $N_3P_3Cl_3(NMe_2)_3$.[9] Three n.q.r. signals were detected in an approximately 2 : 1 : 4 intensity ratio; the number of the signals is consistent with the structure. The crystal structure of the isomeric non-geminal *cis*-trisdimethylamino-derivative, $N_3P_3Cl_3(NMe_2)_3$ (with all dimethylamino-groups on the same side of the ring) reveals[10] that the ring has a slight ' chair ' conformation, and that there are two molecules in the asymmetric unit cell. The P–Cl bond lengths are not significantly different. Its $^{35}Cl$ n.q.r. spectrum at 293 K shows five weak signals in the same region as the $\equiv PCl{\cdot}NMe_2$ signal in the geminal isomer, one of which is possibly twice the intensity of the others. Unfortunately, no signal was detected at 77 K.

Of the chlorocyclophosphazenes with larger ring size, only the crystal structures of the two forms (K[11] and T[12]) of the tetramer, $N_4P_4Cl_8$, and of the pentamer, $N_5P_5Cl_{10}$,[13] are known. The $^{35}Cl$ n.q.r. spectra of the tetramers have been reported in detail[14,15] and the multiplicity of the n.q.r. signals in each case related to molecular symmetry. The pentamer $N_5P_5Cl_{10}$ shows eight n.q.r. signals,[16] possibly reflecting the relatively wide range of P–Cl bond lengths, although the latter were not considered to be significantly different.[13]

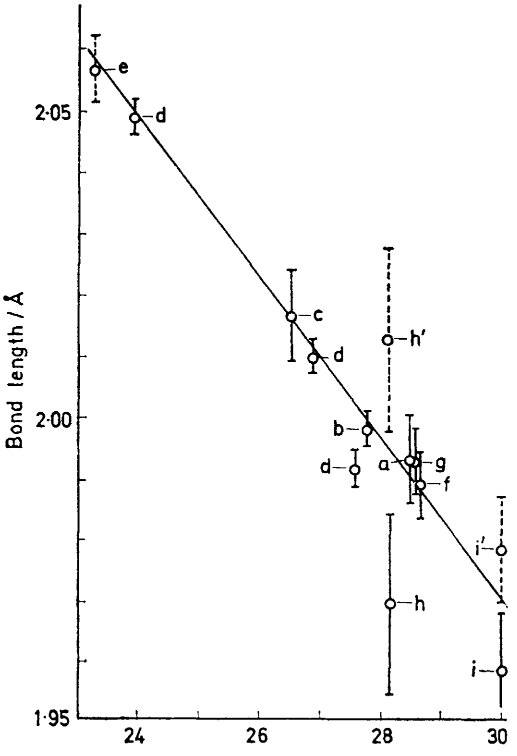
One of the shortest P–Cl bond lengths in a cyclophosphazene has been reported[17] for $NPCl_2(NSOCl)_2$, which has the structure (1). The P–Cl bond lengths are not significantly different but, as expected on chemical grounds, can be distinguished by n.q.r. spectroscopy.[6]



(1)



(2)



Plot of P–Cl bond lengths against $^{35}Cl$ n.q.r. frequencies at 77 K for cyclophosphazenes; a, $N_3P_3Cl_6$; b, $N_3P_3Cl_4Ph_2$; c, $N_3P_3Cl_2Ph_4$; d, $N_3P_3Cl_3(NMe_2)_3$ geminal; e, $N_3P_3Cl_3(NMe_2)_3$ *cis*-non-geminal *; f, $N_4P_4Cl_8$ (K-form); g, $N_4P_4Cl_8$ (T-form); h,h′ $N_5P_5Cl_{10}$ †; and i,i′ $NPCl_2(NSOCl)_2$ †

* Since no signal was detected at 77 K, the value plotted is the mean of the frequencies at 293 K. As the frequencies generally increase by 0·5—1 MHz on cooling to 77 K the point for the lower temperature would be expected to be very close to the line drawn. † See discussion on p. 1650.

The P–Cl bond lengths for the chlorocyclophosphazenes are plotted against $^{35}Cl$ n.q.r. frequencies in the Figure, showing that there is an approximately

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[5] G. J. Bullen, *J. Chem. Soc.* (*A*), 1971, 1450.

[6] R. Clipsham, R. M. Hart, and M. A. Whitehead, *Inorg. Chem.*, 1969, **8**, 2431.

[7] N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, 1965, **19**, 693.

[8] N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, 1966, **21**, 375.

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

[10] F. R. Ahmed and D. R. Pollard, personal communication.

[11] R. Hazekamp, T. Migchelson, and A. Vos, *Acta Cryst.*, 1962, **15**, 539.

[12] A. J. Wagner and A. Vos, *Acta Cryst.*, 1968, **B24**, 707.

[13] A. W. Schlueter and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1968, 2317.

[14] M. Dixon, H. D. B. Jenkins, J. A. S. Smith, and D. A. Tong, *Trans. Faraday Soc.*, 1967, **63**, 2852.

[15] M. Kaplansky and M. A. Whitehead, *Canad. J. Chem.*, 1967, **45**, 1669.

[16] M. A. Whitehead, *Canad. J. Chem.*, 1964, **42**, 1212.

[17] J. C. van de Grampel and A. Vos, *Acta Cryst.*, 1969, **B25**, 651.

linear relationship between the two. The equation for the straight line of best fit (the criterion of least squares being used) is given by: $y = -0{\cdot}12_8x + 2{\cdot}355$ ($y$ = bond-lengths in Å; $x$ = n.q.r. frequencies in MHz). The coefficient of linear correlation is found to be of absolute magnitude 0·98 and for eight points considered [a, b, c, d (three), f and g] this represents a confidence level of well above 99%. The observed deviations from exact linearity, especially for points h and i, can be attributed, at least in part, to underestimation of the bond lengths owing to high thermal vibration of the atoms. When the P–Cl bond lengths of $N_5P_5Cl_{10}$ and $NPCl_2(NSOCl)_2$, represented by points h and i, are corrected for thermal vibration by assuming the riding motion model,[18] the mean P–Cl bond lengths can take values as high as 2·013 and 1·978 Å, which are shown by points h′ and i′, respectively. However, in view of the assumptions involved in the corrections for thermal motion, these points should be given less weight than the others.

Where one molecule contains bonds of significantly different length, we have assigned the higher frequencies to the shorter bonds. Justification for this comes from the observed increase in the mean P–Cl bond length on passing along the series $N_3P_3Cl_{6-n}Ph_n$ ($n$ = 0, 2, 4), which is paralleled by a decrease in the mean n.q.r. frequencies (Table 1). The same conclusion can be reached by consideration of P–Cl bond lengths and n.q.r. frequencies in $(Cl_3PNMe)_2$ below. The uncertainty indicated in bond lengths in the Figure is taken as three times the standard deviations of the variates (not the means). The n.q.r. data obtained at 77 K and for selected compounds at 273 K gave similar plots although, as expected,[1,14,15] the frequencies were always lower at the higher temperature. A study[19] of the variation of $^{35}Cl$ n.q.r. frequencies and Pt–Cl bond lengths in platinum(II) chloride complexes also shows a general decrease in frequency with increasing bond length. Our data cannot be used to estimate the extent of $\pi$-bonding between chlorine and phosphorus, such as by a $3p_\pi$–$3d_\pi$ interaction, but this appears to be relatively small, as on the Townes and Dailey theory[20] increased $\pi$-bonding (presumably associated with a shortening of P–Cl bonds) would be expected to result in a drop in n.q.r. frequencies. In these compounds a decrease in the $^{35}Cl$ n.q.r. frequency and an associated increase in P–Cl bond length can therefore both be essentially ascribed to an increase in the degree of ionic character in the P–Cl bond.

It is clear that $^{35}Cl$ n.q.r. spectroscopy holds considerable promise as a method for predicting P–Cl bond lengths in the chlorocyclophosphazenes. A further feature of these spectra is that $^{35}Cl$ n.q.r. frequencies for the $\equiv PCl_2$ group occur in the range 26—30 MHz, whereas in geminal $N_3P_3Cl_3(NMe_2)_3$ the $\equiv PCl{\cdot}NMe_2$ group gives a signal at 23·97 MHz, and in non-geminal *cis*-$N_3P_3Cl_3(NMe_2)_3$ the $\equiv PCl{\cdot}NMe_2$ groups give signals at <24 MHz. Measurements on other aminochlorocyclophosphazenes containing the $\equiv PCl{\cdot}NR^1R^2$ group show[21] that here also $^{35}Cl$ n.q.r. signals occur at less than 26 MHz, so that it may be possible to distinguish positional isomers of chlorocyclophosphazenes by this technique.

The phosphorus atoms in the cyclodiphosphazanes $(Cl_3PNR)_2$ (R = Me, 2) are five-co-ordinated,[22,23] with the chlorine atoms occupying positions analogous to axial ($Cl_a$) and equatorial ($Cl_e$) sites in a trigonal bipyramid. Our results (Table 2) show that these are readily distinguished by the large separation of their $^{35}Cl$ n.q.r. frequencies, their relative intensities, and in the greater decrease of frequency associated with the equatorial chlorine atoms relative to the axial chlorine atoms, when the temperature is raised.

TABLE 2

$^{35}Cl$ n.q.r. data for $(RNPCl_3)_2$

| R | Position of Cl | Frequency/MHz 77 K | 293 K | Temperature[b] increment/ MHz |
|---|---|---|---|---|
| Me[a] | Axial | $25{\cdot}82_3$ | $25{\cdot}61_7$ | $-0{\cdot}20_6$ |
| | Equatorial | $30{\cdot}00_7$ | $29{\cdot}58_7$ | $-0{\cdot}42_0$ |
| | | $30{\cdot}35_1$ | $29{\cdot}77_8$ | $-0{\cdot}57_3$ |
| Et | Axial | $26{\cdot}18_6$ | $26{\cdot}03_3$ | $-0{\cdot}15_3$ |
| | Equatorial | $30{\cdot}45_6$ | $30{\cdot}01_0$ | $-0{\cdot}44_6$ |
| | | $30{\cdot}54_0$ | $30{\cdot}09_6$ | $-0{\cdot}44_6$ |
| Ph | Axial | $26{\cdot}28_8$ | $26{\cdot}13_9$ | $-0{\cdot}14_9$ |
| | Equatorial | 30·53 (±0·02) | $30{\cdot}08_1$ | −0·45 |
| | | 30·74 (±0·02) | $30{\cdot}12_2$ | −0·62 |
| *Cf.* $PCl_5$[24] | Axial | 29·242 | | |
| | | 29·274 | | |
| | Equatorial | 33·751 | | |

[a] $(MeNPCl_3)_2$, crystals monoclinic, $P2_1/n$, P–Cl, 2·018(5), 2·022(5), and 2·152(5) Å[22]. [b] Difference in frequencies at 77 and 293 K.

Additionally, the two signals obtained from the two equatorial chlorine atoms are possibly a reflection of slight differences in equatorial P–Cl bond lengths. The assignment of axial chlorine atoms to the lower frequencies is consistent with n.q.r. results obtained on molecular phosphorus pentachloride[24] (Table 2) and on $PCl_nF_{5-n}$ ($n$ = 1, 2, or 3).[25] The n.q.r. spectra of $(Cl_3PNR)_2$ (R = Et or Ph), are similar to that of the methyl compound, confirming their dimeric, centrosymmetric nature in the solid state. As might be expected from the fact that the phenyl group can compete with phosphorus for conjugation with the lone pair on nitrogen, the $^{35}Cl$ n.q.r. frequencies are higher when R = Ph than when R = Me or Et. It is rather unexpected, however, that the frequencies when R = Et

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[18] D. W. Cruickshank, *Acta Cryst.*, 1956, **9**, 749, 754, 757.

[19] C. W. Fryer, *Chem. Comm.*, 1970, 902.

[20] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, 1949, **17**, 782.

[21] R. Keat, A. L. Porte, R. A. Shaw, and D. A. Tong, unpublished results.

[22] D. Hess and H. Först, *Z. anorg. Chem.*, 1966, **342**, 240.

[23] L. G. Hoard and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1966, 1203.

[24] H. Chihara, N. Nakamura, and S. Seki, *Bull. Chem. Soc. Japan*, 1967, **40**, 50.

[25] R. R. Holmes, R. P. Carter, and G. E. Peterson, *Inorg. Chem.*, 1964, **3**, 1748.

lie closer to those for R = Ph than to those where R = Me. A plot of the P–Cl bond lengths for five-co-ordinated phosphorus atoms in $(Cl_3PNMe)_2$ against the $^{35}Cl$ n.q.r. frequencies does not fall on the same line as that of the cyclophosphazenes. This is not unexpected in view of the considerably different structural environments. Possibly changes in hybridisation, and in contributions from $p_\pi$–$d_\pi$ bonding may be superimposed on the changes arising from differences in ionic character. It may well be that the relationship shown in the Figure is limited to compounds of closely related structure, and substituents of similar electronegativities.

Most *X*-ray determinations have been carried out at ambient temperatures, whilst the bulk of $^{35}Cl$ n.q.r. measurements was done at 77 K. Whilst, where available, the n.q.r. measurements at 77 K agree with those at 273 K, the existence of the K- and T-forms of $N_4P_4Cl_8$, together with observations obtained by d.t.a. on some phosphazenes,[26] suggest that changes in crystal packing and/or molecular conformations may occur on heating individual compounds from 77 K to their m.p.s.

## EXPERIMENTAL

All n.q.r. spectra were obtained with either a locally-constructed super-regenerative spectrometer or a Decca Radar n.q.r. spectrometer, both of which were based on automatic equipment previously described.[27,28] Resonances were initially detected during unattended overnight sweeps covering *ca.* a 2 : 1 frequency range by use of bi-directional Zeeman modulation with automatic frequency calibration and a recording time constant of 10 s. Each resonance line was then re-examined by use of an expanded frequency scale and with sideband suppression. Frequencies were measured by interpolation between calibration markers automatically printed on the recorder chart paper at 10 kHz intervals.

This procedure was carried out for each sample at both 77 K and 273 K, these temperatures being maintained by immersion of the complete n.q.r. probe, containing the sample, in liquid nitrogen and an ice–water slush respectively.

The powdered samples were tightly packed into Pyrex tubes of outside diameter 12·5 mm and of 1 mm wall thickness, if possible to a depth of 2 cm in order to maximise the signal-to-noise ratio.

The compounds were synthesised as previously described: *gem*-$N_3P_3Ph_2Cl_4$,[29] *gem*-$N_3P_3Ph_4Cl_2$,[29] *gem*-$N_3P_3Cl_3(NMe_2)_3$,[30] *cis*-$N_3P_3Cl_3(NMe_2)_3$,[30] $(AlkNPCl_3)_2$,[31] and $(PhNPCl_3)_2$.[32]

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[26] W. Gee and R. A. Shaw, unpublished results.

[27] J. A. S. Smith and D. A. Tong, *J. Sci. Instr.*, 1968, **1** (Ser. 2), 8.

[28] D. A. Tong, *J. Sci. Instr.*, 1968, **1** (Ser. 2), 1162.

[29] K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J. Chem. Soc.*, 1964, 121.

[30] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215.

[31] I. N. Zhmurova and B. S. Drach, *Zhur. obshchei Khim.*, 1964, **34**, 1441.

[32] I. N. Zhmurova and A. V. Kirsanov, *Zhur. obshchei Khim.*, 1960, **30**, 3044.