Chlorine-35 Nuclear Quadrupole Resonance Studies of some Chlorine-containing Phosphorus–Nitrogen Compounds

By **William H. Dalgleish, Rodney Keat,*** and **Andrew L. Porte,*** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ
Robert A. Shaw, Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX

The ^{35}Cl n.q.r. spectra of a series of chlorine-containing phosphorus–nitrogen compounds including $[Cl(X)PNR]_2$ (X = lone pair, R = Bu^t; X = O, R = Bu^t or Me), $PCl_2(NBu^tH)O$, $Cl_2P{\cdot}NBu^t{\cdot}PCl_2$, $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$, $Cl_2(X)P{\cdot}NMe{\cdot}P(X)Cl_2$ (X = O or S), $Cl_2(O)P{\cdot}NR{\cdot}P(S)Cl_2$ (R = Me or Ph), the heterocycle $C_{17}H_{20}ClN_2OP$ (see Table 1), and $Cl_2(O)P{\cdot}N{:}PPh_3$ have been recorded at ambient temperatures and/or 77 K. The results are discussed in terms of the structures, where known, and a linear correlation between P–Cl bond lengths and n.q.r. frequencies has been deduced for phosphoryl compounds: this is different from the correlation previously deduced for cyclophosphazenes. Data for $Cl_2(O)PCH_2P(O)Cl_2$ are also included. The n.q.r. results enable some comparisons to be made of the relative electron supply of some common substituents encountered in phosphorus chemistry.

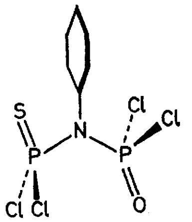
CHLORINE-35 n.q.r. spectroscopy has been widely applied in recent years to structural problems connected with phosphorus–chlorine compounds.[1] It has also been shown [2] that there is a linear correlation between P–Cl bond lengths and ^{35}Cl n.q.r. frequencies for chlorocyclophosphazenes. The applicability of this correlation for other types of phosphorus–chlorine compound has not been established because of a lack of accurate P–Cl bond-length data relevant to the solid state. In this study we describe the ^{35}Cl n.q.r. spectra of a series of cyclic and acyclic phosphorus–nitrogen compounds with phosphorus in oxidation states III and/or V, particular emphasis being placed on the spectra of phosphoryl compounds. Information is obtained on the relation between ^{35}Cl n.q.r. frequencies and P–Cl bond lengths and on the electron supply to phosphorus.

RESULTS AND DISCUSSION

N.q.r. signals can be obtained from most of the compounds listed in Table 1 at or near ambient temperatures. The appearance of two signals in the ^{35}Cl n.q.r. spectrum of $(ClPNBu^t)_2$ is consistent with the slight deviation from mirror symmetry (*cis* arrangement of chlorine atoms) established by a crystallographic study.[3] Both this compound and its oxidation product, $[Cl(O)PNBu^t]_2$,[4] contain only one type of molecule in the crystallographic unit cell, but in the latter compound the chlorine atoms are related by a centre of symmetry and only one signal is obtained. The results indicate that there is little difference in the P–Cl bond properties in $[Cl(O)PNBu^t]_2$ and $[Cl(O)PNMe]_2$.

Many of the acyclic phosphorus–nitrogen compounds reported here showed the same number of signals as chlorine atoms and it therefore follows that in these solids rotational averaging is not complete.[5] Thus in $Cl_2P{\cdot}NBu^t{\cdot}PCl_2$, if the asymmetric unit contains only one molecule, the conformation adopted must be one which does not have a mirror plane of symmetry. It is well established that many molecules of this type have preferred conformations in which phosphorus and nitrogen lone pairs (the latter presumably in a nearly pure *p* orbital because of planarity at nitrogen) lie orthogonal to one another.[6] This introduces a mirror plane of symmetry in the preferred conformations in the related compounds $F_2P{\cdot}NMe{\cdot}PF_2$ (vapour phase) [7] and $PCl_2(NMe_2)$ (liquid phase),[8] although in the solid state at 77 K the latter compound shows two or more ^{35}Cl n.q.r. signals, depending on the phase.

Provided that the following compounds contain only one molecule in the asymmetric unit, then the chlorine atoms in a given $Cl_2P(X)$ group (X = lone pair, O, or S) are not equivalent in $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$, $Cl_2(X)P{\cdot}NMe{\cdot}P(X)Cl_2$ (X = O or S), or $Cl_2(O)P{\cdot}NPh{\cdot}P(S)Cl_2$, but they are apparently equivalent in $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$,[9] possibly indicating a greater degree of symmetry. Of these molecules only the crystal structure of $Cl_2(O)P{\cdot}NPh{\cdot}P(S)Cl_2$ has been determined [10] and this shows that



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

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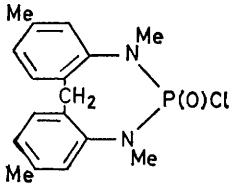
[10] T. S. Cameron, K. M. Ghouse, K. D. Howlett, R. Keat, H. H. Mills, C. K. Prout, and J. M. Robertson, *Phosphorus*, 1972, **2**, 47; T. S. Cameron, K. D. Howlett, and C. K. Prout, personal communication and unpublished results.

there is only one molecule in the asymmetric unit and that the conformation shown is devoid of symmetry elements. In Table 2, the mean frequencies associated *with* PCl_2, $P(O)Cl_2$, and $P(S)Cl_2$ groups are listed for these acyclic compounds. The assignment of frequencies to these groups is based on a consideration of the frequencies of PCl_3, PCl_3O, and PCl_3S (see Table 2). Lower ^{35}Cl n.q.r. frequencies of phosphoryl compounds reflect longer (see below) and presumably more polar P–Cl bonds, which in turn may be related to greater electron withdrawal from the bridging nitrogen atom. Comparison of the ^{35}Cl n.q.r. frequencies of $Cl_2(O)P{\cdot}NMe{\cdot}P(O)Cl_2$ and $Cl_2(S)P{\cdot}NMe{\cdot}P(S)Cl_2$ with those of $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ shows that the signals arising from the $P(O)Cl_2$ group of the non-symmetric compound occur at lower frequencies, and those from the $P(S)Cl_2$ group occur at higher frequencies, than in the respective symmetric compounds. Thus the $P(O)Cl_2$ group is more electron withdrawing than the $P(S)Cl_2$ group, and similar reasoning may be applied to the frequencies observed for the remaining compounds to conclude that the $P(O)Cl_2$ group is also more electron withdrawing than the PCl_2 group. The first conclusion is strongly supported by the crystal structure of the compound, $Cl_2(O)P{\cdot}NPh{\cdot}P(S)Cl_2$, where the P–N bond to the $P(O)Cl_2$ group is significantly shorter than that to the $P(S)Cl_2$ group.[10] Unfortunately, a comparison of the P–N bond lengths in related molecules $PCl_2(NMe_2)$ and $PCl_2(NMe_2)O$ is not possible because of the large errors that arise from their electron-diffraction study.[11] There is, however, evidence, from other crystallographic studies [10,12] that the P^{III}–N bond in general is longer than the P^{V}–N bond, for a given set of substituents on phosphorus.

TABLE 1

Chlorine-35 n.q.r. data

Compound	Frequency ±0.005 MHz	T/K	P–Cl Bond length [a] (Å)
$(ClPNBu^t)_2$	19.659, 19.711	295	2.105 (9) [3]
$Cl_2P{\cdot}NBu^t{\cdot}PCl_2$	24.428, 24.851 25.123, 25.136	293	
$[Cl(O)PNMe]_2$	27.168 [b]	77	
	26.587	293	
$[Cl(O)PNBu^t]_2$	26.345	298	2.007 (2) [4]
$PCl_2(NBu^tH)O$	26.343, 26.390	77	
	24.993, 24.998	295	
$Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$	26.755, 26.771 26.997, 27.008	293	1.985 (2) [c] 1.986 (2)
$Cl_2(O)P{\cdot}NMe{\cdot}PCl_2$	25.321, 25.392 (PCl_2) 25.750, 25.833 27.135, 27.201 [$P(O)Cl_2$] 27.917, 27.987	77	
	24.704, 25.164 (PCl_2) 26.644, 27.229 [$P(O)Cl_2$]	292	
$Cl_2(O)P{\cdot}NMe{\cdot}P(O)Cl_2$	27.408, 27.674 [d] 27.847, 28.817	77	
	26.695, 26.859 27.305, 28.210	290	
$Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$	27.571 [$P(O)Cl_2$] 29.310 [d] [$P(S)Cl_2$]	77	
	26.802 [$P(O)Cl_2$] 28.625 [d] [$P(S)Cl_2$]	290	
$Cl_2(S)P{\cdot}NMe{\cdot}P(S)Cl_2$	28.490, 28.785 28.999, 29.377	77	
	28.259, 28.605	295	
$Cl_2(O)P{\cdot}NPh{\cdot}P(S)Cl_2$	27.617, 28.009 [$P(O)Cl_2$] 28.793, 29.375 [$P(S)Cl_2$]	77	1.963 (4), 1.974 (3) [10] 1.998 (4), 1.994 (4)
	23.977	293	2.069 (3) [e]
$Cl_2(O)P{\cdot}N{:}PPh_3$	25.088, 25.463	293	2.025 (1) [15]
PCl_3O	28.938, 28.986 [f]	77	1.990 (10) [g] 1.972 (10) 1.966 (5)

[a] Not corrected for librational motion. [b] See also W. H. Dalgleish and A. L. Porte, *J. Magnetic Resonance*, 1975, **20**, 359. [c] W. S. Sheldrick, *J.C.S. Dalton*, 1975, 943. [d] Two incompletely resolved signals observed for each frequency (mean given). [e] T. S. Cameron, *J.C.S. Perkin II*, 1972, 591. [f] Data from R. M. Hart and M. A. Whitehead, *J. Chem. Soc.* (*A*), 1971, 1738. [g] K. Olie, *Acta Cryst.*, 1971, **B27**, 1459.

We have also investigated the relation between P–Cl bond lengths of the $>P(O)Cl$ moiety, and their ^{35}Cl n.q.r.

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frequencies. The results for a somewhat limited set of data are shown in the Figure. The correlation between these two parameters is very close to being linear, in fact, surprisingly so when it is considered that the mean of a range of frequencies covering anything up to 0.8 MHz is used. The relation holds for cyclic as well as acyclic compounds.

The straight line of best fit for the phosphoryl compounds is $y = -0.026\,4x + 2.701$ [y = bond length (Å), x = n.q.r. frequency (MHz)], which may be compared with $y = -0.012\,8x + 2.35$ for cyclophosphazenes. The ^{35}Cl n.q.r. frequencies of phosphoryl compounds are less sensitive to changes in bond length than is the case in the chlorocyclophosphazenes (broken line in Figure).

The phosphoryl-group correlation does not apply to thiophosphoryl or to phosphorus(III) chlorides. For example, thiophosphoryl chlorides generally have higher ^{35}Cl n.q.r. frequencies and, where known, longer P–Cl bond lengths than analogous phosphoryl chlorides. This is exemplified by the crystal structure of $Cl_2(O)P{\cdot}NPh{\cdot}P(S)Cl_2$, where the frequency differences do not reflect differences in P–Cl bond lengths in chemically different functional groups.

TABLE 2

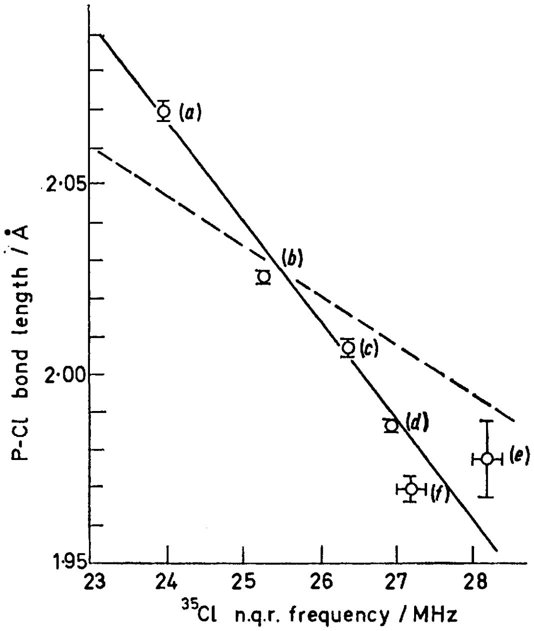
Mean ^{35}Cl n.q.r. frequencies (MHz) observed at 293 ± 3 K in acyclic compounds containing the P–N–P skeleton

	Group		
Compound	PCl_2	$P(O)Cl_2$	$P(S)Cl_2$
$Cl_2P{\cdot}NBu^t{\cdot}PCl_2$	24.885		
$Cl_2(O)P{\cdot}NMe{\cdot}PCl_2$	24.934	26.936	
$Cl_2(O)P{\cdot}NMe{\cdot}P(O)Cl_2$		27.267	
$Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$		26.802	28.625
$Cl_2(S)P{\cdot}NMe{\cdot}P(S)Cl_2$			28.432
PCl_3 [a,c]	26.155		
PCl_3O [b,c]		28.962	
PCl_3S [b,c]			29.822

[a] R. Livingston, *J. Phys. Chem.*, 1953, **57**, 496. [b] Table 1, footnote *f*. [c] At 77 K.

The ^{35}Cl n.q.r. frequency found for the tervalent phosphorus compound $(ClPNBu^t)_2$ is far too low to fit the relation shown in the Figure for a P–Cl bond length of 2.105(9) Å.[3] Whilst this is the only P^{III}–Cl bond length known for the solid state, the lengths of P–Cl bonds determined by electron diffraction for compounds in the series $PCl_{3-n}(NMe_2)_n$ (n = 0—2) [13] show a linear correlation with ^{35}Cl n.q.r. frequency which is yet again different from those above. In view of these findings it is not surprising that a plot of P–Cl bond length against ^{35}Cl n.q.r. frequency for a range of phosphorus(III) and -(V) compounds produces a relatively wide scatter of points.[14]

Of the phosphoryl compounds, it may be noted that those with a $Cl_2(O)P{\cdot}NR{\cdot}P$ skeleton have n.q.r. frequencies intermediate between those of PCl_3O (*ca.* 29 MHz) and $PCl_2(NMe_2)O$ (*ca.* 26 MHz).[5] (Measurements on the latter two molecules were made at 77 K.) The intermediate frequencies are presumably a reflection of the two phosphorus atoms competing for the available bonding electrons on nitrogen. The position of $Cl_2(O)PCH_2P(O)Cl_2$ in the Figure indicates that the CH_2 and NMe groups have similar effects on the P–Cl bond character. The cyclodi-λ^5-phosphazane $[Cl(O)PNBu^t]_2$ has a ^{35}Cl n.q.r. frequency considerably higher than found for the analogous acyclic compound $PCl(NMe_2)_2O$ [5] (22.224 MHz at 77 K). In $[Cl(O)PNBu^t]_2$, the two phosphorus atoms are each bound to two nitrogen atoms, but there are also conformational effects to be considered. It has recently been recognised [15] that the reactivity and structure of phosphorus-containing heterocycles is determined by conformational constraints and that these may render phosphorus in heterocycles electron deficient relative to analogous acyclic compounds. These effects may also be implicated in determining the relatively high frequency of the ^{35}Cl n.q.r. signal of the eight-membered heterocycle $C_{17}H_{20}ClN_2OP$ (see Table 1), relative to $PCl(NMe_2)_2O$, and of the cyclodiphosphazane $(ClPNBu^t)_2$ relative to $PCl(NMe_2)_2$ (18.508 MHz at 77 K).[5]



Plot of P–Cl bond length (not corrected for librational motions) against ^{35}Cl n.q.r. frequency for (*a*) $C_{17}H_{20}ClN_2OP$, (*b*) $Cl_2(O)P{\cdot}N{:}PPh_3$, (*c*) $[Cl(O)PNBu^t]_2$, (*d*) $Cl_2(O)PCH_2P(O)Cl_2$, (*e*) PCl_3O, and (*f*) $Cl_2(O)P{\cdot}NPh{\cdot}P(S)Cl_2$. Points are mean frequencies where more than one is observed, and the broken line shows the gradient of a similar plot for chlorocyclophosphazenes (ref. 2). The n.q.r. frequencies of (*e*) and (*f*) were measured at 77 K and 0.5 MHz has been subtracted from these values; the resulting uncertainty in frequency is shown

The two ^{35}Cl n.q.r. frequencies observed for $Cl_2(O)P{\cdot}N{:}PPh_3$, which are to be expected from the non-equiv-

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alence of the two chlorine atoms in the crystal structure,[16] are marginally higher (mean *ca.* 0.3 MHz) than in $PCl_2(NBu^tH)O$. It is evident that the properties detected by n.q.r., which essentially relate to the ground state, do not reflect the ability of the $N{:}PPh_3$ group to confer relatively high basicities on cyclophosphazenes and related compounds [17] relative to other primary and secondary amine residues. However, it may be noted that the =N–P bonds in $Cl_2(O)P{\cdot}N{:}PPh_3$,[16] $Ph_2(O)P{\cdot}N{:}PPh_3$,[16] $N_3P_3Cl_5{\cdot}N{:}PPh_3$,[18] and geminal $N_3P_3PhCl_4{\cdot}N{:}PPh_3$ [19] are generally shorter by *ca.* 0.06 Å than the Me_2N–P bond in analogous dimethylamino-derivatives $PCl_2(NMe_2)O$,[11] $PPh_2(NMe_2)O$,[20] and $N_3P_3Cl_3(NMe_2)_3$.[21]

The difference in ^{35}Cl n.q.r. frequencies of $PCl_2(NBu^tH)O$ at 77 and 295 K(mean *ca.* 1.4 MHz) is greater than in all the other compounds reported here (generally *ca.* 0.7 MHz). This is the only case where hydrogen bonding could play a role in determining the conformation and barrier to rotation about the P–N bond. The difference in ^{35}Cl n.q.r. frequencies at 77 and 293 K is also greater in the primary amine derivative $N_3P_3Cl_5{\cdot}NPr^iH$ than in the secondary amine derivatives of $N_3P_3Cl_6$, and it is known that the larger frequency increment is caused by a phase transformation in this case.[22,23] Exceptionally large increments in n.q.r. frequencies recorded at liquid-nitrogen and room temperature may provide a ready way of spotting phase transitions in these solids.

EXPERIMENTAL

The compounds $(ClPNBu^t)_2$,[24] $Cl_2P{\cdot}NBu^t{\cdot}PCl_2$,[25] $[Cl(O)PNMe]_2$,[26] $[Cl(O)PNBu^t]_2$,[27] $PCl_2(NBu^tH)O$,[25] $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$,[28] $Cl_2(O)P{\cdot}NMe{\cdot}PCl_2$,[29] $Cl_2(O)P{\cdot}NMe{\cdot}P(O)Cl_2$,[29] $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$,[29] $Cl_2(O)P{\cdot}NPh{\cdot}P(S)Cl_2$,[30] $C_{17}H_{20}ClN_2OP$,[31] and $Cl_2(O)P{\cdot}N{:}PPh_3$ [32] were prepared by literature methods. Nuclear quadrupole resonance spectra were recorded on a Decca n.q.r. spectrometer as before.[2,22,23]

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