Carbon-13 Nuclear Magnetic and Chlorine-35 Nuclear Quadrupole Resonance Spectra of Chloro(trifluoromethyl)phosphines and Chloro(trifluoromethyl)phosphine Oxides

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The ^{35}Cl n.q.r. and ^{13}C n.m.r. spectra of the series of compounds $P(CF_3)_nCl_{3-n}$ and $P(CF_3)_nCl_{3-n}O$ with $0 < n < 3$ have been recorded. The results show that both the ^{35}Cl n.q.r. frequencies and the ^1J(CP) coupling constants are very sensitive to substitution on the phosphorus atom. The trends in these parameters are discussed; they are consistent with a high electronegativity for the CF_3 group.

THERE has been considerable interest for some time in the investigation of chloro-derivatives of phosphorus by n.q.r. spectroscopy.[1-3] Furthermore, the insertion of trifluoromethyl groups in the phosphorus environment has led to new series which exhibit unusual properties. The present work is concerned with the ^{13}C n.m.r. and ^{35}Cl n.q.r. spectra of the series of compounds $P(CF_3)_nCl_{3-n}$ (1)—(4) and $P(CF_3)_nCl_{3-n}O$ (5)—(8) with $0 < n \leqslant 3$. To the best of our knowledge, neither the quadrupole resonance nor the ^{13}C magnetic resonance data (for the phosphine oxides) have yet been reported in the literature.

EXPERIMENTAL

Compounds. All the compounds used in this study were prepared and purified according to published methods.[4] The nature and purity of the samples were checked by ^{19}F and ^{31}P n.m.r. tests.

Spectra.—The ^{13}C n.m.r. spectra were obtained at room temperature on a Brüker WH 90 instrument (22.62 MHz) using the Fourier-transform technique. The shifts were measured relative to the solvent ($CDCl_3$) which also served as the lock: however, δ values reported in Table 1 are quoted with respect to $SiMe_4$ using the conversion $\delta(SiMe_4) = \delta(CDCl_3) + 77.06$ p.p.m. The δ and *J* measurements are considered to be accurate to ±0.03 p.p.m. and ±0.7 Hz.

All the n.q.r. spectra were recorded with sideband suppression, using Zeeman modulation, on a Decca spectrometer. A frequency counter was used to provide the initial calibration of the automatic frequency-marker system. The samples (*ca.* 3 cm^3) were sealed in Pyrex phials under dry argon. Considerable difficulties were met in crystallizing some of the products which exhibit low melting points. In order to observe n.q.r. signals it was necessary to precool the liquid samples slowly down to liquid-nitrogen temperature with the help of standard slush baths; notwithstanding this, reproducible results were obtained when these materials were melted and recrystallized several times. The recording time constant was usually 10 s; frequencies are estimated to be within ±5 kHz. In all cases the ^{35}Cl frequencies were checked by observation of ^{37}Cl signals at a frequency ratio of 1.2688 : 1.

RESULTS

Carbon-13 *N.M.R. Spectra.*—The spectra basically consist of quartets (1 : 3 : 3 : 1) of doublets corresponding to the joint effects of the ^1J(CF) and ^1J(CP) coupling constants. Each member of this pattern is eventually further split into a quartet [compounds (3) and (7)] or a heptuplet [compounds (4) and (8)] by the longer-range coupling ^3J(CPCF) which is clearly observable.

From the first-order analysis of the ^{13}C spectra, the identity of the investigated compounds is apparent and the detection of organic impurities is straightforward. During this work, it came to our attention that the ^{13}C spectra of some phosphorus(III) compounds had been independently published by Burg.[5] Comparison of our results (Table 1) with Burg's paper shows generally good agreement for both the δ and coupling-constant values: in the present study, the carbon shieldings are *ca.* 0.3 p.p.m. downfield from Burg's measurements; these systematic differences may be reconciled if the experimental conditions are considered. Burg's spectra were run on neat samples with external standards, while our own determinations were performed with $CDCl_3$ solutions.

TABLE 1

Carbon-13 n.m.r. spectra for the chloro(trifluoromethyl)phosphines and the chloro(trifluoromethyl)phosphine oxides

		δ [a]	*J*(CP)	*J*(CF)	*J*(CPCF)
	Compound	p.p.m.		Hz	
(2)	$P(CF_3)Cl_2$	126.49	60.3	322.8	
		[126.21]	[60.5]	[323.0]	
(3)	$P(CF_3)_2Cl$	126.25	36.8	320.6	6
		[125.93]	[35.5]	[320.1]	[5.8]
				320.2 [b]	
(4)	$P(CF_3)_3$	125.97	11.5	318.0	5
		[125.70]	[10.7]	[318]	[5.35]
(6)	$P(CF_3)Cl_2O$	118.84	272.1	314.7	
(7)	$P(CF_3)_2Cl(O)$	119.29	205.2	316.2	4
(8)	$P(CF_3)_3O$	119.50	163.3	316.9	3

[a] From internal $SiMe_4$; values taken from ref. 5 are enclosed in square brackets. [b] R. K. Harris, *J. Phys. Chem.*, 1962, **66**, 768.

Chlorine-35 *N.Q.R. Spectra.*—The frequencies measured for the two series are listed in Table 2; in the fifth column of this table appear the mean values averaged over the solid-state splittings. Compounds (2), (3), and (7) show a single ^{35}Cl line whereas (6) exhibits a doublet, presumably indicating either a slight inequivalence of the two chlorine atoms in the lattice or the presence of at least two molecules in the asymmetric unit of the crystal structure. For this latter compound, $P(CF_3)Cl_2O$, we have been able to record the temperature dependence of the two signals between 77 and 210 K (see Figure 1) both dynamically in the manner described in the literature[6] and with the spectrometer probe immersed in constant-temperature slush baths which were prepared by mixing pure organic solvent with liquid nitrogen.[7] The two lines are characterized by a normal negative coefficient whereas the doublet splitting increases significantly with increasing temperature (Δν *ca.* 0.17 MHz at 77 K compared with a value of 0.19 MHz at 210 K); it follows that the framework of the molecule $P(CF_3)Cl_2O$ is reasonably rigid and there is very little change in its structure with temperature. The curves are continuous and there is no evidence of any phase changes within the temperature range examined. These experimental results were analysed by least-squares fitting under two polynomial forms taken from the simplest expression of the Bayer theory [8] and from a more recent proposal formulated by Weiss.[9] The least-squares fits were performed on a

$$\nu(T) = a_0 + a_1T + a_{-1}T^{-1} \qquad (1)$$

$$\nu(T) = a_0 + a_1T + a_{-1}T^{-1} + a_2T^2 \qquad (2)$$

Hewlett-Packard programmable calculator and the parameters obtained are collected in Table 3.

TABLE 2

Chlorine-35 n.q.r. frequencies for the chloro(trifluoromethyl)phosphines and the chloro(trifluoromethyl)-phosphine oxides at 77 K

	Compound	$\nu(^{35}Cl)$ / MHz	S/N [a]	$\nu_{av.}$ / MHz	Population of the chlorine σ bonds
(1)	PCl_3 [b]	26.208	20	26.173	1.513
		26.104	10		
(2)	$P(CF_3)Cl_2$	27.650	70	27.650	1.496
(3)	$P(CF_3)_2Cl$	30.090	20	30.090	1.452
(5)	PCl_3O [b]	28.975	20	28.960	1.472
		28.930	10		
(6)	$P(CF_3)Cl_2O$	28.138	20	28.054	1.489
		27.970	20		
(7)	$P(CF_3)_2Cl(O)$	27.615	4	27.615	1.497

[a] Peak-to-peak signal to peak-to-peak noise ratio obtained with a 10-s recording-time constant. [b] Ref. 1*b*.

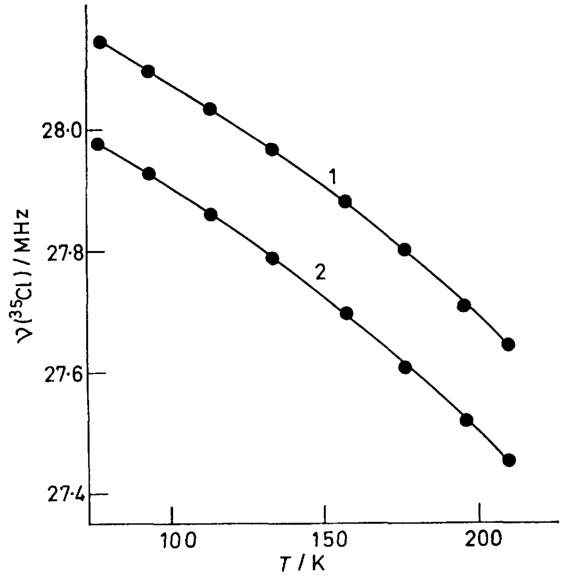

FIGURE 1 Temperature dependence of the ^{35}Cl quadrupole resonance frequencies in $P(CF_3)Cl_2O$

DISCUSSION

Besides the purely structural aspects of the ^{13}C n.m.r. and ^{35}Cl n.q.r. spectra, respectively in solution and in the solid state, considerations of the general trend of the main parameters within the series should give an insight into the extent of the variations in electron population of the bonds surrounding the central phosphorus atom. Thus, the ^{13}C spectra of the CF_3 group show that these nuclei are situated in a typical area for sp^3 trifluoromethyl groups,[10] *i.e.* they are markedly shifted towards low fields relative to their methyl analogues.

TABLE 3

Parameters obtained from least-squares analyses of the experimental n.q.r. frequencies at 77—210 K for $P(CF_3)Cl_2O$

Line	Equation	a_0 / MHz	$10^3\ a_1$ / MHz K^{-1}	a_{-1} / MHz K	$10^5\ a^2$ / MHz K^{-2}	10^4 × Standard deviation
1	(1)	28.665	−4.51	−13.46		6.43
1	(2)	27.469	4.69	34.5	−2.21	1.13
2	(1)	28.518	−4.75	−13.63		4.0
2	(2)	27.637	2.03	21.7	−1.63	1.11

The phosphine chemical shifts appear systematically *ca.* 7 p.p.m. downfield of the corresponding oxide values; this difference indicates an electronic deficiency in carbon bonded to a three-co-ordinate compared with four-co-ordinate phosphorus. However, this behaviour is at variance with the general trend observed for the methyl species; in that particular case, on going from three- to four-co-ordinate phosphorus compounds $\delta(^{13}C)$ usually moves to lower fields [*e.g.* [11,12] $\delta(^{13}C)$ 31.7 p.p.m. for $PMeCl_2O$, and 15.2 p.p.m. for $PMeCl_2$, 17.6 p.p.m. for PMe_3O, and 17.3 p.p.m. for PMe_3 relative to $SiMe_4$]. From a naive point of view, one might speculate that the phosphous atom is releasing more electronic charge to the trifluoromethyl groups when it is linked to an oxygen through a dative bond than when its lone pair is free.

Now, concerning the main spin–spin coupling constants, Burg has already pointed out [5] the contrast existing between ^1J(CF) and ^1J(CP) in the phosphine series: indeed, while ^1J(CF) is hardly affected by substitutions on the phosphorus atom, the value of ^1J(CP) increases by a factor of five between $P(CF_3)_3$ and $P(CF_3)Cl_2$. This remark is also valid for the phosphine oxide series since ^1J(CF) remains constant at *ca.* 316 Hz when, at the same time, ^1J(CP) appears larger than in the corresponding phosphine and highly affected by substitution effects. On the one hand, recent theoretical calculations have shown that, at least in phosphorus(IV) compounds,[13] there is a direct relation between the magnitude of ^1J(CP) and the percentage *s* character in the P–C hybrid orbital. On the basis that *J*(CP) is normally positive for phosphorus(IV) derivatives,[14] and, if the above relation is shown to be valid, the trend in the values reported in Table 1 supports the argument that the CF_3 group demands more and more 3*s* character from the central phosphorus when substitution by a chlorine atom occurs. On the other hand, the variations of ^1J(CP) within the phosphine series are much more ambiguous since theoretical calculations of the coupling constants in such compounds show that simple considerations of the percentage *s* character in the P–C bond cannot be considered alone:

however, it is interesting to note that, if ^1J(CP) is taken as negative in the $P(CF_3)_nCl_{3-n}$ series, successive replacement of CF_3 by Cl is followed by a decrease in the phosphorus–carbon coupling constant. This must be compared with the parallel decrease in the binding energy of the P–Cl molecular orbital which has been measured by Cowley *et al.*,[15] and which reflects a decrease in the *s* character of the sp^x hybrid orbital.

The dependence of the ^{35}Cl n.q.r. frequencies on substitution of a chlorine atom by a trifluoromethyl group may be conveniently appreciated from graphs (see Figure 2). In the $P(CF_3)_nCl_{3-n}$ series, the average ^{35}Cl resonance frequency increases as n increases, according to the sequence $PCl_3 < P(CF_3)Cl_2 < P(CF_3)_2Cl$; the higher frequencies in $P(CF_3)Cl_2$ and $P(CF_3)_2Cl$ are qualitatively consistent with high electronegativities for the CF_3 group in the sense that substitution of Cl by more electronegative groups results in an enhancement of the effective electronegativity of the phosphorus and, therefore, in a reinforcement of the covalent character of the P–Cl bond. The behaviour of chloro(trifluoromethyl)-phosphines deviates entirely from those of their alkyl,[1b] alkoxy,[16] or dialkylamino-analogues [17] since, in those instances, the increase in n causes a decrease of the chlorine n.q.r. frequencies (see Figure 2). This tendency, instead of the quasi-invariability (NR_2) or the increase (OR) which would have been predicted on the grounds of the electronegativity of the NR_2 or OR groups, has been previously attributed to back co-ordination of the nitrogen or oxygen lone-pair electrons.[17-19] Another noteworthy feature of Figure 2 lies in the abnormally weak decrease observed for the PEt_nCl_{3-n} derivatives when n increases: this might be proof of the existence of slight p_π–d_π bonding between chlorine and the central phosphorus atom.

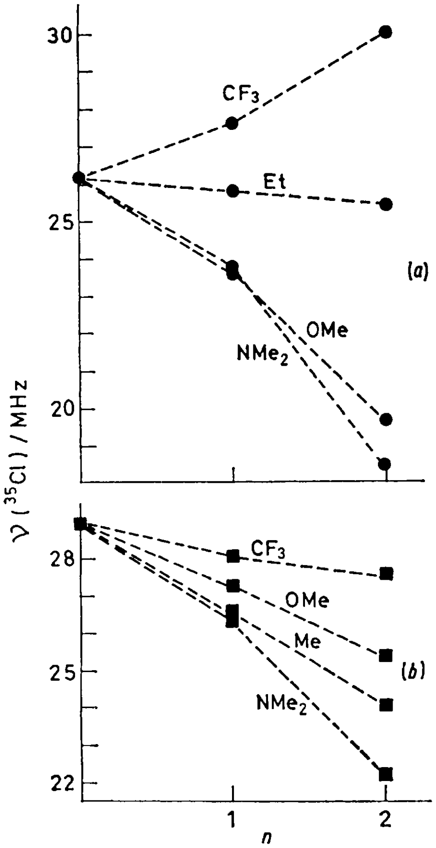

FIGURE 2 Chlorine-35 n.q.r. frequencies for (*a*) $PCl_{3-n}X_n$ and (*b*) $PCl_{3-n}OX_n$ series. Data are taken from refs. 1*b*, 16, 17, and the present work

Following the Townes and Dailey treatment,[20] the ionicity of a covalent singly bonded chlorine atom may be calculated from the observed n.q.r. frequencies. For the compounds investigated in this work the P–Cl bond is regarded as a σ bond polarized towards chlorine, with some slight π character from the chlorine lone pair in the correct orientation to overlap with the *d*-orbital system of the phosphorus atom. If the asymmetry parameter is not higher than 10%, which, in these cases, is a reasonable assumption, the charge q_{Cl} on chlorine is related to the quadrupole coupling constant in the molecule and to that in atomic chlorine by relation (3). The approximations implicit in the use of this equation have been discussed elsewhere;[21] even if the absolute quantities derived from this simple calculation must be regarded as approximate, the relative variations in the population of the chlorine σ bonds given in the final column of Table 2 undoubtedly reflect actual differences in the properties of the P–Cl bonds.

$$\frac{(e^2Qq)_{\text{mol.}}}{(e^2Qq)_{\text{at.}}} = 1 - q_{\text{Cl}} \qquad (3)$$

Thus, in the phosphine series, the population of the chlorine σ bonds throws some light on the variations of the P–Cl ionic character: the ionicity of the P–Cl bond strongly decreases [*ca.* 3% for $P(CF_3)Cl_2$ and 12% for $P(CF_3)_2Cl$ towards PCl_3] when the number of electron-withdrawing CF_3 groups increases. In the oxide series the trend observed for the phosphines is not followed since ^{35}Cl undergoes a decrease in frequency on going from PCl_3O to $P(CF_3)_2Cl(O)$: however, among the different series appearing on the graph, the magnitude of the variation is very small for the trifluoro-compounds [$\Delta\nu \sim -1.3$ MHz between $P(CF_3)_2Cl(O)$ and $PCl_3(O)$ as compared with $\Delta\nu \sim -7$ MHz between $[PCl(NMe_2)_2O$ and $PCl_3O]$. This difference in behaviour might result in a simultaneous variation of the P–O bond multiplicity since the accumulation of σ-electron-attracting groups on the phosphorus atom would enhance the conjugation between the lone electron pairs of oxygen and the vacant phosphorus *d* orbital.[22] Therefore, this effect could be responsible for the simultaneous increase of electron density at the chlorine sites, and then for the shifts towards lower values of ν(^{35}Cl). This tendency perfectly agrees with the observed trend in the coupling constant between carbon and phosphorus since ^1J(CP) also decreases when a chlorine atom is substituted by a much more electronegative CF_3 group.

[8/519 *Received, 20th March,* 1978]

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