View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1976. Downloaded by University of Birmingham on 31/10/2014 15:16:47.

Structural Studies on Organoarsenic(v) Compounds by means of Chlorine-35 Nuclear Quadrupole Resonance Spectroscopy

By **Keith B. Dillon,* Roderick J. Lynch, and Thomas C. Waddington,** Department of Chemistry, University of Durham, Durham DH1 3LE

A ^{35}Cl n.q.r. study of $AsPhCl_4$, $AsPh_2Cl_3$, and $AsPh_3Cl_2$ indicates that they have trigonal-bipyramidal structures in the solid state, with the phenyl groups occupying equatorial positions. The mono- and di-phenyl compounds are thought to be isostructural with the corresponding phosphorus compounds. Trichlorodimethylarsenic(v) and $AsMe_3Cl_2$ also have the trigonal-bipyramidal form in the solid, with the methyl groups occupying equatorial sites, unlike their phosphorus analogues which are ionic. Attempts to synthesise $AsMeCl_4$ by chlorination of $AsMeCl_2$ have led to explosions at low temperatures, and this compound appears to be extremely unstable if it exists at all. 1 : 1 Adducts of the arsenic(v) compounds with Lewis acids, X, such as BCl_3, $SbCl_5$, or ICl, have been prepared; these showed the expected ionic structure $[AsR_nCl_{4-n}][XCl]$. Substituent effects in the cations, where R = Me or Ph, are similar to those in the analogous phosphonium, silane, and germane series, and support the involvement of As($d\pi$)–Cl($p\pi$) bonding. Chlorine-35 n.q.r. frequencies are also reported for the compounds Ph_3CCl, $SiPh_3Cl$, $GePh_2Cl_2$, and $GePh_3Cl$.

As mentioned in a previous paper,[1] various solid-state structures are possible for quinquevalent organohalogeno-derivatives MR_nX_{5-n} of Group 5 elements M. The structures, moreover, may be changed on dissolution,[2,3] so that techniques which examine the solid state directly are desirable if reliable information is to be obtained. A combination of ^{35}Cl n.q.r. and ^{31}P n.m.r. spectroscopy has shown that solid $PPhCl_4$ and PPh_2Cl_3 are molecular with phenyl groups occupying equatorial sites,[1,4] confirming earlier work,[5] but that PPh_3Cl_2 and the chloromethylphosphoranes PMe_nCl_{5-n} (n = 1—3) have ionic structures $[PR_nCl_{4-n}]Cl$. These conclusions were supported by spectral data for the ionic 1 : 1 adducts with strong Lewis acids such as BCl_3, $AlCl_3$, or $SbCl_5$. The results also suggested that some variation in the extent of P–Cl d_π–p_π bonding may occur in the cations.

We now report an extension of these ^{35}Cl n.q.r. investigations to the corresponding arsenic(v) compounds, apart from $AsMeCl_4$ which could not be prepared (see Experimental section). An earlier n.q.r. investigation by Brill and Long [6] suggested that $AsMe_3Cl_2$ and $AsPh_3Cl_2$ are molecular with the organo-substituents occupying equatorial positions, since only one low-frequency ^{35}Cl line was observed, as expected for the axial chlorines in such a structure. They thought that $AsBr_2Me_3$ might have the salt-like formulation $[AsBrMe_3]Br$, however. Revitt and Sowerby [7] recorded the vibrational spectra of $AsPhCl_4$, $AsPh_2Cl_3$, $AsPh_3Cl_2$, and $AsMe_2Cl_3$, and concluded that these were probably molecular, with the phenyl group equatorial in $AsPhCl_4$. Our results show unequivocably that the organoarsenic(V) compounds studied are all molecular, with the organo-groups occupying equatorial sites. This has been confirmed by preparing their 1 : 1 adducts with Lewis acids X such as BCl_3, $SbCl_5$, or ICl, which have been characterised as salts $[AsR_nCl_{4-n}][XCl]$ by means of ^{35}Cl n.q.r. where signals were obtained, and (where appropriate) by ^{11}B n.m.r. spectroscopy. Comparison of the results for the phenyl series of ions with those for the analogous phosphonium, silane, and germane species supports the involvement of d_π–p_π bonding in these compounds. To facilitate this comparison, the ^{35}Cl n.q.r. frequencies of Ph_3CCl, $SiPh_3Cl$, $GePh_2Cl_2$, and $GePh_3Cl$ have been measured. Several attempts were made to record the spectrum of $SiPh_2Cl_2$, both as a pure solid and in solid solution in inert diluents such as CCl_4 and Ph_2CCl_2, but in each case a glass formed on cooling and no Si–Cl resonances could be detected.

EXPERIMENTAL

All the manipulations, including the filling of sample tubes, were under an atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used, generally without further purification. The chloro(organo)-arsenic(V) compounds were prepared by direct chlorination with dry chlorine gas of the corresponding arsenic(III) compounds in methylene chloride solution. The solvent was removed *in vacuo*, the compounds washed with low-boiling light petroleum, and dried on the vacuum line. Tetrachloroborates were prepared as described previously,[1] and showed the expected broad bands in the i.r. spectrum between 650 and 700 cm^{-1}. The compounds $[AsPh_2Cl_2][SbCl_6]$ and $[AsMe_2Cl_2][SbCl_6]$ were also prepared in the same way as hexachloroantimonates of substituted phosphoranes.[1] The compound $[AsMe_2Cl_2][ICl_2]$ was obtained from the stoicheiometric quantities of $AsMe_2Cl_3$ and ICl in methylene chloride solution. The yellow precipitate was separated and washed with low-boiling light petroleum. Pumping was not attempted in case decomposition occurred. Elemental analyses (C, H, Cl, and I) for all the compounds prepared are given in Table 1. Attempts to prepare $AsMeCl_4$ by chlorination of $AsMeCl_2$ in methylene chloride solution at 273 K gave no solid product, and the ^{35}Cl n.q.r. spectrum of the residue remaining after removal of the solvent, on solidification, showed only the signal expected for $AsCl_3$.[8] The compound $AsMeCl_4$ has been reported to

---

[1] K. B. Dillon, R. J. Lynch, R. N. Reeve, and T. C. Waddington, *J.C.S. Dalton*, 1976, in the press.

[2] I. R. Beattie, K. Livingston, and T. Gilson, *J. Chem. Soc.* (*A*), 1968, 1.

[3] D. B. Denney, D. Z. Denney, and B. C. Chang, *J. Amer. Chem. Soc.*, 1968, **90**, 6332.

[4] R. J. Lynch and T. C. Waddington, in 'Advances in Nuclear Quadrupole Resonance,' ed. J. A. S. Smith, Heyden, London, 1974, vol. 1, p. 37.

[5] V. I. Svergun, V. G. Rozinov, E. F. Grechkin, V. G. Timokhin, Yu. K. Maksyumin, and G. K. Semin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1970, 1918.

[6] T. B. Brill and G. G. Long, *Inorg. Chem.*, 1970, **9**, 1980.

[7] D. M. Revitt and D. B. Sowerby, *Spectrochim. Acta*, 1970, **A26**, 1581.

[8] I. P. Biryukov, M. G. Voronkov, and I. A. Safin, 'Tables of N.Q.R. Frequencies,' Israel Program for Scientific Translations, Jerusalem, 1969.

View Article Online

Published on 01 January 1976. Downloaded by University of Birmingham on 31/10/2014 15:16:47.

decompose at 273 K into $AsCl_3$ and chloromethane,[9] so the experiment was repeated by condensing the calculated quantities of $AsMeCl_2$ and chlorine together at 77 K in an ampoule and allowing the mixture to warm up gradually. **CAUTION**: successive ampoules exploded while still well below 273 K, however, and the preparation was abandoned. Samples of $AsMe_2Cl_3$ were also observed to decompose to liquids in a few days at room temperature, even when stored in closed containers in an inert-atmosphere box.

All the n.q.r. spectra were recorded on a mid-range Decca spectrometer (5—55 MHz), using Zeeman modulation. Sideband suppression was used to clarify line centres when their positions were difficult to determine otherwise. The resonances were measured both at 77 K and at room temperature where observable. Resonance frequencies were determined within an accuracy of ±10 kHz by interpolation between the spectrometer frequency markers, which were calibrated by means of a frequency counter (Advance Instruments T.C.16). Boron-11 n.m.r. spectra of the boron trichloride adducts were recorded at 307.2 K on a Perkin-Elmer R10 spectrometer operating at 19.25 MHz, with a Digiac signal-averaging accessory, using stationary sample tubes (outside diameter, 8.4 mm). The technique of recording solid-state ^{11}B spectra on a high-resolution instrument has been described in an earlier paper.[10] Chemical shifts were measured relative to external trimethyl borate, and were reproducible to ±2 p.p.m. in each case.

TABLE 1

Elemental analyses (%)

Compound	Found C	Found H	Found Cl	Found I	Calc. C	Calc. H	Calc. Cl	Calc. I
$AsPhCl_4$	24.55	1.80	47.1		24.55	1.70	48.25	
$[AsPhCl_3][BCl_4]$	17.4	1.35	59.85		17.55	1.25	60.4	
$AsPh_2Cl_3$	42.0	3.95	32.0		42.95	3.00	31.7	
$[AsPh_2Cl_2][BCl_4]$	31.7	2.40	47.05		31.85	2.25	47.0	
$[AsPh_2Cl_2][SbCl_6]$	24.45	1.70	44.1		22.7	1.60	44.7	
$AsPh_3Cl_2$	57.6	3.60	18.8		57.3	4.00	18.8	
$[AsPh_3Cl][BCl_4]$	45.15	2.90	35.9		43.75	3.05	35.85	
$AsMe_2Cl_3$	11.3	3.05	49.85		11.35	2.85	50.3	
$[AsMe_2Cl_2][BCl_4]$	7.75	2.00	64.75		7.30	1.85	64.75	
$[AsMe_2Cl_2][SbCl_6]$	5.15	1.45	54.75		4.70	1.20	55.55	
$[AsMe_2Cl_2][ICl_2]$	6.85	1.90	37.1	34.15	6.45	1.60	37.95	33.95
$AsMe_3Cl_2$	18.8	5.20	38.4		18.85	4.75	37.15	
$[AsMe_3Cl][BCl_4]$	11.45	3.10	57.65		11.7	2.95	57.55	

RESULTS AND DISCUSSION

The ^{35}Cl n.q.r. frequencies obtained for the arsenic compounds are listed in Table 2. Where signals were sufficiently intense the corresponding ^{37}Cl signals were observed. From tetrachlorophenylarsenic(v), for example, ^{37}Cl resonances were recorded at 18.91, 19.65, 26.92, and 27.32 MHz at 77 K, corresponding to $^{35}Q/^{37}Q$ values of 1.2692, 1.2682, 1.2697, and 1.2687 respectively (theoretical 1.2688). No ^{75}As n.q.r. frequencies were observed for these compounds. This was not unexpected since their range is usually above the maximum attainable by our spectrometer. Although frequencies for approximately tetrahedrally co-ordinated arsenic should lie appreciably lower than those for five-co-ordinate compounds, searches up to 55 MHz failed to reveal any further resonances.

For nuclei of spin $\frac{3}{2}$, such as ^{35}Cl, the n.q.r. frequency is related to the nuclear quadrupole coupling constant, e^2Qq/h, by equation (1).[11] When the electric-field-

$$\nu_Q = \frac{1}{2}\frac{e^2Qq}{h}\left(1+\frac{\eta^2}{3}\right)^{\frac{1}{2}} \qquad (1)$$

gradient (e.f.g.) asymmetry parameter, η, is small, as often found for chlorine, the n.q.r. frequency is approximately equal to half the coupling constant. On an approximate basis, the coupling constant may be related to the ionic character, i, of the M–Cl bond, provided that the extent of chlorine

TABLE 2

Chlorine-35 n.q.r. frequencies (MHz) for chloroarsenic(v) compounds

Compound	$\nu(^{35}Cl\text{-}As)$ at 77 K	$\nu(^{35}Cl\text{-}As)$ at 293 K	$\nu(^{35}Cl)$(anion) at 77 K
$AsPhCl_4$	34.66		
	34.18		
	24.92		
	24.00		
$AsPh_2Cl_3$	34.00	33.42	
	20.375	20.215	
	20.31	20.135	
$AsPh_3Cl_2$	19.25	18.75	
	18.80	18.46	
$[AsPhCl_3][BCl_4]$	34.32	33.22	21.67 [a]
	33.94		20.90
			20.66
$[AsPh_2Cl_2][BCl_4]$	32.86	32.17	21.46
	31.535	30.97	21.415
			21.24
			21.08
$[AsPh_3Cl][BCl_4]$	31.78	31.20	21.48
			21.35
			21.245
			21.19
$AsMe_2Cl_3$	32.66	31.975	
	19.42	[b]	
	18.915	[b]	
$AsMe_3Cl_2$	16.675	16.475	
$[AsMe_2Cl_2][ICl_2]$	31.85	[b]	[b]
$[AsMe_3Cl][BCl_4]$	30.265	[b]	21.89
			21.08
			20.93
			20.66

[a] Double intensity line. [b] Not observed.

---

[9] E. Krause and A. von Grosse, ' Die Chemie der metallorganischen Verbindungen,' Verlag von Gebruder Borntraeger, Berlin, 1937.

[10] K. B. Dillon and T. C. Waddington, *Spectrochim. Acta*, 1974, **A30**, 1873.

[11] E. A. C. Lucken, ' Nuclear Quadrupole Coupling Constants,' Academic Press, London, 1969.

View Article Online

Published on 01 January 1976. Downloaded by University of Birmingham on 31/10/2014 15:16:47.

sp hybridisation (*s*) and M–Cl π bonding (π) is small. The Townes–Dailey expression (2)[12] is often used,

$$\frac{(e^2Qq)\text{ molecule}}{(e^2Qq)\text{ atom}} = (1-s)(1-i)-\pi \qquad (2)$$

where the symbols have their usual significance. Widely different n.q.r. frequencies are therefore expected to reflect M–Cl bonds of rather different ionic character, bond length, *etc.* N.q.r. spectroscopy can thus supply some direct bonding information, without further treatment of the data.

For trigonal-bipyramidal molecules of the type under investigation an atom in an axial position has a much lower n.q.r. frequency than a similar atom in an equatorial site.[5] This is expected since the axial bonds are longer and therefore more ionic in character. The ^{35}Cl n.q.r. spectra of tetrachlorophenylarsenic(V) and trichlorodiphenylarsenic(V) bear a strong resemblance to those of the analogous phosphoranes, $PPhCl_4$ and PPh_2Cl_3.[1,4,5] Four independent chlorine sites are indicated for $AsPhCl_4$ and $PPhCl_4$, two of which appear from the frequencies to be considerably more ionic than the others. This is entirely consistent with a trigonal-bipyramidal structure for the molecule, with the phenyl group occupying an equatorial site. The two resonances at 24.00 and 24.92 MHz (77 K) in $AsPhCl_4$ are assigned to axial chlorines and those at 34.18 and 34.66 MHz to equatorial chlorines. These conclusions are in complete agreement with the results of a vibrational-spectroscopic study,[7] which also suggested a trigonal-bipyramidal molecule with an equatorial phenyl group. The multiplicity of lines observed for $AsPh_2Cl_3$ and PPh_2Cl_3 indicates three independent chlorine sites, two of which are assigned to axial chlorine atoms and the third to an equatorial chlorine atom, so that both phenyl groups are equatorially located. The ^{35}Cl n.q.r. frequencies for $PPhCl_4$ and PPh_2Cl_3 are indeed directly proportional to those for $AsPhCl_4$ and $AsPh_2Cl_3$, suggesting that these compounds may be isostructural with strong similarities in the bonding.

Both the present study and a previous n.q.r. investigation[6] of $AsPh_3Cl_2$ are consistent with a molecular structure. The resonance frequencies indicate that the chlorine atoms are axially located, and that all three phenyl groups must occupy equatorial sites in the molecule. The presence of two independent axial chlorine sites implies that no molecular two-fold symmetry axis is present if there is only one molecule in the crystalline asymmetric unit. There is disagreement between the present values for the room-temperature ^{35}Cl n.q.r. frequencies of $AsPh_3Cl_2$ (18.46 and 18.75 MHz) and a previously reported value of 17.62 MHz at 300 K.[6] Despite several attempts, we were unable to find a resonance at this frequency. A single resonance would imply the presence of a two-fold symmetry axis. Unless the compound is polymorphic, we are unable to account for this discrepancy. These results contrast with those expected for PPh_3Cl_2, for which no ^{35}Cl n.q.r. signals could be observed,[1,*] but which was shown to have the ionic form $[PPh_3Cl]Cl$ by solid-state ^{31}P n.m.r. spectroscopy. This conclusion was supported by n.q.r. results for the adduct $PPh_3Cl_2{\cdot}0.5CCl_4$, which showed a single P–Cl resonance frequency ascribed to $[PPh_3Cl]^+$.[1]

The ^{35}Cl resonance frequencies observed for trichlorodimethyl- and dichlorotrimethyl-arsenic(V) are also compatible with molecular rather than ionic structures, unlike the corresponding phosphorus compounds which are ionic $[PMe_nCl_{4-n}]Cl$.[1] For $AsMe_2Cl_3$, the ^{35}Cl resonances at 18.91 and 19.42 MHz (77 K) are assigned to axial chlorines and the single resonance at 32.66 MHz to an equatorial chlorine. Our measurements on $AsMe_3Cl_2$ confirm the ^{35}Cl resonance frequency at 16.49 MHz (room temperature) previously reported by Brill and Long.[6] A single chlorine frequency implies a two-fold molecular axis relating the axial chlorine atoms in this molecule. In both $AsMe_2Cl_3$ and $AsMe_3Cl_2$, methyl groups occupy only equatorial positions, in agreement with the expectation that the most electronegative groups in five-co-ordinate species should occupy the axial sites.[13]

In three compounds of the type AsR_3Cl_2, Brill and Long[6] observed that the chlorine resonance frequency increased as the nucleophilic nature of R decreased, *i.e.* as R changed from methyl to phenyl. In the present work a similar effect was observed for AsR_2Cl_3 molecules. A change of R from Me to Ph increased the equatorial chlorine frequency by 1.34 MHz (4.1%) and the average axial chlorine frequency by 1.175 MHz (6.1%). This can be compared with the rise in the axial chlorine frequency for AsR_3Cl_2 of 2.35 MHz (14.1%). Indeed the net percentage change in frequency, per group R, appears to be approximately constant. For the AsR_2Cl_3 system the total ^{35}Cl frequency change was 16.3%, *i.e.* 8.15% shift per group R, and for AsR_3Cl_2 the total change was 28.2%, *i.e.* 9.4% per group R.

The adducts of phenyl- or methyl-chloroarsenic(V) compounds with boron trichloride, except for the $AsMe_2Cl_3$ derivative, gave n.q.r. spectra (Table 2) which in the lower-frequency region (*ca.* 21 MHz) are consistent with the presence of the tetrachloroborate ion in the lattice. Frequencies within the range 20.38—21.66 MHz have previously been reported for $[BCl_4]^-$.[1,14,15] The presence of $[BCl_4]^-$ is further confirmed by measurements of the ^{11}B n.m.r. chemical shifts (Table 3) which are in good agreement with previous values for this anion in both solution[16] and the solid state.[1,10] We therefore propose that the solid-state structures are of the form $[AsR_nCl_{4-n}][BCl_4]$. Similar structures have been deduced for the analogous solid phosphorus(V) compounds.[1]

---

[*] A signal at 30.12 MHz was previously reported for PPh_3Cl_2 by two of the present workers,[4] but this was not observed when a new sample of PPh_3Cl_2 was prepared.[1]

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

[13] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613.

[14] J. A. S. Smith and D. A. Tong, *J. Chem. Soc.* (*A*), 1971, 178.

[15] R. M. Hart, M. A. Whitehead, and L. Krause, *J. Chem. Phys.*, 1972, **56**, 3038.

[16] J. S. Hartman and G. J. Schrobilgen, *Inorg. Chem.*, 1972, **11**, 940.

View Article Online

Published on 01 January 1976. Downloaded by University of Birmingham on 31/10/2014 15:16:47.

The only resonance observed in the ^{35}Cl n.q.r. spectrum of the adduct of $AsMe_2Cl_3$ with BCl_3 was a very weak signal at 32.66 MHz, identical with the value for the equatorial chlorine in $AsMe_2Cl_3$ itself, and ascribed to a small quantity of unchanged starting material. The solid-state ^{11}B chemical shift and elemental analysis are compatible with almost complete formation of the adduct, but no signals which could be assigned to either the cation or anion were detected. Similar problems have been found with BCl_3 adducts of chloromethylphosphoranes.[1] The compound $[AsMe_2Cl_2][SbCl_6]$ was also prepared, but no n.q.r. signals were observable. The failure to detect resonances from these pseudo-spherical ions may be due to disorder effects in the solid state, possibly because of random orientations of the methyl and chloro-groups, or because of rotation occurring even at low temperature. In an attempt to resolve this difficulty the 1 : 1 adduct with ICl was prepared, where the expected counterion is linear. A very strong ^{35}Cl n.q.r. signal at 31.85 MHz (77 K), readily assignable to the $[AsMe_2Cl_2]^+$ cation, was recorded, but the signals expected for the $[ICl_2]^-$ ion could not be observed either at 77 K or room temperature. Difficulty in detecting n.q.r. signals from this anion has been reported previously.[1,17]

TABLE 3

Boron-11 chemical shifts (p.p.m.) for solid organoarsenic(V) tetrachloroborates

Compound	$\delta(^{11}B)$
$[AsPhCl_3][BCl_4]$	13.5
$[AsPh_2Cl_2][BCl_4]$	12.7
$[AsPh_3Cl][BCl_4]$	11.7
$[AsMe_2Cl_2][BCl_4]$	13.4
$[AsMe_3Cl][BCl_4]$	13.4

The two ^{35}Cl resonances assigned to the $[AsPhCl_3]^+$ ion had intensities in the ratio *ca.* 2 : 1. The spectrum is therefore compatible with C_s symmetry for this species. In the case of $[AsPh_2Cl_2]^+$, a wide splitting (1.32 MHz) of the ^{35}Cl n.q.r. signals was observed. This may indicate the presence of considerable distortion in the ion, with rather different As–Cl distances. The analogous salt $[AsPh_2Cl_2][SbCl_6]$ was examined to see if the same situation exists, but unfortunately no resonances could be found. We did, however, observe a splitting of 1.12 MHz between the ^{35}Cl resonance frequencies of dichlorodiphenylgermane (20.40 and 21.52 MHz at 77 K).

In both the methyl- and phenyl-substituted arsonium and phosphonium ions,[1] $[MR_nCl_{4-n}]^+$, the average ^{35}Cl resonance frequency decreases as n increases, *i.e.* $[MCl_4]^+ > [MRCl_3]^+ > [MR_2Cl_2]^+ > [MR_3Cl]^+$. This is expected from the substituent inductive effects, in which the decreasing number of electron-withdrawing groups (Cl) and increasing number of electron-releasing groups (R) causes increased ionicity of the remaining P–Cl or As–Cl bonds. Figure 1 shows that the resonance frequencies of the methyl-substituted phosphonium and arsonium ions for which data are available deviate significantly less from linearity than those of their phenyl analogues. This behaviour also occurs in the series SiR_nCl_{4-n} and GeR_nCl_{4-n}, but not in R_nCCl_{4-n}, where the phenyl compounds also show an approximately linear decrease with n (Figure 2). All these elements except carbon possess d orbitals which are available for conjugation with chlorine p_π orbitals. The involvement of d orbitals in bonding is aided in the Group 5 compounds by the positive charge on the central atom, which should contract the orbitals and increase their availability for π bonding. The non-linearity of the n.q.r. frequency as a function of the number of phenyl substituents is thus probably due to variations in the extent of p_π–d_π bonding between chlorine and the central element. This in turn may be affected by the amount of conjugation between the phenyl group and the chlorine atom. When $n = 1$ or 3, *i.e.* when the molecule has C_{3v} symmetry, conjugation is unlikely to be very significant since π bonds with carbon and chlorine would use different d orbitals.[18] Conjugation is more likely in the diphenyl compounds (C_{2v} symmetry), where the same d orbitals can overlap both with $C(p_\pi)$ and $Cl(p_\pi)$ orbitals. In this case the amount of overlap between $M(d_\pi)$ and $Cl(p_\pi)$ orbitals may be somewhat lower than in the C_{3v} system. The degree of π bonding is also expected to be a sensitive function of the interbond angle at the central element. It is perhaps significant that the interbond angles in the related compounds $SnPh_2Cl_2$ [19] and $SnMe_2Cl_2$ [20]

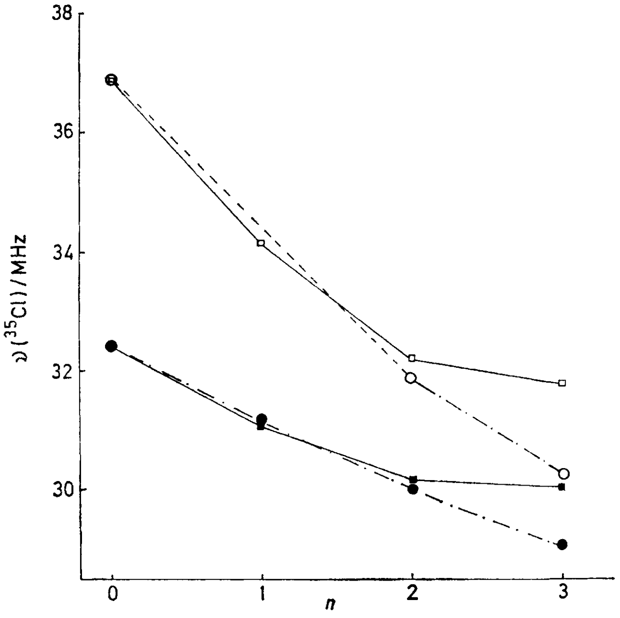

FIGURE 1 Chlorine-35 n.q.r. frequencies in $[PR_nCl_{4-n}]^+$ where R = Me (●) or Ph (■) and $[AsR_nCl_{4-n}]^+$ where R = Me (○) or Ph (□)

---

[17] E. F. W. Riedel, Dissertation, Washington State University, 1973 (*Diss. Abs.*, 1973, **33**, 5757).

[18] R. F. Hudson, 'Structure and Mechanism in Organo-Phosphorus Chemistry,' Academic Press, London, 1965.

[19] P. T. Greene and R. F. Bryan, *J. Chem. Soc.* (*A*), 1971, 2549.

[20] A. G. Davies, H. J. Milledge, and D. C. Puxley, *J. Chem. Soc.* (*A*), 1970, 2862.

View Article Online

Published on 01 January 1976. Downloaded by University of Birmingham on 31/10/2014 15:16:47.

differ considerably from the tetrahedral angle (CSnC 125.5 and 123.5° respectively). The factors affecting π character are thus complex.

In the absence of π bonding, the substitution of a phenyl for a methyl group is expected to cause an increase in the chlorine resonance frequency, because of the greater electronegativity of an sp^2 than an sp^3 hybridised carbon atom. This effect is observed for all members of the carbon series. The resonance frequencies of $[PMeCl_3]^+$ and $[PPhCl_3]^+$ show no such increase, in common with the related silicon and germanium compounds (there are unfortunately no data for the arsenic analogue), although $[PPh_2Cl_2]^+$, $[AsPh_2Cl_2]^+$, $[PPh_3Cl]^+$, and $[AsPh_3Cl]^+$ have higher resonance frequencies than their methyl analogues. The lower frequency in $[PPhCl_3]^+$ is possibly attributable to the occurrence of P–Cl d_π–p_π bonding, which lowers the p_π population on chlorine. This effect is smaller in the diphenyl and triphenyl ions, and the frequency variation shown in Figure 2 suggests that the π character decreases in the same order as the resonance frequencies, *i.e.* $[MCl_4]^+ > [MPhCl_3] > [MPh_2Cl_2]^+ > [MPh_3Cl]^+$.

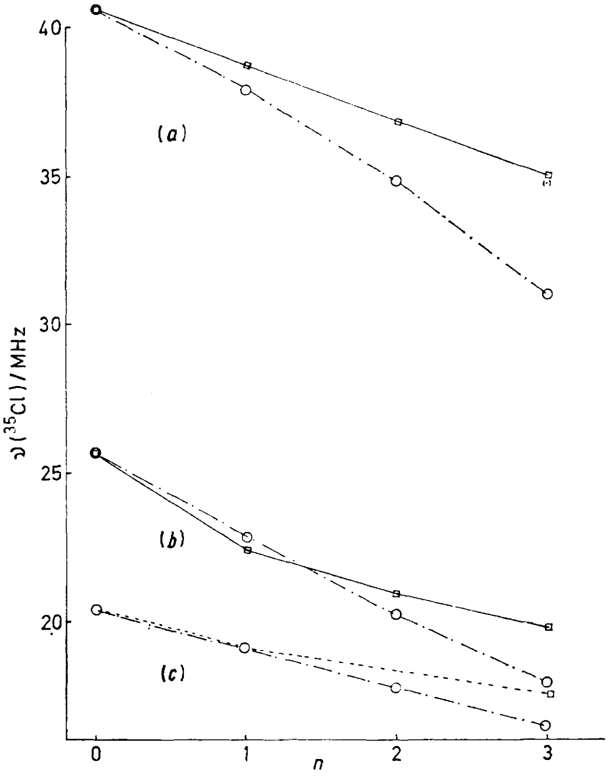

FIGURE 2 Chlorine 35 n.q.r. frequencies for MR_nCl_{4-n}, where R = Me (○) or Ph (□) and M = C(*a*), Ge(*b*), or Si(*c*). [Data are taken from tables of n.q.r. frequencies,[8,22] except for Ph_3CCl (35.10), $SiPh_3Cl$ (17.49 and 17.67), $GePh_2Cl_2$ (20.40 and 21.52), and $GePh_3Cl$ (19.65 and 19.96 MHz) which were observed at 77 K in the present work.]

The lack of data for $[AsMeCl_3]^+$ makes a detailed comparison of π bonding in the phosphorus and arsenic series difficult. Furthermore, such a comparison would only be valid if the central atoms possessed equal inductive and conjugative transmission coefficients. That this is not so is demonstrated by the relation between ^{35}Cl–As frequencies and ^{35}Cl–P frequencies in analogous compounds, from which it is calculated that substituent effects are transmitted 2.14 ±0.05 times more efficiently by arsenic in the phenyl series and 2.02 ± 0.09 times more efficiently in the methyl series (Table 4). (The numbers represent the gradients of the best straight lines, ± the calculated standard deviations.) Phosphorus is known to be a poor transmitter of inductive effects,[21] so the greater sensitivity of the arsenic compounds is not unexpected.

TABLE 4

Comparison of transmission of substituent effects (relative to phosphonium compounds)

Compound	R = Me	R = Ph
$[AsR_nCl_{4-n}]^+$	2.02 ± 0.09	2.14 ± 0.05
R_nCCl_{4-n}	2.31 ± 0.31	2.04 ± 0.44 * 2.12 ± 0.58
SiR_nCl_{4-n}	1.17 ± 0.07	1.17 ± 0.18
GeR_nCl_{4-n}	2.30 ± 0.05	2.28 ± 0.23

* From frequency for Ph_3CCl in present work (see text).

In a similar way, the ability of phosphorus to transmit substituent effects may be compared with those of the Group 4 elements carbon, silicon, and germanium, for which sufficient n.q.r. data are available.[8,22] The results for the methyl- and phenyl-substituted chloro-compounds are given in Table 4. Two values are quoted for the phenylcarbon series, where Semin *et al.*[22] reported 34.77 MHz as the average frequency of five lines in Ph_3CCl, for which a single line at 35.10 MHz was observed in the present work.

As expected from Figure 2, the carbon compounds, particularly the phenyl derivatives, show large standard deviations since their frequencies do not follow the same trends as those of the other elements. The remaining results for both sets of substituents follow the sequence P < Si < As < Ge. (Carbon has been omitted since its position in the phenyl series cannot be established.) Moreover, all the elements except silicon, including carbon, are at least twice as effective as phosphorus in transmitting substituent effects. The positively charged Group 5 ions also appear to be slightly less effective than the isoelectronic Group 4 neutral species.

Despite the limitations discussed above, it is possible to compare generally the extent of π bonding in the chloro-phosphorus and -arsenic(V) cations from the n.q.r. frequencies, if certain simplifying assumptions are made. From the Townes–Dailey expression,[12] we obtain equation (3).

$$\frac{\nu(\text{As–Cl})}{\nu(\text{P–Cl})} = \frac{(1-s)(1-i)_{\text{As}} - \pi_{\text{As}}}{(1-s)(1-i)_{\text{P}} - \pi_{\text{P}}} \tag{3}$$

On the assumption that the $(1 - s)$ terms will be approximately equal for P and As, and may be

---

[21] E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 1961, 2459.

[22] G. K. Semin, T. A. Babushkina, and G. G. Yakobson, 'Applications of N.Q.R. in Chemistry,' Khimiya, Leningrad, 1972.

View Article Online

Published on 01 January 1976. Downloaded by University of Birmingham on 31/10/2014 15:16:47.

expressed as a constant K, this relation simplifies to (4).

$$\frac{\nu(\text{As–Cl})}{\nu(\text{P–Cl})} = \frac{K(1 - i)_{\text{As}} - \pi_{\text{As}}}{K(1 - i)_{\text{P}} - \pi_{\text{P}}} \qquad (4)$$

The experimental ^{35}Cl–As frequencies are higher than the corresponding ^{35}Cl–P frequencies, so that we can write expression (5). On the basis of electronegativities, P–Cl

$$K(1 - i)_{\text{As}} - \pi_{\text{As}} > K(1 - i)_{\text{P}} - \pi_{\text{P}} \qquad (5)$$

bonds are expected to have a smaller degree of ionic character than As–Cl bonds. Hence $K(1 - i)_{\text{P}}$ should be larger than $K(1 - i)_{\text{As}}$. From these inequalities, it follows that $\pi_{\text{As}} < \pi_{\text{P}}$. Thus the frequencies suggest that π bonding is more important in the phosphorus cations. Similarly, it appears that $\pi_{\text{Ge}} < \pi_{\text{Si}}$ in the Group 4 compounds, but it is not possible to deduce the relative extent of π bonding in pairs such as Si and P, or Ge and As, on this basis.

In order to account for substituent effects in Group 4 compounds of the type $MR^1R^2R^3Cl$, and in phosphorus(V) compounds PR^1R^2ClO and PR^1R^2ClS, Semin and Bryuchova[23] proposed the relation (6) where α and β are

$$\frac{\nu - \nu_0}{\nu_0} = (\alpha\Sigma\sigma_{\text{I}} + \beta\Sigma\sigma_{\text{C}}) \pm \mu \qquad (6)$$

transmission coefficients, σ_{I} and σ_{C} are inductive and conjugative Taft parameters, ν_0 is a constant for a particular M, and μ is the average absolute error. For consecutive members of a series, MR_nCl_{4-n}, there will be a constant change in $(\alpha\Sigma\sigma_{\text{I}} + \beta\Sigma\sigma_{\text{C}})$ resulting from the replacement of a chlorine by a group R, and equation (6) thus predicts a linear variation of n.q.r. frequency with n. Figures 1 and 2 show that this relation is followed much more closely by methyl- than by phenyl-substituted ions, probably because of the additional π effects caused by conjugation in the latter, as discussed above. The equation is thus more likely to be valuable for predicting n.q.r. frequencies when σ effects predominate.

Since the bonding in $[PPhCl_3]^+$ is likely to be similar to that in PCl_3O,[24] it is pertinent to compare their ^{35}Cl n.q.r. frequencies. The phosphonium salt has the higher frequency (average 30.97 MHz at 77 K),[1] compared with PCl_3O (average 28.96 MHz at 77K).[8] If inductive effects are considered, replacement of a phenyl group by the more electronegative oxygen would be expected to raise the n.q.r. frequency. This expectation conflicts with the observed frequency shift. The reason may be a substantial difference in $P(d_\pi)$–$Cl(p_\pi)$ bonding which overrides the inductive effects, since these are poorly transmitted by phosphorus. Molecular geometry suggests that there is greater π bonding in $[PCl_4]^+$ than in PCl_3O,[25] however, so the overall order of decreasing P–Cl π bonding may therefore be: $[PCl_4]^+ > PCl_3O > [PPhCl_3]^+ > [PPh_2Cl_2]^+ > [PPh_3Cl]^+$. A similar sequence is probable for the corresponding arsenic species.

We thank J. Lincoln for preparing the compounds, R. Coult for some microanalyses, and the S.R.C. for a grant for the purchase of equipment and a postdoctoral research assistantship (to R. J. L.).

[6/150 *Received*, 23*rd January*, 1976]

[23] G. K. Semin and E. V. Bryuchova, *Chem. Comm.*, 1968, 605.

[24] K. A. R. Mitchell, *Canad. J. Chem.*, 1968, **46**, 3499.

[25] R. M. Hart and M. A. Whitehead, *J. Chem. Soc.* (*A*), 1971, 1738.