Nuclear Magnetic Resonance Investigations of Carbonium Ion Intermediates. Part III.† A Chlorine-35 Quadrupole Resonance Study of Several (R-Chloromethylene)dimethylammonium Salts (Vilsmeier–Haack and Viehe reagents)

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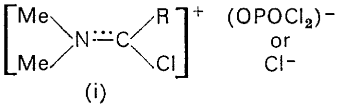
The ^{35}Cl n.q.r. frequencies observed in a series of solid chloromethylenedimethylammonium salts are in agreement with the general structure (i). The variations in the C–^{35}Cl resonance frequency indicate a large polarisability



(i)

of the $[\gt N \overset{\cdots}{-} C \lt]^+$ group, both with respect to the σ and π electron systems. The charge on the Cl atom increases in the order R = Cl < Ph < Pr^i < H.

THE formulation of chloroiminium salts has been a matter of controversy for some time.[1] At the present moment, most work [2-4] in solutions is in agreement with an ionic structure, although there are still some reservations. In the present paper, we give the results obtained from ^{35}Cl quadrupole resonance studies of the pure *solid* compounds. The presence of chlorine atoms within these molecules provides us with a probe that gives information [5] not only about the structural position of this element but also about the nature of the bond in which it is involved.

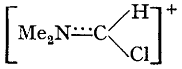
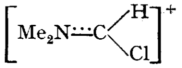
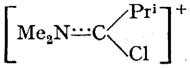
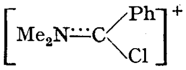
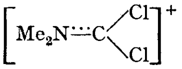
EXPERIMENTAL AND RESULTS

The iminium salts (I) or (II) (Table 1) were obtained from stoicheiometric quantities of pure *NN*-dimethylformamide and the Lewis acids POCl$_3$ or COCl$_2$. To avoid hydrolysis, the complexes were directly prepared in the n.q.r. tube attached to a vacuum line and the sample tube sealed. The salts derived from other amides [(III) and (IV)] were obtained in a similar way. The dichloroiminium chloride (V) was prepared following the procedure described by Viehe and Janousek.[6] The structure of these compounds was checked by comparison between their ^{1}H n.m.r. and data previously recorded; [2,4] the purity is as high as 99%.

All ^{35}Cl quadrupole resonance spectra were recorded on a Decca spectrometer utilising Zeeman modulation, sideband suppression, and automatic frequency calibration. The recording time constant was 10 s and the accuracy of frequency measurement was ±5 kHz. Searches were conducted in the frequency range from 10 to 45 MHz at the standard temperature of liquid nitrogen (77 K). The room temperature liquid samples were frozen very slowly in a cold petroleum–ether bath and then maintained at liquid nitrogen temperature for at least 1 h before the spectra were recorded. When the signal-to-noise ratio allowed, the ^{35}Cl frequencies were checked by the observation of ^{37}Cl signals at a frequency ratio of 1·2688. The experimental frequencies are listed in Table 1. Most other frequencies cited in the text are taken from the Tables of Semin *et al.*[7]

TABLE 1

^{35}Cl N.q.r. frequencies in some (R-chloromethylene)-dimethylammonium salts at 77 K

	Compounds		$\nu_{Cl^{35}}$/MHz	Average
(I) *	 $[Me_2N\overset{\cdots}{-}C(H)Cl]^+$	OPOCl$_2^-$	36·31$_5$ 24·53$_1$ 24·73$_1$	24·63
(II) *	 $[Me_2N\overset{\cdots}{-}C(H)Cl]^+$	Cl$^-$	35·78$_6$	
(III)	 $[Me_2N\overset{\cdots}{-}C(Pr^i)Cl]^+$	Cl$^-$	36·45$_5$	
(IV)	 $[Me_2N\overset{\cdots}{-}C(Ph)Cl]^+$	Cl$^-$	37·05$_0$	
(V) *	 $[Me_2N\overset{\cdots}{-}C(Cl)Cl]^+$	Cl$^-$	39·52 39·60 39·86 39·99	39·74

* ^{37}Cl Signals also detected.

DISCUSSION

The Dimethylformamide–OPCl$_3$ *Adduct*.—The structure of the formylating agent obtained by mixing dimethylformamide (DMF) and phosphoryl chloride has been a matter of some controversy. Several formulations have been proposed, among which the most likely are (A)—(C). ^{1}H N.m.r. studies [2] give strong evidence for structure (B) in solution. A rapid equilibrium between (B) and (C), which had not been previously excluded, may now be disregarded.[8]

The ^{35}Cl n.q.r. spectrum of the solid adduct gives new information on its structure. We assume that the three frequencies in Table 1 are directly ascribed to a C–^{35}Cl

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[1] G. Hazebroucq, *Ann. Pharm. France*, 1966, **24**, 793.

[2] G. J. Martin and M. L. Martin, *Bull. Soc. chim. France*, 1963, 1637.

[3] Z. Arnold and A. Holy, *Coll. Czech. Chem. Comm.*, 1962, **27**, 2886.

[4] G. J. Martin and S. Poignant, *J.C.S. Perkin II*, 1972, 1964.

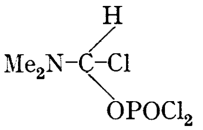
[5] *Cf.* for example, E. A. C. Lucken, 'Nuclear Quadrupole Coupling Constants,' Academic Press, New York and London, 1969, ch. 10.

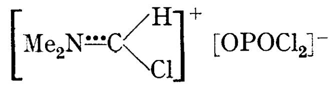
[6] H. G. Viehe and Z. Janousek, *Angew. Chem. Internat. Edn.*, 1973, **12**, 806.

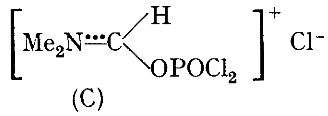
[7] G. K. Semin, T. A. Babushkina, and G. G. Jacobson, 'Nuclear Quadrupole Resonance in Chemistry,' Izdatelistvo 'Ximia,' Leningrad, 1972.

[8] G. J. Martin and S. Poignant, *J.C.S. Perkin II*, 1974, 642.

resonance (36·31 MHz) and to P–^{35}Cl resonances (24·53 and 24·73 MHz). First, the characterisation of a resonance for a chlorine atom directly bonded to carbon allows us to reject structure (C) in which there is no bond of this kind (similarly, the presence of a C–^{35}Cl signal eliminates any structure based on molecular complex formation, such as $\mathrm{Me_2NCHO}\cdots\mathrm{POCl_3}$). Secondly, although the *two* lower frequency lines, which lie in a range typical of P–Cl bonds, are consistent with both structures (A) and (B) and with the unique C–^{35}Cl resonance, the absolute values of the frequencies allow us to eliminate structure (A). On the one hand, for structure (A), the P–^{35}Cl frequencies should lie close to those of an alkyl phosphorodichloridate such as MeOP(O)Cl$_2$ for which we have found, at 77 K, two ^{35}Cl signals at 27·08$_0$ and 27·45$_8$ MHz (in good agreement with previous determinations).[9] The difference of 2·6 MHz between the average of these two frequencies and those of (I) seems too large to be ascribed either to a change in the nature of the R radical in ROP(O)Cl$_2$ or simply to a solid state effect. This decrease in frequency on going from ROP(O)Cl$_2$ to the oxo-anion form (OPOCl$_2$)$^-$ strengthens our arguments in favour of structure (B). The negative charge on the latter is expected to be largely located on the oxygen atoms; the shift towards low frequencies can then be explained by a decrease of the phosphorus electronegativity leading to an increase of the electron charge density on the chlorine atoms. On the other hand, the C–^{35}Cl resonance at 36·31 MHz seems too low to be consistent with (A), in which the central carbon atom would be attached to three highly electronegative atoms or groups (Me$_2$N, Cl, and O); *cf.* the ^{35}Cl frequencies in CHCl$_3$ at 77 K, *viz.* 38·254 and 38·308 MHz.


(A)


(B)


(C)

Our conclusion is that the ^{35}Cl n.q.r. data strongly support structure (B) for the DMF–OPCl$_3$ adduct. They therefore confirm previous ^{1}H n.m.r. studies in solution which relied both on the lack of any $^3J_{POCH}$ spin–spin coupling and on the particular value of the ^{31}P chemical shift.[4] We therefore take the value of 36·31 MHz for the C–^{35}Cl nucleus as typical for the $[\mathrm{Me_2N}\overset{\cdots}{-}\mathrm{C(Cl)H}]^+$ ion in the solid state.

The NN-*Dimethylcarboxamide*–COCl$_2$ *Adducts*.—The chemical reaction of Me$_2$NCOR with phosgene (COCl$_2$) occurs with evolution of CO$_2$: the possibilities for the chemical formulation of these adducts are therefore very much less. The ionic structure $[\mathrm{Me_2N}\overset{\cdots}{-}\mathrm{C(Cl)R}]^{+-}$ Cl was proposed at an early stage.[10] Moreover, it has been shown [11] by ^{1}H and ^{13}C n.m.r. spectroscopy that the *NN*-dimethylcarboxamide–POCl$_3$ adducts are structurally very closely related to the organic part of the COCl$_2$ derivatives. It may therefore be assumed that the conclusions concerning the n.q.r. data for the POCl$_3$ adducts may be extrapolated to those of COCl$_2$.

In solution, the ^{1}H and ^{13}C n.m.r. spectra of the complexes show that these nuclei are strongly deshielded with respect to the carboxamides and the $^1J_{^{13}\mathrm{C}-\mathrm{H}}$ values of the methyl groups of the adducts are relatively high. This behaviour argues for an electronic deficiency and charge delocalisation in the organic ions.

In the solid state, the ^{35}Cl n.m.r. data are in agreement with these conclusions; all four compounds (II)—(V) show C–^{35}Cl signals in the expected region, with some variations in frequency to be discussed later. Compounds (II)—(IV) show a single C–^{35}Cl line whereas (V) shows two doublets, presumably indicating the presence of at least two molecules in the asymmetric unit of the crystal structure. In none of these compounds have we detected any signals attributable to the chlorine anion, despite searches going down to 10 MHz. This is not, however, inconsistent with its presence; in (Coen$_2$Cl$_2$)Cl,HClxH$_2$O (en = ethylenediamine), for example, the ^{35}Cl frequency of the ionic chlorine is 2·86 MHz.[12] In ^{35}Cl n.q.r. studies of α-halogenated amines,[13] the absence of any ^{35}Cl signal in R$_2$N–CH$_2$Cl has been taken as evidence for their formulation as $(\mathrm{R_2N}\overset{\cdots}{-}\mathrm{CH_2})^+\mathrm{Cl}^-$.

The variations of the C–^{35}Cl frequencies quoted in Table 1 are of some interest. First the difference of 0·5 MHz between compounds (I) and (II) shows the small influence of the nature of the anion on the electronic state of the cation. Secondly, Table 1 shows a general trend of the frequency shift within the series in relation to the nature of R which appears to indicate that the extent of delocalisation of the nitrogen lone pair into the carbocation system, $>\!\ddot{\mathrm{N}}-\overset{+}{\mathrm{C}}(\mathrm{Cl})\mathrm{R}$, is dependent upon the nature of R. The C–Cl bond is regarded as a σ-bond polarized towards chlorine, with some slight π-character, principally from the chlorine lone pair in the correct orientation to overlap with the π-system of the carbocation. Substitution of a phenyl group for hydrogen is expected to increase the π-interaction of the substituent R with the $[>\!\mathrm{N}\overset{\cdots}{-}\mathrm{C}\!<]^+$ system, thereby diminishing that of the chlorine atom, leading to an increase in the ^{35}Cl quadrupole coupling constant. If the asymmetry parameter,

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

[10] Z. Arnold and F. Sorm, *Coll. Czech. Chem. Comm.*, 1958, **23**, 452.

[11] M. L. Martin, G. Ricolleau, S. Poignant, and G. J. Martin, 2nd IUPAC Conference on Physical Organic Chemistry, Noordwijkerhout, 1974.

[12] H. Hartmann, M. Fleissner, and H. Sillescu, *Theor. Chim. Acta*, 1964, **2**, 63.

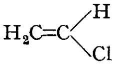
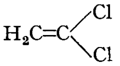
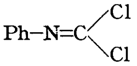
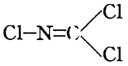
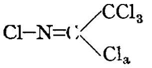
[13] A. A. Neimysheva, G. K. Semin, T. A. Babushkina, and I. L. Knunyants, *Doklady Akad. Nauk. S.S.S.R.*, 1967, **173**, 585.

η, is small in both compounds, then the decrease in this quantity can be neglected, and a substantial part of the increase in frequency of 1·3 MHz on going from (II) to (IV) may be attributed to this change in the $3p_\pi$ populations on the Cl atom.

The frequency shift produced by the Pr^i group also has the same sign, but is almost half as large (*ca.* +0·7 MHz), in apparent contradiction with the usual σ-donor behaviour of this alkyl group: Pr^i should tend to repel electrons to the carbon atom and consequently to the adjacent chlorine atom, thereby decreasing the chlorine frequency. Since it is the reverse that is observed, it seems that hyperconjugation might well be important, for there is then a reversal of electron-donating ability in going from H to Pr^i [consistent with the behaviour of the Pr^i group adjacent to an *unsaturated system* [14]]. Once again, therefore, the ^{35}Cl frequency is susceptible to a change in the π-electron distribution within the cation system.

With the last substituent to be considered, R = Cl, we have a strong σ withdrawing effect from the $[{>}N\cdots C{<}]^+$ system combined with a small reduction in π back-co-ordination along the C–R bond. Both effects will tend to raise the chlorine quadrupole coupling constant. Experimentally, the frequency shift is large (*ca.* +4 MHz), once again underlining the large polarisability of the carbonium ion. These qualitative conclusions are supported by a comparison of the ^{35}Cl frequencies for compounds (II) and (V) with those for some related compounds (Table 2). The observed frequencies for the iminium salts are similar to those observed in PhN=CCl$_2$ and related molecules.[15,16] The changes with substituent are comparable to those observed in chloro-substituted ethylenes,[7] the frequency shifts being in the same direction; in each case, however, a larger value for the chloroiminium salt is observed, in agreement both with the fact that the carbon atom is linked to a group of stronger electronegativity (Me$_2$N instead of CH$_2$) and with the conclusion that the whole system $[{>}N\cdots C{<}]^+$ has a larger polarisability with respect to both the σ and π electrons.

TABLE 2

Compounds	^{35}Cl/MHz*	Average	η
	33·414	33·414	0·07
	36·837 36·524 36·268	36·54$_5$	
	36·128 37·047		
	37·405 37·580 38·595 38·720		
	36·920(Cl$_a$) 37·190(Cl$_a$)	37·06	

* At 77 K.

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[4/2240 *Received*, 30*th October*, 1974]

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[14] P. Sykes, 'A Guidebook to Mechanism in Organic Chemistry,' Longmans, London, 1965, pp. 20—21.

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

[16] H. G. Fitzky, *Adv. Nuclear Quadrupole Resonance*, 1974, **1**, 79.