592. *Chemical Applications of Nuclear Quadrupole Resonance Spectroscopy. Part III.*[1,2] *The Inductive Effect of Substituents belonging to the First Row of the Periodic Table.*

By E. A. C. LUCKEN.

Nuclear quadrupole resonance spectra of chloro-derivatives of a number of aliphatic ethers, sulphides, fluoro-, allyl, and propargyl compounds, have been measured with a frequency-modulated, externally quenched, super-regenerative spectrometer. The anomalously low frequencies of the compounds containing fluorine and oxygen substituents have been interpreted in terms of overlap between the *p*-orbitals of the first-row substituent and the carbon–chlorine σ-bond. A molecular-orbital treatment of the effect is given in an Appendix. In allyl and propargyl compounds little or no anomaly occurs.

PREVIOUS Parts [1,2] in this series have been primarily concerned with the effects of conjugation on nuclear quadrupole resonance frequencies of ^{35}Cl. In this paper is discussed the effect of the first-row substituents fluorine and methoxyl in the α-position to the chlorine nucleus under investigation. It was first observed by Livingstone [3] that the nuclear quadrupole resonance frequencies of ^{35}Cl of the chlorofluoromethanes were anomalously low, and in an attempt to confirm and explain this anomaly for similar α-fluoro-substituted aliphatic compounds and the related α-chloro-ethers this investigation has been carried out.

Experimental.—The ^{35}Cl resonances were detected by the method described in Part I.[1] Propargyl chloride [4] and 2-chloroethyl methyl ether [5] were prepared by standard methods, and the latter was fractionated before use. A commercial specimen of chloromethyl methyl ether was dried and fractionated, and specimens of chloromethyl methyl sulphide, bischloromethyl sulphide, 2,2′-dichlorodiethyl ether, allyl chloride, and methallyl chloride were distilled before use. The remaining commercial specimens were used without further purification. 2,2-Dichloro-1,1,1-trifluoroethane was a gift from Imperial Chemical Industries Limited. The observed frequencies are shown in Table 1.

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[1] Part I, Dewar and Lucken, *J.*, 1958, 2653.
[2] Part II, Dewar and Lucken, *J.*, 1959, 426.
[3] Livingstone, *J. Phys. Chem.*, 1953, **57**, 496.
[4] Hatch and Chiola, *J. Amer. Chem. Soc.*, 1951, **73**, 360.
[5] Swatten and Boord, *ibid.*, 1930, **52**, 651.

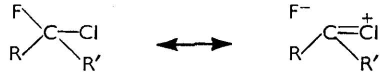
TABLE 1. *Nuclear quadrupole resonance frequencies of* ^{35}Cl, *at* 77° K *unless otherwise stated, in Mc. per sec.*

Chlorodimethyl ether	30·181	1,1,3,3-Tetrachloro-1,3-difluoroacetone	39·312 39·104
2-Chloroethyl methyl ether	33·453	2,3-Dichloro-1,1,1,4,4,4-hexafluorobut-2-ene	39·491
2,2′-Dichlorodiethyl ether	33·392 33·483	1,2-Dichloro-3,3,4,4,5,5-hexafluorocyclopentene	38·039
Chlorodimethyl sulphide	33·104	1,1-Dichloro-2,2,2-trifluoroethane	38·694
2,2′-Dichlorodimethyl sulphide	34·749 34·526	Allyl chloride	33·398 (86° K)
Dichlorofluoroacetic acid	39·594	Methallyl chloride	33·777
Chlorodifluoroacetic acid	37·485	Propargyl chloride	35·753 (86° K)

DISCUSSION

The frequencies of the chlorofluoroacetic acids are both lower than those of trichloroacetic acid (39·96, 40·165, 40·240 Mc./sec. at 77° K), the frequency decreasing with an increasing degree of substitution by fluorine. This trend is similar to that noted by Livingstone in the chlorofluoromethanes, and the effect on the chlorine-resonance frequency of a fluorine atom in a position α to the chlorine atom may thus be said to be established.

In order to explain the anomalously low ^{35}Cl nuclear quadrupole resonance frequencies of the chlorofluoromethanes it was suggested that in those compounds the carbon–chlorine bond is endowed with some π-character by hyperconjugation of form (II). Moderate amounts of such double-bond character can be shown to lower the resonance frequency. Since a structure such as (II) involves a positive charge on the chlorine atom, it is supposed to be favoured by the high electronegativity of fluorine.



(I) (II)

Although it is probable that such carbon–chlorine double-bonding does occur in saturated molecules, the effect is likely to be small. Even when the chlorine atom is attached to an unsaturated residue, *e.g.*, vinyl chloride, it has been shown by measurements of the nuclear quadrupole resonance asymmetry parameter that the carbon–chlorine bond has only 5—15% of π-character. In any case, according to the above hypothesis the amount of π-character in the carbon–chlorine bond will be proportional to the electronegativity of the substituents, and thus its effect on the nuclear quadrupole resonance frequency of chlorine could not be separated from that due to inductive polarisation. There is thus no reason why the effect of fluorine substituents should be anomalous.

An alternative explanation was suggested by the frequency of bischloromethyl ether. It is well known that elements in the first row of the Periodic Table are particularly suited to the formation of π-bonds by the overlap of *p*-orbitals. This effect, in the case of fluorine, is well illustrated by the acid and base dissociation constants of the *para*-halogeno-phenols and -anilines respectively (Table 2),[6] where the expectedly high inductive effect of the fluorine atom is offset by its ability to conjugate with the benzene ring. In view of the above a structure such as (III) may contribute significantly to the ground state of chlorofluoromethane or a related molecule. This would increase the ionic character of the carbon–chlorine bond and so lower the nuclear quadrupole resonance frequency of chlorine.

TABLE 2. *Acid* ($K_A \times 10^{11}$) *and base* ($K_B \times 10^{12}$) *dissociation constants of* para-*halogenophenols and -amines.*

X =	F	Cl	Br	I	H
p-X·C_6H_4·OH	2·6	13·2	15·5	21·9	3·2
p-X·C_6H_4·NH_2	120	28·8	21·9	15·1	12·6

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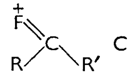
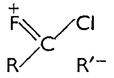
[6] Sharpe and Haszeldine, " Fluorine and its Compounds," Methuen, London, 1951.

The type of interaction invoked is essentially similar to the previous one but it is immediately obvious why fluorine should be different from chlorine, for its ability to form double bonds is so much greater.


(III)


(IV)

The problem has so far been discussed in valence-bond terms which here have the advantage of pictorial clarity and permit a ready comparison with the previous explanation of the anomaly. A molecular-orbital discussion is equally possible and in this case enables an estimate of the magnitude of the effect to be obtained in a straightforward manner. A calculation along these lines has been carried out in the Appendix and it is shown that the magnitude of the interaction between the substituent *p*-orbital and the carbon–chlorine σ-bond is quite sufficient to account for the observed reduction in frequency.

FIG. 1.

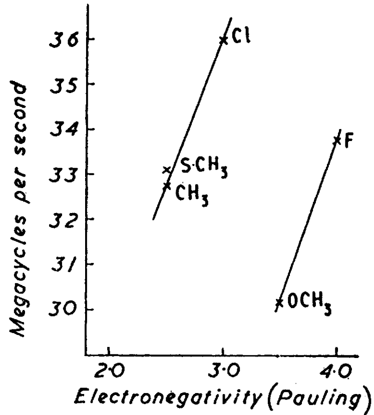
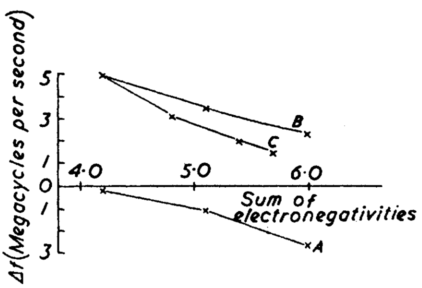


FIG. 2



From this hypothesis we may draw a number of conclusions. First, that the chlorine nuclear quadrupole resonance frequencies of molecules XRR′CCl will also be anomalously low when X is RO or RR′N. Secondly, that the frequencies of these molecules will be in the order X = F > OMe > NMe_2. Thirdly, that if either of the substituents R,R′ is appreciably electronegative then the effect of the postulated hyperconjugation on the chlorine frequency will be reduced since structures such as (IV) will also contribute to the ground state of the molecule

Fig. 1 has been constructed by plotting the chlorine nuclear quadrupole resonance frequency of the molecule $R{\cdot}CH_2Cl$, where R is an atom or radical, against the electronegativity of the atom in R directly attached to the carbon atom. It illustrates the correctness of the first two conclusions. The points corresponding to chlorofluoromethane and chlorodimethyl ether lie at a much lower frequency than those corresponding to molecules in which hyperconjugation is not expected to occur. The results are sparse, but there is no doubt that the frequency of chlorodimethyl ether is much lower than would have been expected on the grounds of a simple inductive effect. It is possible, though with perhaps little justification, to draw two roughly parallel lines through the points on the Figure, one through those in which hyperconjugation occurs and one through those in which it does not. The parallelism, if real, implies that the reduction in frequency due to hyperconjugation is the same in chlorofluoromethane as in chlorodimethyl ether and hence that the amount of π-character in the carbon–fluorine bond is approximately the same as that in the carbon–oxygen bond. If the lower of these two lines is produced to cut the electronegativity axis at 3·0, corresponding to a NMe_2 substituent, a frequency of approximately 27 Mc./sec. is predicted for the molecule $NMe_2 \cdot CH_2Cl$, corresponding to a highly polar carbon–chlorine bond. Such a molecule would be very reactive and this could account for the lack of success in attempts to prepare α-chloro-amines.

TABLE 3. ^{35}Cl *Nuclear quadrupole resonance frequencies of chlorofluoromethanes at* 20° K.

R	R′	(f_1) RR′CHCl	(f_2) $RR'CCl_2$	(f_3) RR′CFCl	$f_1 - f_3$	$f_2 - f_3$
H	H	68·40	72·47	67·6	+0·8	+4·9
H	Cl	72·47	76·98	73·53	−1·06	+3·45
Cl	Cl	76·98	81·85	79·63	−2·65	+2·22

The correctness of the third conclusion may be illustrated by reference to the frequencies of the chlorofluoromethanes. In Table 3 are shown the chlorine nuclear quadrupole resonance frequencies of the molecules RR′CHCl, RR′CFCl, and $RR'CCl_2$, and the frequency differences between the pairs RR′CFCl–RR′CHCl and $RR'CCl_2$–RR′CFCl. In Fig. 2 these differences are plotted against the sum of the electronegativities of R and R′. It is seen that, as expected, two parallel lines are obtained, one (*A*) for substitution of hydrogen by fluorine, and the other (*B*) for the substitution of chlorine by fluorine.

The evidence for the present hypothesis, although far from conclusive, is thus strong enough to justify its use as a basis for discussion. Reference to Fig. 1 shows that the effect of this hyperconjugation is to reduce the effective electronegativity of the first-row substituent by approximately 1·3 electronegativity units. The frequency of 2-chloroethyl methyl ether is thus comparable with that of n-propyl chloride (33·0 Mc./sec.), while that of 1,1-dichloro-2,2,2-trifluoroethane is close to that of pentachloroethane. The frequencies of 2,3-dichloro-1,1,1,4,4,4-hexafluorobut-2-ene and 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentadiene are likewise consistent with this.

In Fig. 2 are also plotted points (line *C*) corresponding to line *B*, for which at least one of the substituents R, R′ is a fluorine atom. The electronegativity of fluorine is taken as 2·7 in accordance with the conclusions of the preceding paragraph, and it is seen that the trend is very similar to that shown in lines *A* and *B*. It must be emphasised, however, that this effective electronegativity of fluorine is not a constant but will depend very much on its molecular environment.

The interaction invoked may also be used to explain the observed bond-shortening in the chlorofluoromethanes. The statement that the hyperconjugation appears to reduce the electronegativity of the fluorine atom can be re-expressed by saying that hyperconjugation appears to increase the electronegativity of the chlorine atom. If we assume, by extrapolation of the upper line in Fig. 1, that the expected frequency of chlorofluoromethane is about 42 Mc./sec., then the lowering is 8 Mc./sec. Making use of the approximate relationship[7] between the electronegativity difference and quadrupole resonance frequency of diatomic molecules, *viz.*,

$$\text{Electronegativity difference} = 2\left\{\frac{\text{Observed frequency}}{\text{Atomic coupling frequency}}\right\}$$

we find that the change in electronegativity of the chlorine atom is approximately 0·3 electronegativity unit. From the Schomaker–Stevenson rule[8] this would produce a shortening in the carbon–chlorine bond length of 0·09 × 0·3 = 0·027 Å. The observed difference in the carbon–chlorine bond lengths between methyl chloride and chlorofluoromethane is 0·015 ± 0·007 Å. Although this calculation is far from exact, particularly in view of the uncertainty in the mutual relation of atomic and bond parameters, it gives an answer of the correct magnitude.

The frequencies of the two sulphides accord with the accepted electronegativity of sulphur (2·5) and thus may be said to support the contention in Part II[2] that the high

[7] Gordy, Smith, and Tramburolo, " Microwave Spectroscopy," Wiley, 1953.

[8] Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

chlorine nuclear quadrupole resonance frequencies of the chlorothiophens are due to sulphur's use of *d*-orbitals in these compounds.

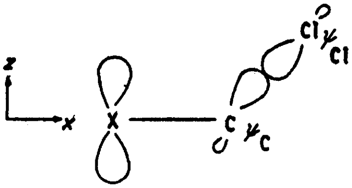
For allyl and propargyl chloride the frequencies are consistent with the assumption that vinyl and ethynyl groups act only as electronegative inductive substituents. From Fig. 1 we may calculate the electronegativity of the sp^2-carbon atom as 2·7 and of the *sp*-carbon atom as 2·9. These values are in accord with other independent estimates.[7] Although at first sight the situation in these compounds is analogous to that in fluoro- and methoxy-compounds, it is in fact fundamentally different. The important point is that, whereas the latter compounds form an odd conjugated system, the former form an even system. There is considerable evidence [9] which suggests that conjugation in even systems is very much less important than in odd ones and, if this is the case, it would probably be impossible to detect hyperconjugation in allyl and propargyl chlorides. It is hoped to discuss this question in more detail in a subsequent paper.

APPENDIX

Molecular-orbital treatment of the interaction between an α*-substituent* p*-orbital and the carbon–chlorine* σ*-bond.*

The following discussion is not intended to be rigorous; it does, however, show that the observed magnitude of the anomaly is consistent with the interaction invoked.

FIG. 3.



Chlorine nuclear resonance experiments show that an average aliphatic carbon–chlorine bond has about 35% of ionic character. In a simple L.C.A.O. treatment of a single bond, with neglect of overlap, this is consistent with a coulomb integral for chlorine of $\alpha_C + \beta$, where α_C is the carbon coulomb integral and β is the carbon–chlorine resonance integral. With these values for the parameters involved, the linear combination of atomic orbitals treatment of the carbon–chlorine single bond gives

$$\Psi_{\text{bonding}} = 0{\cdot}526\psi_C + 0{\cdot}850\psi_{Cl}$$
$$\Psi_{\text{antibonding}} = 0{\cdot}850\psi_C - 0{\cdot}526\psi_{Cl}$$

where ψ_C and ψ_{Cl} are the appropriate atomic orbitals for carbon and chlorine respectively.

It is convenient to assume that the substituent *p*-orbital interacts only with the empty antibonding orbital. This method has been used with success to explain the effect of substituents on the ultraviolet spectrum of benzene.

It is next required to determine the matrix elements of the second-order secular determinant describing the interaction. Let

$$\chi_1 \equiv \Psi_{\text{antibonding}}$$
$$\chi_2 \equiv \text{the substituent } p\text{-orbital}$$

then

$$\int \chi_1 H \chi_1^* d\tau \equiv H_{11} = \alpha_C - 0{\cdot}618\beta$$

and let

$$\int \chi_2 H \chi_2^* d\tau \equiv H_{22} = \alpha_C + b\beta$$

where *b* is a parameter which depends on the electronegativity of the substituent and will have values between 0 and 2, and

$$\int \chi_1 H \chi_2^* d\tau = \int \chi_2 H \chi_1^* d\tau \equiv H_{12} = x\beta$$

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[9] Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 166.

where x is a parameter depending on the amount of interaction between the substituent p-orbital and the antibonding carbon–chlorine molecular orbital.

An order of magnitude of x may be obtained from the following considerations. In Fig. 3 the orbitals in question are shown against a set of axes. All three atoms lie in the plane of the paper and χ_2 is a p_z-orbital. Then

$$\int \chi_2 H \chi_1 d\tau \equiv 0{\cdot}850 \int \chi_2 H \psi_C d\tau - 0{\cdot}526 \int \chi_2 H \psi_{Cl} d\tau$$

We may reasonably put
$$\int \chi_2 H \psi_{Cl} d\tau = 0$$

Now
$$\psi_C = \frac{1}{2}s + \frac{\sqrt{3}}{2}\left(\frac{1}{3}p_x + \frac{2\sqrt{2}}{3}p_z\right)$$

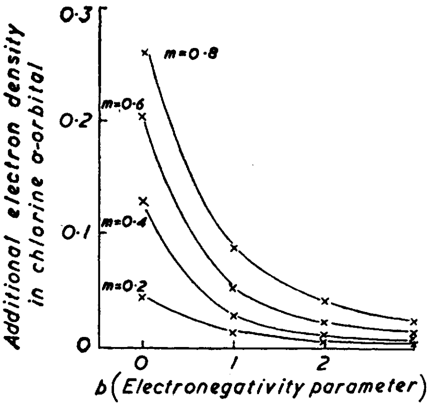
where s, p_x, p_z, are the $2s$, $2p_x$, and $2p_z$ orbitals of carbon. Thus

$$\int \chi_2 H \psi_C d\tau = \frac{1}{2}\int \chi_2 H s d\tau + \frac{\sqrt{3}}{2}\left[\frac{1}{3}\int \chi_2 H p_x d\tau + \frac{2\sqrt{2}}{3}\int \chi_2 H p_z d\tau\right]$$

From the symmetry properties of s and p_x orbitals it is evident that the first two integrals on the right-hand side are equal to zero. Thus

$$\int \chi_2 H \chi_1 d\tau = 0{\cdot}850 \sqrt{\frac{2}{3}} \int \chi_2 H p_z d\tau \simeq 0{\cdot}7 \int \chi_2 H p_z \, d\tau$$

FIG. 4.



Now, in general, $\int \chi_2 H p_z d\tau$ will be less than β, the carbon–chlorine resonance integral; *i.e.*, the ratio

$$\int \chi_2 H p_z d\tau / \beta \equiv m$$

will probably be less than unity. The secular determinant is thus:

$$\begin{vmatrix} \alpha + b\beta - E & 0{\cdot}7m\beta \\ 0{\cdot}7m\beta & \alpha - 0{\cdot}618\beta - E \end{vmatrix} = 0$$

Putting $A = (\alpha - E)/\beta$, we may expand this to give

$$A^2 + A(b - 0{\cdot}618) - (0{\cdot}49m^2 + 0{\cdot}618b) = 0$$

The electron density in the chlorine σ-orbital may then be obtained from the roots of this equation.

In Fig. 4 are plotted curves relating the electron density in the chlorine σ-orbital to the electronegativity of the substituent for various values of m. If it is remembered that 0·1 on the electron-density scale corresponds to a decrease of approximately 5·5 Mc./sec., it can be seen that the interaction is of the right order. In view of the approximation that interaction is only with the antibonding orbital, it is likely that the above analysis will underestimate the frequency-lowering. Qualitatively, it can be seen that it is very sensitive to the choice of the electronegativity and resonance integrals. Resonance integrals are functions of bond length, and since the carbon–fluorine bond length (1·33 Å) is less than the carbon–oxygen bond length (1·42 Å), this would account for the observed equality of the hyperconjugative interaction in the fluoro- and methoxy-compounds.

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