77. *Chemical Applications of Nuclear Quadrupole Resonance Spectroscopy. Part II.[1] Chloro-derivatives of Maleic Anhydrides, Thiophen, and Anilinium Salts.*

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Measurements of chlorine nuclear quadrupole resonance frequencies are reported for *p*-chloroanilinium chloride and bromide, for mono- and di-chloromaleic anhydrides, and for 2-chloro-, 2 : 5-dichloro, and 2 : 3 : 4 : 5-tetrachlorothiophen. The results are discussed in terms of hydrogen bonding in the *p*-chloroanilinium salts, carbon–chlorine π-bonding in the maleic anhydrides, and inductive effects in thiophen due to an increased electro-negativity of sulphur, brought about by promotion of a $3p$ electron to a $3d$ orbital in forming the appropriate valence state.

IN Part I [1] we described a study of inductive and conjugative effects in chloro-derivatives of nitrogen heterocycles by nuclear quadrupole resonance spectroscopy; here we describe some further studies of compounds containing chlorine attached to unsaturated carbon atoms.

EXPERIMENTAL

The chlorine resonances were observed as described in Part I.[1] Chlorothiophens were prepared by chlorination of thiophen and separated by fractional distillation.[2] *p*-Chloro-anilinium chloride and bromide were prepared from *p*-chloroaniline and the corresponding acid and recrystallised from dilute hydrochloric or hydrobromic acid. Monochloromaleic anhydride (a commercial specimen) and dichloromaleic anhydride (supplied by Imperial Chemical Industries Limited) were used without further purification.

The observed frequencies are shown in the Table.

Observed nuclear quadrupole resonance frequencies.

	Frequency (Mc./sec.)		
Compound	86° K	195° K	Room temp.
p-Chloroanilinium chloride	35·448	35·201	34·939 (297°)
p-Chloroanilinium bromide	34·752	34·636	34·440 (297°)
Chloromaleic anhydride	37·159	36·750	36·283 (297°)
Dichloromaleic anhydride	37·945, 38·013	37·565, 37·593	37·049, 37·065 (297°)
2-Chlorothiophen	A series of medium intensity lines in the region 34—39 Mc./sec.		
2 : 5-Dichlorothiophen	36·669 36·875		
	36·696 37·046		
	36·840 37·078		
2 : 3 : 4 : 5-Tetrachlorothiophen	37·517 38·500		36·906, 36·931
			37·740 (294°)

[1] Part I, Dewar and Lucken, *J.*, 1958, 2653.
[2] Conrad, Hartough, and Johnson, *J. Amer. Chem. Soc.*, 1948, **78**, 2564.

<div align="center">DISCUSSION</div>

It is necessary to decide to what extent it is legitimate to ascribe to purely electronic effects the differences in nuclear quadrupole resonance frequencies between different molecules, when it is known that electrostatic crystalline fields can cause an unpredictable lowering of frequency of up to several megacycles/sec. from that of the molecule in the gas phase.[3]

The number of molecules whose nuclear quadrupole coupling frequencies have been measured by microwave spectroscopy as well as by direct nuclear quadrupole resonance is unfortunately so small that no general conclusions can be drawn. It is therefore profitable to consider those compounds in which multiple resonances occur and in which no extraordinary factor, such as hydrogen-bonding, can account for this multiplicity. Results for compounds as varied as the Group IV tetrachlorides [4] and the polychlorobenzenes [5] show that splittings of up to 0·6 Mc./sec. are possible although in most cases they are not greater than 0·3 Mc./sec. A further indication of magnitude of solid-state effects can be obtained from the correlation between the Hammett function and the nuclear quadrupole resonance frequencies of substituted chlorobenzenes where the standard deviation between observed resonance frequencies and those predicted by the linear relationship derived by Bray and Barnes [6] is 0·36 Mc./sec. These facts, in conjunction with the success of pure quadrupole resonance measurements in demonstrating inductive effects in the alkyl halides,[4] indicate that a difference of more than 0·5 Mc./sec. between the chlorine nuclear quadrupole frequencies of two molecules is very probably due to electronic effects. This " limit of confidence " is considerably reduced when comparisons are being made between two *series* of different molecules.

The chlorine nuclear quadrupole resonance frequencies for the two salts of *p*-chloroaniline are much higher than that for the free base [7] (34·146 Mc./sec. at 77° K). Protonation of the amino-group can have several consequencies: (*a*) protonation will destroy the conjugative ($-E$) effect of the nitrogen which normally leads to an increased π-electron density at the *para*-carbon atom; (*b*) protonation will increase the inductive ($+I$) effect of nitrogen, and the resulting polarisation of the π-electrons will decrease the charge density at the *para*-carbon atom; (*c*) the increased electronegativity of nitrogen on protonation will, by a relayed (inductoelectromeric [8]) effect, increase the degree of π-bonding between chlorine and the ring. Now effects (*a*) and (*b*) will lead to a decrease in negative charge at the *para*-carbon atom, and so to a decrease in σ-bond polarity of the C–Cl bond and a consequent increase in nuclear quadrupole resonance frequency; effect (*c*) will lower [1] this frequency. The observed frequencies imply that the former effects predominate.

It is interesting that the frequencies for the two salts differ markedly, that for the hydrochloride being much the greater. This difference is most probably due to differences in hydrogen-bonding between the ammonium groups and halide anions in the salts. Such hydrogen-bonding will reduce the effective positive charge at the nitrogen atom and so lower its electronegativity; the argument of the previous section implies that there should be a corresponding increase in polarity of the C–Cl σ-bond, and a corresponding decrease in π-bonding between chlorine and the ring. Since the former effect will raise, and the latter lower, the quadrupole resonance frequency, one cannot be sure what the net effect will be. One cannot tell from the observed frequencies whether hydrogen-bonding is greater in *p*-chloroanilinium chloride or in the bromide—only that there must be a difference. We are investigating this problem further, for such measurements offer a most interesting method for studying hydrogen bonds in such salts.

[3] Allen, *J. Phys. Chem.*, 1953, **57**, 502.
[4] Livingstone, *J. Phys. Chem.*, 1953, **57**, 496.
[5] Bray, Barnes, and Bersohn, *J. Chem. Phys.*, 1956, **25**, 813.
[6] Bray and Barnes, *J. Chem. Phys.*, 1957, **27**, 551.
[7] Heal, *J. Amer. Chem. Soc.*, 1952, **74**, 6121.
[8] Brown and Dewar, *J.*, 1953, 2406.

The frequencies of the mono- and di-chloromaleic anhydrides can be predicted approximately as follows. The frequencies at 20° K for vinyl chloride [9] (33·6 Mc./sec.) and for *cis*-dichloroethylene [4] (35·0 Mc./sec.) are known; the frequencies at 87° K will be about 0·2 Mc./sec. lower. The effect of the α-carbonyl group in the anhydride can be estimated approximately from the difference (2·3 Mc./sec.) between the nuclear quadrupole resonance frequencies for chloroacetic acid [3] and methyl chloride; [4] and that of the β-carbonyl group from the corresponding difference (1·8 Mc./sec.) between *o*-chlorobenzoic acids and chlorobenzene.[6] Together, these comparisons suggest that the nuclear quadrupole resonance frequency for a chloromaleic anhydride should be 2·3 + 1·8 = 4·1 Mc./sec. greater than that for the corresponding chloroethylene. The predicted frequencies for mono- and dichloromaleic anhydride at 86° K are therefore 37·5 Mc./sec. and 38·9 Mc./sec. respectively, values which are greater than those observed (37·2 and 38·0 Mc./sec. respectively). These differences suggest that C–Cl π-bonding is greater in the anhydrides, for such π-bonding lowers the frequency; this is what one might expect in view of our work on chloro-derivatives of heterocycles, for the more electrophilic character of the C=C bond in maleic anhydride should lead to an increase in π-bonding to chlorine.

The frequencies of the thiophen compounds are interesting in that they seem to be much higher than those for the corresponding benzene derivatives (chlorobenzene, 34·622 Mc./sec.; *p*-dichlorobenzene, 34·779 Mc./sec.; 1 : 2 : 3 : 4-tetrachlorobenzene, 37·557, 37·455, 37·013 Mc./sec.).[5] This is surprising, for sulphur and carbon are thought to have closely similar electronegativities (2·5 on the Pauling scale). The difference cannot reasonably be ascribed to decreased π-bonding in the chlorothiophens, for since vinyl chloride has a lower frequency (33·4 Mc./sec.) than chlorobenzene, any decrease in aromatic character in thiophen as compared with benzene should if anything lower the nuclear quadrupole resonance frequency.

The electronic structure of thiophen has been discussed by Longuet-Higgins,[10] whose conclusions may be briefly summarised: The π-molecular orbitals of benzene can be written as combinations of six ethylenic π-molecular orbitals, three bonding and three antibonding, whose symmetries are indicated in (I) and (II); the resulting molecular orbitals are identical with those given by the usual LCAO approach. Likewise the π-molecular orbitals of thiophen can be constructed from a set of six orbitals, two pairs of ethylenic π-molecular orbitals and a pair of sulphur orbitals, 3*p* (III) and 3*d* (IV).
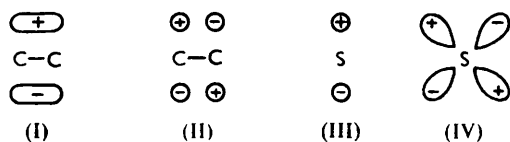
It is obvious from this diagram that the sulphur atomic orbitals resemble the ethylenic π-molecular orbitals in symmetry; they also have similar dimensions and binding energies. This representation therefore explains very clearly the close resemblance between benzene th ophen. As a result the π-electrons are uniformly shared between the six orbitals, so that the mean π-electron charge density is unity at each carbon atom and two at sulphur. This argument suggests that any differences between benzene and thiophen in π-electron distribution at the carbon atoms are small; the differences in nuclear quadrupole resonance frequencies for the chloro-derivatives cannot therefore be explained in terms of π-electron distributions.

However, this analysis requires the sulphur atom in thiophen to be in an excited valence state, with one 3*p* electron promoted into a 3*d* orbital. Since the screening effect of 3*d* electrons is small, the effective electronegativity of sulphur, as regards the 3*s* and 3*p* electrons,

[9] Livingstone, *J. Chem. Phys.*, 1951, **19**, 1613.
[10] Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 173.

will be increased; indeed, Slater's rules imply an increase in effective nuclear charge of 0·35 unit for the $3s$ and $3p$ electrons. This will lead to a strong inductive polarisation (C —➤ S) of the C–S σ-bond, formed by a $3s$–$3p$ orbital, and this by a relayed inductive effect will lead a decreased σ-bond polarity (and increased nuclear quadrupole resonance frequency) for the C–Cl bonds in the chlorothiophens.

A similar change in electronegativity must occur in other compounds where sulphur atoms use d orbitals to form bonds; the very strong inductive effect of the sulphonyl group may be due largely to this.

Since the publication of Part I, our attention has been drawn to the paper by Kojima *et al.*[11] in which piezoelectric resonances in a variety of inorganic compounds were reported. The radiofrequency spectra here observed consisted of a series of sharp resonances occurring over a considerable frequency range—some tens of megacycles— and in which one or more series obeying an interval-rule could be detected. It is probable that the multiple resonances of 2 : 4 : 6-trichloropyrimidine and of 2-chlorothiophen should be ascribed to this cause rather than to any randomness in the orientation of molecules in the crystal.

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[11] Kojima, Tsukada, Ogawa, and Shimauchi, *J. Phys. Soc. Japan*, 1955, **10**, 265.