544. *Chemical Applications of Nuclear Quadrupole Resonance Spectroscopy. Part I. Some Chloro-derivatives of Nitrogen Heterocycles.*

By M. J. S. DEWAR and E. A. C. LUCKEN.

Nuclear quadrupole resonance spectra of a number of chloro-derivatives of pyridine, pyrimidine, 1 : 3 : 5-triazine, and quinoline have been measured with a frequency-modulated externally quenched, super-regenerative spectrometer. The observed frequencies indicate appreciable π-bonding between chlorine and the ring, more than in the isoconjugate benzene and naphthalene derivatives. Inductive effects are also important, but appear to be mainly of short range, transmitted through the σ-bonds. The theoretical implications are discussed.

NUCLEAR quadrupole resonance spectroscopy provides a novel and promising method for investigating the electron distributions in molecules. Radio-frequency absorption due to nuclear quadrupole resonance transitions was first observed in 1950 by Dehmelt and Kruger [1] and a number of papers have since been published on this field. Such transitions are possible whenever a nucleus of spin at least unity is surrounded by an electron cloud which is not completely symmetrical. In this case the nucleus must orient itself relatively to the electron cloud in one of $(2I + 1)$ ways, where the spin of the nucleus is I. If $I > \frac{1}{2}$, the nucleus will not in general be spherically symmetrical, but will possess a quadrupole moment; the electrostatic interaction between the unsymmetrical nucleus and the unsymmetrical electron cloud will depend on their mutual orientation, and so the various orientational states have different energies. Transitions between them can, as usual, be induced by electromagnetic radiation, but the frequencies are so low that they lie in the radio region, usually in the range 1—1000 Mc./sec. The energy differences are functions of the quadrupole moment of the nucleus and the asymmetry of the electron distribution; the transition frequencies for a given nucleus in different molecules are therefore a measure of the electronic asymmetry, and it can be shown that the only significant contribution to this arises from the p-electrons present.[2] Consequently measurements of nuclear quadrupole resonance frequencies provide information concerning the distribution of p-electrons in molecules—information which cannot be obtained directly in any other way and is of great interest in the case of conjugated systems in organic molecules. The mathematical theory has been well reported by Ramsey.[3]

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[1] Dehmelt and Kruger, *Naturwiss.*, 1951, **37**, 111.

[2] Townes and Dailey, *J. Chem. Phys.*, 1949, **17**, 782.

[3] Ramsey, " Nuclear Moments," Wiley, New York, 1954.

Measurements of this kind have been used mainly to study inductive effects and hybridisation in σ-bonds. The number of " organic " atoms that possess spins of unity or greater is unfortunately limited, and most of the work has been confined to halogen derivatives. Halide ions are spherically symmetrical and show no nuclear quadrupole resonance transitions; in covalent compounds RX, the halogen has effectively seven valency electrons (six unshared electrons and a half share in the pair forming the bond), one less than in the ion X^-. The resulting asymmetry gives rise to nuclear quadruple resonance transitions. If the bond $R \longrightarrow X$ is polar, as indicated, X will have effectively more than seven valency electrons; the electronic asymmetry is then less, and so the nuclear quadrupole resonance frequency is also lowered. For a variety of alkyl chlorides, for example, the frequencies of chlorine run parallel[4] to the expected inductive effect of the alkyl group.

One application of this idea concerns the chlorine and bromine frequencies in substituted chloro- and bromo-benzenes. In each case the nuclear quadrupole resonance frequency follows the Hammett relation.[5] This would be expected, since the Hammett σ-constant provides a measure of the change in inductive effect of phenyl due to substituents. For chlorine, the observed relation is:

$$f = 1{\cdot}0248\sigma + 34{\cdot}826\ (\pm 0{\cdot}36) \quad \ldots\ldots\ldots \quad (1)$$

where f is the observed nuclear quadrupole resonance frequency in Mc./sec.

When the halogen is attached to an unsaturated system, π-bonding is possible between halogen and the adjacent carbon atom. Moderate π-bonding can be shown to lower the nuclear quadrupole resonance frequency; this accounts for the fact that the chlorine frequencies in chlorobenzene[5] (34·6 at 76° K) and vinyl chloride[6] (33·6 at 20° K) are similar to those in alkyl chlorides (31—34 Mc./sec. at 96° K) although the sp^2-carbon atoms in the former are much more electronegative than the sp^3-carbon atoms in the latter.

Measurements of nuclear quadrupole resonance frequencies therefore provide a method for studying the distribution of π-electrons in conjugated systems. This paper is the first of a series describing investigations of this kind. In it we report preliminary work on a number of chloro-derivatives of nitrogen-containing heterocycles.

EXPERIMENTAL

Materials.—2-Chloropyridine was distilled before use, and 2- and 6-chloroquinoline were prepared by standard methods.[7] Cyanuric chloride and 2-chlorolepidine were commercial specimens used without purification. A sample of 7-chloroquinoline was lent by May and Baker Ltd. and the pyrimidine derivatives by Imperial Chemical Industries Limited; we gratefully acknowledge their assistance.

Measurements.—The resonances were detected at temperatures ranging from 86° K to room temperature with a frequency-modulated, externally quenched, super-regenerative spectrometer similar to that of Dean,[8] and the spectra were displayed on an oscilloscope whose time-base was locked to the modulation frequency. Resonance frequencies were measured with a war-surplus frequency meter, type BC221, the side bands being distinguished from the fundamentals by carrying out the measurements at two different quench frequencies. The frequencies are thought to be accurate to ±0·001 Mc./sec. Details of the spectrometer and associated equipment are given in a thesis by one of us.[9]

Results.—The observed frequencies are tabulated.

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[4] Livingstone, *J. Phys. Chem.* 1953, **57**, 1792.

[5] Bray and Barnes, *J. Chem. Phys.*, 1957, **27**, 551.

[6] Goldstein and Bragg, *Phys. Rev.*, 1949, **75**, 1943.

[7] Robinson and Perkin, *J.*, 1913, 1977; Fourneau, Trefoud, and Wancolle, *Bull. Soc. chim. France*, 1930, **47**, 738.

[8] Dean, Thesis, Harvard, 1952.

[9] Lucken, Thesis, London, 1958.

Nuclear quadrupole resonance frequencies.

	Frequency (Mc./sec.) at			
Compound	86° K	195° K	276° K	Room temp.
2-Chloropyridine	34·173	—	—	—
2-Chloroquinoline	33·287	33·102	32·939	32·874 (297°)
6-Chloroquinoline	34·600	34·334	34·132	34·057 (297°)
7-Chloroquinoline	34·681	—	—	—
2-Chlorolepidine	33·655	—	—	33·258 (296°)
2 : 4-Dichloro-3-methylquinoline	34·268	—	—	33·829 (292°)
	35·627	—	—	34·902
4 : 6-Dichloro-2-methylpyrimidine	35·156	34·949	—	34·695 (294°)
5-Benzyl-4 : 6-dichloro-2-methylpyrimidine	35·015	—	—	34·598 (293°)
4 : 6-Dichloro-2-methyl-5-phenylpyrimidine	35·248	—	—	—
6-Amino-2 : 4-dichloro-5-ethylpyrimidine	34·879	—	—	34·260 (292°)
	35·044	—	—	34·488
2 : 4 : 6-Trichloropyrimidine	A series of strong closely spaced lines in the region 30—40 Mc./sec. at 86° K.			
Cyanuric chloride	36·724	36·537	36·346	36·300
	36·752		36·360	36·316

DISCUSSION

Segel, Barnes, and Bray[10] have reported nuclear quadruple resonance frequencies for the first three compounds in the Table, our values agreeing well with theirs (2-chloropyridine 34·194, 2-chloroquinoline 33·271, 6-chloroquinoline 34·628 Mc./sec. at 76° K). Our values for cyanuric chloride also agree well with those reported by Negita and Satou[11] (36·323, 36·338 Mc./sec. at 285° K).

For cyanuric chloride the relative intensities of the lines in the doublet vary with temperature. At high temperatures the higher-frequency line is the weaker, at 84° it is the stronger. Our results suggest that this is due to a difference in variation of frequency with temperature, the lines coinciding near 195° K.

The most striking features of the Table are the low frequencies observed for 2-chloropyridine and 2-chloroquinoline. That for 2-chloropyridine is much less than that (34·6 Mc./sec. at 77° K) reported[6] for chlorobenzene, although the inductive effect of the nitrogen might have been expected to raise the frequency. The difference is too large to be ascribed to the effects of stray fields in the crystal, so one must conclude that the C–Cl bond in chloropyridine has a larger π-order than that in chlorobenzene.

The case of 2-chloroquinoline is probably still more striking, but unfortunately the frequency for 2-chloronaphthalene is not yet known. We tried to obtain a spectrum for this substance but could observe no absorption. However, one can use the observed dissociation constants of 2-naphthylamine ($\mathrm{p}K_b = 4{\cdot}11$ at 25° C) or 2-naphthoic acid ($\mathrm{p}K_a = 4{\cdot}17$ at 25° C) to calculate an effective σ-constant for the β-naphthyl group; the values so found (0·17 and 0·00 respectively) in conjunction with equation (1) lead to a predicted value 34·9 ± 0·4 Mc./sec. for 2-chloronaphthalene. The difference (1·6 Mc./sec.) between this and the value observed for 2-chloroquinoline is much greater than the difference between chlorobenzene and 2-chloropyridine.

The explanation of these differences in terms of π-bonding seems quite reasonable. Measurements of the microwave spectrum of vinyl chloride[12] and of the Zeeman splitting of the nuclear quadrupole resonance spectrum of *p*-dichlorobenzene[13] show that the C–Cl bond in such compounds has a double-bond character of 5—15%. Since the π-bond between chlorine and the ring is a dative π-bond, and since the corresponding charge displacement should be easier in the case of the more electrophilic heterocyclic systems, one would expect the C–Cl π-bond orders to be greater in the 2-chloro-heterocycles.

The difference in nuclear quadrupole resonance frequency between 2-chloroquinoline

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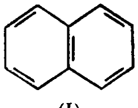
[10] Segel, Barnes, and Bray, *J. Chem. Phys.*, 1956, **25**, 1286.

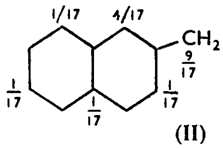
[11] Negita and Satou, *ibid.*, 1957, **27**, 602.

[12] Goldstein and Bragg, *Phys. Rev.*, 1950, **78**, 347.

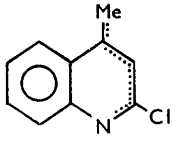
[13] Dean, *ibid.*, 1954, **96**, 1053.

(33·287 Mc./sec.) and 2-chloropyridine (34·173 Mc./sec.) implies that the C–Cl bond order is greater in the former compound. It is true that the β-naphthyl group has a somewhat greater conjugative power than the phenyl group,[14] but the disparity seems too small to account for the large difference (0·886 Mc./sec.). We believe that the difference is due to partial bond-fixation in quinoline. Both theoretical calculation and experiment suggest that naphthalene approximates to the classical structure (I); and the same should be true of quinoline. In that case the conjugative interaction between nitrogen and chlorine in 2-chloroquinoline should be larger than in 2-chloropyridine, since the N=C π-bond order will be larger in the former. Consequently the C–Cl π-bond order should be greater, and the nuclear quadrupole resonance frequency of chlorine less, in 2-chloroquinoline.


(I)



(II)



(III)

This argument implies that the chlorine frequency should be still less in imidoyl chlorides, where the N=C π-bond order is nearly unity; we are investigating this. It is noteworthy in this connection that the chlorine frequencies for acid chlorides[15] (*e.g.*, sebacoyl chloride 29·118; adipoyl chloride 29·978 Mc./sec.) are very much lower than for vinyl chloride[7] (33·6 Mc./sec.), although the carbonyl-oxygen atom must exert a very large inductive effect. Clearly the conjugation in acid chlorides must be strong, as it should be, if our argument is correct.

The chlorine frequencies in 6- and 7-chloroquinoline are very close to the value predicted for 2-chloronaphthalene; this is in accord with the values of the Hammett σ-function for the 6- and the 7-quinolyl group (0·23, 0·24 respectively[16]) which are similar to the value for 2-naphthyl. The effect of nitrogen does not seem to be transmitted to the 6- or 7-position.

One can assess the effect of the nitrogen atom by an approximate method derived by Longuet-Higgins.[17] The chloroquinolines are isoconjugate with the 2-naphthylmethyl anion, in which the formal charge is distributed approximately as in (II). Since the charge is much greater in the 1-position than in the 5- or the 8-position, nitrogen should have a much greater effect in the 1-position (as in 2-chloroquinoline) than in the 5- or 8-position (as in 6- or 7-chloroquinoline). The actual difference will be still greater, for the values in (II) are calculated on the assumption that the C–C bonds are identical; the fixation of bonds in quinoline [cf. (I)] will accentuate the difference between the 1-position and the others.

Any difference in conjugation between 6- and 7-chloroquinoline should, according to (II), make the nuclear quadrupole resonance frequency smaller for the 7-isomer; in fact it is somewhat greater. However, this argument neglects the inductive effect of nitrogen. In the first place this will raise both frequencies by an inductive effect operating through the intervening σ-bonds; and the effect should be more than twice as great[14] in the 7-position as in the 6-position which is one atom further removed from nitrogen. In the second place, the inductive effect will raise the electronegativities of the atoms adjacent to nitrogen and make them behave qualitatively like heteroatoms; when allowance is made for this, the conjugative influence of nitrogen on the 6- and the 7-position is predicted to be much the same.[18]

The frequencies for chlorine in the pyrimidine derivatives are much higher than for

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[14] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3361.
[15] Bray, *J. Chem. Phys.*, 1955, **23**, 703.
[16] Elderfield and Siegel, *J. Amer. Chem. Soc.*, 1951, **73**, 5622.
[17] Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265, 275, 283.
[18] Brown and Dewar, *J.*, 1953, 2406.

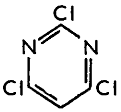
2-chloropyridine; evidently the inductive effects of the extra nitrogen and chlorine atoms outweigh any increase in conjugation due to the extra nitrogen atom. The same is true for cyanuric chloride, the chlorine frequencies being much higher than those for any of the pyrimidine derivatives. A comparison of the frequencies for 4 : 6-dichloro-2-methylpyrimidine with those for its 5-phenyl and 5-benzyl derivative indicates that phenyl exerts a small $+I$ effect, benzyl a small $-I$ effect, as current theory and the values of the corresponding σ-constants [19] suggest.

It is therefore surprising that the nuclear quadrupole resonance frequency for 2-chlorolepidine (33·655 Mc./sec.) is greater than for 2-chloroquinoline (33·287 Mc./sec.). We think this can be ascribed to mutual conjugation between the methyl group and the nitrogen atom, which tends to even out the bond orders in the nitrogen-containing ring, as indicated in (III), and so lower the order of the 1 : 2-bond. If we are correct in assuming that the very low chlorine frequency in 2-chloroquinoline is due to a high 1 : 2-bond order, any decrease in the order of this bond should raise the nuclear quadrupole resonance frequency.

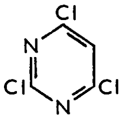
Further evidence for the bond fixation is provided by 2 : 4-dichloro-3-methylquinoline, where the two chlorine frequencies presumably correspond to the two dissimilar chlorine atoms. The inductive effects of the 3-methyl group and the 4-chloro-atom on the 2-chlorine atom can be estimated from the results for the pyrimidines. For 5-benzyl-4 : 6-dichloro-2-methylpyrimidine, the effect of the distant methyl group and the 1-nitrogen atom on the 4-chlorine atom must be small. The main inductive effects arise from the 3-nitrogen atom, the 5-benzyl group, and the 6-chlorine atom. The difference in total inductive effect between the pyrimidine and 2-chloropyridine is then essentially that of an *o*-alkyl group and a *m*-chlorine atom; the corresponding difference in frequency is 0·842 Mc./sec. The difference between the 2-chlorine frequencies in 2-chloroquinoline and 2 : 4-dichloro-3-methylquinoline should therefore be about 0·85 Mc./sec., since the same inductive grouping is involved. This identifies the line at 34·268 Mc./sec. with the 2-chlorine atom (difference from 2-chloroquinoline, 0·895 Mc./sec.), and the line at 35·627 Mc./sec. with the 4-chlorine atom (difference from 2-chloroquinoline, 2·340 Mc./sec.). Now if the difference between the two chlorine frequencies were due to inductive effects, one would expect the 4-chlorine atom to have the lower frequency, for the 2-chlorine is nearer to the nitrogen. If all the bonds in the ring were similar, one would expect the conjugative effect to be greater in the 4-position, and this would also lead to a lower frequency for the 4-chlorine atom. In fact the frequency for the 4-chlorine is very much the higher. The only reasonable explanation seems to be that partial bond-fixation in quinoline [cf. (I)] isolates the 4-chlorine atom from the nitrogen atom; the C–Cl π-bond order is therefore greater, and the frequency consequently less, for the 2-chlorine atom.

Unfortunately no physical data (structure determinations or C–Cl bond stretching frequencies) have been reported which would enable one to deduce the relative C–Cl bond orders in 2- and 4-chloroquinoline. However the much greater chemical reactivity of chlorine in the 4-isomer may be partly due to a lower C–Cl bond order and consequent lower conjugation energy.

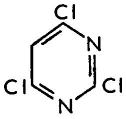
The spectrum of 2 : 4 : 6-trichloropyrimidine, unlike those of the isoconjugate 1 : 3 : 5-trichlorobenzene or cyanuric chloride, contains a multitude of lines covering a wide frequency range. This can probably be attributed to the asymmetry of the pyrimidine derivative. The orientations (IV), (V), (VI) are not identical for the solid state, but differ very little in geometry. We think it likely that the molecules are in consequence packed



(IV)



(V)



(VI)

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[19] Jaffe, *Chem. Rev.*, 1953.

randomly in the crystal, just like the molecules in crystals of nitric oxide. Each chlorine can therefore find itself in one of a number of possible environments; and each environment gives rise to a different chlorine frequency. We are examining trichloropyrimidine in a spectrometer of a different type, where it should be possible to resolve the individual lines, and we shall also examine 2 : 4 : 6-trichloropyridine, which should show similar behaviour, in the hope of relating the number of observed lines to the structure of the crystal.

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QUEEN MARY COLLEGE, MILE END ROAD, LONDON, E.1.

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