# *Studies on Carbon-Chlorine Bonds in Some Aromatic Compounds by Their Pure Quadrupole Spectra*

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Pure quadrupole spectra of many chlorine compounds have been reported so far and their resonance absorption frequencies or nuclear quadrupole coupling constants have been interpreted from various points of view[1]. Some years ago, Meal[2] found a nearly linear relationship between the frequencies and Hammett's $\sigma$ of various substituents in monosubstituted chlorobenzene. Later, the same result as this has been recognized also in bromobenzene, iodobenzene[3], and dichlorobenzene[4].

In this paper we studied other effects on the frequencies, that is, the frequency shifts which resulted from replacement of one or more carbon atoms in the benzene ring by the corresponding numbers of nitrogen atoms. The compounds used for comparison were chlorobenzene, 2-chloropyridine, 1, 3, 5-trichlorobenzene, and cyanuric chloride. As the frequencies due to $^{35}Cl$ of the first three compounds were already known[5-7], we measured only those of the last, which were closely spaced and higher than those of trichlorobenzene. This result is evidently contrary to that of chloropyridine, where its frequency is lower than that of chlorobenzene. However, these opposing phenomena due to nitrogen atoms may be correlated with each other by the theoretical consideration, for the decrease of $\pi$-electron density at chlorine atoms, which accompanies that of $\sigma$-electron necessarily, is much more remarkable in the former than in the latter, compared to the increase of bond order of carbon-chlorine bonds.

## Experimental

**Sample.**—To obtain cyanuric chloride $(CNCl)_3$, cyanuric acid $(CNOH)_3$ was prepared from urea and anhydrous zinc chloride, and then it was chlorinated by phosphorus pentachloride in phosphorus oxychloride as the solvent[8,9]. The product was purified by recrystallization from chloroform and then by sublimation in a long test tube. The sample thus obtained melted around 146°C, which was in good agreement with the value already known.

**Apparatus.**—The resonance absorption frequencies due to $^{35}Cl$ were measured by the frequency modulated super-regenerative spectrometer described in the previous paper[4,10] and was ascertained by those due to $^{37}Cl$, which should be found at the lower frequency region[11]. To obtain the data at lower temperature, solid carbon dioxide and toluene were used as the freezing mixture, and the temperature was measured with copper-constantan and a potentiometer.

The experimental error in frequency would be introduced from reading off both frequency and temperature of the sample, and amounts to several kilocycles/sec., which might not be so serious in the following considerations.

## Results and Discussions

The experimental results are shown in Table I. From this table, it is seen that two resonance absorption lines are so closely spaced, especially at a lower temperature, that they are observed without any interferences from side bands.

TABLE I

NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES ($\nu$) DUE TO $^{35}Cl$ OF CYANURIC CHLORIDE

| Temp. | 195°K | 285°K |
|---|---|---|
| $\nu$ (Mc./sec.) | 36.533—Weak | 36.323—Strong |
| | 36.537—Strong | 36.338—Weak |

At room temperature, 285°K, the lower line was much stronger than the other, which would tell the fact that the chlorine atoms corresponding to the former are

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are more abundant than the others, the ratio presumanbly being 2 : 1. However, the situation is reversed at 185°K. Thus, it may be concluded that the two lines are different from each other in the temperature gradient and they seem to overlap at some intermediate temperature, or else there are some transition points. In spite of this extraordinary behavior, our present interest is in the following fact.

The average value of the frequencies of cyanuric chloride is higher than that of trichlorobenzene, taking account of the temperature effect. To see this more precisely, the two average values in Table I were extrapolated to 77°K and about 36.725 Mc./sec. was obtained as the value at that temperature. It is obviously higher than that of trichlorobenzene(7) and this fact is contrary to the case of 2-chloropyridine(6) and chlorobenzene(5).

For comparison, the frequencies of these compounds are tabulated in Table II. At first sight, the replaced nitrogen atom in the ring will be thought to attract more electrons from the chlorine atom, with the result that the electron density around the latter is decreased, which in turn increases the frequency. However, this is not the case in the first row of Table II. Accordingly, the decrease in the frequency may be attributed to the increase in double bond character induced simultaneously, as pointed out by Segel et al.(6)

TABLE II
NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES ($\nu$) DUE TO $^{35}$Cl OF SOME AROMATIC COMPOUNDS AT 77°K

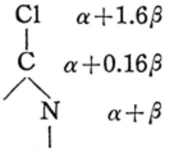
| Compd. | $\nu$ (Mc./sec.) | Compd. | $\nu$ (Mc./sec.) |
|---|---|---|---|
| Chlorobenzene | 34.6216 | 2-Chloropyridine | 34.194 |
| 1, 3, 5-Trichlorobenzene | 35.851 (Average) | Cyanuric chloride | 36.725 (Average) |

On the contrary, the increase in the frequency in the second row is supposed to result from the decrease in electron density, compensating the increase in the double bond character of carbon-chlorine bond. As a rule, circumstances around a molecule in the solid are more complex than in the vapor, owing to the neighboring molecules. However, such compounds as listed in the same row of Table II may be compared with each other by their isolated molecules, since they form molecular crystals alike in size and shape. Thus it will be worth while to examine the data of pure quadrupole spectra with reference to electronic structures computed from molecular orbital theory.

Now the ionic character and double bond character of carbon-chlorine bond may be considered in terms of $\pi$-electron density ($q$) at chlorine atom and mobile bond order ($p$) of the bond, respectively(12). These two quantities are calculated in Table III for the compounds concerned.

TABLE III
$\pi$-ELECTRON DENSITIES ($q$) AT CHLORINE ATOMS AND MOBILE BOND ORDERS ($p$) OF CARBON CHLORINE BONDS

| Compd. | $q$ & $p$ | Compd. | $q$ & $p$ |
|---|---|---|---|
| Chlorobenzene | $q=1.9225$<br>$p=0.2728$ | 2-Chloropyridine | $q=1.9084$<br>$p=0.3391$ |
| 1, 3, 5-Trichlorobenzene | $q=1.9209$<br>$p=0.2744$ | Cyanuric chloride | $q=1.8650$<br>$p=0.4167$ |

Parameters adopted in calculation are as follows. Coulomb integrals are such that 

and resonance integral of C—Cl is 0.8 $\beta$, where $\alpha$ and $\beta$ are the Coulomb and the resonance integral in benzene, respectively.

As seen in Table III, the decrease in the $\pi$-electron density at chlorine atom in the second row amounts to about four times as much as that of the first row, whereas the increase in carbon-chlorine bond order in the former is only twice as large as that of the latter. From these figures, the resonance frequency may decrease or increase as illustrated in Fig. 1,

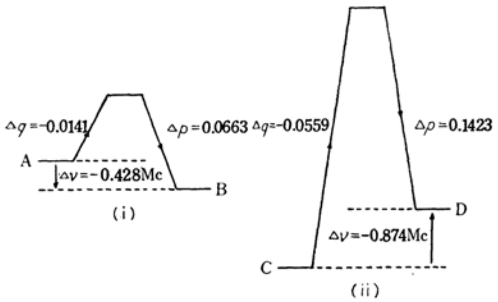


Fig. 1. Correlation of molecular constants and nuclear quadrupole resonance frequencies due to $^{35}$Cl.
(i) A···chlorobenzene,
B···2-chloropyridine.
(ii) C···1, 3, 5-trichlorobenzene,
D···cyanuric chloride.

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where A, B, C and D represent chlorobenzene, 2-chloropyridine, 1, 3, 5-trichlorobenzene, and cyanuric chloride, respectively.

It may be noted that the decrease in the $\pi$-electron density at a chlorine atom accompanies the decrease in the $\sigma$-electron and results in an increase in the frequency. As seen in Fig. 1, this increase is assumed for convenience to be proportional to the decrease in the former, for there is no straightforward way to compute the latter, but the frequency shifts are not so large in our cases. Thus, from the simplified schemes, it follows that $\Delta\nu/\Delta q \simeq -69$ Mc./sec. and $\Delta\nu/\Delta p \simeq -21$ Mc./sec..

The absolute value of the former is relatively large, though it includes the effect of the $\sigma$-electron. However, it is very difficult to justify the value. Thus it will be fair only to say that there is considerable transfer of the $\sigma$-electron accompanied with the $\pi$-electron. On the other hand, the latter value may be accepted easily, for it is near to the value $-27.4$ Mc./sec., which is computed as follows. From the experimental value of the coupling constant of free chlorine atom[13] and the number of unbalanced $p$-electrons, the frequency is assumed to be 54.8 Mc./sec. for pure —Cl state and $54.8\times\frac{1}{2}=27.4$ Mc./sec. for $=\mathrm{Cl}^+$, while the bond order is 0 for the former and 1 for the latter, so that $\Delta\nu/\Delta p = -27.4$ Mc./sec. when $\Delta p=1$. It will be interesting to see whether the above relations might hold also in other cases, or not.

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