The Zeeman Effect of ^{35}Cl Nuclear Quadrupole Resonance Spectra in *p*-Chlorophenol

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The Zeeman effect of the ^{35}Cl nuclear quadrupole resonance spectrum was studied on a single crystal of *p*-chlorophenol in order to obtain information about the crystal and molecular structures in the solid state and in order to explain the doublet separation of the spectrum.1)

A commercial product was distilled and then purified by zone-melting before use; the single crystal was prepared by Bridgeman's method. The Zeeman effect was observed at room temperature by means of a superregenerative spectrometer and a goniometer equipped with a Helmholtz coil.

Two zero-splitting loci, for each element of the doublet, ν_1 and ν_2, were obtained. This suggests that the unit cell is composed of four molecules.

The asymmetry parameters obtained are listed in Table I. Asymmetry parameters in several chlorobenzene derivatives have been obtained by the studies of the Zeeman effect: for example, 0.08 in *p*-dichlorobenzene,2) 0.06 in *p*-chloroaniline,3) and 0.08 in *p*-chlorobenzoic acid.4) In comparison with these values, the η_1 value of the present molecule is considerably larger. This indicates that two of the four chlorine nuclei in the unit cell are placed in an unusual intermolecular interaction, such as hydrogen bonding.

The double-bond character, the ionic-bond character, and the single-bond character of the C–Cl bond in *p*-chlorophenol were evaluated by the method proposed by Townes and Dailey5) and developed by Bersohn,6) from the asymmetry parameter, η_2, and the resonance frequency, ν_2, extrapolated to 0°K. In this calculation, we used the values of 0.155) for the *s*-characters of the σ and π bonds, and of 0.157) for the screening correction for a positive formal charge at the chlorine atom. The results are shown in Table I.

The double-bond character thus evaluated is plotted against Hammett's σ-value in Fig. 1, together with the findings for other chlorobenzene derivatives without an ortho substituent. It may be concluded from the linear correlation in the figure that the double-bond character becomes larger as the substituent is more electron-attractive. A future study of the electronic structure of chlorobenzene derivatives with reference to this correlation seems of interest. A similar correlation has already been obtained for iodobenzene derivatives.8)

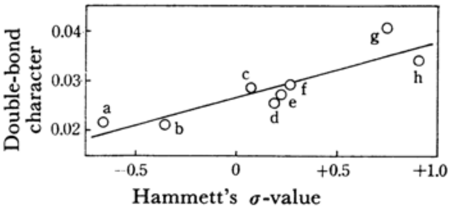

Fig. 1. Relation between double-bond character and Hammett's σ-value

a) *p*-Chloroaniline: Ref. 3. b) *p*-Chlorophenol: Present work. c) 2, 5-Dichloroaniline: T. Sakurai, M. Sundaralingam and G. A. Jeffrey, *Acta Cryst.*, **16**, 354 (1963). d) *p*-Chlorobenzyl chloride: Ref. 3. e) *p*-Dichlorobenzene: Ref. 2. f) *p*-Chlorobenzoic acid: Ref. 4. g) 1, 3, 5-Trichlorobenzene: Y. Morino and M. Toyama, *J. Phys. Soc. Japan*, **15**, 288 (1960). h) 1, 4-Dichloro-2-nitrobenzene: V. Nagarajan and C. R. Murty, *Current Science*, **6**, 254 (1963)

TABLE I

Resonance frequency (17°C)	ν_1=34.367 Mc./s.	ν_2=34.145 Mc./s.
$\lvert e^2 Qq \rvert$ (0°K)	—	69.565 Mc./s.
Asymmetry parameter	η_1=0.223±0.035	η_2=0.058±0.013
Double-bond character	—	0.021
Ionic-bond character	—	0.243
Single-bond character	—	0.736

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1) C. Dean and R. V. Pound, *J. Chem. Phys.*, **20**, 195 (1952).

2) C. Dean, *Phys. Rev.*, **86**, 607 (1952).

3) H. C. Meal, *J. Chem. Phys.*, **24**, 1011 (1956).

4) S. Ogawa and K. Ohi, *J. Phys. Soc. Japan*, **15**, 1064 (1960).

5) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

6) R. Bersohn, ibid., **22**, 2078 (1954).

7) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Co., Inc., New York (1955), p. 239.

8) M. Kubo and Y. Kurita, *Kagaku* (*Chemistry*), **12**, 566 (1957)) obtained the correlation by using the data given by G. W. Ludwig (*J. Chem. Phys.*, **25**, 159 (1956)).