Studies on the Electronic Structures of 2,5-Dichloroaniline and 2,5-Dichloronitrobenzene by Their Pure Quadrupole Spectra

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Since Dehmelt and Krüger(1) succeeded in observing the pure quadrupole spectrum due to Cl^{35} and Cl^{37} of *trans*-1,2-dichloroethylene, many workers have reported spectra of various chlorine compounds, a few of them, however, from chemical viewpoints.

Among them, Meal(2) has pointed out that there is a rough linearity between Hammett's σ(3) of substituents and the resonance absorption frequencies in the spectra of several monosubstituted chlorobenzenes. But, as the absorption frequencies of *p*-nitrochlorobenzene and *o*- and *m*-chloroaniline have not so far been observed, i. e., data of the corresponding isomers of the two series have been missed, the electronic behaviors of amino- and nitro-groups in the benzene ring can not be compared with each other by the spectra of monosubstituted chlorobenzenes.

So we studied those of 2,5-dichloroaniline and 2,5-dichloronitrobenzene, each of which was observed at 77°K independently by Weatherly et al.(4), and by Bray et al.(5), and both of which were observed at 292°K by us.

Experimental

As pointed out by several workers,(1,6) the absorption frequency ν of chlorine compounds is expressed as follows, provided that the electronic distribution around the chlorine nucleus is axially symmetric:

$$\nu = |eqQ|/2h,$$

where e is the proton charge, q the electric field gradient at the nucleus, Q the nuclear quadrupole moment of the atom, which is negative,(7) and h Planck's constant. As the moment Q is regarded as constant in each compound, ν may be con-

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1) H. G. Dehmelt and H. Krüger, *Z. f. Physik*, **129**, 401 (1951).

2) H. C. Meal, *J. Am. Chem. Soc.*, **74**, 6121 (1952).

3) L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co. Inc., New York, N. Y. (1940), p. 188.

4) T. L. Weatherly and Q. Williams, *J. Chem. Phys.*, **21**, 2073 (1953).

5) P. J. Bray and P. J. Ring, *J. Chem. Phys.*, **21**, 2226 (1953).

6) H. C. Allen, *J. Phys. Chem.*, **57**, 501 (1953).

7) C. H. Townes and S. Geschwind, *Phys. Rev.*, **74**, 626 (1948).

sidered to be proportional to q, which, by its definition, has a maximum value in the pure covalent bond and is zero in the pure ionic. Accordingly, it is only necessary to determine ν in order to have an insight into the electronic structures of the chlorine compounds.

Apparatus.—To find the absorption frequencies, we used the frequency-modulated super-regenerative spectrometer,[1] its main oscillator being shown in Fig. 1. The frequencies generated were between about 25 Mc. and 38 Mc., for the absorption frequencies of the most organic chlorine compounds are known to lie in this range.

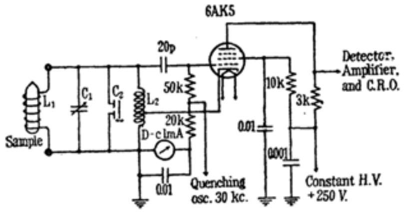


Fig. 1. Main oscillator of the spectrometer.
L_1; removable, ca. 1μH., L_2; fixed, ca. 1μH., tap being variable, C_1; variable, max. 50 pF., C_2; vibrating for freq. modulation.

For the frequency measurement, both the heterodyne frequency meter and the crystal oscillator of 1 Mc. were used. The experimental error was several kc., which was not serious in the following considerations.

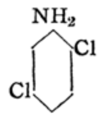
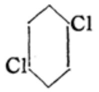
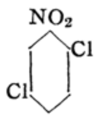
Samples.—2,5-Dichloronitrobenzene and 2,5-dichloroaniline were prepared by nitration and successive reduction of *p*-dichlorobenzene[8]. These compounds were recrystallized to the constant melting points, 54°–55° and 50°C respectively.

The *p*-dichlorobenzene used as the reference material was commercial pure grade.

Results and Considerations

Results obtained are shown in Table I. The absorption lines of the two *p*-dichlorobenzene derivatives are more feeble than that of *p*-dichlorobenzene itself, the reason for which is not evident.

TABLE I
RESONANCE ABSORPTION FREQUENCIES DUE TO Cl^{35} OF *p*-DICHLOROBENZENE AND ITS DERIVATIVES (292°K)

Compounds			
Resonance freq. (Mc.)	33.927 (2) 34.044 (5)	34.286 (1,4)	35.545 (5) 37.290 (2)

In this Table, the numbers in the brackets stand for ordinal numbers of chlorine atoms in the benzene ring. These numbers were assigned in reference to the data of absorption frequencis of Cl^{35} in *o*- and *m*-nitrochlorobenzene (37.260 and 35.457 Mc. respectively[2]) and Br^{81} in *o*- and *m*-bromoaniline (220.255 and 222.614 Mc. respectively[9]) at 77°K; there were no available data of *o*- and *m*-chloroaniline to identify the lines of 2,5-dichloroaniline.

The lower values of frequencies of 2,5-dichloroaniline compared with that of *p*-dichlorobenzene indicate that the amino-group in the benzene ring releases elctrons, and more powerfully towards the *o*-position than towards the *m*-position. On the contrary, the greater values of 2,5-dichloronitrobenzene indicate that the nitro-group attracts electrons, and preferentially from the *o*-position; while the unique value of *p*-dichlorobenzene results from the fact that the state of the two chlorine atoms in this compound are equivalent, which is different from the cases of the other two derivatives.

These facts are in good agreement with the views of the "Electronic Theory of Organic Chemistry" by Robinson and Ingold and the results obtained from data of the dipole moments of amino- and nitro-groups[10]. Though the former is rather qualitative and the latter indirect, the quadrupole data show explicitly the state of electron shift.

Meal[3] suggested that there was a linear relation between resonance absorption frequency ν due to Cl^{35} and Hammett's σ of a substituent in monosubstituted chlorobenzene. We examined whether this relation existed or not in the *p*-dichlorobenzene derivatives, and found that there was a more excellent linearity between them, although the value of Hammett's σ for Cl (2) in the 2,5-dichloroaniline was not seen. These results are shown in Table II and Fig. 2.

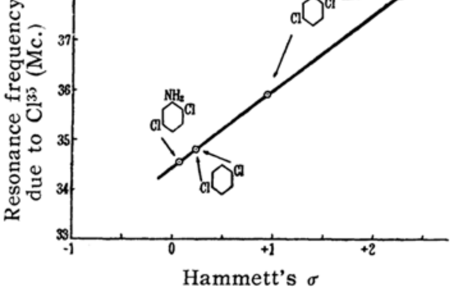


Fig. 2. Relation between the resonance absorption frequencies due to Cl^{35} and Hammett's σ of the substituents in *p*-dichlorobenzene and its derivatives.

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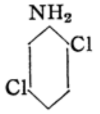
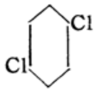
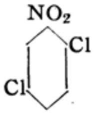
[8] E. Jungfleisch, *Ann. chim.*, [4], **15**, 257, 259 (1868).

[9] P. J. Bray, *J. Chem. Phys.*, **22**, 950 (1954).

[10] L. F. Fieser and M. Fieser, "Textbook of Organic Chemistry", Maruzen Publishing Co. Ltd., Tokyo, (1952), p. 449.

TABLE II
RESONANCE ABSORPTION FREQUENCIES AT 0°K AND HAMMETT'S σ OF p-DICHLOROBENZENE AND ITS DERIVATIVES

Compounds					
Positon of Cl	Cl (2)	Cl (5)	Cl (1, 4)	Cl (2)	Cl (5)
Hammett's σ	o-NH$_2$? p-Cl +0.227 ?	m-NH$_2$ −0.161 p-Cl +0.227 +0.066	p-Cl +0.227 +0.227	o-NO$_2$ +2.03 p-Cl +0.227 +2.257	m-NO$_2$ +0.710 p-Cl +0.227 +0.937
Resonance freq. at 0°K (Mc.)	34.42	34.55	34.80	37.92	35.92

In Table II, the value of Hammett's σ of o-nitro-group was taken from Meal's data and the resonance absorption frequencies at 0°K were obtained to ignore effects of lattice vibrations, by extrapolating the data[4,5] at 77°K and our data at 292°K, referring to the curve of p-dichlorobenzene. Assuming the linearity between ν and σ, we may compute σ of o-amino-group as -0.26 from Fig. 2.

Summary

The pure quadrupole spectra of 2,5-dichloroaniline and 2,5-dichloronitrobenzene were observed at room temperature (292°K), and the effects of electron releasing or attracting power of amino- and nitro-group in the benzene ring were compared with each other. On the other hand, a linear relation between resonance absorption frequencies due to Cl^{35} and Hammett's σ of the substituents in these compounds was found, and Hammett's σ of o-amino-group was assumed to be -0.26. We are indebted to Prof. T. Ichikawa and Prof. D. Nakae for their generarity in granting us the use of their facilities, and to Prof. T. Kawano for the loan of the frequency meter.

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