Assignments of the ^{35}Cl Nuclear Quadrupole Resonance Spectra in Multichlorobenzenes by the Measurement of the Zeeman Effect

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The ^{35}Cl nuclear quadrupole resonance lines in multichlorobenzenes were first assigned by Bray, Barnes, and Bersohn to the chlorine atoms in the molecules[1]. The assignment was, however, based on the assumption that the atoms having more numbers of ortho chlorine neighbors give rise to the resonances at the higher frequencies. This assumption is supported by the fact that the resonance frequencies in *ortho*-dichlorobenzene are higher than those in meta- and para-derivatives. The frequency shifts were interpreted in terms of the induction effect due to the substituted chlorine atoms, in particular, at the ortho neighbors. For the confirmation of this effect, it is necessary to make assignments without any assumption for the derivatives with more than two chlorine atoms. The Zeeman effect of a single crystal is suitable for this purpose, as was shown in the study of benzene hexachlorides[2].

A quadrupole resonance line splits into several Zeeman components in the presence of a static magnetic field. The splittings depend on the orientation of the applied field with respect to the principal axes of the electric field gradient at the nucleus. It has been realized that in the case of the chlorine atom in a C–Cl bond, the bond direction coincides to a high degree of approximation with that of the principal z axis, the direction giving the largest component of the electric field gradient ($|q_{xx}| \leqq |q_{yy}| \leqq |q_{zz}|$). The bond direction can, therefore, be determined by observing the angular depedence of the Zeeman effect in a single crystal. If the crystal structure is known, each resonance frequency can be assigned to one of chlorine atoms in a unit cell, by comparing the directions of the z axes with those of the C–Cl bonds, or the observed Zeeman patterns with those expected from the structure. Even when the crystal structure is unknown, the assignment is made to some extent, if the molecular structure can be inferred from other information: for instance, the resonance lines due to two chlorine atoms disposed mutually at the para positions of a benzene ring are expected to display the same Zeeman patterns at any orientation of the applied field.

The present study was originally made for the purpose to investigate the steric repulsion between the ortho chlorine neighbors in multichlorobenzenes. It was reported by Bastiansen and Hassel that the interatomic distances in hexachlorobenzene observed in electron diffraction were accounted for with assuming the distortion of the C–Cl bonds by 12° successively above and below the plane of the benzene ring[3]. The samples studied in the present work are 1, 3, 5-trichlorobenzene, 1, 2, 3, 4-tetrachlorobenzene and pentachlorobenzene. In 1, 3, 5-trichlorobenzene, the principal z axis of a chlorine atom was found to be inclined at $1.6 \pm 1.0°$ with respect to the plane determined by those of the other two[4]. Since the chlorine atoms in this

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1) P. J. Bray, R. G. Barnes and R. Bersohn, *J. Chem. Phys.*, **25**, 813 (1956).

2) Y. Morino, T. Chiba, T. Shimozawa, M. Toyama and K. Itoh, *Rev. Univ. des Mines*, 9e Sér. T. XV, 591 (1959).

3) O. Bastiansen and O. Hassel, *Acta Chem. Scand.*, **1**, 489 (1947).

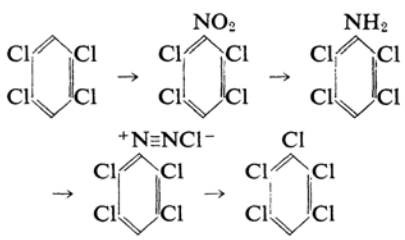
4) Y. Morino and M. Toyama, *J. Phys. Soc. Japan*, **15**, 288 (1960).

molecule are substituted at the meta positions with respect to one another, the observed distortion was attributed to the effect of crystal field. In the other compounds, it was difficult to prepare single crystals large enough for the Zeeman study. The crystals obtained were imperfect so that it was unsuccessful to perform a precise determination of the principal axes[5]. This article will present the assignments of the spectral lines for these multichlorobenzenes made in the course of the investigations.

Experimental

A self-quenched super-regenerative oscillator-detector of Dean's type[6] was used for detecting the absorption spectra. The signals detected were suitably amplified by a narrow-band amplifier, and then recorded through a phase-sensitive detector followed by a pen-recorder, for obtaining a high signal-to-noise ratio. The modulation frequency was 230 c/sec. and the quench frequency was nearly 50kc./sec. The magnet used for the Zeeman study was an air-cooled Helmholtz coil described previously[7], which supplied up to 150 gauss of magnetic field in the continuous operation. All the Zeeman experiments were carried out at room temperature.

The sample of pentachlorobenzene was synthesized from 1, 2, 4, 5-tetrachlorobenzene by Sandmeyer's method:



The product recrystallized from alcoholic solution was colorless needle-like crystals with m. p. 84~85°C. The infrared spectrum indicated little contamination in the reactants and the intermediate products. Further purification was performed by the repetition of zone-melting to remove impurities at the tracer level. The existence of such a small amount of impurities as those detected neither by the melting point nor by the infrared spectrum made the intensity of the nuclear quadrupole resonance spectrum considerably weak. For other samples, use was made of the commercial products after the purification by the similar procedures.

Single crystals were prepared by Bridgeman's method[7]. The apparatus for this purpose was an electric furnace, whose lower end was followed by a cooler place to give a large temperature gradient between the two regions. About 10 g. of each sample, put in an evacuated glass ampule with a capillary sealed at the bottom, was heated in the furnace and then slowly lowered down into the cooler place (at a rate of 2~4 mm./hr.). A single crystal gradually grew up from the bottom of the capillary, when it came to this cooler region.

Results

1, 3, 5-Trichlorobenzene

Zeeman study was made for three ^{35}Cl resonance lines designated ν_a, ν_b and ν_c in the order of increasing frequency, as was reported previously[4]. In Table I are listed the quadrupole coupling constants, the asymmetry parameters of the electric field gradients, and the direction cosines of the principal z axes with respect to the symmetry axes of the crystal, X, Y and Z. The relative orientation of the principal axes led to the unit-cell structure with the orthorhombic symmetry. The analysis of the crystal structure by X-ray diffraction was reported by Milledge and Pant[8]. As was expected from the Zeeman study, the crystal was found to be orthorhombic with the space group $P2_12_12_1$ and the unit-cell dimensions:

TABLE I. QUADRUPOLE COUPLING CONSTANTS, ASYMMETRY PARAMETERS, AND DIRECTION COSINES OF THE PRINCIPAL AXES AND OF THE CORRESPONDING C-Cl BONDS WITH RESPECT TO THE CRYSTAL AXES IN 1,3,5-TRICHLOROBENZENE

Lines (^{35}Cl)		eQq_{zz}[a] Mc./sec.	η	Direction cosines			$\Delta\alpha$[b]
				a(X)	b(Y)	c(Z)	
ν_a	z axis	71.1_2	0.09_3	-0.423_1	0.864_7	0.270_3	1.1°
	C-Cl_3			-0.436_4	0.854_9	0.280_6	
ν_b	z axis	71.8_6	0.11_1	-0.474_4	-0.865_9	0.158_9	1.1°
	C-Cl_1			-0.486_1	-0.861_9	0.144_2	
ν_c	z axis	72.2_8	0.12_9	0.913_6	-0.000_0	-0.406_7	0.8°
	C-Cl_5			0.908_1	-0.006_2	-0.418_7	

a) The value extraporated to 0°K.
b) The angle between the principal z axis and the corresponding C-Cl bond.

5) Recently, Dean, Richardson and Sakurai also made a Zeeman study of 1, 2, 3, 4-tetrachlorobenzene [*Molecular Physics*, **4**, 95 (1961)]. Their results showed that the molecule was planar within ±3/4°. Bastiansen reinvestigated hexachlorobenzene by the electron diffraction method and concluded a planar structure, in contrast with the previous results (private communication).

6) C. Dean and M. Pollak, *Rev. Sci. Instr.*, **29**, 630 (1958).

7) Y. Morino, T. Chiba, T. Shimozawa and M. Toyama, *J. Phys. Soc. Japan*, **13**, 869 (1958).

8) H. J. Milledge and L. M. Pant, *Acta Cryst.*, **13**, 285 (1960).

$a=13.93$ Å, $b=13.19$ Å, $c=3.91$ Å
and $Z=4$ at 20°C

Fractional coordinates in the unit-cell were also given for each constitutive atom.

The assignment of spectral lines is made by comparing the directions of the principal z axes with those of the C–Cl bonds calculated from the fractional coordinates. The results are best explained by assigning the lines ν_a, ν_b and ν_c to the atoms Cl_3, Cl_1 and Cl_5, respectively, with the symmetry axes X, Y and Z corresponding to the crystal axes *b*, *a* and *c*, respectively. Here the suffixes 1, 3 and 5 represent the ring positions designated by Milledge and Pant. Agreement of the directions of the principal z axes with those of the C–Cl bonds is satisfactory as seen in Table I. Table II shows the mutual angles of the principal z axes of the three chlorine atoms in a molecule and those of the corresponding C–Cl bonds. It is to be noted that each principal z axis is appreciably inclined with respect to the plane determined by the remaining two, while the three C–Cl bonds are coplanar within the experimental uncertainty. In this respect the further improvement of the X-ray analysis would be desirable.

Table II. Angles between the principal z axes of the field gradients and those between the corresponding C–Cl bonds in 1, 3, 5-trichlorobenzene

	Cl_1Cl_3	Cl_3Cl_5	Cl_5Cl_1	$\Delta\theta$[a]
z Axes	120.3°	119.8°	119.9°	1.6°
C–Cl bonds	119.0°	121.3°	119.8°	0.0°

a) The angle which each z axis or each C–Cl bond makes with respect to the plane determined by the remaining two. The experimental uncertainty is estimated to be ±1.0° for the Zeeman study and ±2.5° for the X-ray study.

1, 2, 3, 4-Tetrachlorobenzene

Four resonance lines were observed by Bray et al.[1]: $\nu_a=36.297$, $\nu_b=36.333$, $\nu_c=36.635$ and $\nu_d=36.763$ Mc./sec. at 301°K; the two lower frequency lines ν_a and ν_b coalesce to one line at the liquid-nitrogen temperature. The crystal structure has not been reported. The present Zeeman study of a single crystal revealed that the lines ν_a and ν_b gave similar Zeeman patterns at any orientation of the applied magnetic field, while ν_c and ν_d gave the patterns different from any of others. The lines ν_a and ν_b are, therefore, assigned to the pair of chlorine atoms Cl_1 and Cl_4, which are substituted at the para positions with respect to each other, and the lines ν_c and ν_d to Cl_2 and Cl_3. The assignments completely agree with those expected by Bray et al.

Pentachlorobenzene

Five resonance lines were observed by Bray et al.[1] (Table III). with the single hydrogen atom bonded to the ring carbon 1, they also made a tentative assignment on the basis of Hammett sigma values and the frequency grouping: two lowest frequencies ν_a and ν_b to the chlorines 2, 6; a middle frequency ν_c to the chlorines 3, 5; two highest frequencies ν_d and ν_e to the chlorine 4. The assignment, however, seems to be very unusual. If it were true, the relative intensity of the five resonance lines should be 1 : 1 : 2 : 1/2 : 1/2 in the order of increasing frequency. In the actual spectrum, all the lines have nearly the same absorption intensities, and do not split further by the change in temperature.

The study with a single crystal indicates that the resonace lines are classified into three groups: (ν_a, ν_c), (ν_b, ν_e) and ν_d. The lines in each group show the Zeeman pratterns similar to each other but entirely different from those in other groups. The single line ν_d is then assigned to the chlorine 4 whose bond direction is different from those of other chlorines. The other line pair, (ν_a, ν_c) or (ν_b, ν_e), is assigned to either of the atom pairs, (Cl_2, Cl_5) or (Cl_3, Cl_6), the atoms in each pair being substituted at the para positions with respect to each other. Here eight possible choices of the assignments remain unexcluded, as shown in Table III. For

Table III. Assignments of the ^{35}Cl resonance frequencies in pentachlorobenzene with the single hydrogen atom bonded to carbon 1

Resonance frequency at 306°K, Mc./sec.	Assignment[a]								
	I	I′	II	II′	III	III′	IV	IV′	0
ν_a 36.782	2	6	2	6	5	3	5	3	2,6
ν_b 36.961	6	2	3	5	6	2	3	5	6,2
ν_c 37.112	5	3	5	3	2	6	2	6	3,5
ν_d 37.413	4	4	4	4	4	4	4	4	4
ν_e 37.512	3	5	6	2	3	5	6	2	4

a) The assignments I–IV′ are the possible ones revealed by the present Zeeman study, of which I and I′ are the most probable. The last column 0 presents the assignment by Bray et al.

discussing the effect of the ortho chlorine neighbors, it is necessary to assign each line to each atom in the molecule. It is, however, impossible by the present study alone. An assumption, which is not so serious as that made by Bray et al., will be employed here: the line of the highest frequency ν_e comes from one of the atoms Cl_3, Cl_4 and Cl_5, and that of the lowest one ν_a from the atom Cl_2 or Cl_6. The possible assignments are then reduced to the two cases denoted by I and I′ in Table III. These two cases are completely equivalent to each other, so long as the effect of the crystal field is ignored. The result is more reasonable than that by Bray et al., since one absorption line corresponds to one chlorine atom in a molecule. It is to be noted that the line ν_d is assigned without any assumption to the Cl_4, and the line of the highest frequency ν_e to the other one.

The angular dependence of the Zeeman patterns suggests that the orientation of the molecules in a unit-cell is symmetric with respect to three planes perpendicular to one another. It is then likely that the crystal system is orthorhombic with $Z=4$, the molecules in a unit-cell being all equivalent to one another.

Discussion

First of all it should be noted that the four resonance lines in 1, 2, 3, 4-tetrachlorobenzene have been grouped into two groups: two lower frequencies due to Cl_1 and Cl_4 and two higher ones due to Cl_2 and Cl_3; similarly the five resonance lines in pentachlorobenzene into two groups: two lower frequencies due to Cl_2 and Cl_6 and three higher ones due to Cl_3, Cl_4 and Cl_5. This fact indicates that the intramolecular effect is of predominant importance for the shifts of resonance frequencies. As for the origin of these shifts, considerations will be first made on the contribution from the charges at the neighboring atoms within the molecule. The direct field produced by the charges, which is, in general, very weak, distorts the electronic cloud around the nucleus in resonance to make a considerable contribution to the field gradient. Sternheimer has theoretically shown that the total increment of the field gradient may be approximated by the direct one Δq times a constant factor[9]:

$$\Delta q^{\text{total}} = \Delta q(1-R)$$

R is usually called Sternheimer factor which has been estimated for a Cl^- ion to be -57.7[10]. Actually, the differences in the six resonance frequencies of α-isomer of benzene hexachloride and those of γ-isomer have been satisfactorily interpreted in terms of this effect by assuming the multiplying factor $(1-R)\cong 50$[2]. Similar interpretation may be applied to the frequency differences in multichlorobenzenes.

Figure 1 presents a diagram of the observed frequencies in multichlorobenzenes plotted against the zz component of the direct field gradient calculated with disregarding the intermolecular effect. In the calculation, a formal charge placed at the center of each atom has been assumed from the information of the bond moment and of the coupling constant of the chlorine nucleus in monochlorobenzene: $-0.20e$ at the chlorine atom, $0.20e$ at the carbon atom bonded to the chlorine atom, $-0.05e$ at the carbon atom bonded to a hydrogen atom, and $0.05e$ at the hydrogen atom. The interatomic distances have been assumed to be $r(C-C)=1.39$ Å, $r(C-Cl)=1.71$ Å and $r(C-H)=1.08$ Å, and the bond angles to be all hexagonal. The plot has been made on the basis of the above assignments for 1, 2, 3, 4-tetrachlorobenzene and for pentachlorobenzene, and also of those by Bray et al.[1] for other derivatives. Roughly speaking, the frequencies are linearly correlated with Δq_{zz}, and the frequency shifts are accounted for by assuming the same multiplying factor as that in benzene hexachlorides. It will be recognized by a closer examination, however, that the frequencies are aligned on three nearly parallel lines, depending on the number of ortho chlorine neighbors. It is apparent from the trends of the three lines that the contributions from the ortho neighbors are relatively over-estimated by this direct interaction alone. Similar tendencies have been found by Bray et al. in the diagram of frequency versus Hammett sigma values[1].

Two origins should be mentioned in relation to such complicated feature of the resonance frequencies. One is the displacement of the center of the electronic charges from that of the nucleus. A simple estimate will then be attempted here for the position of the formal charge on each atom. If sp^2 hybrid orbitals are assumed for the carbon atoms, the average position of the positive charge in the C^+Cl^- bond or of the negative charge in the C^-H^+ bond is calculated by the following formula:

$$\langle z_C \rangle = (2\sqrt{2}/3)\int z_C \chi_{2s}\chi_{2pz}\mathrm{d}\tau$$

where z_C denotes the displacement of the charge measured from the center of the carbon nucleus towards that of either the chlorine or the hydrogen nucleus, and χ_{2s} and χ_{2pz} the 2s and $2p_z$ atomic orbitals of the carbon atom, respectively. The displacement of the charge

9) R. M. Sternheimer, *Phys. Rev.*, **95**, 736 (1954).
10) R. M. Sternheimer and H. M. Foley, ibid., **102**, 731 (1956).

centers also takes place in the chlorine atom of the covalent C–Cl bond: a negative charge at the center of the chlorine nucleus and a positive charge at the distance

$$\langle z_{Cl}\rangle = 2\sqrt{s(1-s)}\int z_{Cl}\chi_{3s}\chi_{3pz}d\tau$$

from the chlorine nucleus to the carbon one[11], s denoting the s character of the bonding orbital of the chlorine atom. By making use of Slater functions[12] for the atomic orbitals χ's, the equation gives $\langle z_C\rangle = 0.453$ Å and $\langle z_{Cl}\rangle = 0.376$ Å, where the s character is assumed to be 0.15 for the chlorine atom according to the estimate by Townes and Dailey[13]. This amount of displacement of the charges in the covalent C–Cl bond produces a bond moment of 1.80 D, slightly larger than the observed one[14]. The change in the field gradients thus estimated, however, rather enhances the trends of the three lines found in Fig. 1, contrary to the expectation.

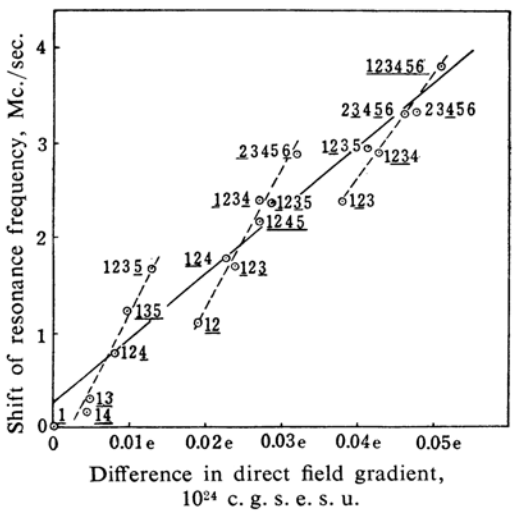


Fig. 1. Plot of the ^{35}Cl resonance frequency in multichlorobenzenes versus the direct field gradient arising from the distribution of the effective charges within the molecule. The diagram is drawn with reference to monochlorobenzene. The names of the compounds are represented by the ring positions of the substituted chlorine atoms and the assignment of each spectral line is indicated with underlines.

Another origin to be mentioned is the indirect induction effect propagated through the chemical bonds. Since chlorine is more electronegative than carbon, the bonding electrons in the C–Cl bond are, in general, attracted towards the chlorine atom. In multichloro-derivatives, however, the attractive forces of other chlorine atoms counteract that of the one in question through the bonds to produce a decrease in the ionic character of the C–Cl bond. The resonance frequency thus tends to increase with increasing number of chlorine atoms substituted in the molecule. The observed trend of the frequencies suggests that such indirect induction effect is considerably propagated to the meta and the para positions, too. An evidence for such effect was also observed in the nuclear magnetic resonance spectra[15]: the protons in monochlorobenzene, for example, give rise to a single resonance with a chemical shift $\tau = 2.756$, independent of the ring positions relative to the chlorine atom.

The contribution of the intermolecular effect has been estimated for the three resonance lines in 1, 3, 5-trichlorobenzene, on the basis of the crystal structure. Table IV shows the direct field gradients calculated by assuming an effective charge at the center of each atom in the crystal as mentioned above. The convergence has been substantially reached by the summation up to the first neighboring lattices along the a and b axes and to the third neighbors along the c axis. The sequence of the field gradients Δq_{zz} thus calculated does not agree with that of the observed coupling constants, except for Cl_3. The agreement does not seem to be attained by making any plausible

Table IV. Calculated field gradients at the chlorine nuclei directly arising from the charge distribution in crystalline 1, 3, 5-trichlorobenzene

Chlorine site	Δq_{zz}-$\Delta q_{zz}(Cl_3)$ in 10^{24} c. g. s. e. s. u.	Δq_{xx}-Δq_{yy} in 10^{24} c. g. s. e. s. u.
Cl_1	$0.0130e$	$-0.0125e$
Cl_3	$0.0000e$	$-0.0124e$
Cl_5	$0.0086e$	$0.0015e$

11) With regard to the charge distribution in the covalent C-Cl bond, one may be tempted to presume a model with the positive charge at the position of the chlorine nucleus and the negative charge at the distance $<z_{Cl}>$ from the nucleus in the direction of the anti-bonding orbital. Such a model, however, has neglected the quadrupolar field due to the lone-pair electrons in the $3p_x$ and the $3p_y$ orbitals which is expected to have a significant influence, especially, on the ortho neighbors. In this respect, the model employed above seems more reasonable, because the positive charge has been treated as a defect of an electronic charge from the spherically symmetric configuration Cl^-.

12) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

13) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949); C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy", McGraw-Hill Inc., New York (1955), p. 237*ff*.

14) Even if the s character is taken to be 0.10, the moment is only reduced to 1.52 D. The consideration suggests that the distribution of the effective charges in the C-Cl bond should be approximated by that in a purely covalent bond with an appropriate amount of s character.

15) P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956); A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

TABLE V. DISTANCES BETWEEN THE CHLORINE ATOMS IN THE MOLECULE 1 AND THE ATOMS IN THE NEIGHBORING MOLECULES IN THE CRYSTAL OF 1, 3, 5-TRICHLOROBENZENE

Atoms in molecule 1[a]	Atoms in the neighboring molecules			
	Cl		H	
Cl_1	(5—6)[a)]	3.63 Å	(4—7)	2.96 Å
	(3—5)	3.75 Å		
	(1—8 and 8′)	3.91 Å		
	(5—7)	4.04 Å		
	(3—5′)	4.15 Å		
Cl_3	(1—5′)	3.75 Å	(2—5)	2.97 Å
	(3—8 and 8′)	3.91 Å	(6—3)	2.98 Å
	(5—3)	4.13 Å	(2—5′)	3.21 Å
	(1—5)	4.15 Å		
Cl_5	(1—2)	3.63 Å		
	(5—4)	3.65 Å		
	(5—4′)	3.65 Å		
	(5—8 and 8′)	3.91 Å		
	(1—3)	4.04 Å		
	(3—7)	4.13 Å		

a) The first figure in each parenthesis denotes the ring position of the neighboring atom and the second one the molecule in which the atom locates. The position of each molecule must be interpreted as follows: 1, (x,y,z); 2, $(1/2+x,1/2-y,1-z)$; 3, $(1-x,1/2+y,1/2-z)$; 4, $(3/2-x,1-y,1/2+z)$; 4′, $(3/2-x,1-y,-1/2+z)$; 5, $(1/2-x,1-y,-1/2+z)$; 5′, $(1/2-x,1-y,1/2+z)$; 6, $(-1/2+x,1/2-y,1-z)$; 7, $(1-x,-1/2+y,1/2-z)$; 8, $(x,y,z+1)$; 8′, $(x,y,z-1)$, where the fractional coordinates (x,y,z) correspond to those given by Milledge and Pant (see Table 1 in Ref. 8).

correction to the amounts nor to the position of the effective charges. The situation is quite the same for the asymmetry parameters. Since the three chlorine atoms are substituted symmetrically with respect to one another in the molecule, the intramolecular effect is not expected to produce any difference in the field gradients. The shifts of the resonance frequencies in this derivative should, therefore, be produced only through the intermolecular interactions. The disagreement may suggest either a limitation to the application of the Sternheimer theory to molecular crystals, or the existence of an extra process to propagate the effects between the neighboring molecules.

A process to be considered is the one through the distortions of the bonds. In 1, 3, 5-trichlorobenzene, however, there are no significant differences in the lengths of the C–Cl bonds, in particular, between C_1–Cl_1 and C_5–Cl_5; $r(C_1\text{–}Cl_1)=1.710$ Å, $r(C_3\text{–}Cl_3)=1.714$ Å and $r(C_5\text{–}Cl_5)=1709$ Å[8]. Considerable differences have been observed rather in the interatomic distances between the neighboring molecules. As easily seen from Table V, the number of the neighboring atoms increases in the order of positions 3, 1 and 5 for the chlorine neighbors, and in the inverse order for the hydrogen ones. Since the hydrogen atom, in general, has an electric property opposite to the chlorine atom, the observed order of the coupling constants is reasonably interpreted by considering an intermolecular induction effect independent of the directions, such as those analogous to the intramolecular one propagated through the chemical bonds. An evidence for such an extra process may also be seen in the fact that the resonance lines due to the chlorine atoms, which should be equivalent in the free molecule, are distributed over a wide range of frequency, compared with those in other chloro-derivatives of benzene.

Summary

Assignments of the ^{35}Cl nuclear quadrupole resonance spectra have been made for some multichlorobenzenes by the Zeeman studies of single crystals. Three resonance lines in 1, 3, 5-trichlorobenzene, have been assigned, in the order of increasing frequency, to Cl_3, Cl_1 and Cl_5 designated by Milledge and Pant in their X-ray study; two lower frequencies in 1, 2, 3, 4-tetrachlorobenzene to Cl_1 and Cl_4 and two higher ones to Cl_2 and Cl_3; and in pentachlorobenzene, the second highest frequency to the chlorine atom at the para position with respect to the single hydrogen atom. The shifts of the resonance frequencies have been accounted for in terms of the induction effect. It is likely that the ortho

effect is produced by the direct field arising from the charges on the neighboring atoms rather than the indirect one propagated through the chemical bonds. The interpretation of the three frequencies in 1, 3, 5-trichlorobenzene has also been attempted from the viewpoint of the intermolecular effect. It has been suggested that an induction effect independent of the directions takes place in this crystal among the neighboring molecules.

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