The Zeeman Effect of Nuclear Quadrupole Resonance Spectrum in α-BHC Crystal

By Gen SODA, Masaharu TOYAMA and Yonezo MORINO

(Received April 17, 1965)

Pure quadrupole resonances of the ^{35}Cl-nuclei for crystals of various isomers of benzene hexachlorides (BHC) have been studied by Duchesne, Monfils and Depireux,[1] and by Morino and others,[2-4] and the assignments of each spectral line to one of the six chlorine atoms have been carried out for α- and γ-isomers, with reference to the crystal structure obtained by van Bommel[5] by the X-ray diffraction method. The apparatus and the method of analysis have been so greatly improved that the Zeeman study enables us to determine the

---

[1] J. Duchesne, A. Monfils and J. Depireux, *Compt. rend.*, **243**, 144 (1956).

[2] Y. Morino, I. Miyagawa, T. Chiba and T. Shimozawa, *J. Chem. Phys.*, **25**, 185 (1956).

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

[4] Y. Morino, T. Chiba, T. Shimozawa, M. Toyama and K. Ito, *Rev. Univ. des Mines, 9e Ser. T.*, XV, 591 (1959).

[5] A. J. Van Bommel, Private communication (1956).

exact locations of the principal axes of the field-gradient tensors at the chlorine nuclei. For instance, for δ-BHC the direction of each axis was determined with an uncertainty of only 0.1° to 0.5°.[6] It has also been revealed that some of the C–Cl bonds are considerably distorted from the directions to be expected from the tetrahedral bond angles for each carbon atom. The purpose of the present study is to locate the field-gradient tensors in the racemic α-BHC crystal by the use of the refined technique that was used for δ-BHC.

The molecule of α-BHC has two axial C–Cl bonds and four equatorial C–Cl bonds, one for each carbon atom in the cyclohexane ring. The configuration, which is shown in Fig. 1, is expressed as "*aaeeee*", where *a* and *e* denote the axial and equatorial C–Cl bonds respectively. The crystal is monoclinic, and the four molecules contained in a unit cell are all equivalent, although they are different in orientation. They may be classified into two groups; two molecules in each group are arranged antiparallel to each other, while the molecules in one group are located symmetrically with the molecules in the other group with respect to the crystal ac-plane.

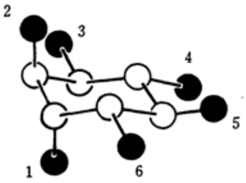


Fig. 1. Model structure of the α-BHC molecule. Black and white circles denote the chlorine and carbon atoms respectively. The locations of hydrogen atoms are omitted.

Experimental and Results

Apparatus and Material. — The spectrometer used was the same as that described in a previous paper on δ-BHC.[6] The absorption spectra were detected by using a self-quenched super-regenerative spectrometer similar to that described by Dean, the modulation and the quench frequencies being 230 cycle/sec. and about 50 kc./sec. respectively. The magnetic field for the Zeeman study was supplied by an air-cooled Helmholtz coil. The field strength was continuously variable from zero to 162 gauss. All the Zeeman studies were carried out at room temperature.

The α-BHC was recrystallized from a benzene solution. A single crystal with dimensions of $0.6\times2.0\times4.0\ \mathrm{cm}^3$ was prepared from the saturated solution by carefully evaporating the solvent. The crystal thus obtained was a good single crystal, as was supported by the fact that the spectra of this crystal did not show, even under a strong magnetic field, any unexpected disturbance, such as line-splitting and broadening, due to the coexistence of crystals with a different orientation.

Principle of the Measurement.—The principle used for the measurement was exactly the same as that used for δ-BHC in the preceeding paper. The direction of the principal z-axis of the field-gradient tensor was determined by the method of "no-splitting locus" proposed by Das and Hahn.[7] The no-splitting locus is expressed by the formula of the first order with respect to η:

$$(\boldsymbol{H}\cdot\boldsymbol{Z})=\frac{1}{\sqrt{3}}\left\{1+\frac{\eta}{3}[1-3(\boldsymbol{X}\cdot\boldsymbol{H})^2]\right\} \qquad (1)$$

where $\boldsymbol{H}$ represents a unit vector in the direction of the generating line of the locus, and $\boldsymbol{Z}$ and $\boldsymbol{X}$, those in directions parallel to the principal z- and x-axes of the field-gradient q-tensor respectively. Equation 1 shows that, in the case of $\eta=0$, the no-splitting locus is a circular cone whose axis is parallel to $\boldsymbol{Z}$, and that the first-order term in η represents a distortion from the circular cone. It would, therefore, be possible to determine not only the direction of $\boldsymbol{Z}$ from the axis of the observed cone, but also the asymmetry parameter, η, and the direction of $\boldsymbol{X}$ from its distortion. This method was, however, not applicable to the latter purpose in the present case, because our apparatus, because of its construction, does not give the whole locus; furthermore, the distortion of the locus from the circular cone is small for α-BHC. Thus, η and $\boldsymbol{X}$ were obtained by the measurement of the splitting and the intensity ratio of the outer and inner components of the Zeeman pattern when the magnetic field was applied nearly parallel to the direction of the intersection between the crystal ac-plane and the principal xy-plane of the field-gradient q-tensor.[6] At this setting of the magnetic field, the relative intensity, P_r, of the outer and the inner components of the Zeeman pattern is expressed by these formulae;

$$\begin{aligned} P_r &= P(-)/\{P(+)+P(-)\} \\ &= \frac{1}{2}\{1-(\eta/\Delta\nu)\cos 2\varphi_r\} \end{aligned} \qquad (2)$$

and

$$\Delta\nu=(\eta^2+9\cos^2\theta_s)^{1/2} \qquad (3)$$

where $P(-)$ and $P(+)$ indicate the intensities

---

[6] Y. Morino, M. Toyama and K. Itoh, *Acta Cryst.*, **16**, 129 (1963); M. Toyama, *J. Phys. Soc. Japan*, **14**, 1727 (1959).

[7] T. P. Das and E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy," Academic Press, New York (1958).

of the outer and the inner components respectively, and (θ_r, φ_r) and (θ_s, φ_s) indicate, respectively, the directions of the r. f.-field and of the static magnetic field with reference to the principal coordinate system. $\Delta\nu$ designates a half of the difference between the frequency separations of the two pairs in units of $\nu_H = \gamma H/2\pi$, where γ is the gyromagnetic ratio and H, the strength of the applied magnetic field.

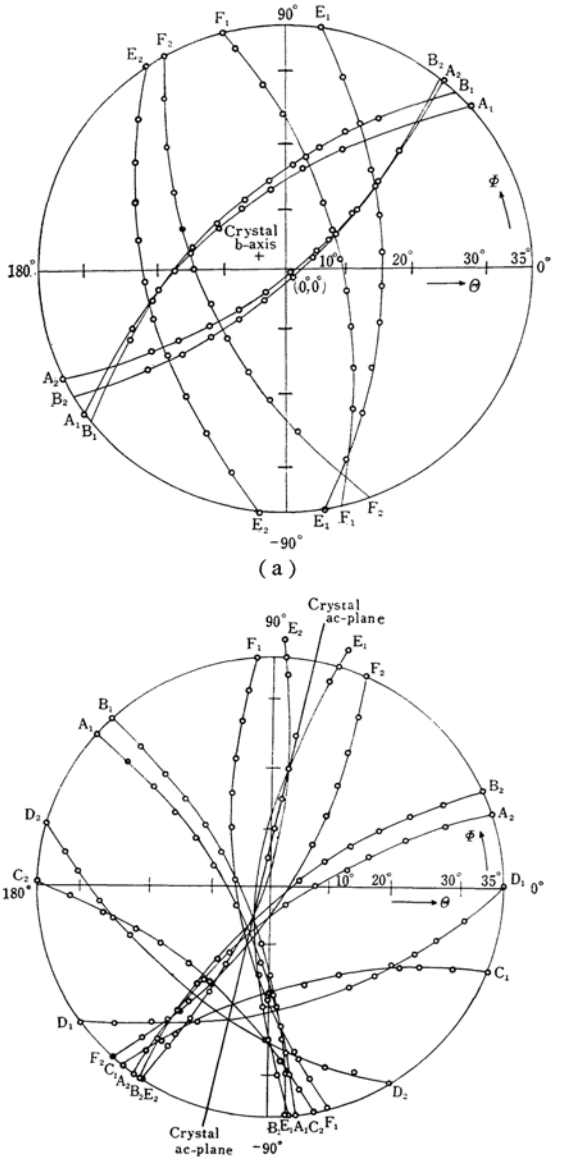
No-splitting Loci and the Principal z-Axes of Field-gradient Tensors.—An approximate location of the no-splitting locus was first determined by observing the Zeeman pattern of each spectral line at various orientations of a relatively weak magnetic field (50—70 gauss). Next, a magnetic field of a suitable strength, from 100 to 160 gauss, was applied in directions near the locus thus roughly determined; the directions giving a no-splitting Zeeman component were determined within an uncertainty of about 0.2°. A no-splitting locus was drawn by tracing the directions thus obtained at intervals of 3—5°.

TABLE I. PURE QUADRUPOLE RESONANCE FREQUENCIES OF ^{35}Cl NUCLEI OF α-BHC AND THEIR TEMPERATURE DEPENDENCE (Mc./sec.)

	291°K	197°K	77°K	197—291°K	77—197°K
A	36.817	37.015	37.219	0.198	0.204
B	36.487	36.680	36.879	0.193	0.199
C	36.230	36.456	36.705	0.226	0.249
D	36.230	36.408	36.589	0.178	0.181
E	35.693	35.878	36.081	0.185	0.203
F	35.608	35.813	36.038	0.205	0.225

The six absorption lines are designated, for convenience, A, B, C, D, E and F, in the order of decreasing frequency, as is shown in Table I. The no-splitting loci of the spectral lines A, B, E and F were first determined with a single crystal mounted in such a way that the crystal b-axis was nearly parallel to the Z_l-axis of the laboratory coordinate system. The loci of the spectral lines C and D were not determined, because the frequency difference between the two lines was so small that the Zeeman pattern was complicated at this mounting. This run is called Experiment 1. Next, the crystal was remounted at such a position that the b-axis was located nearly parallel to the X_l-axis. At this mounting the no-splitting loci of the spectral lines from A through F were all determined. This run is called Experiment 2.

Figures 2a and 2b illustrate the no-splitting loci in a stereographic projection; they are projected on a horizontal plane, namely, on the X_lY_l-plane which passes through the center of the crystal as its origin. The symbols Θ and Φ denote the polar coordinates with reference to the laboratory coordinate system. The figures show that two no-splitting loci were found for each spectral line. This means that each line corresponds to two distinct field-gradient tensors which are equal in magnitude but different in direction; in other words, one



(a)

(b)

Fig. 2. Stereographic projection of the no-splitting loci.

(a) Experiment 1. Crystal b-axis oriented nearly parallel to the Z_l-axis of laboratory coordinate system.

(b) Experiment 2. Two pairs of no-splitting loci of each spectral line located symmetrically with respect to the crystal ac-plane.

TABLE II. DIRECTION COSINES OF THE PRINCIPAL Z-AXES OF THE FIELD-GRADIENT TENSORS FOR THE MOLECULES 1 AND 2, WITH REFERENCE TO THE CRYSTAL-FIXED COORDINATE SYSTEM

	X_c	Y_c	Z_c
A_1	0.3293 ± 0.0023	-0.6735 ± 0.0020	0.6818 ± 0.0015
A_2	0.3283 ± 0.0018	-0.6730 ± 0.0020	-0.6628 ± 0.0011
B_1	0.3634 ± 0.0030	-0.6379 ± 0.0021	0.6790 ± 0.0025
B_2	0.3607 ± 0.0030	-0.6369 ± 0.0017	-0.6815 ± 0.0025
C_1	0.0544 ± 0.0137	-0.8879 ± 0.0062	-0.4568 ± 0.0119
C_2	0.0516 ± 0.0155	-0.8940 ± 0.0069	0.4452 ± 0.0133
D_1	0.9370 ± 0.0014	0.2340 ± 0.0040	0.2594 ± 0.0024
D_2	0.9381 ± 0.0032	0.2304 ± 0.0075	-0.2588 ± 0.0055
E_1	-0.5832 ± 0.0014	0.0669 ± 0.0022	0.8097 ± 0.0009
E_2	-0.5819 ± 0.0018	0.0660 ± 0.0041	-0.8106 ± 0.0012
F_1	0.6859 ± 0.0020	0.0803 ± 0.0050	-0.7233 ± 0.0017
F_2	0.6850 ± 0.0018	0.0761 ± 0.0044	0.7250 ± 0.0017

spectral line corresponds to two distinct C-Cl bonds which are different in direction. As will be seen later, the principal z-axes of the two field-gradients determined by two no-splitting loci were found to be symmetrical with respect to an axis which is common to all the six lines. This axis is the crystal b-axis. These results agree with those obtained by X-ray diffraction;[5] four equivalent C-Cl bonds in a unit cell are classified into two groups, as has been described in the introduction. All principal z-axes of the field-gradient tensors determined above were, therefore, uniquely classified into two groups according to the criterion that the mutual angles between the two directions of the principal z-axes which belong to the same group were nearly 180° or close to the tetrahedral angle. These two groups are distinguished by the suffixes 1 and 2; for example, A_1 and A_2 denote the field-gradient tensors belonging to group 1 and group 2 respectively.

There are two symmetry planes with respect to which two principal z-axes of the q-tensors of each spectral line are equivalent. One is the crystal ac-plane, and the other is a plane which is perpendicular to it. The latter symmetry planes intersect, on the crystal b-axis, with those for other field-gradient tensors. Accordingly, a bisecting line of the angle between the z-axes of A_1 and A_2 should be either on the ac-plane or parallel to the b-axis. This gives a method for determining the b-axis; that is, a direction common to either one of the bisecting lines for all of the six spectral lines, A to F, is parallel to the b-axis. As the observed directions of these bisecting lines deviated from A to F within a possible range of experimental error, an average of them was taken and designated as the Z_c-axis, the suffix c denoting a crystal-fixed coordinate system.

The X_cY_c-plane was easily given by a plane perpendicular to the Z_c-axis thus determined. The X_c- and Y_c-axes were defined, for the sake of convenience, by taking the direction of a bisecting line between the projections of the z-axes of the E and F tensors on the X_cY_c-plane. As the X_cY_c-plane does not exactly coincide with the ac-plane of the crystal because of experimental uncertainties, the projections of the two z-axes belonging either to the E or to the F tensors on the X_cY_c-plane are slightly different from each other. Thus, the Y_c-axis was determined by taking an average of them. The X_c-axis was determined as perpendicular to both the Y_c- and Z_c-axes.

Table II shows the final values of the directions of the principal axes referred to the crystal-fixed coordinate system. The details of the elimination of one of the two choices of φ_r will be described later.

Asymmetry Parameters and the Principal x- and y-Axes of Field-gradient Tensors.—When a static magnetic field is applied in a direction which is in either of the two symmetry planes mentioned above, then the Zeeman pattern is reduced to a simple four-line pattern. For example, Fig. 3 shows a Zeeman pattern of a spectral line, F, for such a setting of the magnetic field. The spectra were recorded from the right to the left, with the magnetic field applied 12′ and 44′, respectively, from the intersection of the crystal ac-plane and the principal xy-plane of the q-tensor. The asymmetry parameter of α-BHC is so small that the outer and the inner components of the Zeeman pattern overlap appreciably, as is shown in Fig. 3, and the apparent peak-to-peak separation recorded in the first derivative form is smaller than the correct value. Therefore, the values of $P(+)/P(-)$ and $\Delta\nu$ were determined from the observed Zeeman pattern in the following way.

If the shape of a single spectral line is

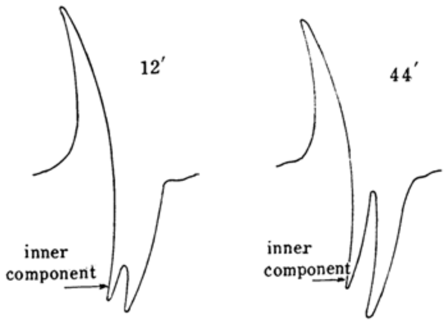


Fig. 3. Typical patterns of the Zeeman splittings of the spectral line F when the static magnetic field is applied near the principal xy-plane in the crystal ac-plane. Zeeman components on the higher frequency side were recorded in the first derivative form. The frequency increase from the left to the right.

assumed to be expressed by a Gaussian distribution function, then the first derivative curve of a doublet is given by the following equation:

$$g(x)=\frac{\{P(+)(x+\Delta\nu)\mathrm{e}^{-a(x+\Delta\nu)^2}+P(-)x\mathrm{e}^{-ax^2}\}}{(P(+)+P(-))} \tag{4}$$

where $\Delta\nu$ denotes the frequency separation. The two lines are assumed to have the same width, $(2/a)^{1/2}$. The three parameters, a, $\Delta\nu$ and $P(+)/P(-)$, involved in this formula were obtained by comparing the calculated curve with the observed one, with reference to the peak-to-peak separation and the widths at half-height positions of the two peaks. The asymmetry parameters of the six field-gradient tensors thus determined are given in Table III.

TABLE III. ASYMMETRY PARAMETERS OF FIELD-GRADIENT TENSORS

Absorption line	Asymmetry parameter η
A	0.0166±0.0014
B	0.0231±0.0031
C	0.0286±0.0031
D	0.036 ±0.010
E	0.0220±0.0025
F	0.0311±0.0031

The angle, θ_r, of the r. f.-field with respect to the principal axes was determined, with an uncertainty of 10°, on the assumption that the r. f.-field was parallel to the axis of the r. f.-coil. The values of φ_r are obtained from the intensity ratio, P_r, by the use of Eq. 2. However, the sign of φ_r was not determined uniquely, because φ_r is involved in Eq. 2 in the form of $\cos 2\varphi_r$. One of the alternatives was discarded by the following procedure. The approximate directions of the principal z-axes obtained above were refined for the first-order term given in Eq. 1, the magnitude of which depended on the choice of the direction of the principal x-axes. By using one of the values of the principal x-axes, the corrected directions of the principal z-axes for the two experiments, 1 and 2, coincided within the range of experimental error, whereas, for the other choice, they did not coincide beyond the range of experimental error. The former direction was, therefore, taken as the correct one. The measurements at different mountings were thus efficient in excluding the alternative choice of φ_r.

This method, however, could not be used for the spectral lines, C and D, not measured in Experiment 1. Nevertheless, in the case of D the direction of the principal x-axis was determined, because $|\varphi_r|$ was accidentally close to 90°. In the case of C, the directions of the principal axes were examined by the same method as was employed in a previous report:⁶⁾ first, two directions of the principal z-axes of the q-tensors were calculated, corresponding to the choices of the two principal x-axes, which are designated by $\mathrm{C_I}$ and $\mathrm{C_{II}}$, and then two directions of the intersection between the principal xy-plane and the crystal ac-plane were determined. The directions of the intersections for the other spectra were similarly calculated; the mutual angles between these

TABLE IV. OBSERVED AND CALCULATED ANGLES BETWEEN THE INTERSECTIONS OF THE PRINCIPAL XY-PLANES OF FIELD-GRADIENT TENSORS WITH THE CRYSTAL ac-PLANE

	Observed	Calculated	Difference
∠AB	3°32′	3°32′	0′
$\angle\mathrm{AC_I}$	22°22′	22°32′	10′
$\angle\mathrm{AC_{II}}$	22°22′	22°51′	29′
$\angle\mathrm{BC_I}$	25°54′	26°05′	11′
$\angle\mathrm{BC_{II}}$	25°54′	26°25′	31′

TABLE V. DIRECTION COSINES OF THE PRINCIPAL X- AND Y-AXES OF THE FIELD-GRADIENT TENSORS WITH REFERENCE TO THE CRYSTAL-FIXED COORDINATE SYSTEM (molecule 1)

		X_c	Y_c	Z_c
A	x	0.25	−0.61	−0.75
	y	0.91	0.41	−0.03
B	x	0.90	0.44	−0.07
	y	0.25	−0.64	−0.73
C	x	0.62	−0.32	0.72
	y	−0.78	−0.32	0.54
D	x	0.17	0.34	−0.92
	y	0.30	−0.91	−0.28
E	x	0.28	−0.92	0.28
	y	0.76	0.39	0.52
F	x	0.68	0.26	0.68
	y	0.24	−0.96	0.13

directions of the intersections are listed in Table IV, along with the values obtained in the course of the determination of η. If the choice is correct, the mutual angles among these calculated intersections should agree with those among the observed intersections. As Table IV shows, this requirement was actually satisfied for both assignments; of these, however, C_I seems to be preferable because in it the deviation was found to be smaller. The final values of the directions of the principal z-axes and those of the principal x- and y-axes are tabulated in Tables II and V respectively.

Discussion

Assignment.—Six absorption lines are assigned to six chlorine atoms by comparing the directions of the principal z-axes of the field-gradient tensors determined by the present study with those of the C–Cl bonds obtained by X-ray diffraction. Table VI shows the angles between the two principal z-axes of the field-gradient tensors belonging to each spectral line obtained by the Zeeman study and the angles between the C–Cl bonds which are symmetric with respect to the ac-plane. It may easily be seen that a mutual agreement is attained between the corresponding angles, if the absorption lines from A through F are assigned to the bonds shown on the same line in the table. The assignment of A and B has not yet been established because of the experimental error, ±4°, which accompanies the X-ray diffraction. The reliability factor proposed in the previous paper,

$$\langle \Delta\theta^2\rangle^{1/2} = \left\{\frac{1}{6}\sum_{i=1}^{6}(\Delta\theta_i)^2\right\}^{1/2} \qquad (5)$$

decreases when the assignments A and B are interchanged, as is shown in Table VII. Here $\Delta\theta_i$ denotes the angle between the direction of the i-th C–Cl bond and that of the principal z-axis of the corresponding field-gradient tensor. For calculating $\Delta\theta_i$, it is necessary to describe the directions of the C–Cl bonds and those of the principal z-axes of the q-tensors on the same coordinate system. The direction of the Z_c-axis as determined by X-ray diffraction coincides well with that obtained by the Zeeman study, because, as a result of the symmetry, the crystal b-axis was determined accurately in comparison with the other axes. On the other hand, the Y_c-axis which is obtained from the directions of the principal z-axes of the spectra E and F does not always coincide with the Y_c-axis as determined from the directions of the corresponding C–Cl bonds, 2 and 1, by X-ray diffraction. Because of the experimental errors, the directions of the two Y_c-axes thus determined might have a small deviation between them. The description of the results on a common coordinate system may be obtained by rotating either of the two coordinate systems about the Z_c-axis so as to minimize $\langle \Delta\theta^2\rangle^{1/2}$. This minimum value of $\langle \Delta\theta^2\rangle^{1/2}$ was calculated for each probable assignment as in Table VII. Here again the difference in $\langle \Delta\theta^2\rangle^{1/2}$ between the two assignments is so small compared with the error, ±4°, that it would be premature to eliminate one of the two assignments.

TABLE VI. COMPARISON OF THE RESULTS OF THE ZEEMAN STUDY WITH THOSE OF X-RAY DIFFRACTION

	Mutual angles between the two principal z-axes of the field-gradient tensors	Mutual angles between the C–Cl bonds by the X-ray diffraction by van Bommel	
A	82°57′	C_3–Cl_3	82°36′
B	85°43′	C_6–Cl_6	86°22′
C	53°37′	C_4–Cl_4	49°56′
D	30°02′	C_5–Cl_5	30°36′
E	108°13′	C_2–Cl_2	106°48′
F	92°48′	C_1–Cl_1	92°48′

TABLE VII. PROBABLE ASSIGNMENT OF THE ABSORPTION LINES TO THE C–Cl BONDS OF α-BHC AND THE RELIABILITY FACTOR

Spectral line	A	B	C	D	E	F	$\langle \Delta\theta^2\rangle^{1/2}$
Assignment 1	3	6	4	5	2	1	2°58′
Assignment 2	6	3	4	5	2	1	2°44′

The assignment obtained here agrees with the tentative one reported previously, and it is consistent with the temperature dependence of the resonance frequencies listed in Table I. According to Bayer's theory,[8] the absorption lines coming from the parallel C–Cl bonds should have the same temperature gradient. Two pairs of lines, A and B, and E and F, have nearly the same temperature gradients, but the curves of the C and D spectral lines cross each other slightly below room temperature. This indicates that the lines, A and B or E and F, may be assigned to the pair of C–Cl bonds which are parallel to each other, whereas C and D may be assigned to a pair of C–Cl bonds which are not parallel, in accord with the results obtained above.

Molecular Structure.—The α-BHC molecule in the gaseous state has a two-fold symmetry axis which passes through the middle point of the C_1–C_2 bond and that of the C_4–C_5 bond, as is shown in Fig. 1, and each of the pairs of chlorine atoms, (Cl_1–Cl_2), (Cl_3–Cl_6), or (Cl_4–Cl_5), is disposed symmetrically with respect to this axis. The molecules in the crystal are appreciably distorted from the configuration in

---

[8] H. Bayer, *Z. Physik*, **130**, 227 (1951).

the gaseous state. Still, the molecules retain a pseudo-two-fold symmetry, as is easily shown by the fact that the principal z-axes of the q-tensors belonging to each of the above chlorine pairs are symmetrically oriented about the axis; the deviations were found to be within 45′ for the pairs, A and B, or E and F, and 3°, for the pair of C and D. The location of the x-axes is also another test for this symmetry; it shows a tendency to satisfy the symmetry, though fairly large errors were unavoidable in determining the x-axes.

TABLE VIII. MUTUAL ANGLES BETWEEN THE PRINCIPAL Z-AXES OF THE FIELD-GRADIENT TENSORS IN THE α-BHC MOLECULE

	B (6)	C (4)	D (5)	E (2)	F (1)
A (3)	2°59′	70°51′	71°12′	72°32′	72°08′
B (6)	—	73°43′	68°31′	72°40′	73°53′
C (4)	—	—	74°06′	62°51′	72°59′
D (5)	—	—	—	71°18′	61°51′
E (2)	—	—	—	—	11°18′

Table VIII shows the mutual angles of the directions of the principal z-axes of the q-tensors within a molecule, as calculated from the results listed in Table II. It exhibits considerable distortions of bond angles from 180° or from the tetrahedral angle. For instances, neither the opposite equatorial bonds, 3 and 6, nor the opposite axial bonds, 1 and 2, are parallel to each other; the deviations amount to 2°59′, or even to 11°18′. For the bond pairs, 2 and 4, and 1 and 5, which consist of an axial bond and an equatorial bond, the deviations from the tetrahedral angle (70°32′) amount to 7°41′ and 8°41′ respectively. A closer examination indicates that the distorting force tends to make the skeleton of the molecule planar, keeping the symmetry of the molecule at a maximum. Therefore, it is likely that the distortions are mainly due to intramolecular forces which act in accordance with the molecular symmetry, and only partly due to intermolecular forces which are not connected with the symmetry of the molecule.

The asymmetry parameters shown in Table III are of the same order of magnitude as those observed in the δ-BHC crystal.⁶⁾ This is another case in which the asymmetry parameters of the chlorine nuclei substituted to a saturated hydrocarbon have been measured. Two effects have been pointed out concerning the origin of the asymmetry of the field-gradient. One is the intramolecular effect, such as the deviation of the hybridization of carbon atoms from sp³, which would be anticipated from the distortion of bond angles. The other is the effect of the crystal field; the electric charge on the neighboring atoms distorts the charge cloud around the chlorine nucleus, thus producing asymmetry in the field-gradient. For δ-BHC, the asymmetry parameters were of the same order of magnitude as that produced by the crystal field. For α-BHC it is likely that, in addition to the crystal field, the intramolecular effect also makes a considerable contribution to the asymmetry parameters, because the principal x-axes tend to satisfy the symmetry of the free molecule. In the δ-BHC crystal, the orientation of the x-axes were not examined except for line B, because the assignment was accompanied by a large uncertainty originating from the errors of the X-ray study, and because two choices between x-axes remained undetermined for the D, E and F spectra. The α-BHC reported here is a fortunate case where the directions of the x-axes have been determined by the pursuit of the measurement at two different mountings of the crystal.

Summary

The Zeeman effect of the nuclear quadrupole resonance has been studied on the ^{35}Cl-nuclei in the racemic α-BHC single crystal at room temperature. The directions of the principal x-, y- and z-axes of the field-gradient tensor at each nucleus have been determined through two runs of measurements of the no-splitting loci of each absorption line. The asymmetry parameters of the field-gradient tensor have also been determined. The C–Cl bonds have been found to be considerably distorted from the directions to be expected from the tetrahedral bond angles for each carbon atom. The distortion takes place in such a way that the skeleton of each molecule approachs a planar configuration. Since the principal axes show a tendency to satisfy the two-fold symmetry, the distorting force has been attributed mainly to the intramolecular forces, and only partly to the intermolecular forces. The previous assignment of the six absorption lines to the six chlorine atoms in the molecule has thus been confirmed.

The authors wish to express their deep thanks to Dr. Hideo Sueta, of the Research Laboratory of the Mitsubishi Chemical Industries, Ltd., for kindly supplying the pure sample of α-BHC. The expenses of the work were defrayed by the Ministry of Education of Japan, to which their thanks are also due.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo