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Nuclear Quadrupole Resonance Study of β-Chloroisocrotonic Acid

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^{35}Cl nuclear quadrupole resonance frequencies have been measured in powders of β-chlorocrotonic acid and β-chloroisocrotonic acid to be 34.966 and 34.261 MHz, respectively, at 78 K. Zeeman effect experiments were conducted on a single crystal of β-chloroisocrotonic acid and the asymmetry parameter of the electric field gradient has been determined to be 0.174 ± 0.016 at 78 K. The π-electron density on the chlorine site has been estimated from the asymmetry parameter according to Bersohn and discussed on the basis of the semi-empirical Pariser-Parr-Pople molecular orbital treatment.

The electronic structure of organic compounds has been examined extensively by electronic spectra, photoelectron spectroscopy and other experimental techniques and the results of these experiments have been used to check the theoretically elucidated atomic and molecular wave functions and *vice versa*. It is still difficult to obtain good wave functions for such heavy atoms as chlorine, bromine, *etc.* which may play very important roles in determining the molecular and crystal structure as well as the reactivity of simple organic compounds.

Pure nuclear quadrupole resonance (NQR) is a powerful tool to examine the electronic structure of the ground state of molecules in crystals and has been applied to numerous organic compounds which contain quadrupole nuclei such as nitrogen, chlorine, bromine, and iodine. This method can be more effective to determine the molecular wave functions if the nuclear quadrupole coupling constant e^2Qq and the asymmetry parameter η of the electric field gradient (EFG) at the resonating nucleus can be measured, but it is necessary to do Zeeman effect experiments on single crystals to obtain η in the case of chlorine and bromine. Although the electronic structure of the chemical bonds between halogens and the carbon atoms in simple halogen-substituted ethylenes has been studied by the NQR method,[1] only semi-quantitative discussions have been possible because of the lack of precise e^2Qq and η in these compounds. The difficulty in obtaining e^2Qq and η stems mainly from the difficulty in growing large single crystals of halogen-substituted olefinic compounds.

The purpose of the present paper is to measure e^2Qq and η of ^{35}Cl precisely in a single crystal of β-chloroisocrotonic acid which contains a typical olefinic C–Cl bond and to discuss the electronic structure of this substance in detail. The bond parameters of the olefinic system elucidated by a semi-empirical molecular orbital method based on the Pariser-Parr-Pople theory are also evaluated.

Experimental

A mixture of ethyl β-chloroisocrotonate and ethyl β-chlorocrotonate was prepared from ethyl acetoacetate and PCl_5 in benzene solution according to methods in the literature.[2,3] The esters were separated by fractionation, and hydrolyzed with hydrochloric acid to give the free acids. The crystals of the acids thus precipitated were collected, and purified by sublimation *in vacuo*. β-chloroisocrotonic acid (hereafter abbreviated as CICA) and β-chlorocrotonic acid (CCA) were identified by high resolution NMR, the melting points being 56 and 90 °C, respectively. A single crystal of the CICA (approximately $1\times2\times3.5$ cm^3) was grown from a solution of water–methanol system.

The ^{35}Cl NQR frequencies were measured between 20 and 80 K, and at 196 and 291 K by using a Dean-type super-regenerative spectrometer on a powdered specimen. The uncertainty in the frequency measurement was within ±1 kHz. Single crystal Zeeman effect experiments were conducted at the liquid nitrogen and at the room temperatures. The zero-splitting loci of the ^{35}Cl resonance line were determined on an oscilloscope by rotating the magnetic field about two mutually orthogonal axes. Details of the apparatus and the method of the frequency determination and the Zeeman measurements have been previously described.[4]

The analysis of the data of the Zeeman effect measurement was performed by using a high-speed electronic computer (NEAC-2200) which has been programmed by Mano.[5]

Results and Discussion

Description of the Crystal Structure. CICA crystallizes in a monoclinic system with the space group $P2_1/c$ and contains four molecules in the unit cell. Two molecules in the unit cell are connected to each other by hydrogen bonds and form a plane dimer.[6] The center of symmetry lies at the center of the dimer, therefore all the chlorines are at equivalent sites in the crystal. The crystal structure of CCA has not been determined.

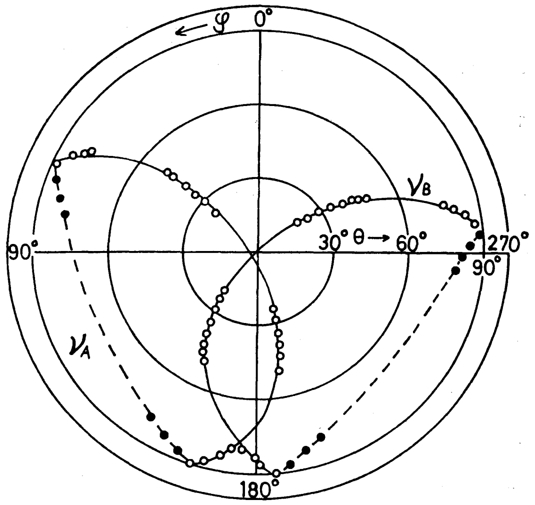

Fig. 1. Zero-splitting loci due to two C–Cl bonds at room temperature. The zero-splitting loci above and below the plane of the paper are distinguished by open and closed circles.

TABLE 1. NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES, QUADRUPOLE COUPLING CONSTANTS, ASYMMETRY PARAMETERS AND THE DIRECTION COSINES OF PRINCIPAL Z-AXIS OF ELECTRIC FIELD GRADIENT TENSORS IN A LABORATORY-FIXED COORDINATE SYSTEM

The standard deviations are given in parentheses.

Resonance line	Temperature/ K	Frequency/ MHz	e^2Qqh^{-1}/ MHz	η	Direction cosines X_L	Y_L	Z_L
ν_A	291	33.605	66.88(0.34)	0.172(0.005)	−0.5397	−0.6151	0.5748
ν_B	291	33.605	66.86(0.27)	0.177(0.004)	−0.3822	0.7451	0.5466
ν_A	78	34.261	68.23(1.10)	0.160(0.016)	−0.5339	−0.6042	0.5916
ν_B	78	34.261	68.11(1.10)	0.190(0.016)	−0.3728	0.7576	0.5358

^{35}Cl Nuclear Quadrupole Resonance. ^{35}Cl NQR frequencies in ClCA were 34.372 ± 0.001 MHz at 20 K and 33.605 ± 0.001 MHz at 291 K. The resonance frequency of ClCA decreases monotonously with increasing temperature as expected by the Bayer-Kushida theory[7,8] and no phase transition was found over the whole temperature range of the measurement. The temperature coefficient $d\nu/dT$ was 2.00 ± 0.25 (Hz K^{-1}) at 50 K which is comparable to that in *trans*-$C_2H_2Cl_2$.[9] The result of the Zeeman effect study on ClCA crystal is shown in Fig. 1. In this figure one may see the location of the two zero-splitting cones in the laboratory-fixed coordinate system. These cones are related to each other by the two-fold screw axis. From these experimental results the nuclear quadrupole coupling constants, the asymmetry parameters and the direction cosines of the principal axes of the electric field gradient tensors were calculated by fitting these zero-splitting data to the relation[10]

$$\sin^2\theta = \frac{2}{3-\eta\cos 2\varphi}, \tag{1}$$

where θ and φ are the polar and the azimuthal angles of the direction of the Zeeman field with respect to the principal coordinate system of the EFG tensors. The number of data collected were 92 for Cl_1 and 99 for Cl_2 at room temperature. The results of the analysis are recorded in Table 1.

The angle between the two principal Z-axes of EFG with different orientations was calculated to be 93.3° which agrees well with 93.1° obtained by the X-ray analysis.[6] It can be seen from Table 1 that the η and the direction cosines of the principal axes X, Y, and Z at 78 K and room temperature were nearly the same.

Semi-empirical Molecular Orbital Treatment of the NQR Parameters. According to the Townes-Dailey theory the electric field gradient eq and the asymmetry parameter η of a free molecule may be expressed in terms of the population difference of the outer p-electron orbitals. If we assume that the population difference of the p_x, p_y, and p_z orbitals are U_x, U_y, and U_z, then

$$q = q_p\left(U_z - \frac{U_x+U_y}{2}\right), \tag{2}$$

and

$$\eta = \frac{3(U_y-U_x)}{U_x+U_y-2U_z} = \frac{3q_p}{2q}(U_y-U_x) = \frac{3e^2Qq_p(U_y-U_x)}{2e^2Qq}, \tag{3}$$

where eq_p is the field gradient due to one p-electron in the valence shell and the Z-axis is assumed to coincide with the C–Cl bond. By putting $e^2Qq_p/h=109.6$ MHz,[11] $e^2Qq/h=68.18$ MHz, $\eta=0.174$, and $U_y=2$ (the population in the chlorine p_y orbital perpendicular to the π-bond between two carbons), U_x was calculated to be 1.93 for the partially π-bonded chlorine orbital p_x in ClCA. Here we have neglected the intermolecular contribution to η.

Grabe[12] calculated the values of U_x for several chlorine-substituted ethylenes by means of a semi-empirical molecular orbital theory proposed by Pariser, Parr, and Pople.[13] In order to examine the reliability of the parameters presented by Grabe we applied the Pariser-Parr-Pople method to ClCA. In the calculation the usual assumptions have been adopted as follows:

$$S_{\mu\nu} = \langle\mu|S|\nu\rangle = \delta_{\mu\nu}$$

$$\alpha_\mu = \langle\mu|H^{\text{core}}|\mu\rangle \neq 0$$

$$\beta_{\mu\nu} = \langle\mu|H^{\text{core}}|\nu\rangle \begin{cases} \neq 0 \text{ when } \mu \text{ and } \nu \text{ are the neighbors} \\ = 0 \text{ when } \mu \text{ and } \nu \text{ are not the neighbors} \end{cases}$$

$$\langle\alpha\beta|r_{ab}{}^{-1}|\mu\nu\rangle = \delta_{\alpha\mu}\delta_{\beta\nu}\gamma_\mu$$

The same notations as in Ref. 12 were used here. The core integral was assumed to be

$$\alpha_\mu = W_\mu - (n_\mu-1)\gamma_{\mu\mu} - \sum_{\mu\neq\nu} n_\nu\gamma_{\mu\nu}.$$

The other parameters were taken as

$$\beta_{\mu\nu} = \beta_0 + \delta_{\mu\nu}{}^{\beta}(R_{\mu\nu}-R_0),$$

$$W_\mu = W_0 + \sum_\nu \Delta W_\mu(\nu),$$

$$\gamma_{\mu\nu} = \gamma_0 + \delta_{\mu\nu}{}^{\gamma}(R_{\mu\nu}-R_0),$$

$$\Delta W_\mu(\nu) = \Delta W_\mu{}^0(\nu) + \delta_{\mu\nu}{}^{W}(R_{\mu\nu}-R_0),$$

where R_0 is the reference distance and $R_{\mu\nu}$ is the real distance between atoms μ and ν. These parameters were determined according to Refs. 12, 14—16 by using the crystal structure data. The ionization potential

TABLE 2. IONIZATION POTENTIAL AND π-ORBITAL POPULATION IN β-CHLOROISOCROTONIC ACID

I_p/eV (calcd)	π-electron density	
9.62	C_{methyl}	1.961
10.19	C_β	0.946
11.75	C_α	1.049
12.68	C_{carboxyl}	0.606
13.55	Cl	1.964
	O_{carbonyl}	1.587
	O_{hydroxyl}	1.885

and the orbital populations calculated by using these parameters are given in Table 2. As there are no available experimental data on the ionization potential of ClCA, the values in Table 2 cannot be evaluated at the present stage.

We now compare the π-electron density in ClCA with those in other olefinic compounds. The π-electron densities on the chlorines in vinyl chloride and *cis*-dichloroethylene in the gaseous state have been deduced to be 1.94[17)] and 1.95,[18)] respectively, from microwave measurements. These values agree fairly well with 1.97 calculated for these compounds by the Pariser-Parr-Pople method.[12)] In the case of ClCA the agreement between the experimental π-electron density 1.93 and the calculated one, 1.96, is comparable to the cases of vinyl chloride and *cis*-dichloroethylene. The experimental π-electron density in ClCA is the smallest of these three olefinic compounds, suggesting that the conjugation of the π-orbitals extends over the whole molecule and makes it easy to form strong π-bonding between the C_β and the terminal chlorine atom. There may be some contribution to η at the chlorine site from the intermolecular interactions which cannot be estimated at the present stage.

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