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An electron spin double resonance study of x-ray irradiated phenacyl chloride single crystals^{a)}

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Single crystals of phenacyl chloride irradiated at room temperature give rise to an EPR spectrum that has been shown by ENDOR and ELDOR studies to be due to the radical



The EPR spectra are complicated by the appearance of a large number of forbidden lines due to the presence of a chlorine quadrupole interaction similar in magnitude to the proton hyperfine coupling. Spectral assignment is not possible by considering the EPR spectra alone. Although ENDOR spectra are difficult to obtain, it is possible to obtain an ENDOR spectrum along one of the crystal axis that identifies the spectra as due to radical I. Furthermore, rather intense and highly resolved ELDOR spectra are obtained at -60 °C as a function of angle enabling the chlorine and proton magnetic hyperfine tensor components of the -CHCl fragment to be determined as -15.4, -8.3, +45.6 MHz and -26.5, -52.5, -80.0 MHz, respectively. The Q_{rr} components of the chlorine quadrupole tensor is -11.2 MHz.

I. INTRODUCTION

The identification and study of α -halogen substituted radicals formed in irradiated organic crystals has always been limited by the complexity of the EPR spectrum. Nevertheless, a number of radicals containing α -halogens have been identified by ESR studies in x- or γ -irradiated crystals of chloroacetamide, ¹ chloroacetic acid,² chlorodifluoroacetamide,³ methyl chloride,⁴ and more recently in x-irradiated five-halogen substituted uracils.⁵ Hyperfine parameters, g values, and quadrupole tensors were obtained for these systems. In addition, 1-monochloro and 1, 1-dichloro substituted radicals have been detected in irradiated alkyl chlorides and α -chlorocarboxylic acid glasses.⁶ Recently the alpha halogen interaction in planar radicals was examined by an INDO study⁷ and shown to be rather consistent throughout different molecular systems and quite predictable by semiempirical molecular orbital theory. In fact an excellent fit was obtained between calculated and experimental hyperfine and quadrupole tensors by retaining the normal INDO scheme for the first and second row elements and parametrizing for best charge densities and relative ionization potentials. It was also found that d orbitals could be neglected as they apparently are not important in calculating the unpaired densities; only s and p orbitals need be retained.

Despite the ability to predict α -chlorine hyperfine couplings, it is still difficult to recognize and to analyze the EPR patterns that appear at an arbitrary crystal orientation for α -chloro-substituted radicals. This is especially true for those orientations where the chlorine quadrupole interaction is similar in magnitude to the chlorine hyperfine couplings, each orientation giving rise to a new and unrecognizable EPR pattern. Unfortunately, to properly examine an oriented radical, it is necessary to select a crystal face that permits easy mounting. However, as luck would have it, the forbidden transitions for such a mounting can be so intense that they may be mistaken as due to another radical. Such a situation occurred when the room temperature EPR spectrum of an x-irradiated phenacyl chloride crystal was recorded. However, after obtaining both ENDOR and ELDOR spectra, it was possible to identify the spectrum as due only to

In addition, it was possible to deduce the α -chlorine and α -proton hyperfine couplings by carrying out a computer diagonalization of the full Hamiltonian.³ The couplings were found to be similar to those previously reported for other chloro-substituted radicals.

In addition to reporting here the hyperfine parameters and structure of

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an important new result is that intense and well resolved ELDOR spectra can be recorded while the observing field is positioned on a forbidden EPR line. This feature greatly expands our ability to identify α -chloro-substituted radicals. Although the ELDOR spectra recorded when the observing field is set on an allowed EPR line is complex to analyze, the ELDOR spectra observed from the forbidden lines can be analyzed and the couplings as a function of angle used as estimates of the hyperfine parameters needed in the computer program MAGNSPEC.^{3,8}

On the other hand, chlorine and proton ENDOR spectra are very difficult to obtain. Only by using very high rf power and long time constants has a signal-to-noise ratio of approximately 8:1 been obtained. It is assumed that the difficulty of obtaining ENDOR spectra may be due to the relaxation conditions being determined by the large chlorine quadrupole interactions. Despite these problems we have been successful in recording ENDOR spectra for the chlorine and proton nucleus and have verified the spectral assignment deduced by ELDOR measurements.

II. EXPERIMENTAL

Single crystals of phenacyl chloride were grown by evaporation of an ethanol solution. The crystals are orthorombic⁹ and belong to the space group $P2_12_12_1$ with Z = 4, a = 19.13, b = 9.6, and c = 4.13 Å. Unfortunately, the identification of the a, b, and c crystal axes with respect to the external crystal morphology is not known so an orthogonal XYZ reference axis system was chosen where the Z axis was taken as the direction perpendicular to the crystal plate, the X axis as the direction parallel to the long direction of the crystal plate, and the Y axis as the orthogonal direction.

The crystals were sealed in a plastic bag (to avoid sublimation) and x-ray irradiated at 30 kV and 20 mA for 4 h at room temperature. The low intensity was used so that the crystals would not melt. The radicals generated were stable providing the crystals were stored below 0°C. The crystals were mounted at one end of a flat machined surface of a 2-mm-o.d. suprasil quartz rod. EPR spectra were obtained with a Varian E-12spectrometer operating at X band (9.5 GHz) and the ELDOR spectra were obtained by use of a Varian E-800 ELDOR spectrometer. The EPR and ELDOR data were collected for every 10 deg in the three-axis system at around -60 °C. The ENDOR spectra were taken with the crystals mounted on the ENDOR probe previously described¹⁰ with the balum transformer rewired so more rf power was available at the crystal. This was necessary because no ENDOR signals were observed between 6 and 240 K using the circuit given in Ref. 10. The balum transformer was wound so that the top and bottom wires in Fig. 2 of Ref. 10 (right hand side) were tied together. The inner pair were also tied together. The top two wires (left side) were used as the ground wire with the bottom wire as input and the remaining wire as output. This has the disadvantage that the balum no longer protects the rf coil from being destroyed by excess rf power. The ENDOR coil system was inserted into a TE₁₀₂ rec-



FIG. 1. EPR of x-irradiated single crystals of phenacyl chloride (x-irradiated at room temperature and spectrum measured at -60° C). Magnetic field is along canonical direction Z of one molecular site of α -chloro radical fragment -CHCl. The three arrows denoted by 1, 2, and 3 indicate the three ELDOR observing positions, and E_2 and E_1 denote the two ENDOR observing positions.

tangular cavity operating at 9.5 GHz. With this modification to the ENDOR system, weak ENDOR spectra were obtained at 77 K. Lowering the temperature to 6 K did not improve the intensity; in fact, even less intense ENDOR spectra were observed.

The rf field was measured by the side-band technique.¹¹ The rf signal from a Wavetek model 1101A sweep generator was amplified by a model 3100 E.N.I. rf power amplifier. The ENDOR spectra were recorded at 77 K along the Z axis using the standard Varian liquid nitrogen accessory.

III. RESULTS

The first derivative EPR spectrum observed at -60 °C for the room-temperature x-irradiated phenacyl chloride single crystals when $H_0 \parallel Z$ is shown in Fig. 1. The arrows in Fig. 1 denote ELDOR and ENDOR observing positions. The EPR spectrum is complex, suggesting two possibilities. One, the spectrum may be due to the breakdown of the first order selection rule as a result of a quadrupole interaction being larger than a hyperfine coupling for a nucleus with I = 3/2. Alternatively, the spectrum may be due to an overlap of the spectra from two or more radicals containing several unequal couplings for I = 1/2 nuclei. However, upon crystal rotation the two lines of lower intensity at high and low field increased in intensity. In addition, the four-line pattern which appears twice by virtue of a I = 1/2 coupling exhibits a marked unequal spacing with angle. Such a spectral feature is typical for a radical containing a strongly coupled nuclei with a quadrupole coupling greater than the hyperfine coupling. Thus the first possibility appears to be the case, and chemically the nucleus with I = 3/2 must be a chlorine. Furthermore, the ENDOR and ELDOR spectra substantiate these findings.

There are two natural abundant isotopes of chlorine, 35 and 37, which occur in an intensity ratio of 3 to 1, respectively. Each isotope has a nuclear spin equal to $\frac{3}{2}$ and each possesses a large nuclear quadrupole moment. The ratio of the magnetic moments $\mu({}^{35}\text{Cl})/\mu({}^{37}\text{Cl})$ = 1.201 and the ratio of the quadrupole moments $Q({}^{35}\text{Cl})/Q({}^{37}\text{Cl})$ = 1.272. To determine **Q** and **A**, the experimental spectra is compared to that calculated using a Hamil-



FIG. 2. ENDOR spectrum at 77°K for the x-ray-irradiated single crystals of phenacyl chloride along the X axis at observing position E_2 . (A) between 17 and 56 MHz, (B) 2 to 12 MHz.

tonian that includes the quadrupole interaction. This is usually tedious^{3, 5, 7} and can require a great deal of computer time, as all transitions (forbidden and allowed in first order) must be calculated and then compared to the observed EPR spectrum. In many cases, the poorly resolved EPR spectrum prevents a unique solution for the quadrupole tensor from being derived. A much more straightforward measure of \mathbf{Q} is by ENDOR, where only a few highly resolved lines are observed.¹²

The ENDOR spectrum obtained at field position E_2 and at 77 K for $H_0 \parallel Z$ is given in Fig. 2(A) and 2(B) for an rf scan between 17 and 56 MHz and 2 and 12 MHz, respectively. In general, the first-order ENDOR frequencies 12,13 are given by

$$h\nu = |G_M + 3P_M(m - 1/2)| , \qquad (1)$$

$$G_M^2 = \mathbf{h} \cdot (\mathbf{T}^M)^2 \cdot \mathbf{h} , \qquad (2)$$

$$G_{M}^{2}P_{M} = \mathbf{h} \cdot \mathbf{T}^{M} \cdot \mathbf{Q} \cdot \mathbf{T}^{M} \cdot \mathbf{h} , \qquad (3)$$

$$\mathbf{T}^{M}h = M^{s}\mathbf{A}h - g_{n}\beta_{n}H_{0} , \qquad (4)$$

where h is a unit vector directed along the magnetic field H_0 ; $M = \pm 1/2$, the electron spin; A = hyperfine coupling matrix; and Q = quadrupole matrix. Along a given direction, these equations can be simplified to those given in Table I if, in addition, the presence of a



radical is assumed. This assumption is based on the analysis of the angular dependence of the EPR lines in the three planes and comparisons to previous studies. The equations in Table I have been listed according to the selection rules $\Delta m_{C1} = \pm 1$, $\Delta m_H = 0$, and $\Delta m_{C1} = 0$, $\Delta m_H = \pm 1$ with $g_n \beta_n H_0 = \nu(\text{Cl})$ or $\nu(\text{H})$. A reasonable first-order fit to the ENDOR lines for $H_0 \parallel Z$ occurs assuming $A(\text{H}) = -80.0 \text{ MHz}, A(^{35}\text{Cl}) = -14.5 \text{ MHz}, P(^{35}\text{Cl}) = -11.2 \text{ MHz}, \nu(^{35}\text{Cl}) = 1.38 \text{ MHz}, \nu(^{37}\text{Cl}) = 1.15 \text{ MHz}, A(^{37}\text{Cl}) = -12.07 \text{ MHz}, P(^{37}\text{Cl}) = -8.82 \text{ MHz}, \text{ and that the radical is a -CHCl type fragment.}$

It is interesting to note that the proton ENDOR lines $(\Delta m_{C1} = 0, \Delta m_{H} = \pm 1)$ that occur at 54.0 and 26.0 MHz exhibit a phase opposite to that observed for the chlorine ENDOR lines. In addition, the intensity for the high frequency proton line (54.0 MHz) is approximately eight times more intense than the low frequency line (26.0 MHz). Apparently this is due to some type of dominant cross relaxation which causes the lower frequency peak of each ENDOR doublet to be quite weak, making it more difficult to analyze the entire spectrum. Although the chlorine ENDOR spectral intensity is in general weaker than that due to proton, ENDOR lines are still detected

TABLE I. ENDOR transitions along the Z axis assuming A(H) = -80.0 MHz, $\nu(H) = 14.0 \text{ MHz}$, $A(Cl^{35}) = -14.5 \text{ MHz}$, $P(^{35}Cl) = -11.2 \text{ MHz}$, $\nu(Cl^{35}) = 1.38 \text{ MHz}$, $\nu(Cl^{37}) = 1.15 \text{ MHz}$, $A(Cl^{37}) = -12.07 \text{ MHz}$, $P(Cl^{37}) = -8.82 \text{ MHz}$.

$\Delta m_{\rm Cl} = \pm 1$, $\Delta m_{\rm H} = 0$	C1(35)	C1(37)
$\nu_1 = \frac{1}{2}A(C1) - \nu(C1) + 3P =$	42.20	33.64
$\nu_2 = \frac{1}{2}A(C1) - \nu(C1) =$	8.60	7.18
$\nu_3 = \frac{1}{2}A(C1) - \nu(C1) - 3P =$	24.97	19.30
$\nu_4 = -\frac{1}{2}A(C1) - \nu(C1) + 3P =$	27.73	21.58
$\nu_5 = -\frac{1}{2}A(Cl) - \nu(Cl) =$	5.87	4.88
$\nu_6 = -\frac{1}{2}A(Cl) - \nu(Cl) - 3P =$	39.47	31.34
$\Delta m_{\rm Cl} = 0$, $\Delta m_{\rm H} = \pm 1$		
$\nu_1 = \frac{1}{2}A(H) + \nu(H) = 26 \text{ MHz}$		
$\nu_2 = \lfloor \frac{1}{2} A(\mathrm{H}) - \nu(\mathrm{H}) \rfloor \approx 54 \ \mathrm{MHz}$		



FIG. 3. ELDOR spectra at -60°C for the x-ray irradiated single crystals of phenacyl chloride along the Z axis at observing positions 1, 2, and 3.

from both the 35 and 37 isotope of chlorine. A perfect fit to the experimental spectra is probably not possible as second-order and off-diagonal effects have not been included. In addition, ENDOR spectra as a function of angle were not attempted as the spectra were in general too difficult to obtain. Instead, to determine the hyperfine tensors, ELDOR spectra were recorded as a func-

 $\frac{3}{2}, -\frac{3}{2}$

-3, 3

1 + 1. 12

 $\frac{1}{2}, \frac{1}{2}$

 $\frac{1}{2}, -\frac{1}{2}$

 $-A(C1) - 2\nu(C1) - 2P = 34.2$

 $-A(C1) + 4\nu(C1) - 2P = 42.3$

tion of angle at observing positions 1, 2, and 3 of Fig. 1. The ELDOR spectra observed along the Z axis are given in Fig. 3. Qualitatively, it is noted that intense and well resolved spectra are obtained for all observing magnetic field positions 1, 2, and 3. The intensity of the spectrum obtained at position 3 is reduced somewhat because the EPR line intensity at position 3 is lower than at position 1 or 2.

It is instructive to examine the complex ELDOR spectra for $H_0 \parallel Z$ by assuming a first-order description of the energy levels given by Eq. (1):

$$W(M, m) = g\beta HM + A(Cl)m_{Cl}M - \nu(Cl)m_{Cl} + P(Cl)[m_{Cl}^2 - \frac{1}{3}I(I+1)] + A(H)m_HM - \nu(H)m_H .$$
(1)

The ENDOR parameters deduced from position E_2 were initially assumed for Eq. (1). Based on these initial values, it was possible to assign $m_{\rm I}$ values to each of the more intense ELDOR peaks in Fig. 3. The first order equations for the ELDOR transitions experimentally observed as a function of $(\nu_p - \nu_o)$ and the calculated frequencies are given in Table II. Since both a pumping as well as an observing frequency are involved, the ELDOR transitions are commonly referred to by the type of observing transition (allowed or forbidden) followed by the

TABLE II. The first-order ELDOR transitions for chlorine-35 in the CHClC- ϕ radical. ELDOR transitions are observed at positions indicated in Fig. 1.

Position 1 pumping transitions		ELDOR frequency (MHz)	Posi pumping	tion 2 transitions	ELDOR frequency (MHz)	
$\frac{C1}{(m_{\rm I} - m_{\rm I})}$	$\begin{array}{c} H\\ (m_{1}-m_{1})\end{array}$		$\frac{Cl}{(m_{\rm I} - m_{\rm I})}$	H $(m_{\rm I} \leftarrow m_{\rm I})$	_	
$-\frac{1}{2}, -\frac{1}{2}$	1/2, 1/2	A(Cl) = - 14.5	$-\frac{3}{2}, -\frac{3}{2}$	$\frac{1}{2}, \frac{1}{2}$	-A(C1) = 14.5	
$-\frac{1}{2}, -\frac{3}{2}$	$\frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}A(Cl) - \nu(Cl) - 2P = 13.8$	$-\frac{1}{2}$, $\frac{1}{2}$	$\frac{1}{2}$, $-\frac{1}{2}$	$\frac{1}{2}A(Cl) + \nu(Cl) - \frac{1}{2}A(H) - \nu(H) = 19, 1$	
$-\frac{3}{2}, \frac{3}{2}$	$\frac{1}{2}, \frac{1}{2}$	$\frac{3}{2}A(Cl) + 3\nu(Cl) = -17.6$	$-\frac{3}{2}, \frac{3}{2}$	$\frac{1}{2}$, $-\frac{1}{2}$	$\frac{1}{2}A(Cl) + 3\nu(Cl) - \frac{1}{2}A(H) - \nu(H) = 21, 9$	
$-\frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}$	$\nu(C1) + \frac{3}{2}A(C1) = -20.4$	$-\frac{3}{2}, -\frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}$	$-\frac{1}{2}A(C1) + \nu(C1) + 2P = -13.8$	
$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}$	$-\nu(C1) + \frac{3}{2}A(C1) = -23.1$	$-\frac{1}{2}, -\frac{3}{2}$	$\frac{1}{2}, \frac{1}{2}$	$-\frac{1}{2}A(C1) - \nu(C1) - 2P = 27.9$	
$-\frac{3}{2}, -\frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}A(C1) + \nu(C1) + 2P = -28.3$	$-\frac{1}{2}, -\frac{3}{2}$	$\frac{1}{2}$, $-\frac{1}{2}$	$-\frac{1}{2}A(CI) - \nu(CI) - 2P - \frac{1}{2}A(H) - \nu(H) = -52.5$	
$-\frac{3}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}$	$A(C1) + 2\nu(C1) + 2P = -34.2$	$-\frac{3}{2}, -\frac{3}{2}$	$\frac{1}{2}$, $-\frac{1}{2}$	$-A(C1) - \frac{1}{2}A(H) - \nu(H) = 39.5$	
$\frac{3}{2}, \frac{3}{2}$	$-\frac{1}{2}, -\frac{1}{2}$	3A(C1) - A(H) = 34.5	$\frac{3}{2}, -\frac{3}{2}$	$-\frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}A(C1) - 3\nu(C1) - \frac{1}{2}A(H) + \nu(H) = 41.6$	
$-\frac{1}{2}, -\frac{1}{2}$	$-\frac{1}{2}, \frac{1}{2}$	$+A(Cl) + \nu(H) - \frac{1}{2}A(H) = 38.5$	$-\frac{1}{2}, -\frac{1}{2}$	$-\frac{1}{2}$, $\frac{1}{2}$	$-\frac{1}{2}A(H) + \nu(H) = 53.0$	
$\frac{1}{2}, -\frac{1}{2}$	$-\frac{1}{2}, -\frac{1}{2}$	$\frac{3}{2}A(C1) - A(H) - \nu(C1) = 54.9$	$-\frac{3}{2}, -\frac{3}{2}$	$-\frac{1}{2}, \frac{1}{2}$	$-A(C1) - \frac{1}{2}A(H) + \nu(H) = 67.5$	
$-\frac{1}{2}, \frac{1}{2}$	$-\frac{1}{2}, -\frac{1}{2}$	$\frac{3}{2}A(Cl) - A(H) + \nu(Cl) = 57.6$	$\frac{1}{2}, -\frac{3}{2}$	$-\frac{1}{2}, \frac{1}{2}$	$-2\nu(C1) - 2P - \frac{1}{2}A(H) + \nu(H) = 72.6$	
$\frac{3}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}$	$\frac{5}{2}A$ (C1) + 2P (C1) - ν (C1) = -60, 0				
$-\frac{3}{2}, -\frac{3}{2}$	$-\frac{1}{2}, -\frac{1}{2}$	- A (H) = 78				
Posi pumping	tion 3 transitions	ELDOR frequency (MHz)	Position 3 pumping transitions		ELDOR frequency (MHz)	
$\frac{Cl}{(m_{\rm I}-m_{\rm I})}$	$\begin{array}{c} H\\ (m_{\rm I} \leftarrow m_{\rm I}) \end{array}$		$\frac{Cl}{(m_{\rm I}-m_{\rm I})}$	$\frac{H}{(m_{\rm I}-m_{\rm I})}$		
$\frac{3}{2}, -\frac{1}{2}$	ź, ż	-A (Cl) = 14.5	$-\frac{3}{2}, -\frac{3}{2}$	$\frac{1}{2}, -\frac{1}{2}$	$-\frac{5}{2}A(Cl) + \nu(Cl) - 2P = 60.0$	
3, 3 2, 2	$\frac{1}{2}$, $\frac{1}{2}$	$\frac{1}{2}A(Cl) + \nu(Cl) - 2P = 16.5$	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}$, $-\frac{1}{2}$	$-A$ (Cl) $-\nu$ (H) $-2P - \frac{1}{2}A$ (H) = 61, 9	
$-\frac{3}{2}, \frac{1}{2}$	1/2, 1/2	$-\frac{3}{2}A(C1) + 3\nu(C1) = 25.9$	$\frac{1}{2}, \frac{3}{2}$	$\frac{1}{2}$, $-\frac{1}{2}$	$2\nu(C1) - 4P - \nu(H) - \frac{1}{2}A(H) = 72.6$	
$-\frac{3}{2}, -\frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}$	$-2A(Cl) + 2\nu(Cl) = 31.7$	$-\frac{1}{2}, -\frac{3}{2}$	$\frac{1}{2}, \frac{1}{2}$	-2A(C1)-4P=73.8	

- ³/₂, 32 $-\frac{1}{2}, \frac{1}{2}$ $-A(Cl) + 4\nu(Cl) - 2P + \nu(H) - \frac{1}{2}A(H) = 95.4$ $-\frac{1}{2}A(C1) - \nu(H) + \nu(C1) - 2P - \frac{1}{2}A(H) = 56.0$ 32 1/2, $-\frac{1}{2}, \frac{1}{2}$ $-2\nu(C1) - 4P + \nu(H) - \frac{1}{2}A(H) = 95.0$

 $-\frac{3}{2}A(C1) - \nu(C1) - 4P - \nu(H) - \frac{1}{2}A(H) = 90, 2$

 $\frac{1}{2}, -\frac{1}{2}$

 $\frac{1}{2}, -\frac{3}{2}$

	Coupling (MHz)	l (with r	Direction cosin espect to XYZ	es reference)	φ	θ
	(-) 26.5	0.5594,	- 0. 8286,	0.0207	- 56.0	88.8
A (¹ H)	(-) 52, 5	0.8286.	0.5597,	0.0104	34.0	89.4
	(-) 80.0	-0.0203,	0.0113,	0.9997	150.5	1.3
	$A_{100} = -53.$	0 MHz				
A (³⁵ C1)	(_) 8,3	0.0724,	- 0, 9120,	0.4037	- 85.5	66.2
	(-) 15.4	-0.0266,	0,4029,	0.9149	93.8	23.8
	45.6	0.9970,	0.0770,	-0.0049	4.4	90.3
	$A_{100} = 7.3$]	MHz				
Q (³⁵ C1)	5.3	0.0713,	- 0. 9974,	0.0089	- 85, 9	89.5
	5.9	-0.9973,	-0.0712,	0.0206	- 175.9	88.8
	- 11.2	0.0199,	0.0104,	0,9998	27.1	1.3

TABLE III. ¹H and 35 Cl hyperfine coupling constants and 35 Cl quadrupole coupling constant for radical I.

type of pumping transition (allowed or forbidden). For example, position 1 is an allowed EPR transition ($m_{\rm H}$ $=\frac{1}{2} - \frac{1}{2}$, $m_{\rm C1} = -\frac{3}{2} - -\frac{3}{2}$) while the identified pumping transitions are all forbidden and thus the lines are referred to as allowed-forbidden transitions (see Table II for assigned list) except lines at 14.5 and 34.5 MHz which are allowed-allowed transitions. For position 2, the observed transition is ($m_{\rm H} = \frac{1}{2} - \frac{1}{2}$, $m_{\rm C1} = -\frac{1}{2} - -\frac{1}{2}$) while all the pumping transitions are forbidden except the allowed pumping transitions at 14.5 MHz.

In both positions 1 and 2, only the more intense spectral lines were assigned. No attempt was made to assign the weaker lines as a fit to the hyperfine parameters given in Table III was possible for the stronger lines.

The most useful ELDOR spectra as a function of angle are obtained while observing position 3-a forbidden line $(m_{\rm H} = \frac{1}{2} - \frac{1}{2}, m_{\rm Cl} = \frac{3}{2} - \frac{1}{2})$ —and pumping various formally forbidden lines. The change in the first-order quantum number for the pumping transition is given in Table II along with the transition frequency. The ELDOR transitions that occur at 14.5, 16.5, 25.9, 31.7, 34.2, and 42.3 MHz are due to $\Delta m_{\rm Cl} = 0, \pm 1, \pm 2, \pm 3, \Delta m_{\rm H}$ = 0 pumping transitions and are of the same phase; those at 56.0 and 60.0 MHz are due to $\Delta m_{C1} = 0$, $\Delta m_{H} = \pm 1$ while the line at 73.8 MHz is due to $\Delta m_{C1} = \pm 1$, Δm_{H} = 0, and the lines at 90.2, 95.0, and 95.4 MHz are due to $\Delta m_{C1} = \pm 2, -1, \pm 3, \Delta m_{H} = \pm 1$ pumping transitions, respectively. Each ELDOR line can be accounted for by the hyperfine parameter $A(^{35}Cl) = -14.50$ MHz, A(H)= -78.0 MHz, and $P(^{35}Cl) =$ -11.2 MHz. Each observed ELDOR line from position 3 is similar in intensity, in contrast to the spectrum obtained at positions 1 and 2 where a variety of intensities are observed. The change in the effective proton hyperfine coupling is due to a small observed temperature dependence. The ELDOR spectra were taken at a higher temperature (213 K) than the ENDOR spectra (77 K).

The fit of the ENDOR derived (observed from magnetic field position E_2) parameters to the ELDOR lines obtained by setting on the weak EPR lines, ¹⁻³ show positive proof that the spectrum in Fig. 1 is due only to one

radical. The angular dependence of the ELDOR and EPR lines in the 3 planes was used to estimate the input couplings needed for the computer program MAGNSPEC. The resulting ¹H and ³⁵Cl hyperfine coupling constants and ³⁵Cl quadrupole coupling observed at 213 K are listed in Table III. These parameters represent a best-fit of the angular dependence calculated from the computer program MAGNSPEC to the EPR and ELDOR data. An example of the fit is given in Fig. 4 for the EPR spectrum along the X axis.

IV. DISCUSSION

The complete ³⁵Cl hyperfine tensor is directly related to the spin density and orbital structure in the -CHCl fragment. Following the analysis given by Kohin¹ for the chlorine coupling tensor yielded the spin densities in the different -CHCl orbitals reported in Table IV. The 3s density is derived from the isotropic coupling and from the $3p_x$ and $3p_z$ densities of the chlorine 3s and 3porbitals deduced from the anisotropic coupling. The $3p_x$ and $3p_z$ densities are calculated by separating the anisotropic dipolar components into two axial sets along x and z in the usual manner. These calculated unpaired spin density distributions are compared in Table V to those calculated for the CHClCOOH₂ radical in α -chloroacetamide¹ and the CHClCOOH radical in 2-chloroacetic



FIG. 4. EPR spectrum of x-ray irradiated single crystals of phenacyl chloride (x-irradiated at room temperature and spectrum measured at -60 °C). Magnetic field is along the canonical direction X of the α -chloro fragment -CHCl. Theoretical line positions resulting from the various hyperfine interactions are indicated.

TABLE IV. Contributions of the 35 Cl hyperfine tensor and spin density in various orbitals in

Orbital		Oį	снсі		
		Chlorine-35	coupling tens	ing tensors (MHz)	
	ρ	A _{xx}	Ayy	Azz	
2 p ^C _x	+ 0. 81 ^a	-0.6	-1.0	+1.6	
$3 p_x^{C1}$	+0,13	+35,8	-17.9	-17.9	
3 p CI	- 0, 023	+3.2 ^b	+3.2 ^b	-6.4 ^b	
3 s ^{Cl}	+0.0015	+7.3	+7.3	+7.3	
Total	+0.91	+45.7	- 8.4	- 15.4	

^aFrom $a^{H} = Q \cdot \rho$ (Q = -23.3 G, R. P. Kohin used Q = 26.3).

Calculated following H. M. McConnell and J. Strathdee, Mol. Phys. 2, 129 (1959).

acid.² A very close similarity is found. The calculated isotropic proton and chlorine hyperfine couplings of -53.0 and +7.3 MHz were slightly smaller than the couplings of -56.6 and +10.4 MHz observed for CCIHCOOH trapped in irradiated α -chloroacetic acid.² The lower isotropic couplings were assumed to be due to the delocalization of the unpaired spin density into the aromatic ring. This is in agreement with the 13 percent spin density in the $3p_x$ orbital of chlorine indicating appreciable delocalization onto atoms other than chlorine. Spin delocalization has been attributed to the low values of α -chlorine interaction in x-ray-irradiated 5-chlorode-oxyuridine single crystals.¹⁴

From the crystal structure data reported⁹ for phenacyl chloride,

$$\phi - C(2) - C(1)H(1)H(2)Cl$$
,

the calculated dihedral angle between the aromatic ring and the O-C(2)-C(1) group equals 1.2°, between O-C(2)-C(1) and C(2)-C(1)-Cl equals 3.9°, between O-C(2)-C(1) and C(2)-C(1)-H(2) equals 123.2°, and between O-C(2)-C(1) and C(2)-C(1)-H(1) equals -115.2° .

TABLE V. Experimental spin densities of $\dot{C}HClC-R$ radicals $(R = \phi, NH_2, OH)$.

Radical	3s(Cl)	3p _x (C1)	3p_(C1)	Reference
сінсіо	+0.0015	0.130	- 0. 023	This work
·CHC1C-NH2	+0.0015	0.132	-0,025	1
· CHCIC-OH	+0.0018	0, 119	-0.0245	2

TABLE VI. Crystallographic directions for

Ų.	
A_C_CH_CL	
w	

Bond	Direction cosines			
plane	a	b	c	
C(1)-C(2)	0.6077	0.7942	0.000	
C(1)Cl	-0.8584	0.3425	0.3819	
C(1)-H(1)	0.3728	-0.7315	0.5702	
C(1)_H(2)	-0.1369	-0.3402	- 0, 9303	
O ∥ C-C plane (⊥) ^a	- 0.3628	0 . 27 76	- 0.8895	
aromatic ring $(\bot)^a$	-0.3760	0.2667	-0.8874	
	0			

^aDihedral angle between the $\overset{\parallel}{C}$ -C plane and the aromatic ring, 1.2°.

Thus, if protons 1 and 2 are removed, the remaining fragment is essentially planar, the C(1)-Cl bond lying in the plane of the aromatic ring. Furthermore, the normal to this plane is approximately parallel to the ccrystallographic axis, the molecular stacking direction. According to a general rule of thumb in crystallography, ¹⁵ crystals of molecules containing aromatic rings grow more rapidly along a direction normal to the plane of the aromatic rings (due to the relatively strong interaction between the π clouds of the ring) than in any other direction. Thus it would appear that the longest dimension of the crystal plate is the c axis. Furthermore, the *a* axis must be the direction perpendicular to the crystal plate since a crystal usually grows the slowest perpendicular to the stacking direction. If this is true than the ZYX reference system chosen for this study is parallel to the abc crystal direction, respectively. This assignment is also consistent with the expected direction of the unpaired electron being approximately along the long dimension of the crystal.

In Table VI are given selected bond directions and the normals to planes. The angle between the C(1)-H(1)bond direction and the smallest proton coupling equals 21.1° while that for the C(1)-H(2) direction equals 76°. Thus it would appear that H(2) was lost upon radical formation. One somewhat disturbing result is that the angle between the normal to the OC(2)-C(1) plane (the expected maximum unpaired electron density direction) and the largest chlorine coupling direction is 25.0°suggesting some reorientation has occurred besides the change in the C(1)-H(2) bond direction. In addition, a rather large angle difference of 29° between the largest chlorine and the medium size proton coupling directions is inconsistent with a planar CHCl fragment but apparently outside the limits of error. The reason for this is not understood.

V. CONCLUSION

The EPR, ENDOR, and ELDOR data support the assignment of radical I as those generated by x irradiation of single crystals of phenacyl chloride. Spectral assignment was not possible by using EPR data alone because the EPR spectra were complicated by the appearance of a large number of forbidden lines. It is shown that the chlorine quadrupole interaction can be measured from ENDOR data taken along one of the crystal axes. This information is combined with the highly resolved angular-dependent ELDOR spectra to yield the chlorine and proton magnetic hyperfine tensor components of -15.4, -8.3, +45.6 MHz, and -26.5, -52.5, - 80.0 MHz, respectively. The Q_{zz} ⁽³⁵Cl) component of the chlorine quadrupole tensor is -11.2 MHz. Based on the values of the ³⁵Cl hyperfine tensor, radical I has been found to exist as a planar π radical. The spindensity assignments in the various orbitals in radical I are $\rho(2p_x^{C}) = 0.81$, $\rho(3p_x^{C1}) = 0.13$, $\rho(3p_x^{C1}) = -0.023$, and $\rho(3s^{C1}) = 0.0015$. The lower chlorine isotropic coupling (7.3 MHz) compared to α -chloroacetic acid (10.37 MHz) and α -chloroacetamide (8.41 MHz) was assumed to be due to delocalization of the unpaired spin density into the aromatic ring.

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