

MAR 4 1964
**TECHNICAL REPORT
of
I S S P**

CONF-403-1

Ser. A No. 90

Sep. 1963

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Published by

THE INSTITUTE FOR SOLID STATE PHYSICS
THE UNIVERSITY OF TOKYO
TOKYO JAPAN

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TECHNICAL REPORT OF ISSP

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ELECTRON SPIN RESONANCE OF AN IRRADIATED SINGLE CRYSTAL
OF POTASSIUM HYDROGEN MALEATE*

by

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September 1963

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ABSTRACT

Electron spin resonance absorptions of X-irradiated single crystals of potassium hydrogen maleate and potassium deuterium maleate were observed mainly at 24 kMc/sec. as well as at 9 kMc/sec. Both compounds gave the same hyperfine structures, although the slightly sharper line widths were observed for the deuterium exchanged compound. The hyperfine structures were reasonably assigned to the two proton system. The direction of the minimum element of the coupling tensor approximately coincides with that of the C - H bond. The two coupling protons should be $\text{H} \geq \text{C} = \text{C} \leq \text{H}$. The line widths for the both compounds were very sharp and from one to two gauss in distance between maximum slopes. The largest difference between the line widths of the two compounds was only 0.5 gauss. This is very much smaller than the smallest possible difference expected for the case that the OH proton exists in the produced radical. The sharp line widths and their small change by the deuterium substitution suggest that the most probable radical is the one which is produced by the removal of the OH hydrogen atom. Since the direction of the minimum element of the *g*-tensor is perpendicular to the molecular plane, the unpaired electron is a π -electron in accordance with the prediction from the simple LCAO calculation presented in this paper.

* This work was presented at the 16th Annual Meeting of the Chemical Society of Japan, April 2, 1963.

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INTRODUCTION

According to an unpublished work of Professor I. Miyagawa, electron spin resonance (ESR) absorptions of irradiated polycrystals of oxalic acid, fumaric acid, and maleic acid are weak and hardly detectable, in contrast to strong absorptions from those of their salts of metal ions such as Na^+ , K^+ , and Ca^{++} . This notable difference in intensity is in harmony with the view of Gordy, Ard, and Shields¹⁾ which has been given in the case of oxalic acid: In a crystal the molecules which have conjugate double bonds are linked by intermolecular hydrogen bonds; thus, holes (or odd electrons) which are produced by irradiation may easily migrate throughout the entire crystal through the conjugate systems and hydrogen bonds, until recombination of the holes and odd electrons takes place. Because of absence of intermolecular hydrogen bonds, no such migrations are expected for the salts, and the molecules with holes or odd electrons will be transformed into radicals.

In connection with the above mentioned results, a crystal of potassium hydrogen maleate is of interest: There is no intermolecular hydrogen bond, though each molecule still has an intramolecular hydrogen bond. Actually, a strong ESR absorption is observed for an irradiated polycrystalline specimen of this compound. This paper deals with identification of the radicals produced in a single crystal of this compound.

EXPERIMENTAL PROCEDURE

The single crystals of potassium hydrogen maleate and its deuterium exchanged compound ($\text{KOOCH}=\text{CHCOOD}$) were grown from aqueous and heavy water solutions, respectively, by the slow cooling method. The purity of the deuterium exchanged compound was tested by the infrared spectra. The single

crystals obtained were typical orthorhombic crystals, the crystal axes of which were identified by taking vibration photographs of X-ray diffraction. The crystal structure of KHM has completely analysed by Darlow and Cochran²⁾ giving the orthorhombic space group *Pbcm*, with four molecules per unit cell and cell dimensions $a = 4.578\text{ \AA}$, $b = 7.791\text{ \AA}$, $c = 15.953\text{ \AA}$. The results of the ESR will be compared with their crystal analysis in the later paragraph of this paper.

The single crystals were irradiated at room temperature by an X-ray source operating at 30 kV. and 15 mA. The ESR of irradiated single crystals was measured mainly at 24 kMc/sec. for various orientations of the crystal in the magnetic field at room temperature. As a reference for the spectroscopic splitting factor, the sharp resonance of DPPH was used. The separations of the hyperfine structures were measured by a proton resonance with a side band technique.³⁾

EXPERIMENTAL RESULTS

The ESR spectra first observed at 9 kMc/sec. showed a marked second order effect⁴⁾ making the spectra somewhat complicated, but the one observed at 24 kMc/sec. showed practically no second order effect making the spectra simpler enough to interpret very easily and accurately. Therefore the measurements for various orientations of the crystal were mainly carried out at 24 kMc/sec. Figure 1 depicts the ESR spectrum measured at 9 kMc/sec. for the orientation of the crystal in the magnetic field parallel to the crystal *c*-axis. The hyperfine structure of the spectrum was interpreted based on the theory of the second order effect⁴⁾ giving a good agreement with the observation. The vertical lines under the absorption lines indicate the theoretical spectral positions and their intensities.

The spectra observed at 24 kMc/sec. for orientations of the crystal in the magnetic field parallel to three crystallographic axes consist of three lines, the relative intensities of which are 1 : 2 : 1. If the crystal is rotated around the a or b -axis, fixing the magnetic field in the (bc) or (ca) plane of the crystal, respectively, the triplet was resolved into quartet which consists of a pair of doublets expected for two non-equivalent protons with spin 1/2 (see Fig. 2 and 3). This suggests that for these orientations the unit cell contains only one kind of radical which has two chemically equivalent protons, and that the two protons are not magnetically equivalent for the field along the intermediate directions of the crystal axes. However if the crystal is rotated around the c -axis, fixing the magnetic field in the (ab) plane of the crystal, the single triplet was resolved into a pair of triplets, the g -factors of which are different each other (see Fig. 1). This means that for this orientation of the crystal there are two kinds of radicals which are magnetically non-equivalent each other. In this case the triplets were not resolved into quartet as in the case of the rotation around the a or b -axis. Therefore the two coupling protons in a radical are magnetically equivalent for any orientation produced by the rotation around the c -axis.

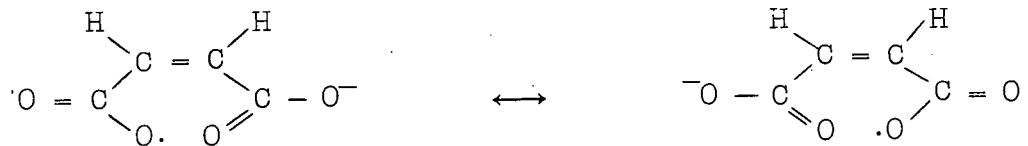
From the interpretation of the observed spectra, it is concluded that there are four coupling protons in a unit cell. The principal values and the direction cosines of the hyperfine tensors for these protons determined from the angular dependence of the coupling constants were tabulated in Table I. The principal values and their direction cosines of the g -tensors were also determined from the angular dependence of the center of the hyperfine patterns and are listed in Table I.

The ESR of an irradiated single crystal of potassium deuterion maleate

(KDM) was also measured in order to get some additional information about the structure of the free radical. The observed spectra, however, did not show any difference from the one for KHM in the coupling values. The line widths for both compounds were very sharp and from one to two gauss in distance between maximum slopes. Although the slightly sharper lines were observed for KDM, it was shown by the comparison of the spectra for rotations around the *a*, *b*, and *c*-axes that the largest difference between the line widths of the two compounds was only 0.5 gauss.

ANALYSIS OF RESULTS AND DISCUSSION

These features of the observed spectra suggest that the radical is produced with the removal of OH hydrogen, and that coupling protons should be two vinylene protons which can be chemically equivalent due to the following resonance:



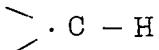
Two vinylene protons were always equivalent for the orientations of the crystal in the magnetic field in the (*ab*) plane, so that the (*ab*) plane should be perpendicular to the C = C bond. Furthermore it is expected from the experimental fact that the two kinds of molecules in a unit cell are oriented in such a way that the (*ca*) or (*bc*) plane of the crystal makes an equal angle to the two planes of molecules corresponding to the two magnetically non-equivalent radicals.

Shown in Fig. 5 is the arrangement of four molecules in the unit cell as determined by Darlow and Cochran²⁾. It is seen that the orientations of the molecules expected from the observed ESR spectra are entirely consistent

with the crystallographic results. The direction cosines of the C - H bond and the directions perpendicular to it can be calculated from the crystallographic data and compared with those of the principal axes of the hyperfine tensor. As indicated in Table I and II the direction for the smallest element approximately coincides with the C - H bond direction and the one for the largest with the direction perpendicular to the C - H bond in the molecular plane. This result indicates that the origin of the hyperfine structure is two vinylene protons, and that the structure of the free radical produced is not very much deformed from the parent molecule as far as the vinylene portion of the molecule is concerned.

The results listed in Table I indicate that the smallest principal element of the g -tensor has its axis perpendicular to the molecular plane and the other two principal elements are approximately equal and are directed in the molecular plane. This means that the spin density is in a p - orbital of the carbon which has its direction perpendicular to the molecular plane.

The nuclear hyperfine interaction constant A of the



fragment consists of an isotropic Fermi term A_f and an anisotropic dipole-dipole interaction term, A_i . The isotropic term, A_f , is obtained from the three principal elements by $(A_1 + A_2 + A_3)/3$ to be 6.4 gauss for the present free radical. With this value the spin density on the vinylene carbon atom is found to be 0.26 employing 25 gauss as the A_f value for unit spin density. The anisotropic hyperfine interaction for π -electron free radicals has been estimated by McConnell and Strathdee⁵⁾ giving the principal elements 15.4, -1.7, and -13.6 gauss along the C - H bond, along the density

axis of the p -orbital, and perpendicular to those two, respectively. For the present radical these principal values should be reduced by 74 % to 3.9, -0.4, and -3.5 gauss, respectively. Since A_f is known to be negative in sign⁶⁾, adding the observed isotropic component $A_f = -6.4$ gauss to the theoretical anisotropic components yields -2.5 gauss for the total coupling constant along the C - H bond, -6.8 gauss along the p -orbital, and -9.9 gauss perpendicular to the C - H bond in the molecular plane. These values are in very good agreement with the observed principal elements of the hyperfine tensor as shown in Table I. Figure 6 indicates the directions of the principal axes, A_1 and A_3 , A_2 not indicated being perpendicular to the molecular plane.

The observed sharp line widths and their small change by the deuterium substitution suggest that no nuclear spin except two vinylene protons exists in the present radical. The difference of line widths in both compounds for the case that the OH proton exists in the produced radical was estimated with the following assumptions: (1) the radical has the same geometrical structure as that of the parent molecule²⁾; (2) the spin density in the vinylene carbon atom is +0.26; (3) the remaining spin density +0.48 is equally assigned to the most distant side oxygen atoms from the OH protons; (4) each spin density is located on the nucleus as a point spin density; (5) the Fermi term of the OH proton coupling constant is assumed to be -0.1 gauss which gives the smallest possible total coupling constant; (6) the contributions from the neighboring molecules to the line width is neglected. As nothing is known about the quantities in the assumptions (3) and (5), they are assumed to give the lowest possible value for difference in line widths as far as these quantities are concerned. Thus the principal elements of coupling constant for the OH proton were estimated to be +1.5, -1.5, and -0.3 gauss for the

direction perpendicular to the C = C bond, respectively. When the OH proton is substituted with deuteron, the line widths are expected to be reduced at least by 1.0, 1.0, and 0.2 gauss for the principal directions. Comparison of this result with observation excludes the possibility that the radical which gives the observed absorption has the OH hydrogen atom as the parent molecule does.

It may be interesting to note that the discrepancy between the observed direction of the C - H bond in the radical and the calculated direction from the X-ray crystallographic data of the parent molecule may be responsible for the loss of the bridge hydrogen bond. Darlow⁷⁾ pointed out that this intramolecular hydrogen bond produces strain in the bond angles of this molecule. The C = C - C angle in unstrained molecules⁷⁾ is about $121.5 \pm 1.0^\circ$ while the same angle in the present molecule²⁾ is $130.4 \pm 0.2^\circ$, the strain angle being $8.9 \pm 1.0^\circ$. Therefore if the strain was removed by the loss of the bridge hydrogen, the C = C - C angle will be closed by an amount of about 8.9° , accompanied by a change of the C = C - C angle which will amount about a half of this strain, that is, 4.5° . Thus the C = C - H angle will change from 115.8° (X-ray value) to 120.3° in the unstrained radical. The observed C = C - H angle in the radical, 121° , is in good agreement with the expected value, 120.3° .

It is of interest that a simple LCAO calculation shows that the unpaired electron must be a π -electron for the proposed radical produced by the removal of the OH hydrogen during irradiation. It is assumed in the calculation that the Coulomb integral of the ring oxygen is smaller than the side oxygen because of the following reasons. (1) According to the X-ray data, the side C - O distance is shorter than the ring C - O in the parent molecule (see Fig. 6). (2) In the radical produced with the removal of the OH hydro-

gen, the ring O...O distance become so close that the β_{OO} may not be ignored. Instead of including β_{OO} , the contribution from the β_{OO} may be replaced by taking the larger value of the Coulomb integral for the ring oxygen. With $\alpha_0(\text{ring}) = \alpha_c + 1.8\beta_c$, $\beta_{co}(\text{ring}) = 0.85\beta_c$, $\alpha_0(\text{side}) = \alpha_c + 1.2\beta_c$, and $\beta_{co}(\text{side}) = 0.95\beta_c$, the energy level of the highest filled π -orbital was found to be higher than that of a $p\pi$ lone-pair electron on an oxygen atom by $0.71|\beta_c|$, where α_c is the Coulomb integral and β_c the resonance integral of a $p\pi$ electron in a C = C bond. An unpaired electron which should be formed on the oxygen atom by the removal of the OH hydrogen atom is equivalent to one of the σ lone-pair electrons. The energy level of the latter electron is equal to that of a $p\pi$ lone-pair electron on the same atom for a simple LCAO approximation. Thus, to minimize the energy of the radical, an electron in the highest filled orbital is re-located to the half-filled σ lone-pair orbital, the remaining π electron becoming an unpaired electron. The spin density in the vinylene carbon atom was found to be +0.28, which is in very good agreement with +0.26 estimated from the proton coupling constant.

After our work was finished, Heller and Cole⁸⁾ published a similar work (HC). Our results may be more accurate than those of (HC), since their results were derived mainly from the measurements at 9 kMc/sec. However, the two independent measurements are in very good agreement with each other. The discrepancies between the principal values in Table I and those given by (HC) are within 0.2 gauss and 2.5° for the values and directions of principal elements of the proton coupling constant, respectively, and within 0.0012 and 1° for those of the g -factor, respectively.

The authors are greatly indebted to Professor Ichiro Miyagawa of Duke University for his suggestion of this problem and his valuable advice, and to Professor Saburo Nagakura for his kind supply of the sample.

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Table I. Values of the proton hyperfine and g -factor tensors in X-irradiated potassium hydrogen maleate.

| Tensor | Principal values* (gauss) obs. theo. | | Direction cosines* with respect to the a , b , and c -axes | | | Directions with respect to the molecule |
|---------------|--|-------|--|-------------|-------------|--|
| Proton | - 2.1 ₁ | - 2.5 | ± 0.649 | ± 0.560 | = 0.515 | $\text{C}_2 \text{ - H}_2^{**}$ |
| H_2 | - 7.0 ₁ | - 6.8 | ± 0.669 | ± 0.743 | 0.000 | \perp molecular plane |
| | - 10.1 ₃ | - 9.9 | ± 0.360 | ± 0.370 | = 0.857 | $\perp \text{C}_2 \text{ - H}_2$ in molecular plane |
| Proton | - 2.1 ₁ | - 2.5 | ± 0.649 | ± 0.560 | ± 0.515 | $\text{C}_2' \text{ - H}_2'$ |
| H_2' | - 7.0 ₁ | - 6.8 | ± 0.669 | ± 0.743 | 0.000 | \perp molecular plane |
| | - 10.1 ₃ | - 9.9 | ± 0.360 | ± 0.370 | = 0.857 | $\perp \text{C}_2' \text{ - H}_2'$ in molecular plane |
| g | 2.0024 | | ± 0.629 | ± 0.778 | 0.000 | \perp molecular plane |
| | 2.0040 | | ± 0.778 | ± 0.629 | 0.000 | $\perp \text{C} = \text{C}$ in molecular plane |
| | 2.0045 | | 0.000 | 0.000 | ± 1.000 | $\text{C} \perp \text{C}$ |

* The uncertainties in the principal values, the g -factor, and the directions of the coupling tensor are estimated to be 0.3 gauss, 0.0006, and 2° , respectively.

** Determined by X-ray diffraction data²⁾.

Table II. Direction cosines of the C - H bond and its perpendicular in the molecular plane obtained from the X-ray data

| Direction | Direction cosines with respect to the <i>a</i> , <i>b</i> , and <i>c</i> -axes | Angle made with the principal axes of the hyperfine tensor |
|-----------------------------------|--|--|
| $\text{C}_2 - \text{H}_2$ | $\pm 0.715 \pm 0.548 = 0.435$ | 6° |
| $\perp \text{C}_2 - \text{H}_2$ | $\pm 0.339 \pm 0.272 = 0.901$ | 6° |
| in plane | | |
| $\text{C}'_2 - \text{H}'_2$ | $\pm 0.715 \pm 0.548 \pm 0.435$ | 6° |
| $\perp \text{C}'_2 - \text{H}'_2$ | $\pm 0.339 \pm 0.272 = 0.901$ | 6° |
| in plane | | |

CAPTIONS FOR FIGURES

Fig. 1 Electron spin resonance curve at 9 kMc/sec. of an X-irradiated single crystal of KHM with the static magnetic field parallel to the *c*-axis. The vertical lines indicate the theoretical positions and intensities.

Fig. 2 Electron spin resonance curves at 24 kMc/sec. of an X-irradiated single crystal of KHM with the static magnetic field in the (*bc*) plane. Angles are measured from the *b*-axis. Arrows show the position for the DPPH resonance.

Fig. 3 Electron spin resonance curves at 24 kMc/sec. of an X-irradiated single crystal of KHM with the static magnetic field in the (*ca*) plane. Angles are measured from the *c*-axis.

Fig. 4 Electron spin resonance curves at 24 kMc/sec. of an X-irradiated single crystal of KHM with the static magnetic field in the (*ab*) plane. Angles are measured from the *a*-axis.

Fig. 5 Projection of the structure of potassium hydrogen maleate to the *c* and *a*-axes.

Fig. 6 The molecular structure of the hydrogen maleate ion and the directions of the proton coupling tensor.

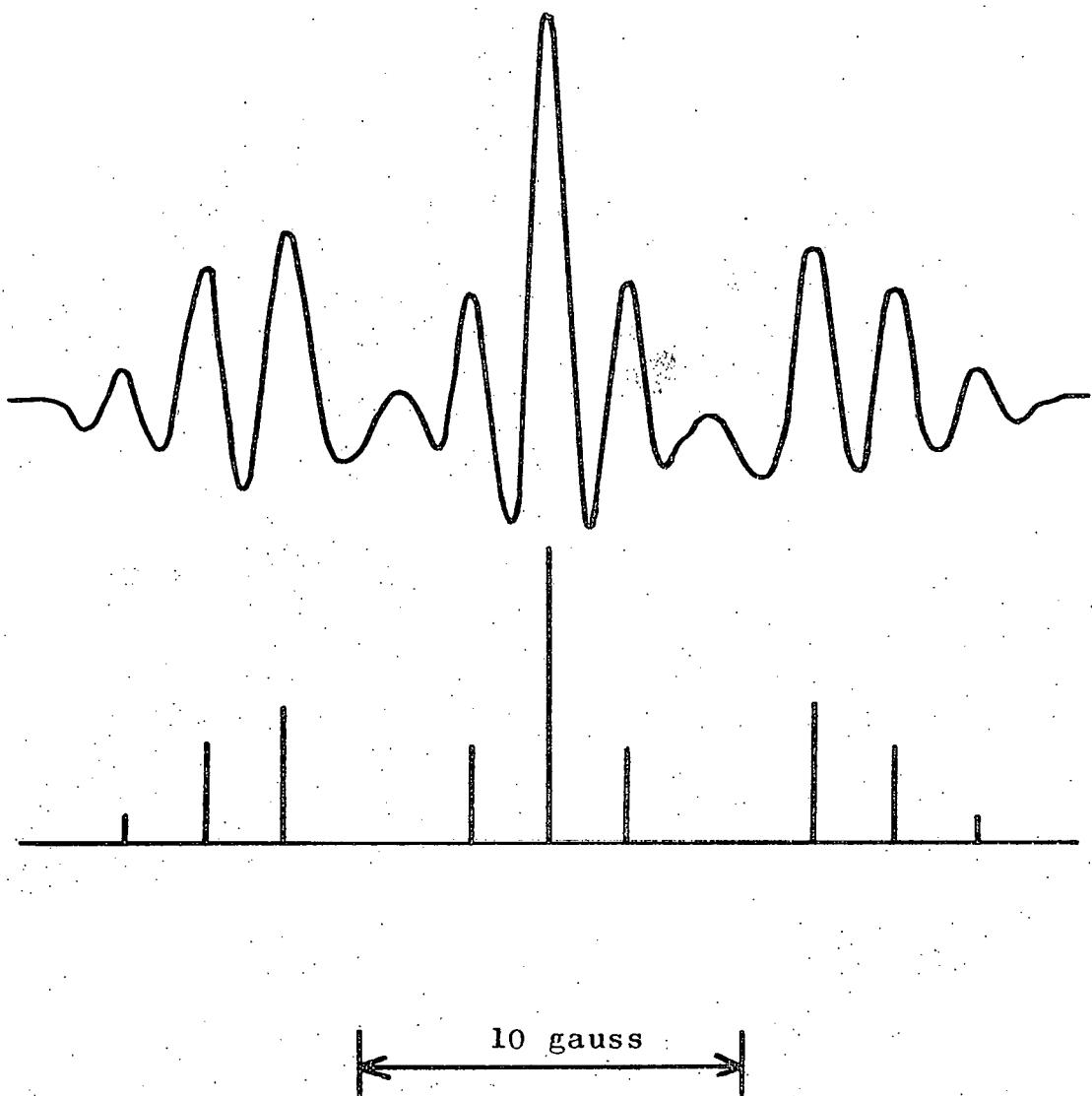


Fig. 1

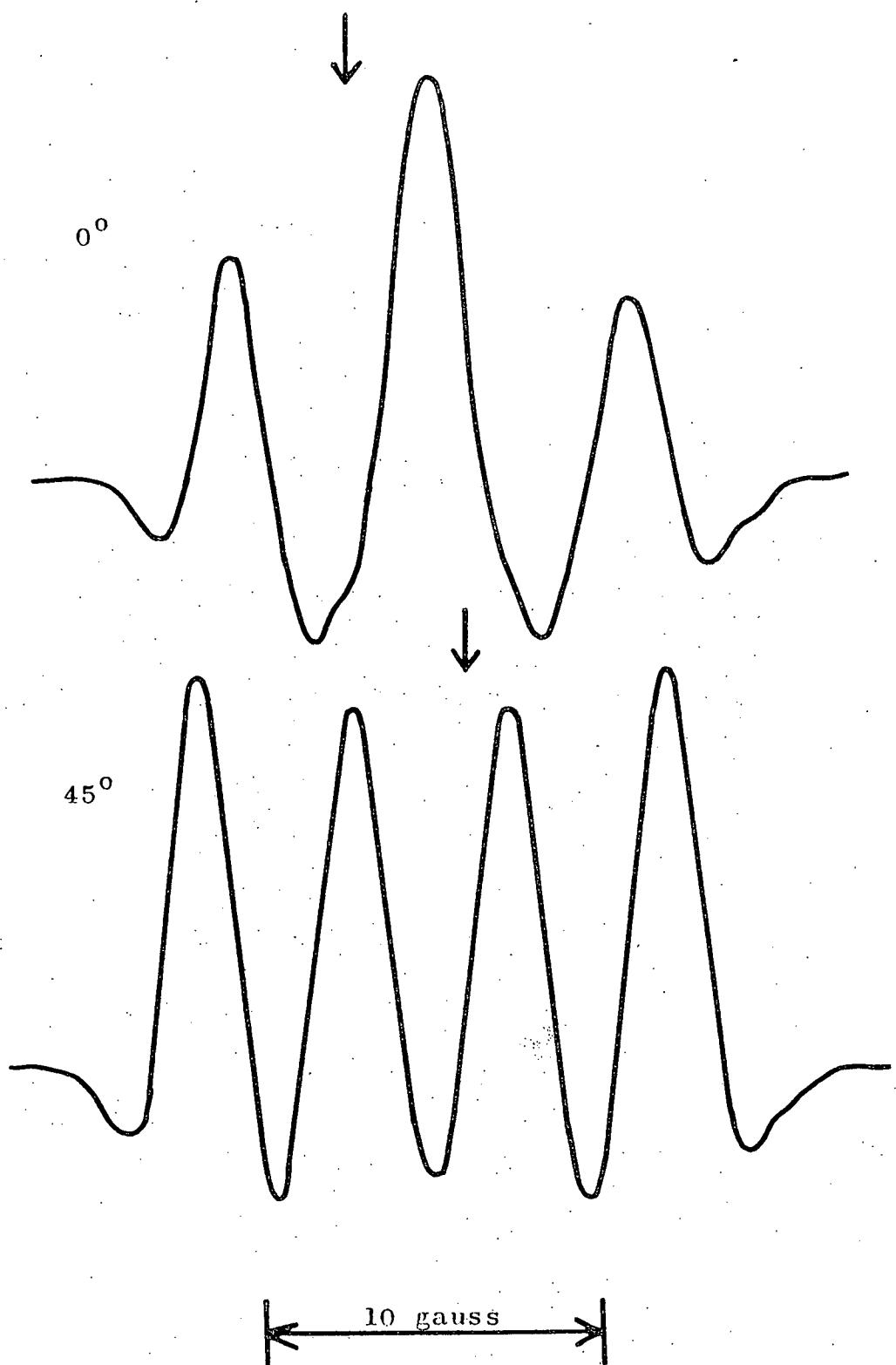


Fig. 2

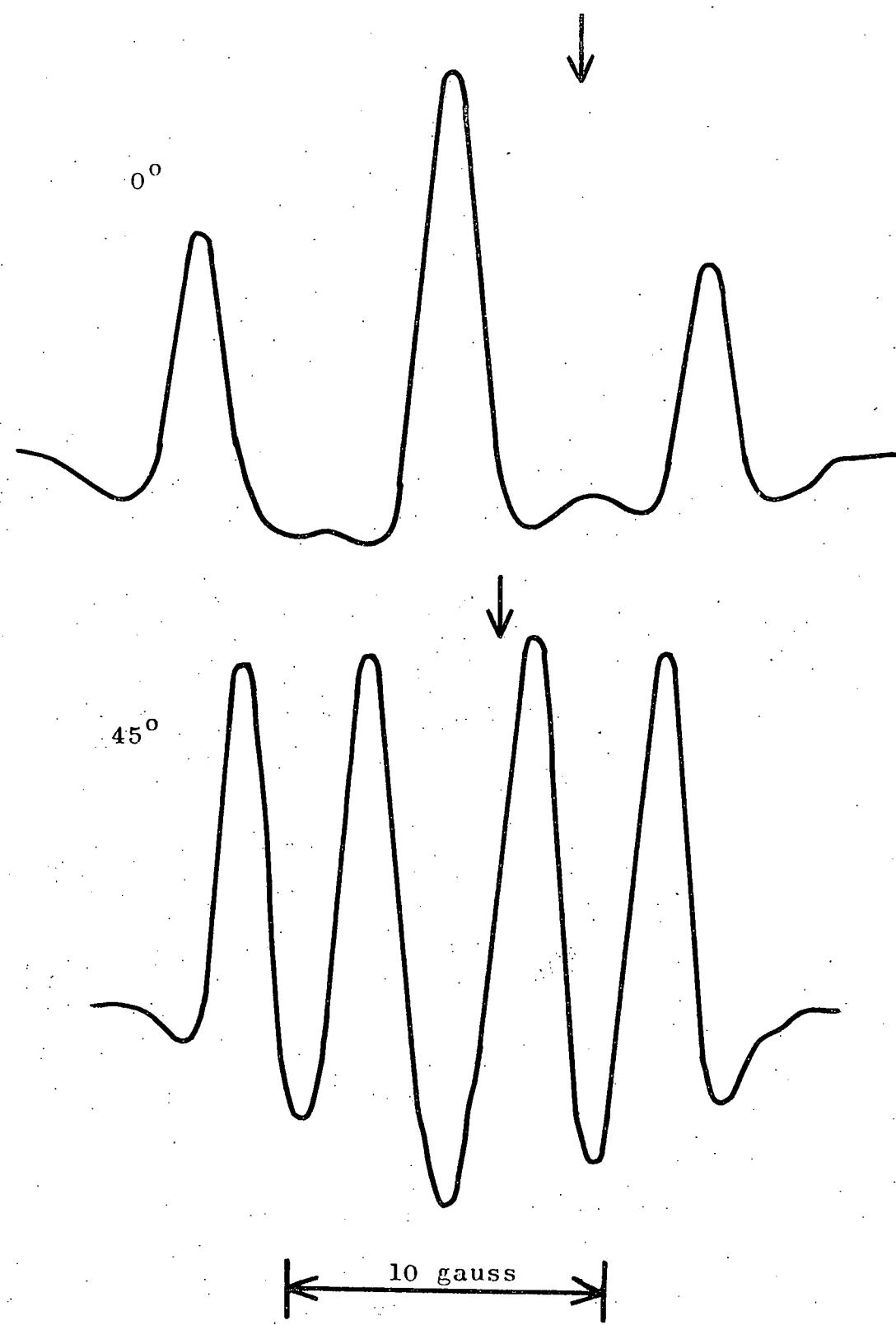


Fig. 3

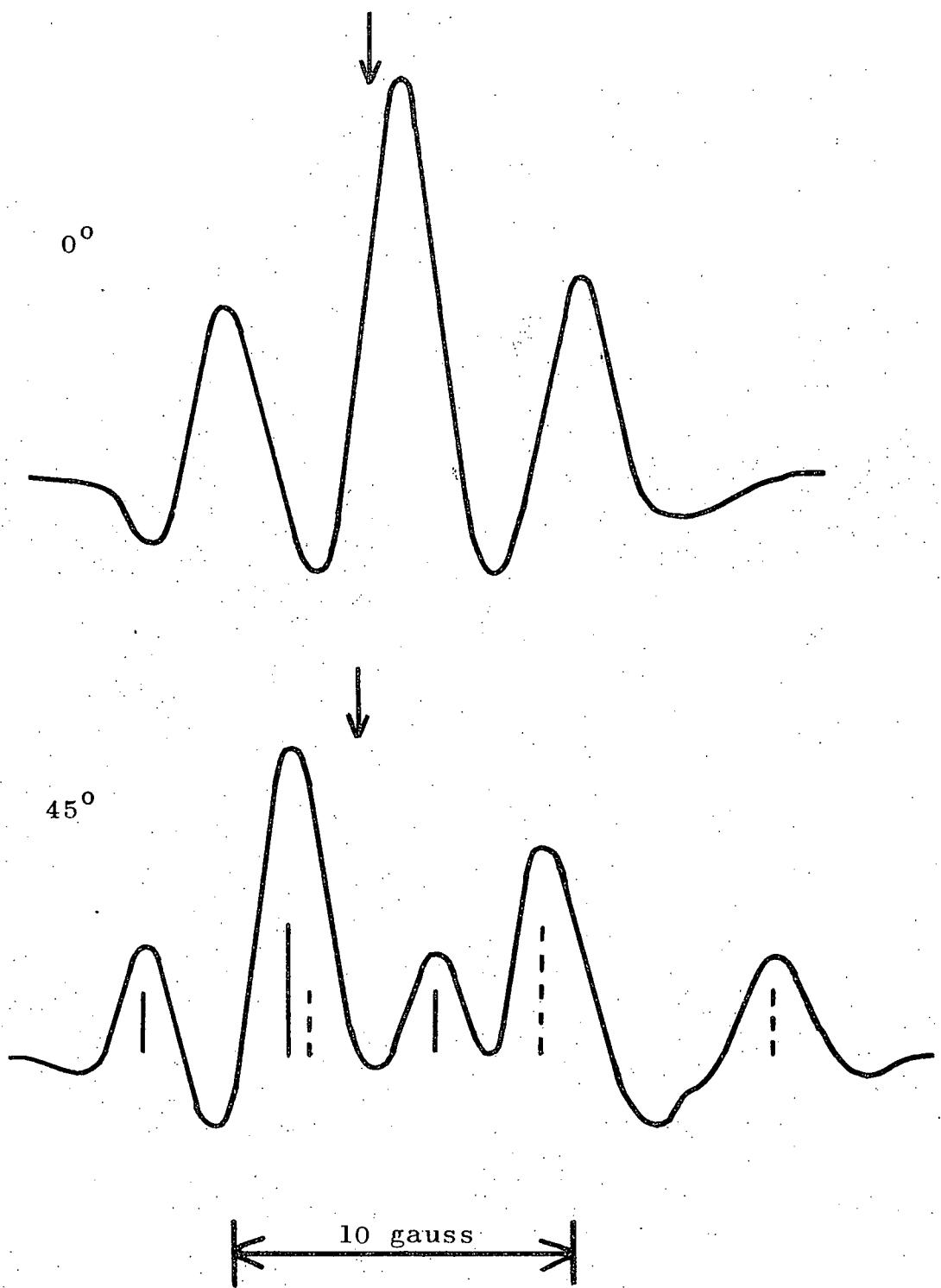


Fig. 4

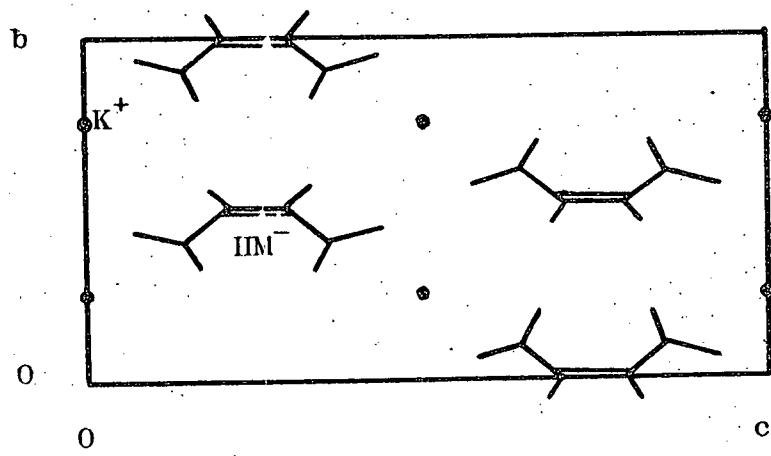
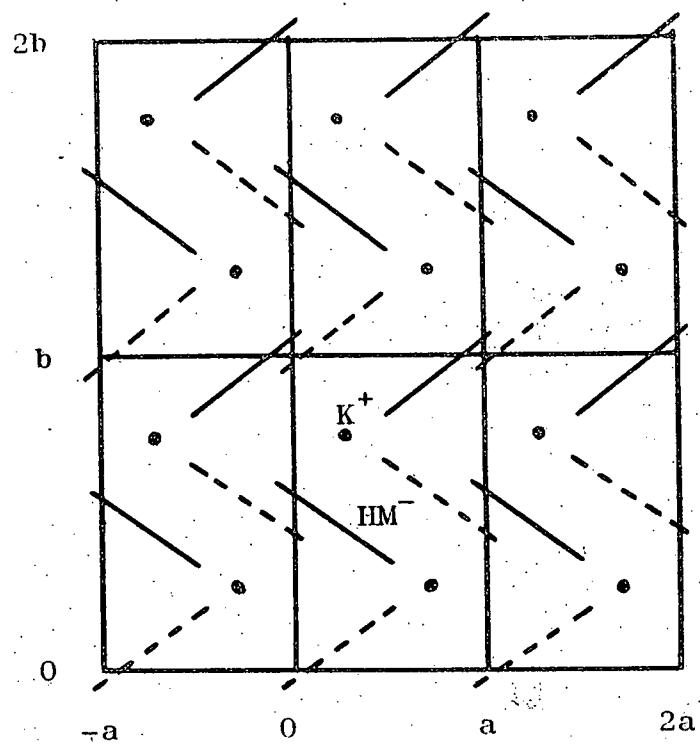


Fig. 5

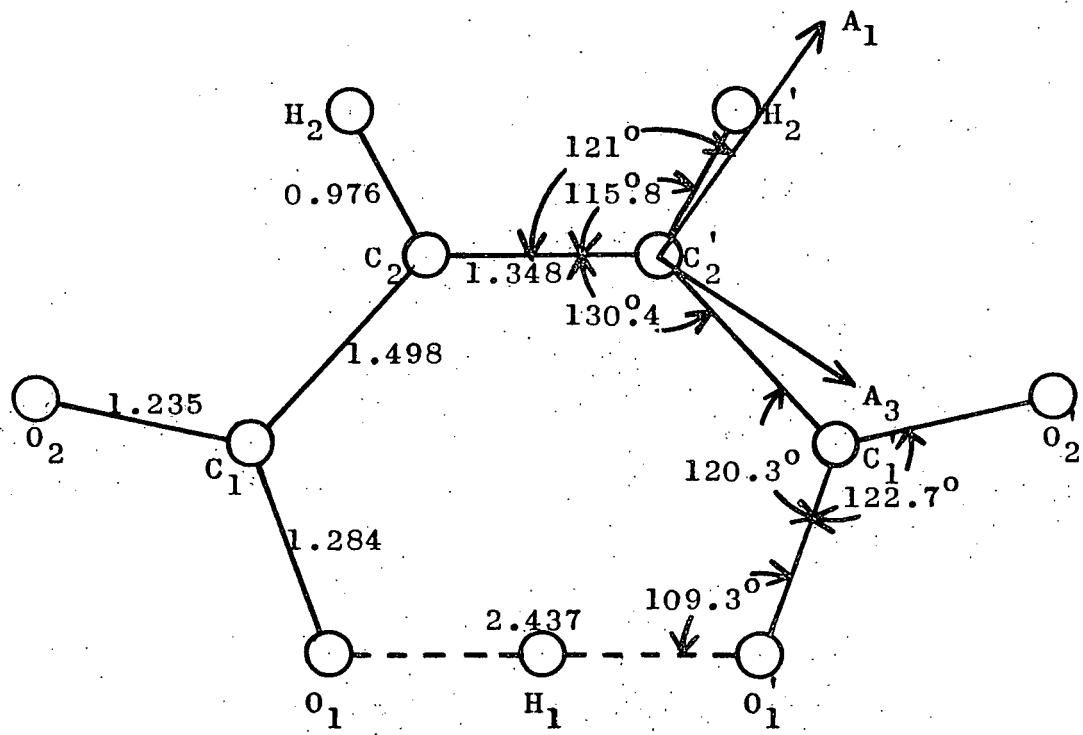


Fig. 6