I. INTRODUCTION

The work described in this paper is a continuation of our efforts to characterize the 13C chemical shielding tensors of various functional groups. The complete determination of a symmetric chemical tensor requires six parameters. These are conveniently selected to be the three principal values and three angles describing the orientation of the principal axes relative to crystal or molecular geometry. The determination of these tensors is important for several reasons: Firstly, they teach us considerably more about the shielding than the isotropic shifts available from conventional liquid experiments. This means that comparison with theoretical calculations is much more sensitive and meaningful. Secondly, they should become quite useful as analytical orientational probes for structural and dynamical studies of oriented and partially oriented systems. We have already exploited this fact for the study of phase transitions and molecular ordering in liquid crystals.1-3

In a previous paper, we outlined some experimental details and described the measurement of chemical shielding tensors for the carboxyl and hydroxyl carbon sites in a single crystal of ammonium tartrate.4 The tensor for the carboxyl group was found to have the most shielded element perpendicular to the carboxyl plane and the least shielded element close to the C-C bonds, displaying the effects of hydrogen bonding. The principal values of the methylene tensors are \( \sigma_{11} = 110.2 \pm 2 \text{ ppm} \), \( \sigma_{22} = 76.3 \pm 2 \text{ ppm} \), and \( \sigma_{33} = 65.6 \pm 2 \text{ ppm} \). The more or less unique, most shielded element, is in the C-C-C plane and is nearly along the C-C bond adjacent to the out-of-plane carboxyl group.

Chemical shielding tensors have been determined in single crystal ammonium hydrogen malonate by proton-enhanced 13C NMR. The average principal values of the carboxyl tensors are \( \sigma_{11} = -12.8 \pm 2 \text{ ppm} \), \( \sigma_{22} = -45.8 \pm 2 \text{ ppm} \), and \( \sigma_{33} = 25.6 \pm 2 \text{ ppm} \) relative to benzene. Using the crystal structure determined in the preceding paper by Chapuis et al., the orientations of the tensor principal axes have been determined and assigned to specific carbon sites. The carboxyl tensor is oriented with the most shielded element perpendicular to the plane of the carboxyl group and the least shielded element \( \sigma_{11} \) in the plane of the carboxyl group making an angle of 25° relative to the bisector of the CO bonds, rotated towards the long CO bond, displaying the effects of hydrogen bonding. The principal values of the methylene tensors are \( \sigma_{11} = 76.3 \pm 2 \text{ ppm} \), \( \sigma_{22} = 65.6 \pm 2 \text{ ppm} \), and \( \sigma_{33} = 110.2 \pm 2 \text{ ppm} \). The more or less unique, most shielded element, is in the C-C-C plane and is nearly along the C-C bond adjacent to the out-of-plane carboxyl group.

Carbon-13 chemical shielding tensors in ammonium hydrogen malonate*

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II. EXPERIMENTAL

Single crystals of ammonium hydrogen malonate were grown by slow evaporation from aqueous solution. A suitable crystal was cut and mounted in a machined Kel-F cube whose edges defined the xyz axis system for determination of the tensors. 13C NMR spectra were

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obtained at 26.7 MHz with proton decoupling fields of ~15 G in the rotating frame. The spectrometer and other experimental details were as described previously. Spectra were obtained with rotation of the crystal about crystal cube \( xyz \) axes and analyzed as before to obtain six tensors for the four orientationally inequivalent carboxyl and two methylene groups in the unit cell. The following parameters were used for the proton-enhanced \(^{13}\)C NMR: mixing time: 6 msec; number of \(^{13}\)C-\(^{1}\)H mixing contacts per cycle: 1; recycle time: 3 sec; total accumulation time: 5 min.

The crystal structure of ammonium hydrogen malonate is described in the preceding paper; space group \( C2/c \) with eight molecules per unit cell. The orientation of the \( xyz \) axis system with respect to the orthogonal \( abc^* \) crystal system was determined by means of x-ray precession techniques.

III. RESULTS AND DISCUSSION

A. Principal values

The unit cell of ammonium hydrogen malonate contains four orientationally inequivalent molecules, two pairs related by a center of symmetry. The two inequivalent molecules are shown in Fig. 1 with a projected view down the \( b \) axis. The atomic numbering is that used in the tables describing the tensor orientation.

Thus, in a general orientation six lines are expected in the \(^{13}\)C NMR spectrum, four from the carboxyl groups and two from the methylene groups. Six or less lines were indeed observed and followed for the three rotational experiments. A typical spectrum showing 4 carboxyl and a degenerate methylene line is shown in Fig. 2. Linewidth is dominated primarily by \(^{14}\)N dipolar broadening.

Carbon-13 NMR spectra were obtained as a function of rotation angle about the three orthogonal axes \( (xyz) \) defined by the Kel–F cube. A rotational plot about an axis close to the crystallographic \( c^* \) axis appears in Fig. 3. The rotational data were analyzed to obtain six complete chemical shielding tensors. The principal values for the tensors are presented in Table I. The carboxyl tensors are easily distinguished from the methylene tensors and are similar to those obtained for other carboxyl groups. The extreme elements \( \sigma_{22} \) and \( \sigma_{33} \) are within experimental errors of those determined in tartrate and benzoic acid, but \( \sigma_{22} \) is significantly larger. It appears that this correlates with the rotation of the in-plane axes for unequal CO bonds.

B. Assignment

1. Carboxyl Tensors

The orientation of the principal axes of the tensors with respect to the crystallographic \( abc^* \) axes is presented in Table II as direction cosines. Although the
principal values of the tensors are determined unequivocally, the assignment of a given tensor to a particular carbon is subject to interpretation. Since there are four carboxyl tensors and four carboxyl groups in the two distinguishable molecules in the unit cell, there are, a priori, 24 ways of assigning the tensors to the carbon sites. However, since the two molecules are related by a symmetry element (rotation about the $b$ axis), the tensors must also be related by the symmetry elements. In Table II the primed tensors are related to the unprimed tensors by a rotation about the $b$ axis and are therefore assigned to different molecules. This symmetry requirement reduces the number of possible assignments to eight. Of the eight remaining possibilities, only one assignment is consistent with the requirements that (a) the tensors should be related to the local molecular environment in the same way and (b) the most shielded element of the tensor should lie along the perpendicular to the plane formed by the carboxyl group. The orientation of the principal tensor axes with respect to molecular bond directions with this assignment is shown in Table III. The bond notation employs the numbering of Fig. 1. The other two principal axes of the carboxyl tensor are in the plane of the carboxyl group. However, unlike the situation in ammonia trtarate and benzoic acid, where $c_{11}$ is approximately along the C-C bond bisecting the OCO angle, this axis is rotated in the plane such that $c_{22}$ comes closer to the shorter of the CO bonds. This situation is depicted schematically in Fig. 4. As shown in the x-ray work, one of the oxygens of each carboxyl group is strongly hydrogen bonded to a hydrogen bridge atom between two molecules. The two CO bonds are therefore close to being pure double (C=O) and single (C–O) bonds. Thus there is no local $C_{2v}$ symmetry axis bisecting the OCO angle as in benzoic acid and thus no requirement for $c_{11}$ and $c_{22}$ to be in any specific direction. The rotation away from the ideal symmetry case is thus a reflection of the hydrogen bonding. We have found this in other cases, too, and have also noticed a correlation between the magnitude of $c_{22}$ and the rotation angle of the axes in the plane.

## 2. Methylene Tensors

The assignment of the methylene tensors is simpler than that of the carboxyl tensors. With two tensors and two methylene groups, there are only two possible assignments. Since one of the principal axes of the tensor is along the $b$ axis, a symmetry axis of the crystal, both assignments give nearly same orientation of the tensors with respect to the local molecular geometry. The two assignments yield orientations which agree within experimental error.

The orientation of the methylene tensors with respect to the methylene group geometry also appears in Table III as tensors 3 and $3'$. The tensor is found to have the most shielded element in the plane defined by the three carbons. The malonate molecule is in a configuration...
such that one of the carboxyl group planes is in the same plane as the molecular (CCC) skeleton plane and the plane of the other carboxyl group is perpendicular to the C–C–C plane. The most shielded element of the tensor is oriented 14.5° away from the CC bond which is adjacent to the out of plane carboxyl group.

In our carbon-13 liquid crystal work, we have noticed that in the isotropic–nematic transitions, the lines from side chain methylene carbons shift upfield. Since the nematic ordering involves an arrangement of the aliphatic side chains parallel to the magnetic field, this means that the most shielded element of the methylene tensor is more or less "along the chain." This is in agreement with the orientation of the malonate methylene tensor described above. It is clear that a detailed study of these tensors and a characterization of relationships between structure and tensor orientation will yield invaluable information for the application of NMR to liquid crystals and biological membranes.

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