

Carbon-13 chemical shielding tensors in ammonium hydrogen malonate*

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Chemical shielding tensors have been determined in single crystal ammonium hydrogen malonate by proton-enhanced ^{13}C NMR. The average principal values of the carboxyl tensors are $\sigma_{11} = -112.8 \pm 2$, $\sigma_{22} = -45.8 \pm 3$, and $\sigma_{33} = 25.6 \pm 2$ 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 σ_{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 $\sigma_{11} = 65.6 \pm 2$, $\sigma_{22} = 76.3 \pm 2$, $\sigma_{33} = 110.2 \pm 2$ ppm. The more or less unique, most shielded element, is in the C-C plane and is nearly along the C-C bond adjacent to the out-of-plane carboxyl group.

I. INTRODUCTION

The work described in this paper is a continuation of our efforts to characterize the ^{13}C 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 direction bisecting the CO bonds. A similar orientation was found for the carboxyl tensor in benzoic acid by Kempf *et al.*⁵ These present two of the few complete single crystal tensors which have been determined to date. Others include calcium carbonate,⁶ durene,⁷ benzophenone,⁸ dimethyl oxalate,⁹ malonic acid,¹⁰ and alanine.¹¹ Clearly, considerably more measurements are required before any general understanding of shielding and trends for various functional groups and bonding geometry can be developed.

Two primary approaches have been taken to the determination of ^{13}C chemical shielding tensors in single crystals. These are proton-enhanced NMR with spin decoupling,¹² and NMR in ^{13}C enriched and deuterated

crystals.^{5,8} The latter has the advantage of permitting the study of individual carbon sites in complex molecules, but involves the specific synthesis of labeled material. We have adopted the former approach which can be applied to natural abundance ^{13}C , eliminating the need for synthesis, but requiring the observation of only small molecules to obtain tractable spectra.

Ammonium hydrogen malonate was found to be an excellent candidate for our continuing work, for several reasons:

- (a) Large single crystals could be grown.
- (b) There are only six magnetically inequivalent carbon sites in the unit cell.
- (c) There are two functional groups of interest, carboxyl and methylene.
- (d) The crystal structure necessary for orientation of the tensor was determined in a parallel study by Chapuis *et al.*¹³ (preceding paper).
- (e) Proton T_1 is short due to the orientationally mobile ammonium groups combined with spin diffusion.

The carboxyl group is interesting, since the π bonding yields a large anisotropy of the chemical shielding and a comparison with other π -bonded systems can be made. A particularly interesting feature of the present study is the fact that one oxygen of each carboxyl group is strongly hydrogen bonded while the other is not, yielding different CO bond lengths. This has a marked effect on the chemical shielding tensor and produces an orientation quite different from that of the more symmetrical carboxyl groups studied previously.

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. ^{13}C NMR spectra were

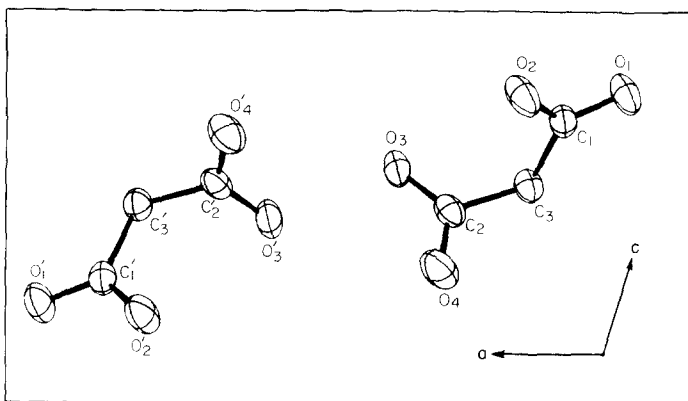


FIG. 1. ORTEP plot of two unequivalent molecules in ammonium hydrogen malonate. The atom numbering is that used in the tensor designation in the text and in the tables. The prime and unprimed atoms are related by a twofold symmetry axis. The C_1 and C_1' carboxyl groups are in the (C-C-C) planes while the other carboxyl groups are perpendicular to the plane.

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.⁴ 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 - ^1H 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 paper¹³; 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.

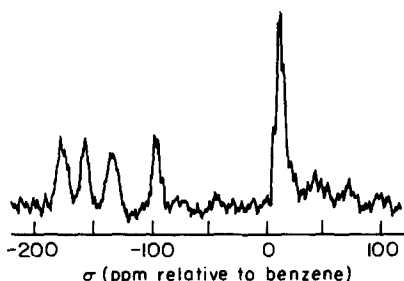


FIG. 2. Typical ^{13}C NMR spectrum of single crystal ammonium hydrogen malonate. The low field lines are from the four unequivalent carboxyl carbons and the high field line is from the methylene carbons.

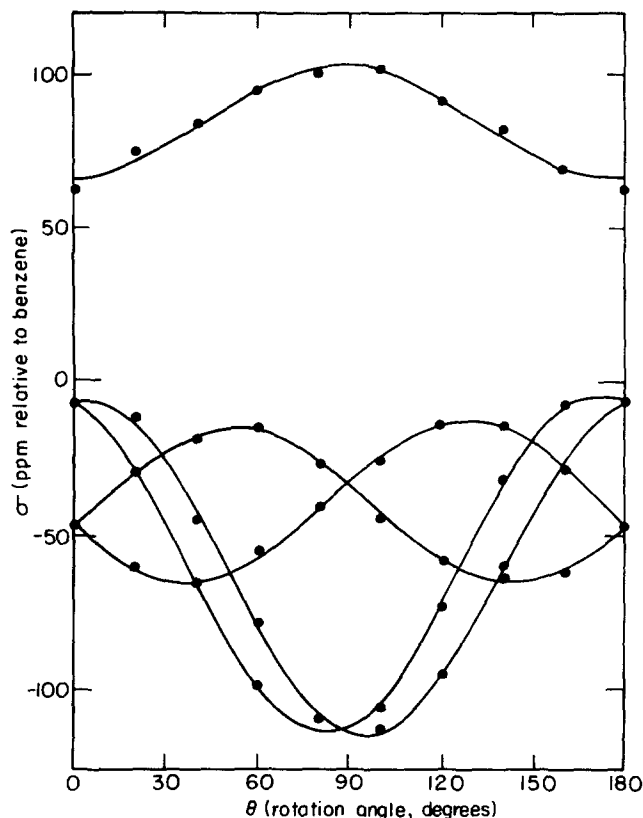


FIG. 3. Plot of ^{13}C NMR lines vs rotation angle of crystal about an axis with direction cosines of 0.07649, 0.04925, -0.99585 relative to the crystallographic a , b , c^* axes. At $\theta = 0$, the b axis was along the magnetic field.

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 σ_{11} and σ_{33} are within experimental errors of those determined in tartrate⁴ and benzoic acid,⁵ but σ_{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

TABLE I. Principal values of tensors relative to external reference of liquid benzene.

	Tensor 1	Tensor 1'	Average
σ_{11}	-112.0	-111.5	-111.7
σ_{22}	-43.9	-45.0	-44.4
σ_{33}	24.8	25.1	25.0
	Tensor 2	Tensor 2'	
σ_{11}	-113.3	-114.7	-114.0
σ_{22}	-45.9	-48.5	-47.2
σ_{33}	26.5	26.0	26.3
	Tensor 3	Tensor 3'	
σ_{11}	64.3	66.9	65.6
σ_{22}	74.9	77.7	76.3
σ_{33}	111.2	109.4	110.2

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 ammonium tartrate and benzoic acid, where σ_{11} is approximately along the C-C bond bisecting the OCO angle, this axis is rotated in the plane such that σ_{22} comes closer to the shorter of the CO bonds. This situation is depicted schematically in Fig. 4. As shown in the

TABLE II. Direction cosines of tensor principal axes relative to crystallographic axes.

	Tensor 1			Tensor 1'		
<i>a</i>	0.0956	0.9265	-0.3639	-0.0329	-0.9099	0.4135
<i>b</i>	0.6701	0.2105	0.7718	0.7335	0.2591	0.6283
<i>c*</i>	0.7362	-0.3119	-0.6007	-0.6789	0.3239	0.6589
	Tensor 2			Tensor 2'		
<i>a</i>	0.9843	-0.1499	-0.0939	-0.9966	0.0805	0.0186
<i>b</i>	-0.1717	-0.6816	-0.7112	-0.0658	-0.6379	-0.7673
<i>c*</i>	0.0426	0.7161	-0.6967	-0.0500	-0.7659	0.6410
	Tensor 3			Tensor 3'		
<i>a</i>	-0.1391	-0.4423	0.8860	0.0080	0.4236	-0.9058
<i>b</i>	-0.9595	0.2815	-0.0101	-0.9956	0.0875	0.0321
<i>c*</i>	-0.2450	-0.8515	-0.4635	0.0929	0.9016	0.4224

TABLE III. Orientation of principal axes of ^{13}C shielding tensors relative to molecular bond directions.^a

	Tensor 1			Tensor 1'		
	σ_{11}	σ_{22}	σ_{33}	σ_{11}	σ_{22}	σ_{33}
$\text{C}_3 \rightarrow \text{C}_1^b$	25.2	115.1	88.3	23.9	113.7	92.6
$\perp(\text{C}_1\text{O})^c$	93.2	91.1	3.4	87.3	88.4	3.2
$\parallel(\text{C}_1\text{O})^d$	65.0	25.2	87.6	66.4	23.8	92.5
	Tensor 2			Tensor 2'		
$\text{C}_3 \rightarrow \text{C}_2$	27.8	117.8	92.0	24.0	113.9	89.4
$\perp(\text{C}_2\text{O})$	86.0	87.1	5.0	90.9	90.9	1.3
$\parallel(\text{C}_2\text{O})$	62.5	28.0	94.5	66.1	23.9	88.8
	Tensor 3			Tensor 3'		
C_3C_1	131.55	111.91	130.45	127.26	121.51	126.89
C_3C_2	104.3	97.58	16.25	99.88	97.90	12.70
$\perp(\text{C}_1\text{C}_3\text{C}_2)$	119.12	29.12	90.29	130.50	40.50	90.40

^aErrors in angles are $\pm 3^\circ$.

^b $\text{C}_i \rightarrow \text{C}_j$ is along the $\text{C}_i\text{-C}_j$ bond bisecting the OC_jO bond angle.

^cPerpendicular to the carboxyl plane.

^dPerpendicular to the above two directions.

x-ray work,¹³ 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 σ_{11} and σ_{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 σ_{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

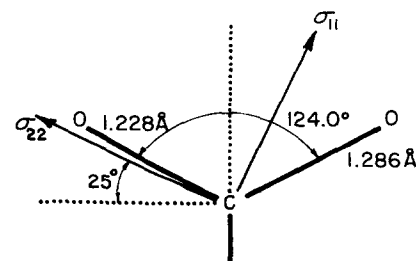


FIG. 4. Orientation of principal axes of ^{13}C chemical shielding tensor for carboxyl groups in ammonium hydrogen malonate. The most shielded element σ_{33} is perpendicular to the carboxyl plane while the other two axes are oriented as shown.

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.¹³ 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.¹⁻³ 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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