

^{13}C chemical shielding in oxalic acid, oxalic acid dihydrate, and diammonium oxalate

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^{13}C chemical shielding tensors in three oxalates were investigated in order to determine the effects of protonation and conformation changes on the tensor elements and their orientations. The experimental results, together with those in the accompanying paper [R. G. Griffin and D. J. Ruben, *J. Chem. Phys.* **63**, 1272 (1975)], indicate that, while neither of these factors seems to seriously effect the magnitudes σ_{11} and σ_{33} , they do perturb σ_{22} and the tensor orientation. Protonation produces an upfield shift (increased shielding) of σ_{22} and in one case a concurrent rotation of the tensor about σ_{33} , the element which is perpendicular to the COO plane. On the other hand, the simple conformational change of the twisting of carboxyl groups relative to one another, which occurs in diammonium oxalate monohydrate, results in small rotation of the tensor around σ_{11} and also may contribute to a decrease in the shielding of the σ_{22} component in this molecule. The orientation of the ^{13}C tensor in oxalic acid dihydrate is different from that observed in other oxalate ions and carboxyl groups. The influence of a change in hydrogen bonding strength on tensor elements is discussed.

I. INTRODUCTION

By employing recently developed double resonance techniques, it has become possible to obtain routinely high resolution NMR spectra of dilute spin systems, such as ^{13}C , in solids.¹⁻⁴ Because molecules are fixed in a crystal lattice, one can now examine the anisotropies of certain magnetic interactions, in particular the chemical shift, and obtain information which is not available from the spectra of the corresponding liquid samples. Using these techniques ^{13}C chemical shift tensors in a number of compounds have been examined, primarily in molecules with aromatic carbons^{3,4} and carboxyl groups,⁵⁻⁷ with the goal in mind of establishing the general characteristics of these tensors, e. g., their orientations and principal values. The results of the studies indicate that some tensor element orientations are relatively invariant to chemical or structural perturbations applied to the functional group. Thus, the interesting possibility arises that measurement of the relative orientations of these elements could suffice for rudimentary crystal and molecular structure determinations. To date, however, there has been only one systematic examination of shift tensors in a series of molecules, in polyalkyl benzenes,⁴ to investigate variations in shift tensors which occur from molecule to molecule. For this and other reasons we have undertaken the present investigation of ^{13}C shift tensors in oxalates in order to elucidate the factors which affect the tensors of carboxyl groups. Specifically we have investigated the effects of protonation and a simple conformational change on the orientations and principal values of carboxyl tensors. As one might suspect, both of these factors influence the tensors to some degree,

and our data illustrate the manner in which these perturbations manifest themselves in oxalates.

We chose oxalate ions for this investigation primarily because the crystal structures of a number of oxalate derivatives have been determined, and consequently one can obtain the orientation of the shift tensors in the molecular frame in several cases. These compounds allow one to examine the effects of protonation and conformational changes on ^{13}C shift tensors. Moreover, the oxalate moiety is small enough so that it should be amenable to theoretical examination, and consequently these measurements should be useful to those interested in the quantum chemical aspects of magnetic shielding. And, finally, in two of the compounds we have studied, anhydrous and hydrated oxalic acid, the proton tensors of the carboxyl protons have been examined.^{8,9} These two compounds, together with malonic acid,^{10,11} represent the first cases where both ^1H and ^{13}C tensors have been studied in the same molecule.

In order to access the effects of protonation on ^{13}C shift tensors we have examined an oxalate salt, diammonium oxalate monohydrate (DAOX), and the partially and fully protonated compounds ammonium hydrogen oxalate hemihydrate (AHOX) (see accompanying paper), and the hydrated (HOX) and anhydrous (AOX) forms of oxalic acid. A comparison of the tensors in this series of compounds permits us to observe the effect of protonation on carboxyl tensors in oxalate ions.

In order to observe the influence of a conformational change we have studied single crystals of diammonium oxalate monohydrate. This compound is unique among

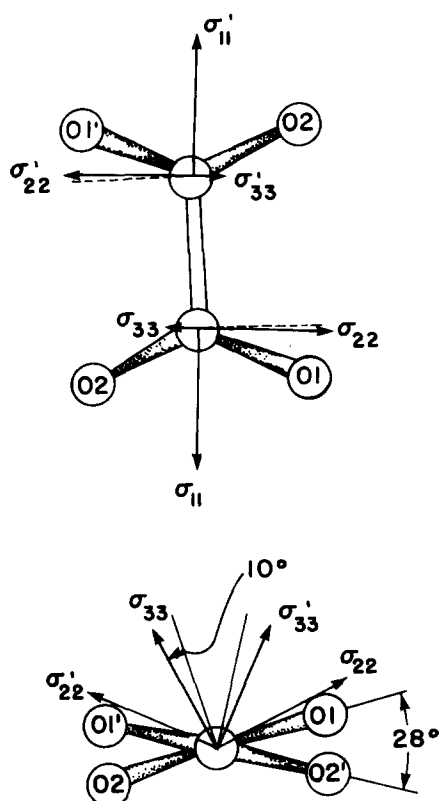


FIG. 1. Illustration of the ^{13}C tensor orientation in $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (DAOX). The top figure is a view from above the carboxyl plane, while the bottom figure is along the C-C bond.

oxalate molecules in that its carboxyl planes are twisted by 28° with respect to one another in the crystal lattice. In all other oxalates the carbon-oxygen framework is flat within experimental error. The ^{13}C shift tensors in this compound seem to reflect this simple conformational change through a small rotation (10°) in the tensor orientation and, perhaps, through a shift in one of the principal elements.

II. EXPERIMENTAL

Finally, we have observed a difference in the tensors of hydrated and anhydrous oxalic acid, which may be attributable to a change in hydrogen bonding strength.

Crystals of diammonium oxalate and oxalic acid were grown by slow evaporation from aqueous solution and were mounted on boron nitride buttons which were transferable between x-ray and NMR goniometers. The morphology of the crystals was employed to determine their initial orientation which was subsequently refined with x-ray techniques. In the case of diammonium oxalate film techniques were employed, and for oxalic acid dihydrate a single crystal diffractometer was used. NMR spectra were taken at 10° intervals for construction of rotation plots which allowed us to determine the orientation of the tensor in the molecular frame. The treatment of the data has been described previously as well as the NMR probe employed in the experiments.³

III. RESULTS AND DISCUSSION

A. Diammonium oxalate monohydrate (DAOX)

The crystal structure of DAOX has been studied by a number of groups and has been found to be orthorhombic (space group $P2_12_12$) with two molecules per unit cell.¹²⁻¹⁴ One half of the molecule is related to the other by a twofold axis along *c*, and the two molecules are related to one another by twofold screw axes along *a* and *b*. These symmetry elements reduce the number of unique shift tensors in DAOX to unity. We note from Fig. 1 that the carboxyl planes in DAOX are twisted with respect to one another. As mentioned above, this twist, which amounts to 28° , is unique for oxalate ions, and permits us to access the effect of this conformational change on oxalate ^{13}C shift tensors.

The principal elements of the ^{13}C shift tensor in DAOX are given in Table I along with their direction cosines with respect to the *a*, *b*, and *c* axes. Also included in Table I are the direction cosines for C-C bond direction, the perpendicular to the COO plane, and the perpendicular to the C-C bond which lies in the COO plane. We can see from Table I and Fig. 1 that the σ_{11} component in DAOX is close (within 3°) to the C-C bond direction. This is not unexpected since the carboxyl group possesses nearly C_{2v} symmetry. A similar orientation has been observed for carboxyl tensors of an ionic carbon in AHOX and in diammonium tartrate.^{6,7} However, the σ_{22} and σ_{33} components in DAOX are oriented somewhat differently than in the latter two compounds. Inspection of Table I and Fig. 1 shows that the σ_{22} and σ_{33} components are rotated about σ_{11} by about 10° so that σ_{33} lies near to the longer C-O bond.¹⁵ This rotation is in contrast to that found for the protonated carboxyl in ammonium hydrogen oxalate and malonate¹¹ where protonation produces a rotation of the tensor around the σ_{33} component rather than σ_{11} . This effect is probably attributable to the twisting of the carboxyl planes rela-

TABLE I. ^{13}C shift tensor components in DAOX and their direction cosines and direction cosines of the reference frame. $\frac{1}{3}\text{Tr}\sigma_{11} = -42.4$ ppm, and $\sigma_{180} = -44.0$ ppm. All shifts relative to external liquid C_6H_6 .

Component	Shift	Tensor element direction cosines ^a	Reference frame direction cosines
σ_{11}	-116.6	0.9361 ^b	0.9369 ^c
	+2.0	0.3468	0.3510
		-0.0536	0.0000
σ_{22}	-29.9	-0.3369	-0.3460 ^d
	+2.2	0.8466	0.9085
		-0.4117	-0.2419
σ_{33}		-0.0974	-0.0860 ^e
	19.9	0.4037	0.2255
	+1.3	0.9094	0.9704

^aRelative to *a*, *b*, and *c*.

^bDirection cosines of the other three tensors and COO groups are $\bar{x}\bar{y}\bar{z}$, $\bar{x}\bar{y}\bar{z}$, and $\bar{x}\bar{y}\bar{z}$.

^cParallel to C-C bond.

^dPerpendicular to C-C bond in COO plane.

^ePerpendicular to COO plane.

TABLE II. Comparison of shift tensor elements of carboxyl groups in oxalate molecules and in other carboxyl-containing compounds. Note the increased shielding of σ_{22} in the oxalates.

Compound	σ_{11}	σ_{22}	σ_{33}	$\frac{1}{3}\text{Tr}\sigma_{11}$	σ_{180}
$\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$					
COO^-	-120.5	-14.4	17.3	-39.2	-38.2
COOH	-123.9	-6.5	17.3	-37.7	-38.2
$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	-116.6	-29.9	19.3	-42.4	-44.0
$(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$	-119.8	-3.2	20.1	-34.3	-32.9
$(\text{COOH})_2$	-121.8	5.6	16.8	-33.2	-32.9
$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ (Tartrate)	-110.5	-61.7	21.6	-50.2	
Glycine	-122.6	-54.0	22.0	-51.5	-44.5
L-Alanine	-115.9	-55.2	19.1	-50.7	-47.8
CaCHO_2	-106	-61	24	-48	
	-111	-57	24	-48	

tive to one another in the crystal lattice.

The principal values for the DAOX tensor are also listed in Table II along with the principal values for shift tensors of some of the other carboxyl compounds that have been studied. We note that the 11 and 33 elements for all of the compounds are very nearly identical, but that the 22 component varies from molecule to molecule.² In DAOX the σ_{22} value is shifted in the direction of decreased shielding by about 15 ppm relative to the ionic carboxyl in AHOX and, although this could be due to a number of factors, it may be attributable in part to the relative orientation of the carboxyl planes.

In regard to the value of σ_{22} in DAOX it is perhaps

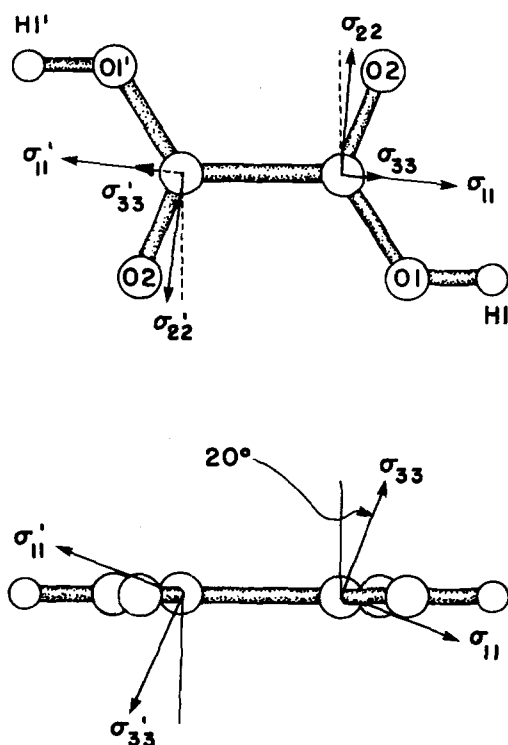


FIG. 2. Illustration of the ^{13}C tensor orientation in $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (HOX). The top figure is a view from above the carboxyl plane, while the bottom figure is along the perpendicular to the C-C bond lying in the C_2O_4 plane.

worth mentioning that σ_{22} in oxalate ions is considerably larger than in other carboxyl groups as is also shown in Table II. Table II is a comparison of carboxyl tensors in oxalates and in some other molecules in which carboxyl tensors have been studied. Excluding DAOX the average value of σ_{22} for the three other oxalate ions is -6.2 ppm. For carboxyl groups which are attached to a methylene carbon such as exist in diammonium tartrate,^{6,7} glycine,¹⁶ L-alanine,¹⁷ and formate⁵ ion, σ_{22} occurs at about -60 ppm. Thus, if we assume that there is some coupling between carboxyl groups in oxalate ions which causes σ_{22} to shift upfield when the molecules are flat, then the twisting of the carboxyl planes in DAOX should break this coupling and result in a downfield shift in σ_{22} as is observed. Such an interaction between the COO groups has been invoked as an explanation for the anomalously long C-C bonds (1.54-1.58 Å) observed in oxalate molecules.¹⁸

Another interesting point concerning the ^{13}C tensor in DAOX is the value of its trace with respect to the shift measured in aqueous solution. That the trace and isotropic shifts are identical could imply that the twisted conformation observed in the solid state is preserved in solution. If the molecule were flat in solution then we would expect a shift in the direction of increased shielding.

B. Oxalic acid dihydrate

HOX crystallizes in the monoclinic space group $P2_1/n$ with two molecules per unit cell.^{19,20} The C-O framework is flat in this molecule, and the oxygens of the oxalate are involved in extensive hydrogen bonding with the water molecules in the lattice. In addition, the hydrogen bond involving the acid proton is rather short (2.51 Å).

The principal values obtained for ^{13}C tensors in this molecule are listed in Table III along with the direction cosines which relate the tensor to the molecular frame, and Fig. 2 is an illustration of this tensor orientation.

TABLE III. ^{13}C shift tensor components in HOX and their direction cosines and direction cosines of reference frame. $\frac{1}{3}\text{Tr}\sigma_{11} = -34.3$ and $\sigma_{180} = -32.9$. All shifts relative to external liquid C_6H_6 .

Component	Shift	Tensor element direction cosines ^a	Reference frame direction cosines
σ_{11}	-119.8	-0.6862 ^b	-0.5861 ^c
	± 0.7	0.0806	0.2569
σ_{22}	-3.2	0.7229	0.7685
	± 0.7	0.6467	0.6292 ^d
σ_{33}	20.1	-0.5286	-0.4533
	± 0.7	0.5499	0.6314
		0.3399	0.5134 ^e
		0.8447	0.8523
		± 0.7	0.4135
			0.1003

^aRelative to a, b and c*.

^bDirection cosines of the other molecule and tensor are at xy_z .

^cParallel to the C-C bond.

^dPerpendicular to the C-C bond in the COO plane.

^ePerpendicular to the COO plane.

Although the general orientation of the tensor is consistent with what we have found for the other oxalates, there are some salient differences.

We first note that the principal values of the tensor are approximately what one would expect on the basis of our other experimental results. That is, that σ_{11} and σ_{33} are about -120 and $+20$ ppm, and that σ_{22} is shifted in the direction of increased shielding due to protonation (-3 ppm) relative to the ionic tensor in AHOX. This result, together with the data on the protonated tensor in AHOX and anhydrous oxalic acid, indicate that effect of protonation on carboxyl tensors is to move σ_{22} in the direction of increased shielding.

Even though the principal values of the tensor are "normal," its orientation is not. We have mentioned above the effect of protonation on the orientation of the carboxyl tensor in AHOX; that is, rotation of the tensor around σ_{33} . And, a twist of the carboxyl planes in DAOX produces a rotation around σ_{11} . The situation in HOX is clearly quite different: inspection of the data in Table III and Fig. 2 shows that σ_{33} is tilted off the perpendicular to the COO plane by $\sim 20^\circ$ by a rotation around σ_{22} . This is the first case in which such a tensor orientation has been observed and consequently it deserves some discussion.

There are a number of structural similarities between this oxalate molecule and the other oxalates we have examined, and thus one would expect the tensor orientations to be somewhat similar. For instance, the C-O bonds on the protonated end of AHOX and those in HOX are of similar length and the bond angles are very nearly identical; in addition, both of the molecules are flat within experimental error. Moreover, the orientation that was observed for the protonated end of AHOX fits well into the general picture of carboxyl shift tensors observed in a number of compounds. Thus, one wonders what causes the tensor in HOX to assume its peculiar orientation.

One possible explanation might be that the hydrogen bonding in the crystal lattice leads to a rotation of the tensor about σ_{22} . However, we note that crystals of all of the oxalate molecules we have examined possess a good deal of hydrogen bonding. For instance, in AHOX and DAOX there are extensive nets of hydrogen bonds between CO oxygens and hydrogens of water molecules and ammonium ions. Thus, if intermolecular hydrogen bonding is responsible for the tilt of the tensor around σ_{22} in HOX, then it seems one could reasonably expect to observe similar effects in other crystals. From the discussion above this is not the case, and, consequently, it is not clear that hydrogen bonding produces the effect we have observed.

Of course, a rigid rotation of the entire molecule, which serves as the framework of our coordinate system, could bring our results into consonance with the other cases discussed (see Fig. 2). This might be the case if the crystal studied existed in a different crystal-line modification than the reputed structure, but with the same space group. However, we have no evidence other than the chemical shielding tensors that this might

be the case. For the moment we have no satisfactory explanation for the orientation of the ^{13}C tensor in HOX, and we can only view it as an interesting case which is quite different from the other carboxyl tensors that have been studied in oxalates and in other molecules.

C. Anhydrous oxalic acid

Because of experimental problems, e.g., a very long proton T_1 , this compound was examined only in powdered samples. The principal values for its tensor elements are given in Table III along with the tensor elements for the other oxalates for comparison. Although there is nothing particularly surprising about the σ_{11} and σ_{33} components in this molecule, the σ_{22} component deserves some discussion. The hydrogen bond length in anhydrous oxalic acid is somewhat longer (2.71 \AA) than in oxalic acid dihydrate, and at first thought one would expect its σ_{22} value to be somewhat *less* shielded than σ_{22} in the dihydrate. However, reference to Table III shows that this is not the case; instead it is more shielded by almost 9 ppm. Although this shift still fits into the general picture that protonation of an ionic carboxyl group results in an upfield shift of σ_{22} , it says, at the same time, that once a hydrogen bond is formed then increasing the strength of the bond (shortening its distance) results in a downfield shift of σ_{22} . This result is in agreement with experiments of Maciel and Ruben obtained on liquid samples.²¹ In going from a weakly to strongly hydrogen-bonding solvent, these workers found a decrease in the shielding of the carbonyl carbon in acetone. In view of the peculiar orientation of the ^{13}C tensor in oxalic acid dihydrate, it would, of course, be interesting to know the orientation of the tensor in this molecule. Data concerning this point will be presented at a later date.

IV. SUMMARY

The general orientation of ^{13}C shift tensors in oxalate molecules is in agreement with data on other ^{13}C carboxyl tensors; that is, σ_{11} is approximately along the C-C bond direction and σ_{33} is perpendicular to the COO plane. In addition, our data confirm that differences in chemical shifts observed in liquids for carboxyl groups are due primarily to changes in the value of σ_{22} rather than σ_{11} or σ_{33} . Protonation of an ionic carboxyl group results in an increased shielding for σ_{22} , at least for the three cases we have examined and, in one case, AHOX also produces a rotation of the tensor by $\sim 25^\circ$ around σ_{33} . In contrast, the twisting of carboxyl planes relative to one another in DAOX results in a rotation of the tensor around σ_{11} by 10° and is also possibly responsible for the relatively large deshielding of σ_{22} in this compound. Although the tensor in HOX has principal values which are not unusual and a general orientation that is similar to those found for the ^{13}C tensors in the other oxalate ions, it nevertheless possesses its own peculiar orientation; that is, it is rotated by about 20° around σ_{22} . Finally, the effect of a change in hydrogen bonding strength was detected by comparing the

tensors of anhydrous and hydrated oxalic acid.

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