Chemical shielding tensors of ^{13}C in solid dimethyl oxalate*

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We recently reported the full chemical shielding tensors for ^{13}C in the hydroxyl and carboxyl groups of tartrate ion in single crystals of ammonium tartrate.[1,2] These tensors are beginning to shed some light on the nature and anisotropy of chemical shielding, and some trends are beginning to emerge. It is clear, however, that this area, although promising, is at a very preliminary and premature stage, and further measurements are necessary before any reliable generalizations can be inferred or any basis for critical testing of shielding theories can be developed. In this Communication, we present a preliminary report of the ^{13}C shielding tensors measured in a single crystal of dimethyl oxalate. These tensors should be useful for comparison with the only other reported full measurements in carbon–oxygen groups: ^{13}C=O in benzophenone,[3] ^{13}C–OH and $^{13}CO_2^-$ in tartrate,[1,2] and $^{13}CO_3^=$ in calcite.[4]

Figure 1 shows proton-enhanced and decoupled ^{13}C NMR spectra[5] from a single crystal of dimethyl oxalate in two orientations, with the static external field H_0 having directions cosines of (a) 0.2183, −0.8371, −0.5015 and (b) 0.8392, 0.0244, 0.5432, respectively, with the a^*, b, c crystallographic axes. Such signal/noise ratios are achieved both by multiple contact and by total cross-polarization experiments.[5,6] The dimethyl oxalate molecule possesses a center of symmetry, and the unit cell contains two inversion-inequivalent molecules[7]; thus, in general orientations, four lines are expected, as indeed observed, in the spectrum of Fig. 1(a). In isotropic liquid solution, only two lines are observed from the averaged magnetically inequivalent carboxyl and methyl carbon nuclei; this is also true, of course, in crystal orientations where the two molecules have the same orientation with respect to H_0, as in the spectrum of Fig. 1(b).

In Fig. 2, we show an example of the dependence of the chemical shielding on orientation, displaying a large anisotropy for the carbonyl ^{13}C nuclei. Such rotations were performed about three mutually orthogonal axes, and the data were then analyzed[2] to yield two similar[8] carbonyl tensors and two similar[8] methyl tensors. The principal values of the carbonyl tensors are (± 4): $\sigma_{11} = -124$, $\sigma_{22} = 13$, $\sigma_{33} = 17$, and for methyl carbons (± 4): $\sigma_{11} = 43$, $\sigma_{22} = 58$, $\sigma_{33} = 114$, in ppm relative to an external reference of liquid benzene. These have previously been determined very roughly in polycrystalline samples.[9]

The unique axes of the two axially symmetric (within experimental error) carbonyl ^{13}C tensors, corresponding to σ_{11}, have direction cosines of −0.3358, −0.5675, −0.7518 and −0.3600, 0.5720, 0.7340 with the a^*, b, c crystallographic axes. Clearly, the assignment of these two tensors to the molecules in the unit cell cannot be made unambiguously. For an isolated planar molecule, symmetry requires that the axes be in, or perpendicular to, the plane, and we expect this to be true to a first approximation in the crystal. Indeed, one of the two assignments places the unique axes in the planes of the molecules (± 3°), making angles of $(14.0 \pm 2)^\circ$ and $(111.5 \pm 2)^\circ$, respectively, with the C=O and C–C bonds of the molecules. It is plausible, though not unequivocal, that this is the correct assignment. In benzophenone, the more or less unique axis of the ^{13}C=O tensor corresponds to the highest shielding and is perpendicular to the plane spanned by the carbonyl ^{13}C and the atoms bonded to it.[3] In our case, the unique axis corresponds to the least shielding (most paramagnetic shift) and appears to lie roughly along the C=O bond. It remains to be seen whether or not these characteristics will appear in other cases and can thus serve as analytical "fingerprints" for structure and orientation.

The shielding values for the methyl group are similar to those for methanol and to values previously determined roughly in powder spectra.[9] Interestingly enough, the principal axes are related not to the local orientation of the methyl groups, but rather to the symmetry of the carbonyl groups, the most shielded axis corresponding to σ_{33} lying along a C=O axis (± 5°) and σ_{22} perpendicular to a molecular plane. The assignment to particular molecules is not clear in this case and is under further study. It thus appears that the methyl ^{13}C- chemical shielding tensor is very susceptible to "through-space" effects from the carbonyl groups. However, these results are preliminary and tentative and further experiments will be reported later.

The experiments were performed on a homebuilt double-resonance spectrometer[10] operating at 106 MHZ for protons. The crystals were grown by slow cooling from

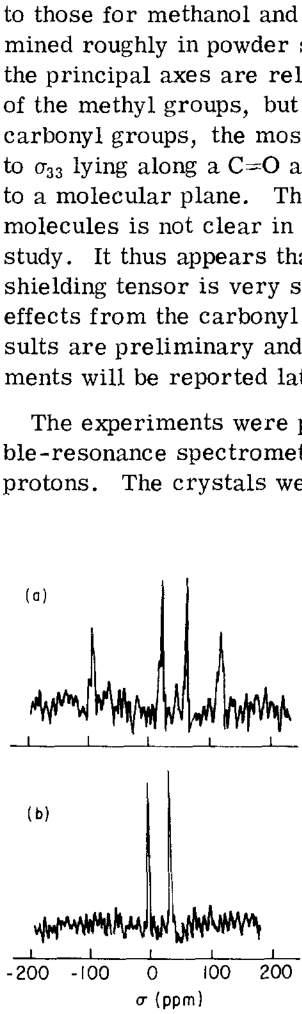

FIG. 1. Proton-enhanced and decoupled ^{13}C NMR spectra of single crystal of dimethyl oxalate in two different orientations. The directions of H_0 relative to the crystal axes are given in the text. The horizontal scale is relative to an external reference of liquid benzene.

the melt and oriented by X-ray precession techniques. The enormous requisite rf power limited total multiple-contact exposures to ~1 sec to avoid evaporation of probe components. Further experimental details will be presented separately.

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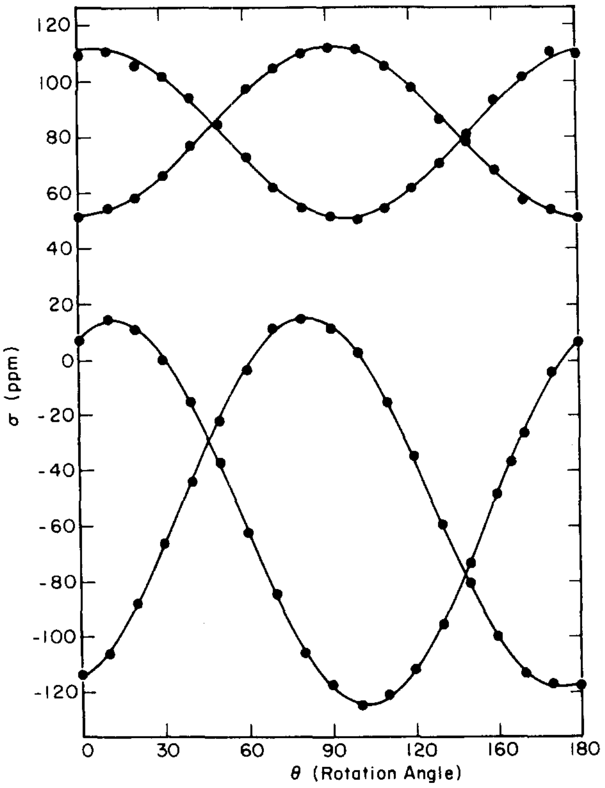

FIG. 2. Dependence of the ^{13}C chemical shifts in dimethyl oxalate on crystal orientation. The points are experimental and the solid lines are from theoretical formulas. The rotation axis had direction cosines of 0.8268, −0.1144, 0.5508, and at $\theta = 0°$, H_0 had direction cosines of −0.4726, −0.6721, 0.5699, respectively, with the a^*, b, c, crystallographic axes.

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[8] Similar here means that the principal values are the same but the orientations of the principal axes are not.

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