

# Chemical shielding tensor of $^{13}\text{C}$ in a carboxyl group\*

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We wish to report the first measurement of the full chemical shielding tensor for  $^{13}\text{C}$  in a carboxyl group. The experiments were performed on a single crystal of ammonium *d*-tartrate employing multiple-contact and

total cross-polarization versions of proton-enhanced nuclear magnetic resonance.<sup>1-3</sup> Full tensors were determined for all the  $^{13}\text{C}$  nuclei in the unit cell; details of these experiments and a complete description and analysis of the results will be presented separately.<sup>4</sup> In this communication, we present a preliminary account of the work to indicate the nature of the spectra observed and the type of information extracted.

Figures 1(a) and 1(b) show a proton-enhanced and decoupled  $^{13}\text{C}$  free induction decay and Fourier transform obtained from a small single crystal of ammonium *d*-tartrate. The unit cell of the crystal (space group  $P2_1$ ) contains two molecules,<sup>5</sup> and thus, in general orientations, four lines are expected from the carboxyl groups. These are the four low field lines observed in the spectrum. The high field lines are from the hydroxyl carbons for which the analysis will be presented separately. In contrast, only two lines are observed using conventional NMR in isotropic solution from the two magnetically inequivalent carbon sites (carboxyl and hydroxyl).

Rotations about three mutually perpendicular axes were performed and analyzed according to Eq. (1):

$$\sigma = \sin^2\theta \cos^2\phi \sigma_{11} + \sin^2\theta \sin^2\phi \sigma_{22} + \cos^2\theta \sigma_{33}, \quad (1)$$

where  $\sigma_{ii}$ ,  $i=1-3$  are the principal elements of the chemical shielding tensor,  $(\theta, \phi, \psi)$  are the Euler angles of the transformation from the principal axes (1, 2, 3) to the laboratory frame ( $x, y, z$ ), and  $\sigma$  is the observed chemical shift,  $\sigma \equiv \sigma_{zz}$ . This yielded four chemical shielding tensors for the carboxyl carbons with similar principal elements; the average values for these shielding elements are  $\sigma_{11} = -109$ ,  $\sigma_{22} = -61$ ,  $\sigma_{33} = 23 (\pm 6)$ , in parts per million relative to liquid benzene.

Of particular interest is the orientation of the principal axes of the chemical shielding tensors in the molecular frame. The orientation of these axes in our experiments is given in the crystal axis system, and these cannot be assigned unambiguously to specific carbon nuclei. However, only one assignment yields reasonable relative orientations of the four sets of principal axes with respect to the local molecular structure at the four carboxyl carbons, and we assume that this is the correct assignment. This assumption is indeed strengthened by experiments on other crystals containing carboxyl groups,<sup>6</sup> and by the fact that the orientation of the axes assigned in this way is related to the local symmetry of the carboxyl group. This is shown in Fig. 1(c); the  $^{13}\text{C}$  nucleus is most shielded when  $H_0$  is roughly perpendicular to the  $^{13}\text{COO}^-$  plane, and least shielded when  $H_0$  is along the C-C bond. There are small deviations and these will be discussed in detail in a full paper.<sup>4</sup> To date, the only other reported  $^{13}\text{C}$  chemical shielding ten-

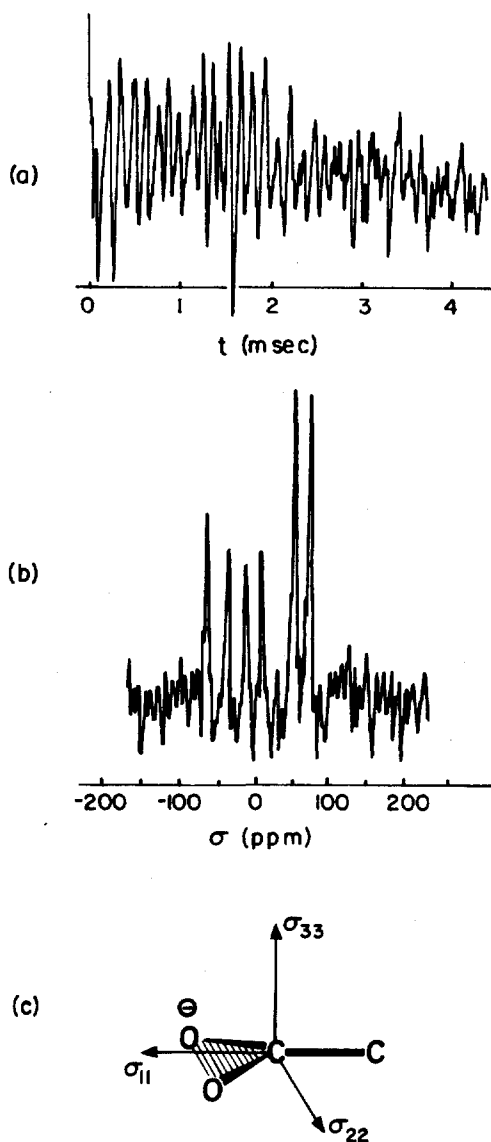


FIG. 1. (a) Portion of proton-enhanced and decoupled  $^{13}\text{C}$  free induction decay in single crystal of ammonium *d*-tartrate, with  $H_0$  making angles of  $60^\circ$  and  $90^\circ$  with the *a* and *b* crystallographic axes of the crystal. (b) Fourier transform of the free induction decay. Horizontal scale is in parts per million ppm relative to an external reference of liquid benzene. Resolution is limited primarily by dipolar coupling to  $^{14}\text{N}$  nuclei. (c) Orientation of principal axes of  $^{13}\text{C}$  chemical shielding tensor in  $^{13}\text{COO}^-$  obtained from crystal rotation analysis of spectra such as that in (b). The average values of the shielding elements,  $\sigma_{11} < \sigma_{22} < \sigma_{33}$ , appear in the text.

sors from single crystal studies are for  $^{13}\text{CO}_3^-$  in calcite,<sup>7</sup>  $^{13}\text{C}$  in durene,<sup>8</sup> and  $^{13}\text{CO}$  in benzophenone.<sup>9</sup> In all cases, the paramagnetically shifted elements of the tensor are in the nodal planes of  $\pi$  molecular orbitals, as expected from simple considerations.<sup>9</sup> Our measurements should provide a sensitive test of detailed molecular quantum mechanical calculations of chemical shielding.

The experiments were performed on a home-built double-resonance spectrometer operating at 106 MHz for protons. Rotating proton decoupling fields averaged several hundred watts, thus limiting total multiple-contact exposure times to  $<0.5$  sec to avoid melting of various components. Typical accumulation times were  $<5$  min per spectrum. The crystals were grown from aqueous solution, oriented by x-ray precession techniques and then transferred, employing a precision transfer device, to a goniometer and high power double coil probe in the field of a wide bore superconducting magnet. Full experimental details will appear separately.

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