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Determination of the orientations for the ^{17}O NMR tensors in a polycrystalline L-alanine hydrochloride

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ABSTRACT

We report a solid-state ^{17}O NMR study of the ^{17}O electric-field-gradient (EFG) and chemical shielding (CS) tensors for the carboxyl oxygen in an L-alanine hydrochloride. Using [^{17}O]– and [^{13}C,^{17}O]–L-alanine hydrochlorides, both the magnitudes and the orientations in the molecular frame of the ^{17}O EFG and CS tensors could be determined by the analysis of the ^{17}O magic-angle spinning (MAS) and stationary NMR spectra. For the carbonyl oxygen, the smallest EFG tensor component, V_{XX}, and the largest EFG component, V_{ZZ}, roughly lies in the carboxyl molecular plane and the direction of V_{XX} is parallel to the dipolar vector between ^{13}C and ^{17}O, that is, the direction of C=O bond. The angles between the intermediate EFG component, V_{YY}, and δ_{33} component, and between δ_{22} component and V_{ZZ} are found to be approximately 10° and 35°, respectively. We also present the results of the quantum chemical calculations for a theoretical hydrogen-bonding model, indicating that hydrogen-bonding strengths make it possible to vary both magnitudes and orientations of the carbonyl ^{17}O EFG tensors in amino acid hydrochlorides.

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1. Introduction

One of the advantages of solid-state nuclear magnetic resonance (NMR) spectroscopy is that NMR parameters expressed by tensor quantities may be experimentally obtained [1]. Moreover, even for macromolecules such as proteins, it is possible to deal with quadrupolar nuclei. Thus, more detailed information on molecular properties will be potentially offered to scientists. Clearly, oxygen is one of the most important elements in biochemistry and biology, and it contains an NMR active nucleus (^{17}O, natural abundance = 0.037%, $I = \frac{5}{2}$, $\gamma = -3.6279 \times 10^7\,\mathrm{rad\,T^{-1}\,s^{-1}}$). Hence, it is expected that solid-state ^{17}O NMR is a very attractive tool for biochemists and biologists. Recently, there have been some literatures reporting ^{17}O electric-field-gradient (EFG) and chemical shielding (CS) tensors for biological solids [2–12]. One of the experimental approaches is that, by analyzing stationary ^{17}O NMR spectra, the magnitudes of ^{17}O NMR tensor components as well as the relative orientations between the ^{17}O CS and EFG tensors are obtained. Assuming that absolute orientation of the EFG tensor in the molecular frame obtained from high-level quantum chemical calculations are correct, then it is possible to deduce the CS tensor orientation using the calculated EFG tensors as in Ref. [13].

In the cases of L-amino acid hydrochlorides, however, it has been reported [14] that it is difficult to obtain reliable information on ^{17}O EFG tensor orientations by theoretical calculations. As shown in Scheme 1, the quantum chemical calculations provided two possible orientations of the carbonyl ^{17}O EFG tensors for L-amino acid hydrochlorides. Two EFG tensor components roughly lie in the molecular plane so that the direction of the remaining component is approximately perpendicular to the molecular plane. In one possible orientation depicted in Scheme 1(a), the V_{XX} component is along the C=O bond, while, in the other orientation depicted in Scheme 1(b), the V_{YY} component is parallel to the C=O bond direction. Apparently, the theoretical calculations for ^{17}O EFG tensors in L-amino acid hydrochlorides provide such uncertain results because the values of V_{XX} and V_{YY} components are too close to predict the accurate values by quantum chemical calculations.

One of the standard experimental NMR methods to determine the tensor orientation in the molecular frame is single-crystal NMR. However, this requires growth of a large single-crystal suitable for the NMR experiments. This may be one of the critical problems for solid-state ^{17}O NMR in biological molecules because of a small quantity of the ^{17}O-enriched sample. Previously, by using a doubly enriched sample (for example, ^{13}C and ^{17}O), orientations of ^{17}O NMR tensors in the molecular frame could be determined even for a powder sample with the aid of a ^{13}C–^{17}O dipolar vector, which

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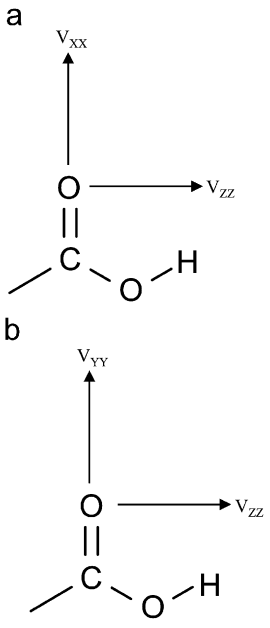

Scheme 1

has a known direction along the C–O bond [15]. Recently, our group has also presented the experimental determination of the ^{17}O NMR tensors in the molecular frame for an L-amino acid [16]. In this paper, we will report the first experimental determination of the orientations of ^{17}O NMR tensors in L-alanine hydrochloride by using a ^{13}C–^{17}O dipolar vector as an internal reference. We believe that the present results will be useful for the future evaluations of quantum chemical calculations for ^{17}O NMR tensors including tensor orientations. We will also discuss whether hydrogen bonds make it possible to change the carbonyl ^{17}O EFG tensor orientations, or not, by carrying out the extensive quantum chemical calculations. This work is part of a systematic investigation of amino acids, peptides, and proteins by solid-state ^{17}O NMR performed at RIKEN Genomic Sciences Center.

2. Experimental

2.1. Sample aspects

^{17}O-enriched L-alanine and doubly isotopic-labeled (^{13}C and ^{17}O of carboxylate groups) L-alanine were previously obtained [9,16]. After the labeled amino acids were treated with 1 mol L^{-1} of hydrochloric acid, the solvent was removed so that white powder samples were obtained. Powder X-ray diffraction was run on Rigaku RINT 2200 V diffractometer using CuK_α radiation at a wavelength of 1.54184 Å. The diffraction patterns for the samples were recorded from $2\theta = 3.00^\circ$ to 50.00° in 0.02° steps with a scan rate of 4.0° min^{-1} at room temperature. These patterns were in good agreement with those calculated from the literature of L-alanine hydrochloride ($P2_12_12_1$, $Z = 4$, $a = 7.148(3)$ Å, $b = 17.590(8)$ Å, $c = 5.202(2)$ Å) [17]. Approximately 40 and 12 mg of the ^{17}O-enriched L-alanine hydrochloride and the doubly isotopic-labeled L-alanine hydrochloride, respectively, were used for the following NMR experiments.

2.2. Solid-state NMR

All the ^{17}O NMR experiments were performed on a Chemagnetics Infinity-400 spectrometer and JEOL ECA 500, 700, and 930 spectrometers operating at frequencies of 54.24, 67.80, 94.91, and 126.07 MHz, respectively. Polycrystalline amino acid hydrochlorides were packed into 4-mm rotors of silicon nitride and 3.2-mm rotors of zirconium oxide for ^{17}O stationary and magic-angle spinning (MAS) NMR experiments, respectively. A sample spinning frequency for the ^{17}O MAS experiment carried out at 11.7 T was 20.53 ± 0.02 kHz. For stationary ^{17}O NMR experiments performed at 9.4, 11.7, and 16.4 T, a single-pulse sequence was used in which the $\pi/2$ pulse lengths were 1.2, 1.4, and 1.2 μs for 9.4, 11.7, and 16.4 T, respectively, and the corresponding preacquisition times were 20, 15, and 20 μs. When the baselines were distorted at the stationary ^{17}O NMR spectra, the baseline corrections were carried out using polynomial functions. For the stationary ^{17}O NMR experiment recorded at 21.8 T, the echo sequence of Oldfield et al. [18] was employed. High-power proton decoupling with the TPPM scheme [19] was used during data acquisition times for all the NMR experiments. A sample of liquid water was employed for chemical shift referencing. The recycle delay was 3–7 s. The number of scans for the MAS and the stationary NMR experiments were approximately 1500 and 15,000–30,000, respectively. All the NMR spectra were processed by Delta (JEOL USA, Inc.) software. Spectral simulations were performed using the WSOLIDS1 program package including the PAIN32 program [20] or the program developed by the authors on MATLAB.

2.3. Quantum chemical calculations

All quantum chemical calculations on ^{17}O EFG tensors were performed with the Gaussian03 program package [21] on RIKEN super combined cluster (RSCC). The crystal structure of L-alanine hydrochloride [17] was calculated using second-order Møller–Plesset perturbation (MP2) theory with standard basis sets such as STO-3G, 6-31G, 6-31+G**, 6-311G, TZVP, 6-311++G**, and cc-pVTZ where the symbols of + and * indicate diffusion and polarization, respectively. It has been demonstrated [9] that all possible intermolecular interactions should be included in the quantum chemical calculations to well reproduce the experimental results. Hence, in addition to the target L-alanine hydrochloride molecule, three L-alanine molecules and three chloride ions were included in the calculation geometries. The quantum chemical calculations yield EFG tensors in atomic units (a.u.), q_{ii}. In solid-state NMR experiments, quadrupolar coupling interactions are expressed as EFG tensors in frequency whose principal components are defined as $|V_{XX}| < |V_{YY}| < |V_{ZZ}|$. To describe a traceless EFG tensor, one uses two NMR parameters, namely, the quadrupole coupling constant, C_Q, and the asymmetry parameter, η_Q. The following equations were employed for making a direct comparison between theoretical and experimental data:

$$C_Q\ [\mathrm{MHz}] = eV_{ZZ}Qh^{-1} = -2.3496Q\ [\mathrm{fm}^2]\, q_{ZZ}\ [\mathrm{a.u.}] \quad (1)$$

and

$$\eta_Q = (V_{XX} - V_{YY})/V_{ZZ} \quad (2)$$

where Q is the electric quadrupole moment of the ^{17}O nucleus and the factor of 2.3496 comes from unit conversion. In the present calculations, $Q = -2.558$ fm^2 [22] was employed in all EFG calculations.

3. Results and discussion

The aim of the present work is to experimentally determine the orientations of the ^{17}O EFG and CS tensors for an L-amino acid hydrochloride with respect to the molecular frame by introducing dipolar vectors between ^{13}C and ^{17}O, which contains known

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