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Research paper

Solid-state ^{17}O NMR analysis of synthetically ^{17}O-enriched D-glucosamine

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HIGHLIGHTS

- D-glucosamine was chemically synthesized with ^{17}O enrichment at position 6.
- Its high-quality ^{17}O NMR data were obtained by high-magnetic-field measurements.
- This enabled estimation of chemical shift and electric field gradient tensors.

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ABSTRACT

The hydroxyl groups of carbohydrates are critical determinants of their conformational dynamics and intermolecular interactions but are difficult to characterize by conventional ^{1}H nuclear magnetic resonance (NMR) approaches in solution. Here, we report a solid-state ^{17}O NMR analysis of synthetic glucosamine with ^{17}O enrichment at position 6. Based on magic-angle spinning and stationary spectral data obtained at varying magnetic fields in conjunction with quantum chemical calculations, we successfully estimated ^{17}O chemical shift and electric field gradient tensors, providing benchmark for ^{17}O NMR analyses of oligosaccharide structures.

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy is indispensable for carbohydrate researches as a useful tool not only to determine covalent structures of oligosaccharides but also to characterize their dynamic conformations and interactions at atomic level [1–3]. Using solution NMR techniques, the information is provided through chemical shifts (CSs), scalar couplings, nuclear Overhauser effects, dipolar couplings, and paramagnetic effects, regarding CH and NH groups of oligosaccharides [4]. In addition, solid-state NMR investigations of carbohydrates have been undergoing rapid development and providing valuable information especially on structures [5–7], dynamics [8,9], interactions [10], and metabolism [11] of polysaccharides.

Carbohydrate structures are characterized by an abundance of hydroxyl groups, which can be steric constraints and involved in hydration and specific hydrogen bonding, thereby serving as critical determinants of their conformational dynamics and intermolecular interactions. Despite such importance, the rapid exchange of carbohydrate hydroxyl hydrogens with solvent preclude their direct observation by ^{1}H NMR measurements in aqueous solution. Hence, information on the carbohydrate hydroxyl groups have been obtained through indirect approaches based on observation of deuterium-induced ^{13}C isotope shifts [12,13] and hydrogen-bond-mediated scalar couplings [14,15].

Solid-state ^{17}O NMR spectroscopy offers an alternative, promising

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approach that enables direct observation of the hydroxyl oxygens of carbohydrates, providing information on microenvironments surrounding the hydroxyl groups through ^{17}O CS and electric field gradient (EFG) tensors. However, in general, ^{17}O NMR observation is precluded by low sensitivity due to low natural abundance (0.037%) and severe line broadening due to quadrupole relaxation. D'Souza and Lowary overcame the low-natural-abundance problem by ^{17}O enrichment [16]. The quadrupole relaxation can be suppressed at higher magnetic fields [17,18]. Indeed, Grandinetti and co-workers reported solid-state ^{17}O NMR data obtained at 19.5 T of position-specific ^{17}O-enriched analogs of glucose, galactose and Glc–Glc disaccharides, which were prepared by nucleophilic substitution using ^{17}O-labeled benzoic acid and its salt [19].

Here, we extend the solid-state NMR approach to determine ^{17}O-derived parameters of D-glucosamine, which is a common metabolic precursor of aminosugars including sialic acids and their derivatized polysaccharides and glycoconjugates. Therefore, solid-state ^{17}O NMR characterization of D-glucosamine will serve as solid starting point of structural studies of these glycoconjugates.

2. Experimental section

2.1. Sample preparations

2.1.1. 6-O-Tosyl-N-acetyl-D-glucosamine

Preparation of 6-*O*-tosyl-*N*-acetyl-D-glucosamine was performed according to the previous report [20] with some modifications. To a solution of *N*-acetyl-D-glucosamine (66.4 g, 0.30 mol) in pyridine (860 mL), a solution of *p*-toluenesulfonyl chloride (68.6 g, 0.36 mol) in pyridine (430 mL) was slowly dropped at 4 °C within 30 min, and the mixed solution was stirred for 4 h at 4 °C under argon atmosphere. The reaction was monitored on silica gel TLC (ethyl acetate : water:-isopropylamine = 18:1:1 and methanol:*tert*-butyl alcohol:water:-ammonia water = 8:2:1:1). The reaction was quenched by adding methanol (43 mL). The mixture was diluted with chloroform (2.1 L) and the organic layer was washed with water (500 mL, 300 mL). The organic layer was dried over $MgSO_4$, and concentrated in vacuo. To remove pyridine, toluene (40 mL × 3) was added and repeatedly evaporated. To the residue, CH_2Cl_2 (500 mL) was added to obtain crude solid. The solid was further washed with CH_2Cl_2 (500 mL) to give white solid (42.8 g, yield 38%).

2.1.2. 6-O-Tosyl-1,3,4-triacetyl-N-acetyl-α-D-glucosamine

To a solution of 6-*O*-tosyl-*N*-acetyl-D-glucosamine (37.5 g, 0.10 mol) in pyridine (500 mL), acetic anhydride (70 mL, 0.74 mol) was slowly dropped at 0 °C under argon atmosphere within 30 min. The mixture was stirred for 5 h at 0 °C. The reaction was monitored on silica gel TLC (ethyl acetate : water : isopropylamine = 18:1:1). The reaction was quenched by adding methanol (24 mL). The solvent was removed by evaporation. Then, toluene (30 mL × 3) was added and repeatedly evaporated to remove pyridine. To the residue, methanol was added to give crude solid. The solid was recrystallized from methanol (100 mL) and a colorless crystal (27.8 g, yield 55%, m.p. 153 °C) was obtained.

2.1.3. Sodium [$^{17}O_2$]acetate

Sodium [$^{17}O_2$]acetate was synthesized using 1 g of [^{17}O]H_2O (^{17}O: 89.9%, ICON) according to the reported procedure [21]. The reaction was conducted under argon atmosphere. The yield of sodium [$^{17}O_2$] acetate was 2.1 g (97%).

2.1.4. [6-$^{17}O_2$]Acetyl-1,3,4-triacetyl-N-acetyl-α-D-glucosamine

Introduction of ^{17}O at the 6 position of glucosamine unit was performed following the previous procedure [22]. To a solution of 6-*O*-tosyl-1,3,4-triacetyl-*N*-acetyl-α-D-glucosamine (10.02 g, 20.0 mmol) in DMF (50 mL), 15-crown-5 (4.76 mL, 24.0 mmol) and sodium [$^{17}O_2$] acetate (2.02 g, 24 mmol) were added under stirring at once. The solution was kept stirring for 4 h at 120 °C. The reaction was monitored with silica gel TLC (ethyl acetate : water : isopropylamine = 18:1:1). After cooling, the mixture was diluted with ethyl acetate (1.5 L). The organic layer was washed with water (500 mL × 5) and brine (500 mL × 1). The organic layer was dried over $MgSO_4$, and evaporated to remove solvents. The product [6-$^{17}O_2$]acetyl-1,3,4-triacetyl-*N*-acetyl-α-D-glucosamine was obtained as a brown oil (4.54 g, 58%).

2.1.5. D-[6-^{17}O]Glucosamine hydrochloride

[6-$^{17}O_2$]Acetyl-1,3,4-triacetyl-*N*-acetyl-α-D-glucosamine (4.54 g, 11.6 mmol) was dissolved in 2 M hydrochloric acid (116 mL) and stirred for 4 h at 100 °C under argon atmosphere. The reaction was monitored with silica gel TLC (ethyl acetate:water:-isopropylamine = 18:1:1 and ethanol:*tert*-butyl alcohol:water:-ammonia water = 8:2:1:1). After cooling, solvent was evaporated and toluene (10 mL × 5) was added to the oil reside. After evaporation, a crude brown solid was obtained. The crude solid was washed with methanol giving colorless material (2.41 g, yield 96%). The purity (> 95%) and anomeric configuration (α-anomer 95%) of the obtained D-[6-^{17}O]glucosamine hydrochloride were assessed based on solution ^1H and solid-state ^{13}C NMR spectra, respectively (Supplementary data).

2.2. Solid-state ^{17}O NMR experiments

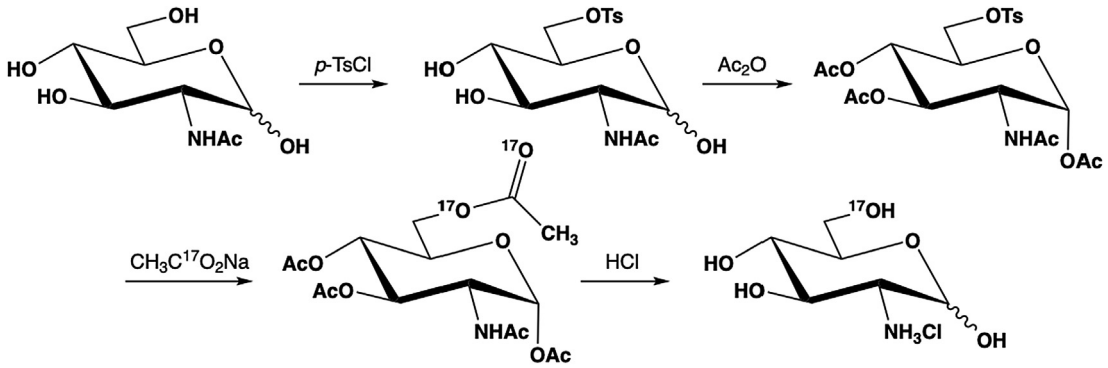
All solid-state ^{17}O NMR spectra of D-[6-^{17}O]glucosamine hydrochloride were obtained on JEOL ECA 600, JEOL ECZR 800, and Bruker Avance-900 spectrometers, operating at 81.356 MHz (14.1 T), 108.469 MHz (18.8 T), and 122.026 MHz (21.1 T), respectively. The polycrystalline samples were packed into 2.5- mm, 3.2- mm, or 4.0- mm rotors of zirconium oxide and/or silicon nitride. An external sample of liquid water was used for pulse adjustments and chemical shift referencing. For all the experiments, an Oldfield echo sequence [23] was used, and high-power ^1H decoupling was applied during the acquisition periods. The recycle delay was typically 1 s, and the $\pi/2$ pulse length was typically 1.0 μs –2.0 μs. Sample spinning frequencies, ω_R, at 21.1 T and 18.8 T were 20 kHz and 8 kHz, respectively, and the inter-pulse delay times were rotor-synchronized. For the stationary ^{17}O NMR experiments, the inter-pulse delay times were set to 40 μs – 50 μs. All the experimental NMR spectra were processed using TOP-SPIN (Bruker) and/or Delta (JEOL Ltd.) software. Spectral simulations were performed using the program written by the authors on MATLAB (The MathWorks Inc.). To describe the relative orientation of ^{17}O CS and EFG tensors, expressed by the rotation parameters in terms of three Euler angles α, β, and γ, the definition of the literature [24] was used.

2.3. Quantum chemical calculations

All quantum chemical calculations on ^{17}O EFG and CS tensors were performed with the Gaussin16 program package [25]. The crystal structure of α-D-glucosamine hydrochloride, determined by X-ray diffraction [26], was used for the input geometry, in which two neighboring molecules were additionally included as the effect of intermolecular interactions. The Gauge-Induced Atomic Orbital (GIAO) approach [27] was used for chemical shielding calculations. In NMR experiments, the frequency of an NMR signal is observed relative to that in a reference system. For ^{17}O NMR, liquid water was used as the reference. Because the quantum calculations give absolute chemical shielding values, σ_{ii}, it is convenient to convert them into chemical shifts relative to water, δ_{ii}, by using

$$\delta_{ii} = 307.9 - \sigma_{ii}\,[\mathrm{ppm}], \qquad [i]$$

where the value of 307.9 ppm is the absolute chemical shielding constant for the ^{17}O nucleus in liquid H_2O [28]. 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, whose principal components are defined as



Scheme 1. Synthesis of D-glucosamine hydrochloride with ^{17}O enrichment at position 6.

$$|Vxx| < |Vyy| < |Vzz|. \quad \text{[ii]}$$

To describe a traceless EFG tensor, two NMR parameters are used, 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:

$$C_Q\,[\mathrm{Hz}] = eVzzQh^{-1} = -2.3496\ Q\ [\mathrm{fm}^2]q_{zz}[\mathrm{a.u.}\ ] \quad \text{[iii]}$$

and

$$\eta_Q = (Vxx\ -\ Vyy)/Vzz, \quad \text{[iv]}$$

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 [29] was employed in all EFG calculations.

3. Results and discussion

We synthesized D-[6-^{17}O]glucosamine efficiently using ^{17}O-labeled sodium acetate (Scheme 1). To realize high isotope enrichment, sodium [$^{17}O_2$]acetate was prepared through consecutive hydrolysis of triethyl orthoacetate using [^{17}O]H_2O (^{17}O: 89.9%) according to the reported procedure [21]. The reaction of the obtained sodium [$^{17}O_2$]acetate with a 6-*O*-tosylated glucosamine derivative allowed the selective introduction of ^{17}O at 6 position of the glucosamine unit. A subsequent deprotection in hydrochloric acid gave D-[6-^{17}O]glucosamine hydrochloride in good yield.

In parallel, D-[6-^{18}O]glucosamine was prepared under the same procedure using [^{18}O]H_2O (^{18}O: 95–98%, CIL) instead of [^{17}O]H_2O to estimate the isotope enrichment ratio. By comparing signal intensities (^{13}C-^{16}O and ^{13}C-^{18}O) in the ^{13}C NMR spectrum, the ^{18}O enrichment ratio in the synthesized D-[6-^{18}O]glucosamine hydrochloride was determined as 89%. Thus, the enrichment ratio of ^{17}O in our D-[6-^{17}O]glucosamine was estimated to be 82%-84%.

The synthetic D-[6-^{17}O]glucosamine was subjected to solid-state NMR measurements and successfully provided ^{17}O spectra with high sensitivity. By the measurement at 21.1 T using magic-angle spinning (MAS) with a fast rotor regime ($\omega_R = 20$ kH), a typical MAS line shape arising from the central transition of second-order quadrupolar interactions for half-integer quadrupolar nuclei was obtained (Fig. 1a). The spectral analysis yielded the following parameters; $\delta_{iso} = -14(2)$ ppm, $C_Q = 9.0(2)$ MHz, and $\eta_Q = 0.91(5)$. Grandinetti and co-workers previously reported a series of solid-state ^{17}O MAS NMR data of carbohydrates [19], providing the ^{17}O NMR parameters of methyl α-D-[6-^{17}O]glucopyranoside, relevant to the present compound, as follows: $\delta_{iso} = 9.5$ ppm, $C_Q = 8.76$ MHz, and $\eta_Q = 1.00$. The C_Q and η_Q values obtained for the oxygen at position 6 of glucosamine are similar to those reported for methyl α-D-[6-^{17}O]glucopyranoside, indicating their comparable EFG tensors. In contrast, the isotropic chemical shifts of the oxygen at position 6 were significantly different between glucose and glucosamine, which suggested that a combined analysis of ^{17}O CS and EFG tensors is effective for investigation of the local electronic structures of oligosaccharides. To further approach the CS and EFG tensors, we also measured ^{17}O MAS spectrum with $\omega_R = 8$ kHz (Fig. 1b). Using this intermediate rotor regime, spinning sidebands appeared in the MAS spectrum, which was well fitted by the theoretical ^{17}O MAS spectrum simulated by the second-order quadrupolar interaction with lower rotor frequency [30]. This result indicated that the magnitude of the ^{17}O CS tensor for D-[6-^{17}O]glucosamine was expected to be much smaller than that of the EFG tensor.

In principle, the analysis of stationary ^{17}O NMR line shape is required to reveal ^{17}O CS tensor components and the relative orientations between CS and EFG tensors [31]. Therefore, the ^{17}O stationary NMR spectra of D-[6-^{17}O]glucosamine were measured and analyzed at 14.1 T, 18.8 T, and 21.1 T (Fig. 2). The high-quality ^{17}O NMR data were obtained at the high magnetic field. All the obtained experimental ^{17}O NMR parameters for the oxygen at position 6 of glucosamine are summarized in Table 1. It was also necessary to carry out the ^{17}O NMR experiments at higher magnetic fields, where the magnitude of EFG tensors decreases while that of CS tensors increases in general. At a lower magnetic field, *e.g.*, at 11.7 T, it was nearly impossible to obtain information on ^{17}O CS tensors and the Euler angles, because that the line shape was insensitive to the changes in their parameters.

For reference, the results of density functional theory (DFT) calculations for the ^{17}O NMR parameters of α-D-[6-^{17}O]glucosamine using various basis sets are summarized in Table 2. While the calculated C_Q values were reasonably consistent in the experimental one, the η_Q value was not reproduced by the DFT calculation. The calculated relative orientations between the two NMR tensors tend to be in good agreement with the experimental ones. Assuming that the orientations of the ^{17}O EFG tensor components obtained from the present quantum chemical calculations were correct, the absolute orientations of the ^{17}O CS tensor components with respect to the molecular frame were determined using the experimentally obtained relative orientations [31]. The ^{17}O NMR tensor orientations thus determined for α-D-[6-^{17}O]glucosamine are depicted in Fig. 3. The largest ^{17}O EFG tensor component, V_{ZZ}, and the smallest component, V_{XX}, lay in the molecular plane of C-O-H, while the V_{ZZ} direction was approximately 20° off the C-O bond. The least shielding component, δ_{11}, and the most shielding component, δ_{33}, slightly lay off the molecular plane, since the direction of δ_{22} component did not coincide with that of V_{YY}, *i.e.*, $\alpha = 16(10)$ and $\gamma = 12(30)$. The angle between δ_{33} and V_{ZZ} components was 108(8)°. Although there remains room to improve quantum chemical calculations for magnitudes of ^{17}O NMR tensors, the present experimental data, in particular the ^{17}O CS tensors, would be useful for the future evaluation of *ab initio* calculations.

4. Conclusions

We successfully interpreted the ^{17}O spectral data, for estimating the ^{17}O CS and EFG tensors, of D-glucosamine by the site-specific ^{17}O

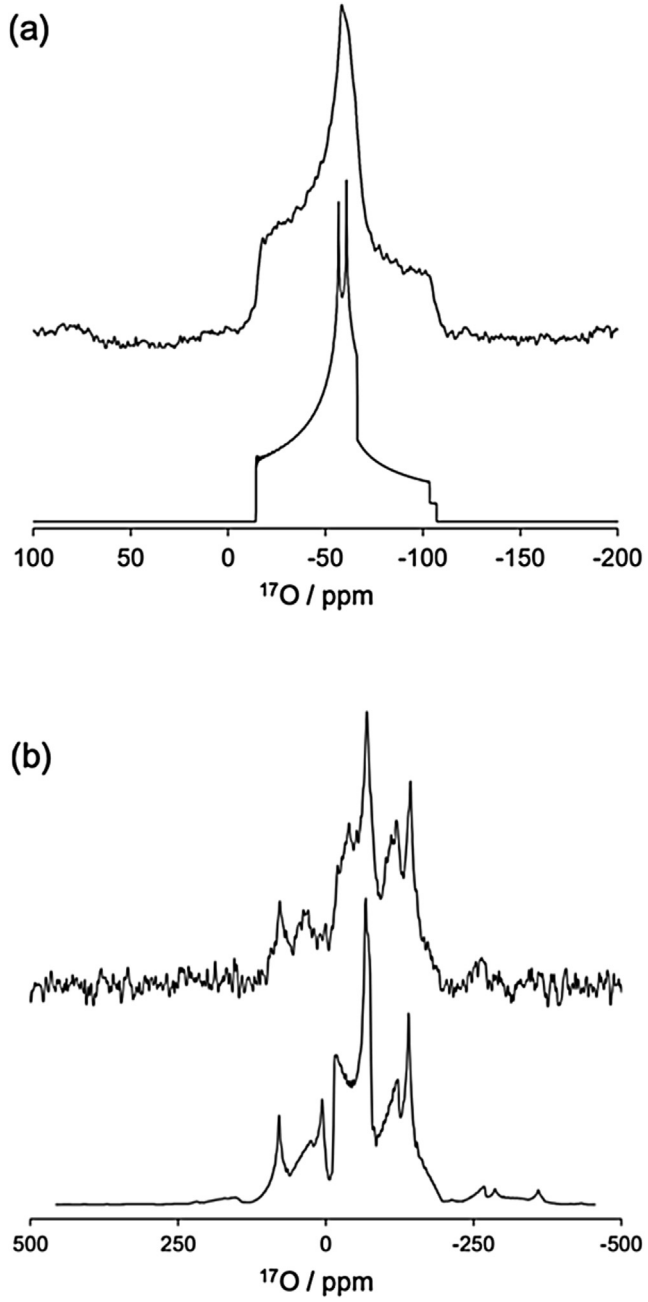


Fig. 1. Experimental (upper trace) and the best-fitted simulated solid-state (lower trace) ^{17}O MAS NMR spectra of D-[6-^{17}O]glucosamine, measured at (a) 21.1 T and ω_R = 20 kHz and (b) 18.8 T and ω_R = 8 kHz. The chemical shift is relative to liquid water.

enrichment in conjunction with the high-field NMR measurements and the quantum chemical calculations. The analyses of ^{17}O MAS and stationary NMR spectra provided the parameters associated with the magnitudes and rotations of the CS and EFG tensors. Furthermore, the orientations of the two ^{17}O NMR tensors with respect to the molecular frame were obtained by the combined analyses with NMR experiments and DFT calculations. To the best of our knowledge, this is the first experimental report on ^{17}O CS tensors for carbohydrates, which provides a benchmark for future solid-state ^{17}O NMR studies of oligosaccharides. This line of approach will be widely applicable to ^{17}O NMR analyses of oligosaccharides, offering sensitive probes for hydrogen bonding and glycosidic linkage conformations.

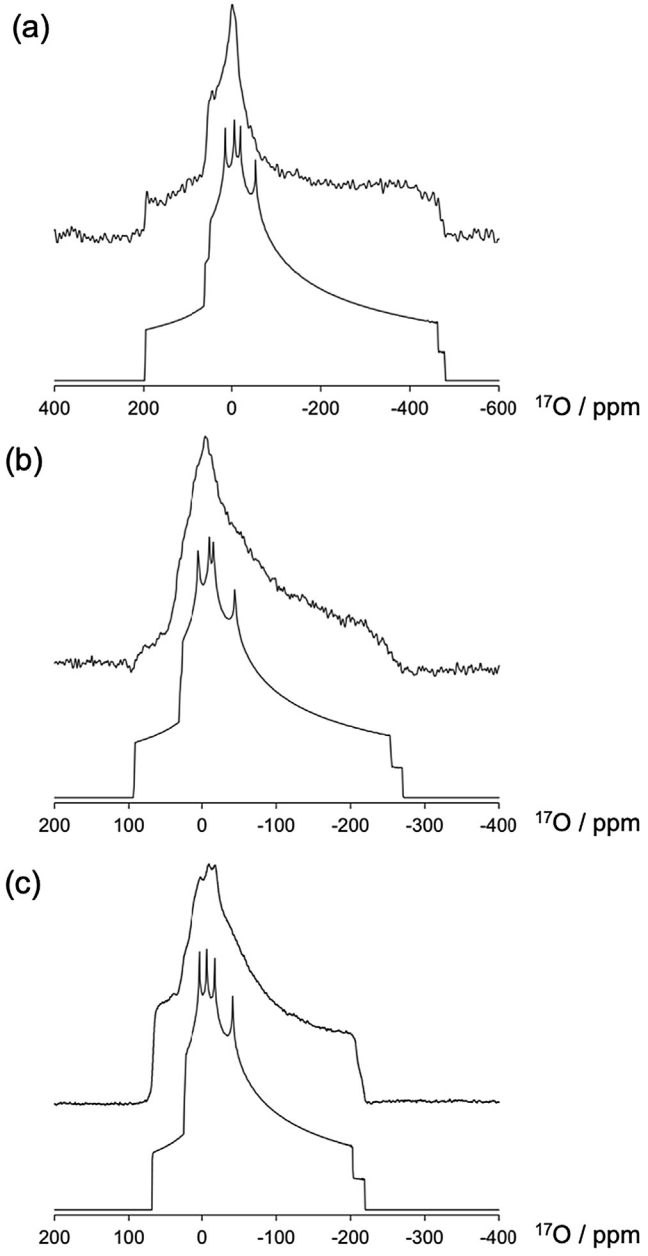


Fig. 2. Experimental (upper trace) and the best-fitted simulated (lower trace) stationary solid-state ^{17}O NMR spectra of D-[6-^{17}O]glucosamine, measured at (a) 14.1 T, (b) 18.8 T, and (c) 21.1 T. The chemical shift is relative to liquid water.

CRediT authorship contribution statement

Kazuhiko Yamada: Conceptualization, Investigation, Writing - original draft. **Yoshiki Yamaguchi:** Conceptualization, Investigation, Writing - original draft. **Yoshinori Uekusa:** Investigation. **Kazumasa Aoki:** Supervision. **Ichio Shimada:** Supervision. **Takumi Yamaguchi:** Investigation, Project administration, Writing - original draft. **Koichi Kato:** Conceptualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 1
The experimentally obtained ^{17}O CS tensors, EFG tensors, and Euler angles for D-[6-^{17}O]glucosamine.

δ_{11} /ppm	δ_{22} /ppm	δ_{33} /ppm	δ_{iso} /ppm	C_Q / MHz	η_Q	α / deg.	β / deg.	γ / deg.
6(5)	−2(7)	−46(7)	−14(2)	9.0(2)	0.91(5)	16(10)	108(8)	12(30)

Table 2
The calculated ^{17}O CS tensors, EFG tensors, and Euler angles for the oxygen at position 6 of α-D-glucosamine. All the calculations were carried out by using B3LYP exchange functional.

Basis set	δ_{11}/ppm	δ_{22}/ppm	δ_{33}/ppm	δ_{iso}/ppm	C_Q/ MHz	η_Q	α/ deg.	β/ deg.	γ/ deg.
6–311++G**	−13.9	−27.6	−49.9	−30.5	10.3	0.76	0.4	107.1	3.8
cc-pVTZ	−17.9	−28.4	−54.9	−33.7	10.0	0.76	3.3	109.5	5.8
spAug-cc-pVTZ	−13.4	−27.5	−51.0	−30.6	9.97	0.75	0.7	105.5	4.7
D95**	−20.6	−37.9	−60.3	−39.8	10.5	0.62	4.4	114.2	−9.2

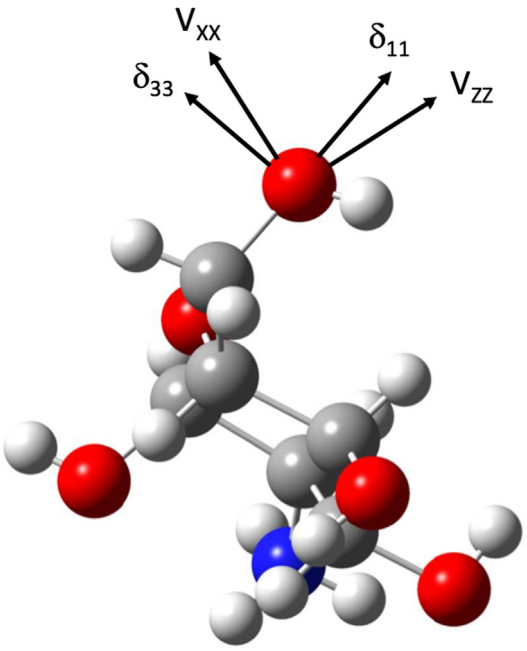


Fig. 3. Schematic representation of the ^{17}O NMR tensors for the oxygen at position 6 of α-D-glucosamine. The direction of V_{YY} components is perpendicular to the molecular plane of C-O-H. Both δ_{11} and δ_{33} components slightly lie off the molecular plane, and δ_{11} component is approximately parallel to the C-O bond direction. Color code: red, O; blue, N; gray, C; white, H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cplett.2020.137455.

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