**Abstract** Anomalous H/D isotope effects were detected in the $^1$H MAS NMR spectra of piperidinium p-chlorobenzoate ($C_5H_{10}NH_2^+\cdot ClC_6H_4COO^-$) upon deuterium substitution of hydrogen atoms which form two kinds of N-H···O H-bonds in the crystal; in contrast to these spectra, only slight chemical shifts were recorded in $^{13}$C CP/MAS NMR spectra. $^2$H NMR spectrum of the deuterated sample show quadrupole coupling constants of 148 and 108 kHz, and reveal that there are a few motions contributing to the electric-field modulation of the $^2$H nucleus. The $^1$H MAS NMR spectra of piperidinium p-chlorobenzoate-$d_{16}$ ($C_5D_{10}ND_2^+\cdot ClC_6D_4COO^-$) and -$d_{14}$ ($C_5D_{10}NH_2^+\cdot ClC_6D_4COO^-$) revealed that the change in the envelope is caused by chemical shifts of each signal upon deuteration. Calculations based on the density-functional-theory showed that the N-H distance along the crystallographic $a$-axis mainly contributes to the anomalous isotope effects on $^1$H MAS NMR envelopes.

**Keywords** $^1$H MAS NMR · $^2$H NMR · $^{13}$C CP/MAS NMR · H/D isotope effect · Hydrogen bond
1 Introduction

By the substitution of H atoms forming the hydrogen bonds in A-H⋯B with D atoms, H/D isotope effects on A⋯B bond lengths have been studied by performing X-ray diffraction measurements [1–4], however, the determination of the exact H positions in hydrogen bonds is difficult. Although $^1$H NMR methods can provide information about electron densities in the case of H atoms, the very strong dipole-dipole interactions among $^1$H atoms make it difficult to measure high-resolution $^1$H MAS NMR spectra for solid samples. The recently developed high-speed magic-angle-spinning (MAS) technique, however, allows us to record high-resolution $^1$H MAS NMR spectra for solid specimens. Further, while $^{13}$C CP/MAS NMR spectra (CP: cross polarization) have occasionally been employed to study H/D isotope effects [5–9], such spectra generally show slight shift after deuteration. We have previously reported that the $^1$H MAS NMR spectra of pyrrolidinium $p$-chlorobenzoate (PYC) display significant envelope changes after deuteration, while the $^{13}$C CP/MAS NMR spectra show only small changes [10]. Further, in the case of piperidinium $p$-bromobenzoate (PIB) and pyrrolidinium $p$-bromobenzoate (PYB), whose crystal structures are similar to that of PYC [11, 12], small H/D isotope effects on the $^1$H MAS NMR spectral lines are observed [13]. Nuclear quadrupole resonance (NQR) methods have often been employed to study H/D isotope effects, because NQR frequencies ($\nu_Q$) are sensitive to very small changes in the electronic environment around the observed atom. Upon deuterium substitution, $\nu_Q$ shifts of dozens of kilohertz for covalently attached Cl atoms and up to several hundred kilohertz (occasionally even of the order of megahertz) for ionic Cl$^-$ atoms have been recorded in $^{35}$Cl NQR measurements [14–25]. An anomalous $^{35}$Cl $\nu_Q$ H/D shift of 309 kHz at 77 K has been observed in the case of PYC crystals, although the Cl atom does not form hydrogen bonds [10]. In contrast, $^{79}$Br $\nu_Q$ have exhibited small H/D shifts in PYB and PIB solids [13].

In piperidinium $p$-chlorobenzoate (PIC) crystals, whose crystal structure is similar to those of PYC, PIB, and PYB, anomalous large $^{35}$Cl $\nu_Q$ H/D isotope shifts have been observed, although the Cl atom forms no hydrogen bonding and deuterium substitution contributes to a little crystal structure changes [26]. In this study, C$_5$H$_{10}$NH$_2$$^+$·ClC$_6$H$_4$COO$^-$ and C$_5$H$_{10}$ND$_2$$^+$·ClC$_6$H$_4$COO$^-$ are, respectively, abbreviated to HPIC(H) and HPIC(D). Single crystal X-ray diffraction measurements of HPIC(H) and HPIC(D) have shown that piperidinium and $p$-chlorobenzoate ions are linked by two types of O⋯H-N H-bonds: one is parallel to the crystallographic $a$-axis and the other lies along the $b$-axis (abbreviated herein as H-bonds($a$) and H-bonds($b$), respectively). These hydrogen bonds form a chain network of hydrogen bonds that progresses parallel to the $a$-axis and perpendicular to the $c$-axis. The crystal structure analysis has indicated that the N-H length of H-bonds($a$) becomes 10 pm shorter and the dihedral angle between the benzene and piperidine rings changes by 1.8$^\circ$ after deuterium substitution [26]. Simulations based on the density-functional-theory (DFT) have revealed that the dihedral angle, rather than the N-H distance, contributes to the anomalous large isotope shift of $^{35}$Cl $\nu_Q$. DFT estimation also shows that the potential curves of H-bonds($a$) are of a double-minimum type with a potential barrier of 41 kJ mol$^{-1}$ and that the energy required to form the N-H bond is lower than that needed for the O-H bond. In contrast, H-bonds($b$) has single-minimum-type potential curves, which shows that the H atom forms a covalent bond.
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with the N atom [26]. These results, which indicate that the probability of each H atom being near the N atom is higher than that of the O side, are consistent with the observed crystal data. Similar results have been obtained in the case of the PYC crystal [10].

In the present study, \(^1\)H MAS NMR, \(^2\)H NMR, and \(^{13}\)C CP/MAS NMR spectral measurements were carried out to reveal the electron density changes that result from deuterium substitution. Moreover, \(^1\)H MAS NMR observation of piperidinium \( p \)-chlorobenzoate-\( d_{16} \) (DPIC(D); \( C_5D_{10}N\text{D}_{2}^+\cdot\text{CIC}_6\text{D}_4\text{COO}^- \)) and -\( d_{14} \) (DPIC(H); \( C_5D_{10}\text{NH}_{2}^+\cdot\text{CIC}_6\text{D}_4\text{COO}^- \)) were performed to obtain more detailed information.

2 Experimental

HPIC(H) crystals were prepared by adding piperidine to a hot benzene solution of \( p \)-chlorobenzoic acid and then evaporating the solvent. The crude samples were subsequently recrystallized from benzene. HPIC(D) was obtained by crystallizing the purified HPIC(H) three times from hot CH\(_3\)OD (99 % deuterated, Cambridge Isotope Laboratories, Inc.), followed by recrystallization from dried benzene under dry N\(_2\) gas. DPIC(H) powder crystals were obtained by mixing piperidine-\( d_{10} \) (98.5 % D, CDN Isotopes Inc.) and \( p \)-chlorobenzoic acid-\( d_4 \) (99.3 % D, CDN Isotopes Inc.) in benzene. DPIC(D) solids were prepared by crystallizing DPIC(H) three times from a hot CH\(_3\)OD solution under dry N\(_2\) gas.

Solid-state high-resolution \(^1\)H NMR experiments were carried out at a Larmor frequency of 600.13 MHz by using a Bruker Avance 600 spectrometer (14.10 T) with a high-speed MAS accessory. The samples were packed in a ZrO rotor with an outer diameter of 2.5 mm, and a spinning rate of 35 kHz was maintained throughout the free-induction-decay (FID) acquisition. NMR spectra were obtained from the Fourier transform of the FID signals after a \( \pi/2 \) pulse. We chose a recycle time of 500 s for HPIC(H) and HPIC(D), and 1000 s for DPIC(H) and DPIC(D). The \(^1\)H chemical shifts (CS) were calibrated relative to an external reference of adamantane (\( \delta = 1.91 \) ppm); the chemical shift is calibrated by using tetramethylsilane (TMS).

The \(^2\)H NMR spectrum was recorded at a Larmor frequency of 46.07 MHz using a Bruker MSL-300 spectrometer (7.01 T). The HPIC(D) powder crystals were sealed in a Pyrex tube with an outer diameter of 5.0 mm, and the spectrum was obtained from echo signals after a \( (\pi/2)_x - \tau - (\pi/2)_y - \tau \) pulse sequence with a recycle delay of 1 000 s. The frequency calibration was carried out by employing a D\(_2\)O external reference (\( \delta = 0 \) Hz).

\(^{13}\)C CP/MAS NMR spectral measurements were performed at a Larmor frequency of 150.92 MHz using a Bruker Avance 600 spectrometer (14.10 T). The sample was packed in a ZrO rotor with an outer diameter of 4.0 mm and the CP/MAS spectra were recorded with a contact time of 1.0 ms and a \(^1\)H TPPM15 decoupling pulse sequence. In order to distinguish peaks from spinning side bands, NMR measurements with three spinning rates of 5, 7, and 12 kHz were carried out, where a ramp pulse [27] was employed for recording spectra at a spinning rate of 12 kHz. The CS of the \(^{13}\)C nuclei was estimated by using an external reference of adamantane (\( \delta = 29.47 \) ppm).

DFT-based calculation was carried out using Gaussian 03w computer program [28] to estimate the theoretical values of the electric-field gradient (EFG) at \(^2\)H
nucleus and the $^1$H and $^{13}$C shielding tensors. All calculations were carried out using a B3LYP/6–311+G** function based on the reported crystal parameters and coordinates [26].

3 Results and discussion

3.1 $^1$H MAS NMR spectra

The spin-lattice relaxation time ($T_1$) was roughly estimated at room temperature by measuring the recycle-time dependences of $^1$H NMR peak areas for HPIC(H) and HPIC(D), and $T_1$ was found to be about 100 s. Since this value is similar to those reported for PYC(H) and PYC(D) [10], it can be concluded that there are a few motional modes effecting the relaxation of the $^1$H nuclear spins in these crystals. $^1$H MAS NMR spectra of HPIC(H) and HPIC(D) observed at a MAS speed of 35 kHz and a recycle time of 500 s are shown in Fig. 1. In order to assign each peak, a $^1$H NMR spectral measurement of HPIC(H) in a benzene-$d_6$ solution, and DFT calculation were carried out. From the obtained results, the signals recorded from 5 to 2 and from 1 to $-5$ ppm can be assigned to H atoms bonding to the C atoms of the benzene and piperidine rings, respectively. Peak assignments are listed in Table 1, where atoms are numbered as in Fig. 2.

This figure shows three significant changes that are due to isotope substitution: (i) The peak observed at 17.8 ppm disappears. (ii) The four sharp signals detected from 5 to 2 ppm change into two broad peaks. (iii) The two signals from 1 to $-5$ ppm become a single broad peak. Using the DFT calculations, the peak at 17.8 ppm is assigned to the H atoms in H-bond($a$), and therefore, the first change listed above (i) guarantees high deuterium substitution (DFT estimation showed that the signal of the H atom in H-bond($b$) would be observed at around 0 ppm, but its range is covered by the $^1$H signals of piperidine ring). The other two changes (ii) and (iii) have also been reported for PYC, but significant changes were detected in the HPIC(H) and HPIC(D) samples. To explain these changes (ii) and (iii), two models can be
Table 1 ¹H NMR chemical shifts in ppm observed for piperidinium p-chlorobenzoate crystals

<table>
<thead>
<tr>
<th>Atom</th>
<th>HPIC(H)</th>
<th>HPIC(D)</th>
<th>DPIC(H)</th>
<th>DPIC(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(a)</td>
<td>17.8</td>
<td>–</td>
<td>17.8</td>
<td>–</td>
</tr>
<tr>
<td>H(b)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>H(1)</td>
<td>5.3</td>
<td>5.4</td>
<td>5.2</td>
<td>5.2</td>
</tr>
<tr>
<td>H(2)</td>
<td>4.6</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>H(3)</td>
<td>4.2</td>
<td>4.1</td>
<td>4.3</td>
<td>4.3</td>
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<tr>
<td>H(4)</td>
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<td>4.1</td>
<td>4.1</td>
</tr>
<tr>
<td>H(5)</td>
<td>0.3</td>
<td>–</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>H(6)</td>
<td>–1.1</td>
<td>–1.2</td>
<td>–1.2</td>
<td>–1.2</td>
</tr>
<tr>
<td>H(7)</td>
<td>–1.2</td>
<td>–2.0</td>
<td>–2.0</td>
<td>–2.8</td>
</tr>
<tr>
<td>H(8)</td>
<td>–2.0</td>
<td>–2.0</td>
<td>–2.0</td>
<td>–2.8</td>
</tr>
<tr>
<td>H(9)</td>
<td>–2.0</td>
<td>–2.0</td>
<td>–2.0</td>
<td>–2.8</td>
</tr>
<tr>
<td>H(10)</td>
<td>–2.8</td>
<td>–2.8</td>
<td>–2.8</td>
<td>–2.8</td>
</tr>
</tbody>
</table>

Fig. 2 Structures of p-chlorobenzoate and piperidinium ions. Dashed lines indicate N-H...O hydrogen bonds

proposed: (a) The line width of each signal increases, and (b) the CS value of each peak is shifted because of deuteration. To reveal the origin of the anomalous H/D isotope effects on the NMR envelope, higher-resolution ¹H MAS NMR spectra are needed. In the case of a ¹H nucleus, the spectral line-widths of solid-state NMR spectra are mainly determined on the basis of the dipole-dipole interactions among the H atoms, while these interactions rarely induce peak shifts. Dipole-dipole interactions among ¹H nuclei are described as the following Hamiltonian [29].

\[
H_{DD} = \frac{1}{4} \sum_{i,j} \frac{\gamma_i \gamma_j}{r_{ij}^3} h^2 (1 - 3 \cos^2 \theta_{ij}) \left( 3I_i Z I_j Z - I_i \cdot I_j \right) \quad \text{[homonucler]}
\]

\[
H_{DD} = \frac{1}{2} \sum_{i,j} \frac{\gamma_i \gamma_j}{r_{ij}^3} h(1 - 3 \cos^2 \theta_{ij}) I_i Z I_j Z \quad \text{[heteronucler]}
\]

Here, \(\gamma\), \(r_{ij}\), and \(\theta_{ij}\) are the gyromagnetic ratio, the distance between nuclei \(i\) and \(j\), and the angle between an \(i\) – \(j\) vector and a magnetic field, respectively. This dipole-dipole Hamiltonian suggests that reducing \(\gamma^2\) and/or \(r^{-3}\) will result in a narrow line-width of a ¹H MAS NMR spectrum. We introduced the DPIC(D) sample where a few
Fig. 3 $^1$H MAS NMR spectra with a spinning ratio of 35 kHz in (a) piperidinium $p$-chlorobenzoate-$d_{14}$ (DPIC(H)) and (b) piperidinium $p$-chlorobenzoate-$d_{16}$ (DPIC(D)) crystals.

Fig. 4 $^{13}$C CP/MAS NMR spectra with a spinning ratio of 5 kHz in (a) piperidinium $p$-chlorobenzoate (HPIC(H)) and (b) piperidinium $p$-chlorobenzoate-$d_2$ (HPIC(D)) crystals. The asterisks denote spinning-side-band peaks.

$^1$H nuclei (ca. 1 %) are included as unsubstituted impurity in the crystals: the $\gamma$ value of the $^2$H nucleus is ca. 15 % of that of the $^1$H, and the average separations among $^1$H nuclei are longer than those of HPIC(D) because a large number of spins around a rare $^1$H nuclei are $^2$H.

$^1$H MAS NMR spectra of DPIC(H) and DPIC(D) are shown in Fig. 3. The strong peak recorded around 8 ppm of each line can be assigned to a signal of H atoms present in a sample rotor (this signal could be detected by measuring a rotor without any samples). This peak is ordinarily very weak for normal samples, and hence, there is no effect on the $^1$H NMR spectra of HPIC(H) and HPIC(D), as shown in Fig. 1. No peak was recorded around 18 ppm of DPIC(D), guaranteeing high deuterium substitution (<1 %) of DPIC(H). The fact that four peaks are detected in the range of $-5$ to 1 ppm in DPIC(D) as shown in Fig. 3, suggests that the broad line observed...
Table 2 $^{13}$C NMR chemical shifts in ppm observed for piperidinium $p$-chlorobenzoate crystals

<table>
<thead>
<tr>
<th>Atom</th>
<th>HPIC(H)</th>
<th>HPIC(D)</th>
<th>Difference</th>
</tr>
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<tbody>
<tr>
<td>C(1)</td>
<td>171.97</td>
<td>171.65</td>
<td>0.32</td>
</tr>
<tr>
<td>C(2)</td>
<td>130.19</td>
<td>129.93</td>
<td>0.26</td>
</tr>
<tr>
<td>C(3)</td>
<td>132.14</td>
<td>132.06</td>
<td>0.08</td>
</tr>
<tr>
<td>C(4)</td>
<td>127.16</td>
<td>126.77</td>
<td>0.39</td>
</tr>
<tr>
<td>C(5)</td>
<td>136.13</td>
<td>135.93</td>
<td>0.20</td>
</tr>
<tr>
<td>C(6)</td>
<td>43.10</td>
<td>42.66</td>
<td>0.44</td>
</tr>
<tr>
<td>C(7)</td>
<td>23.73</td>
<td>23.33</td>
<td>0.40</td>
</tr>
<tr>
<td>C(8)</td>
<td>22.94</td>
<td>22.07</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Fig. 5 $^2$H NMR spectrum of piperidinium $p$-chlorobenzoate-$d_2$ (HPIC(D)) crystals

in the case of HPIC(D) is composed of some signals having very similar CS values. In the case of DPIC(H), three peaks are detected in the same region. These results can be concluded that the anomalous H/D isotope effect on line shape is due to peak shifts rather than dipole-dipole interactions. More detail discussions are presented in Section 3.4.

3.2 $^{13}$C CP/MAS NMR

$^{13}$C CP/MAS NMR spectra obtained at room temperature of HPIC(H) and HPIC(D) are displayed in Fig. 4. Employing three kinds of spinning rates (5, 7, and 12 kHz), we could distinguish signals from spinning-side-band lines. Each peak could be assigned by DFT calculations as listed in Table 2. Peak shifts of ca. 0.3 ppm are of a similar order to those previously reported [5–10].

3.3 $^2$H NMR spectra

The $^2$H NMR spectrum of crystalline HPIC(D), shown in Fig. 5, was obtained by accumulation for a week at a recycle time of 1000 s. By choosing a recycle delay of a few seconds (often, in the case of $^2$H nuclei, $T_1$ extends for a short duration because of quadrupole relaxation), no discernable spectrum was recorded. Therefore, there are a few motions contributing to the electric-field modulation of the $^2$H nucleus in
Fig. 6 Estimated electric-field-graduation values, $eq(\circ)$ and ($\bullet$), and anisotropic parameters, $\eta(\triangle)$ and ($\triangle$) of $^2$H atoms as a function of N-D length along H-bond(a) and H-bond(b). Here, the open and closed symbols denote each parameter of the $^2$H atoms in H-bond(a) and H-bond(b), respectively.

The obtained $^2$H NMR spectrum could be distinguished based on two lines: assuming that the antisymmetric parameter ($\eta$) defined in (2) is equal to 0, quadrupole coupling constants ($e^2Qqh^{-1}$) were estimated from peak widths ($\Delta\nu$) and found to be 148 and 108 kHz.

$$\Delta\nu = \frac{3}{4} e^2 Qqh^{-1}$$
$$eq = V_{zz} \quad \eta = \left| \frac{V_{xx} - V_{yy}}{V_{zz}} \right|$$

In this equation, $eQ$ and $V_{kk}$ ($k = x, y, z$) denote quadrupole moment, which is determined only by the nuclear species, and a principal value of the EFG tensor for $kk$ components, respectively. In order to determine which components correspond to the D atom in H-bond(a) and H-bond(b), DFT calculation was carried out. Since EFG values are inversely proportional to the cube of the distance from a nucleus of interest to the other nuclei in the crystal, the EFG estimation was performed for six molecules around the p-chlorobenzoate ion. Using the B3LYP/6–311+G** function and reported atomic coordinates of HPIC(D) [26], the dependence of $e^2Qqh^{-1}$ and $\eta$ values on the N-D distances are obtained, as shown in Fig. 6; the assumption of $\eta = 0$ around an acceptable N-D length is supported by this figure.

Our DFT estimation also reveals that $eq$ at $^2$H nuclei drastically decreases with increasing N-D length. Since the reported N-D length of 88 pm in H-bond(a) is shorter than that in H-bond(b) (95 pm) [26], the obtained $e^2Qqh^{-1}$ values of 148 and 108 kHz are assigned to D atoms in H-bond(a) and H-bond(b), respectively. Calculated $e^2Qqh^{-1}$ values are generally different (1 or 2 digit smaller than experimental values) from observed frequencies without introducing the Sternheimer antishielding factor [30]. To avoid this empirical value, an $e^2Qqh^{-1}$ ratio of 148/108 = 1.37 was introduced, and to obtain this ratio, N-D lengths for H-bond(a) and H-bond(b) were
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Fig. 7 $^1$H NMR line-shape dependence on the dihedral angle between benzene and piperidine ring estimated by B3LYP/6–311+G**

Chemical Shift / ppm

estimated to be 89 and 94 pm, respectively. These distances are in good agreement with the reported values of 88 and 95 pm [26].

3.4 DFT simulation

To understand the anomalous H/D isotope effect detected in $^1$H MAS NMR spectra, DFT calculations with a B3LYP/6–311+G** function were carried out by utilizing the reported atomic coordinates [26]. Since each ion in the crystal is linked to each other via hydrogen bonds, six units were included in our shielding tensor estimation. Simulated CS values were obtained by subtracting the shielding tensors of HPIC(H) from that of a molecule of the standard TMS sample. $^1$H NMR line shapes simulated as a function of the dihedral angle between the benzene and piperidine rings are displayed in Fig. 7, where a Gaussian function was used for line convolution. Since a change in angle by 1.8° because of deuterium substitution has been observed by performing single-crystal X-ray diffraction measurement [26], a slight change in the line shapes was observed, as shown in Fig. 7.

Therefore, other mechanisms contributing to the anomalous H/D isotope effects on $^1$H MAS NMR line-shapes must be proposed. Since the X-ray diffraction data reports that the N-H bond length in H-bonds(a) shortens by 10 pm upon deuteration [26], we calculated the dependence of $^1$H CS values on the N-H distance. The obtained results are displayed in Fig. 8. The envelope estimated at the N-H length of 115 pm shows four peaks in a range of 5 to 8.5 ppm and two signals at around 0 ppm. In our simulation, the four peaks assigned to the H atoms of the benzene ring merge into two lines at 90 pm, while the two signals due to the piperidine ring eventually become three peaks and one shoulder. Since these tendencies are identical to the
observed isotope effect on $^1$H MAS NMR spectra, as shown in Figs. 1 and 3, it is considered that the shortening of the N-H distance because of deuterium substitution is the main contributor to the anomalous H/D isotope effects observed in these spectra. The absolute value of 90 pm is in good agreement with the estimated N-D distance from our $^2$H NMR measurement as shown in Fig. 6 and with the reported N-D length of 88 pm in HPIC(D) [26].

4 Conclusion

Anomalous H/D isotope effects were detected in $^1$H MAS NMR spectra of piperidinium $p$-chlorobenzoate by substitution of H atoms with D atoms to form two types of N-H···O H-bonds in the crystal; in contrast to these spectra, $^{13}$C CP/MAS NMR spectra showed little CS changes. The resolution of the $^1$H MAS NMR spectra of piperidinium $p$-chlorobenzoate-$d_{16}$ and -$d_{14}$ was high, and these results suggested that the line width of the signal which is assigned to the H atoms of piperidine ring in the HPIC(D) increased because of CS changes due to deuteration. Our DFT calculations with B3LYP/6–311+G** showed that the N-H length in H-bond(a), rather than the change in the dihedral angle between the benzene and piperidine rings, is the main factor contributing to the anomalous H/D isotope effects on the $^1$H MAS NMR envelopes, even though anomalous H/D isotope shifts of $^{35}$Cl NQR frequencies are attributed to the angle rather than the N-H separation [26]. H/D isotope effects on $^1$H MAS NMR spectra can be induced by shortening the N-H length by 25 pm, which is quite smaller than the reported isotope effects on H bonds [1–4]. The present study
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reveals that in the sample, ordinary changes in the molecular arrangements and N-H distances contribute to anomalous isotope effects on $^{35}$Cl $\nu_Q$ and $^1$H MAS NMR line-envelopes because of deuterium substitution. Therefore, both methods are efficient for studying H/D isotope effects on H bonds.

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