Determination of the $^{17}$O NMR tensors in potassium hydrogen dibenzoate: a salt containing a short O···H···O hydrogen bond

Gang Wu* and Kazuhiko Yamada

Department of Chemistry, Queen's University, Kingston, Ont., Canada K7L 3N6

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Dedicated to the memory of Professor Almeria L. Natansohn (1949–2002)

Abstract

Solid-state $^{17}$O NMR spectra were obtained at 4.70, 11.75 and 19.60 T for potassium hydrogen $[^{17}$O$_4$]dibenzoate (PHB) under both magic-angle spinning and stationary conditions. Spectral analyses yielded both the magnitude and orientation of the $^{17}$O chemical shift (CS) tensor and the electric field gradient (EFG) tensor for each of the two chemically distinct oxygen sites in PHB. For the oxygen site that is not involved in hydrogen bonding, the experimental $^{17}$O NMR tensors are: $\delta_{\text{iso}} = 287 \pm 2$ ppm, $\delta_{11} = 470 \pm 5$ ppm, $\delta_{22} = 380 \pm 5$ ppm, $\delta_{33} = 10 \pm 5$ ppm, $C_Q = 8.30 \pm 0.02$ MHz, $\eta_Q = 0.23 \pm 0.05$, $\alpha = 0 \pm 5^\circ$, $\beta = 90 \pm 5^\circ$, and $\gamma = 30 \pm 5^\circ$. For the oxygen site in the short O···H···O hydrogen bond, the experimental $^{17}$O NMR tensors are: $\delta_{\text{iso}} = 213 \pm 2$ ppm, $\delta_{11} = 370 \pm 5$ ppm, $\delta_{22} = 190 \pm 5$ ppm, $\delta_{33} = 80 \pm 5$ ppm, $C_Q = 5.90 \pm 0.02$ MHz, $\eta_Q = 0.55 \pm 0.05$, $\alpha = 5 \pm 5^\circ$, $\beta = 90 \pm 5^\circ$, and $\gamma = 90 \pm 5^\circ$. Extensive quantum mechanical calculations at both restricted Hartree–Fock and density functional theory levels were performed to investigate the effects of an effectively symmetrical O···H···O hydrogen bond on $^{17}$O CS and EFG tensors.

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Keywords: Oxygen NMR; Hydrogen bond; Chemical shift tensor; Electric field gradient; Quantum mechanical calculation

*Corresponding author. Fax: 1-613-533-6669.
E-mail address: gangwu@chem.queensu.ca (G. Wu).

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1. Introduction

Hydrogen bonding is an important feature in biological structures and has been studied extensively in the past 50 years [1–5]. Major experimental techniques proven to be useful in studying hydrogen bonding phenomena include infrared spectroscopy, X-ray and neutron diffraction, and liquid-phase NMR spectroscopy. In recent years, solid-state NMR has also emerged as a useful technique in the study of hydrogen bonded systems [6,7]. Solid-state NMR can provide rich information about the local electronic structures around the nucleus of interest. In particular, solid-state NMR studies can yield information about the tensorial nature of all NMR parameters. This type of information is generally difficult to obtain in liquid-state NMR experiments. While most solid-state NMR studies have focused on the utilization of spin-1/2 probes such as $^1$H, $^{13}$C and $^{15}$N [8–17], several research groups have also attempted to establish $^{17}$O (spin-5/2) as an effective NMR probe to hydrogen-bonded systems in the solid state [18–30]. Recent work from this laboratory has clearly demonstrated the sensitivity of $^{17}$O NMR tensors to hydrogen bonding environment.

Alkali hydrogen salts of carboxylic acids are among the classic examples containing very short O⋯H⋯O hydrogen bonds [5]. Potassium hydrogen dibenzoate (PHB) crystallizes in the space group $C_2/c$ ($Z = 4$) where two carboxylate groups are hydrogen bonded across a centrosymmetric center of symmetry giving rise to an effectively symmetrical O⋯H⋯O hydrogen bond; see Scheme 1. According to the notation introduced by Speakman [31], PHB is a type A acid salt. The O2⋯O2' distance in PHB was determined to be 2.51 Å by an early X-ray diffraction study [32]. To our knowledge, no neutron diffraction study has been reported for PHB, presumably due to practical difficulties in growing suitable single crystals. An early $^{17}$O NQR study of PHB indicated that the $^{17}$O nuclear quadrupole coupling constant ($C_Q$) for the C–O2⋯H site is 6.165 MHz [33]; however, the signal from O1 was not observed in the NQR experiment. Using a solid-state $^{17}$O NMR approach, we recently observed $^{17}$O NMR signals for both oxygen sites in PHB and showed that the two sites exhibit very different $^{17}$O NMR parameters [28]. In particular, the $^{17}$O isotropic chemical shift ($\delta_{iso}$) for the C–O2⋯H site is smaller than that found for the C–O1 site by approximately 70 ppm. The value of $C_Q$ for the C–O2⋯H site is also significantly smaller than that for the C–O1 site.

![Scheme 1.](image-url)
To better understand the influence of a short O···H···O hydrogen bond on $^{17}$O NMR properties, it is necessary to determine all principal components for each of the $^{17}$O NMR tensors involved. Here we present an experimental determination of the $^{17}$O chemical shift (CS) tensors and the electric field gradient (EFG) tensors in PHB. We also perform extensive quantum mechanical calculations to examine the sensitivity of individual tensor components on the formation of a short O···H···O hydrogen bond.

2. Experimental section

Potassium hydrogen [${^{17}$O}]dibenzoate was prepared as previously described [21]. The level of $^{17}$O-enrichment for the sample was approximately 40%. The solid-state $^{17}$O NMR experiments at 4.70 and 11.75 T were carried out on Bruker ASX-200 and Avance-500 spectrometers operating at 27.11 and 67.80 MHz for $^{17}$O nuclei, respectively. A liquid H$_2$O sample (25% $^{17}$O atom) was used for chemical shift referencing and RF power calibration. The solid-state NMR experiments at 19.60 T (112.48 MHz for $^{17}$O nuclei) were performed at the National High Magnetic Field Laboratory (Tallahassee, Florida) using a Bruker DRX spectrometer and a 2.75 mm magic angle spinning (MAS) probe. The sample spinning frequency was 20 kHz. Spectral simulations were performed using WSOLIDS (Klaus Eichele, http://casgm3.anorg.chemie.uni-tuebingen.de/klaus/soft/index.html).

Quantum mechanical calculations were performed using the Gaussian 98 suite of programs [34]. All calculations were performed on a personal computer equipped with a 800 MHz Pentium II processor, 512 MB of memory and 12 GB of disk space. The molecular structure of PHB determined by X-ray diffraction [32] was used in the quantum mechanical calculations. Because hydrogen atoms were not reported in the X-ray study, standard values for the C–C–H angle (120.0°) and the C–H bond length (1.000 Å) were assumed to calculate the hydrogen atom positions. The hydrogen atom involving in the short O···H···O hydrogen bond is assumed to be at the midpoint between the two oxygen atoms (O···H = 1.255 Å), which is required by the crystallographic symmetry.

For the H, C and O atoms, we used standard basis sets of 6-311+ +G** and D95**. For the third-row K atom, we used two different all-electron basis sets. The first one was a 6-31G* basis set recently reported by Rassolov et al. [35,36]. This basis set is a medium-size split valence basis with a contraction scheme of (22s, 16p, 1d)→ [5s, 4p, 1d]. The second all-electron basis set used for K was a 6-311G type valence triple-zeta basis set reported by Bludeau et al. [37]. This basis set uses a general contraction scheme of (14s, 12p, 3d)→ [8s, 7p, 1d]. We refer to these two types of basis sets for K atoms as the DZ and TZ basis sets in this study.

Calculated shielding values were converted to chemical shifts by using the absolute $^{17}$O shielding scale established by Wasylishen et al. [38], $\Delta$ (ppm) = 307.9 – $\sigma$ (ppm). Calculated EFG tensor components ($V_{xx}$, $V_{yy}$, $V_{zz}$) are related to the nuclear quadrupole coupling parameters in the following fashion: $C_Q$ (MHz) = $-2.3496 \times Q^{(17)}O$ (fm$^2$) $\times V_{zz}$ (a.u.) and $\eta_Q$ = ($V_{xx}$–$V_{yy}$)/$V_{zz}$, where the nuclear
quadrupole moment for $^{17}\text{O}$ is $Q(^{17}\text{O}) = -2.558 \text{ fm}^2$ [39]. It should be noted that, when this standard value for $Q(^{17}\text{O})$ is used, the calculated values of $C_Q$ are generally 10% larger than the experimental values. As we have demonstrated previously [22], much better agreement can be obtained between the calculated and observed $C_Q$ values, if a “calibrated” $Q(^{17}\text{O})$ is used to convert the computed electric field gradient to $C_Q$.

3. Results and discussion

3.1. Experimental determination of the $^{17}\text{O}$ NMR tensors in PHB

Fig. 1 shows the experimental and calculated $^{17}\text{O}$ NMR spectra obtained for PHB at 19.60 T under the MAS condition. The two groups of signals observed in the MAS spectrum are consistent with the presence of two types of $^{17}\text{O}$ sites. Analyses of the $^{17}\text{O}$ MAS spectrum for PHB yielded the following parameters: O1, $\delta_{\text{iso}} = 287$ ppm, $C_Q = 8.30$ MHz and $\eta_Q = 0.23$; O2, $\delta_{\text{iso}} = 213$ ppm and $C_Q = 5.90$ MHz. It is rather difficult to accurately determine the asymmetry parameter for O2 because of the relatively narrow line shape and the presence of some residual line broadening as a result of the large $^1\text{H}^{-^{17}\text{O}}$ dipolar coupling.

To obtain further information about the NMR tensors in PHB, we carried out experiments at three different magnetic fields, 4.70, 11.75 and 19.60 T, under the stationary sample condition. Fig. 2 shows experimental and calculated $^{17}\text{O}$ stationary NMR spectra obtained for PHB. Details for analyzing $^{17}\text{O}$ stationary

![Fig. 1. Experimental (lower trace) and calculated (upper trace) $^{17}\text{O}$ MAS spectra for PHB at 19.60 T. The sample spinning frequency was 20.000 kHz. Other experimental parameters are: 444 transients, 10 s recycle delay.](image-url)
NMR spectra have been reported in a previous study [24]. The general approach consists of three steps. First, we obtain $\delta_{\text{iso}}, C_Q$ and $\eta_Q$ for each oxygen site from an analysis of $^{17}$O MAS spectra of the same sample. Second, we perform high-level quantum mechanical calculations to obtain information about $^{17}$O CS and EFG tensor orientations in the molecular frame. Third, the tensor orientations obtained from the previous step are used as a starting point in the simulation for stationary spectra. Subsequently, two remaining (independent) CS tensor components and three Euler angles for describing the relative orientation between the EFG and CS tensors are further refined by matching simulated and observed stationary spectra. The uncertainty in the values of tensor components and orientations is expected to be larger than that in the values of $\delta_{\text{iso}}, C_Q$ and $\eta_Q$, because the latter quantities are obtained from analyses of MAS spectra.

Fig. 2. Experimental (lower trace) and calculated (upper trace) $^{17}$O stationary NMR spectra for PHB. Detailed experimental parameters are: 4.70T, 6600 transients, 10s recycle delay; 11.75 T, 1792 transients, 20s recycle delay; 19.60 T, 1622 transients, 10s recycle delay.
The experimental $^{17}$O NMR results for PHB are given in Table 1. Results from quantum mechanical calculations are summarized in Tables 2 and 3. The molecular cluster models used in the quantum mechanical calculations are depicted in Fig. 3. It should be noted that the NMR spectra shown in Fig. 2 are sensitive only to the relative orientation between the $^{17}$O CS and EFG tensors. To obtain information about the tensor orientation in the molecular frame of reference, we assume that the orientations of the $^{17}$O EFG tensors obtained from high-level quantum mechanical calculations represent the true tensor orientations. Using the calculated EFG tensors as a reference, we were able to deduce the CS tensor orientations in the molecular frame. The resultant tensor orientations in the molecular frame for PHB are shown in Fig. 4.

As seen from Fig. 3, the primary structural difference between O1 and O2 in PHB is the involvement of the latter atom in a short O···H···O hydrogen bond. This

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental $^{17}$O CS and EFG tensors for PHB$^a$</th>
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<tbody>
<tr>
<td>Oxygen site</td>
<td>$\delta_{iso}$ (ppm)</td>
</tr>
<tr>
<td>O1</td>
<td>287(2)</td>
</tr>
<tr>
<td>O2···H···O2'</td>
<td>213(2)</td>
</tr>
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</table>

$^a$Uncertainties in the last digits are given in parentheses.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Calculated $^{17}$O EFG and CS tensors for O1 in PHB</th>
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<tr>
<td>Method/basis set</td>
<td>$C_Q$ (MHz)</td>
</tr>
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<td>Model A</td>
<td>RHF/6-311++G** (K: TZ basis set)</td>
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<tr>
<td></td>
<td>RHF/6-311++G** (K: DZ basis set)</td>
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<td></td>
<td>RHF/D95** (K: DZ basis set)</td>
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<tr>
<td></td>
<td>B3LYP/6-311++G** (K: TZ basis set)</td>
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</tr>
<tr>
<td></td>
<td>B3LYP/D95** (K: DZ basis set)</td>
</tr>
</tbody>
</table>

Model B

| Method/basis set | $C_Q$ (MHz) | $\eta_Q$ | $\delta_{iso}$ (ppm) | $\delta_{11}$ (ppm) | $\delta_{22}$ (ppm) | $\delta_{33}$ (ppm) | $\alpha$ (deg) | $\beta$ (deg) | $\gamma$ (deg) |
| RHF/6-311++G** | 9.79 | 0.18 | 290.6 | 499.2 | 377.9 | $-5.4$ | 11.4 | 90.6 | 27.6 |
| RHF/D95** | 10.0 | 0.30 | 278.0 | 481.6 | 375.2 | $-22.7$ | 6.0 | 90.7 | 27.4 |
| B3LYP/6-311++G** | 9.18 | 0.13 | 325.0 | 521.5 | 440.3 | 13.1 | 13.9 | 90.5 | 42.6 |
| B3LYP/D95** | 9.28 | 0.23 | 310.6 | 496.2 | 434.1 | 1.4 | 6.5 | 90.6 | 48.5 |
Table 3
Calculated $^{17}$O EFG and CS tensors for O2 in PHB

<table>
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<tr>
<th>Method/basis set</th>
<th>$C_0$ (MHz)</th>
<th>$\eta_0$</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\delta_{11}$ (ppm)</th>
<th>$\delta_{22}$ (ppm)</th>
<th>$\delta_{33}$ (ppm)</th>
<th>$\alpha$ (deg)</th>
<th>$\beta$ (deg)</th>
<th>$\gamma$ (deg)</th>
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<tr>
<td>RHF/6-311++G</td>
<td>−6.61</td>
<td>0.51</td>
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<td>328.5</td>
<td>165.4</td>
<td>73.0</td>
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<tr>
<td>RHF/6-311++G</td>
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<td>188.0</td>
<td>328.1</td>
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<tr>
<td>RHF/D95</td>
<td>−7.32</td>
<td>0.43</td>
<td>176.7</td>
<td>313.9</td>
<td>155.8</td>
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<td>0.58</td>
<td>229.3</td>
<td>359.6</td>
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<td>111.2</td>
<td>4.9</td>
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<tr>
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<td>358.8</td>
<td>213.7</td>
<td>110.3</td>
<td>4.6</td>
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<td>88.6</td>
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<td>B3LYP/D95</td>
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<td>RHF/6-311++G</td>
<td>−6.70</td>
<td>0.66</td>
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<td>90.6</td>
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<td>RHF/D95</td>
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<td>194.4</td>
<td>347.5</td>
<td>183.5</td>
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<td>86.0</td>
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<td>B3LYP/6-311++G</td>
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<td>87.6</td>
<td>0.5</td>
<td>86.5</td>
<td>90.4</td>
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Fig. 3. Molecular cluster models used in the quantum mechanical calculations.
situation provides an excellent opportunity to examine the influence of strong hydrogen bonding on $^{17}$O NMR tensors. The assignment of the signals is straightforward, on the basis of a previously known correlation between $^{17}$O quadrupole parameters and hydrogen bonding environment from NQR studies [40,41]. The assignment reported in Table 1 is further confirmed by our quantum mechanical calculations. As expected, both the chemical shift anisotropy and the quadrupole coupling constant observed for O2 are considerably smaller than those found for O1. Interestingly, the orientations of the $^{17}$O CS tensors are essentially the same at O1 and O2. For both oxygen sites, the CS tensor component with the most shielding, $\delta_{33}$, is perpendicular to the molecular plane (O–C–O) and the CS tensor component associated with the least shielding, $\delta_{11}$, is approximately perpendicular to the C–O bond (within 30°). It should be noted that the $^{17}$O CS tensor orientation observed for O1 and O2 in PHB is different from the situation found in compounds containing a C–O double bond [23,24,26,27,29,42,43]. This is interesting because the C–O1 and C–O2 bond distances (1.22 and 1.24 Å) are very similar to those in amides. Clearly, the lack of a double bond character for the C–O bonds in PHB is responsible for the observed $^{17}$O CS tensor orientation. In fact, the $^{17}$O CS tensor orientation in PHB is similar to that found in crystalline urea [25].

In contrast to the case for the $^{17}$O CS tensors, the EFG tensors for O1 and O2 have quite different orientations. In particular, the largest EFG component, $V_{zz}$, is perpendicular to the C–O bond at O1, but is nearly parallel to the C–O bond at O2.

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**Fig. 4.** Experimental orientations of the $^{17}$O CS tensors (top) and EFG tensors (bottom) in the molecular frame of PHB.
As will be discussed in detail in the next section, the discrepancy in the two EFG tensor orientations in PHB is a consequence of the way that $V_{zz}$ is defined. Also related to this problem is the interesting observation that the sign of $C_0$ is positive for O1 but negative for O2; see Tables 2 and 3. The $^{17}$O EFG tensor orientation for O1 is similar to those found in amides [23,24,26] and urea [25], but different from those in formaldehyde [42] and benzophenone [43]. The EFG tensor orientation found for O2 is in agreement with that deduced from the $^1$H–$^{17}$O dipolar fine structure observed in the $^{17}$O NQR spectrum of PHB [33]. It is also worth noting that the EFG tensor orientation at O2 is similar to the situation found for KHCO$_3$ at 77 K [44]. Although the EFG tensor orientations in PHB show some discrepancies from those observed for carboxylic acid dimers, the magnitudes of tensor components fall very nicely into the correlation discovered by Seliger [45] for hydrogen-bonded carboxylic acid dimers. This may indicate the presence of some common characteristics in chemical bonding between these two classes of closely related compounds.

As seen from Tables 1–3, the calculated $^{17}$O NMR tensors are generally in good agreement with the experimental values. The best theoretical results are obtained using the B3LYP method and a 6-311++G** basis set for H, C, N atoms and a triple-zeta basis set for K. In addition, the difference between using the DZ and TZ basis sets for K atoms is negligible for the $^{17}$O NMR tensors in PHB. We also performed quantum mechanical calculations using a LANL2DZ effective core potential (ECP) [46] to describe the K atoms in Model A. However, the calculated results (data not shown) are drastically different from those reported in Tables 2 and 3, suggesting that the LANL2DZ ECP may not be an adequate alternative for all-electron basis sets for K atoms in the calculations of $^{17}$O NMR tensors. This observation is not surprising because in PHB the K$^+$ ions are quite close to both O1 and O2 atoms (K–O distance $\approx 2.8$ Å) [32].

### 3.2. The effects of a symmetrical hydrogen bond

To further examine the effects of the effectively symmetrical O⋯H⋯O hydrogen bond in PHB on $^{17}$O NMR tensors, we construct another cluster model, Model B, which is also shown in Fig. 3. Because Model B does not have the two K atoms, which are present in Model A, the only structural difference between O1 and O2 in Model B is the O⋯H⋯O hydrogen bond. The calculated $^{17}$O CS and EFG tensors for Model B are also given in Tables 2 and 3. To aid analysis, it is convenient to introduce the notation illustrated in Fig. 5 for describing the directions of the individual tensor components. We summarize in Table 4 the difference between individual tensor components for O1 and O2 calculated for Model B.

As seen from Table 4, the $^{17}$O CS tensor components along the directions both parallel ($||$) and perpendicular ($\perp$) to the C–O bond decrease significantly upon hydrogen bond formation, indicating a considerable increase in magnetic shielding along these directions. In contrast to the case in these directions, the CS tensor component perpendicular to the molecular plane ($\delta_{33}$) increases by approximately 80 ppm. In a previous study, we also found that $\delta_{33}$ of the $^{17}$O CS tensor increases with the hydrogen bond strength for C≡O⋯H–N hydrogen bonds [24]. However,
the magnitude of change for \( \delta_{33} \) in PHB is considerably larger than those found for C–O⋯H–N hydrogen bonds, consistent with the nature of the short O⋯H⋯O hydrogen bond. It is also clear from Table 4 that the observed decrease of approximately 70 ppm in the \(^{17}\)O isotropic chemical shift between O1 and O2 is primarily due to the large decreases in the in-plane tensor components (\( \delta_{11} \) and \( \delta_{22} \)), which partially cancel the opposite contribution from \( \delta_{33} \). The opposite changes in \( \delta_{11} \) and \( \delta_{33} \) of the CS tensor also leads to a drastic reduction of the \(^{17}\)O chemical shift anisotropy. In particular, upon formation of a short O⋯H⋯O hydrogen bond, the span of the \(^{17}\)O CS tensor (\( \Omega = \delta_{11} - \delta_{33} \)) is reduced by more than 200 ppm according to the calculated results at the B3LYP/6-311 + + G** level.

We noticed from Table 4 that the \(^{17}\)O EFG tensor exhibits a very different sensitivity to the formation of a short O⋯H⋯O hydrogen bond. In particular, the \(^{17}\)O EFG tensor component along the C–O bond changes only slightly, whereas the other two components vary drastically. For example, the B3LYP/6-311 + + G** results indicate that the changes in the parallel and perpendicular directions are on the order of 4–5 MHz; however, the corresponding change in the direction norm to the molecular plane is less than 1 MHz. The very large EFG change in the direction
perpendicular to the C–O bond also causes a sign inversion in $C_Q$. This is because the sign of $C_Q$ is determined by the sign of $V_{zz}$, which is defined as the EFG tensor component with the largest absolute magnitude. As seen from Fig. 4, the largest EFG component at O1 is found to be perpendicular to the C–O bond. At O2, due to the participation in a short hydrogen bond, the EFG along the C–O direction is significantly reduced, leading to the fact that now the EFG component parallel to the C–O bond becomes the largest in magnitude. Under such a circumstance, the sign of the EFG component along the C–O bond determines the sign of $C_Q$ for O2. Therefore, as noted earlier, the sign inversion of $C_Q$ (as indicated in Tables 2 and 3) and the EFG tensor orientation change between O1 and O2 (as illustrated in Fig. 4) are intrinsically related. Finally, we note in passing an interesting trend observed in the calculated $^{17}$O chemical shifts from Models A and B. That is, the presence of K$^+$ ions causes a shielding increase at both oxygen sites by approximately 20 ppm, regardless of the basis set used in the calculation. Furthermore, this change results from shielding increases only in $\delta_{11}$ and $\delta_{22}$ components.

4. Conclusions

We have presented an experimental determination of the $^{17}$O CS and EFG tensors in PHB. The presence of a short O···H···O hydrogen bond in PHB is responsible for the drastically different $^{17}$O NMR tensors observed at the two oxygen sites. For the oxygen site that is involved in the O···H···O hydrogen bond, the isotropic $^{17}$O chemical shift is considerably smaller (ca. 75 ppm) than that for the oxygen site free of hydrogen bonding. Similarly, upon the hydrogen bond formation, the span of the $^{17}$O CS tensor is also reduced by 170 ppm. The reduction of $C_Q$ at the hydrogen-bonded oxygen site is also strikingly large, ca. 2.4 MHz. By combining experimental NMR data obtained at multiple fields with high-level quantum mechanical calculations, we have also determined the $^{17}$O NMR tensor orientations in the molecular frame of PHB. We have found that the NMR tensors are oriented differently at the two oxygen sites. The precise knowledge about these $^{17}$O NMR tensor orientations has been proved important in analyzing the sensitivity of individual tensor components to hydrogen bond formation. The present work represents the first determination of complete $^{17}$O NMR tensors for an effectively symmetrical O···H···O hydrogen bond. We believe that continuous accumulation of fundamental $^{17}$O NMR tensors for important functional groups will lead to practical use of $^{17}$O solid-state NMR as a tool for probing hydrogen bond environment in biological structures in the future.

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References


