17O NMR parameters of some substituted benzyl ethers components: Ab initio study

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Abstract The 17O NMR chemical shielding tensors and chemical shift for a set of substituted benzyl ethers derivatives containing (methyl, ethyl, isopropyl, t-butyl, bromo and lithium) have been calculated. The molecular structures were fully optimized using B3LYP/6-31G(d,p). The calculation of the 17O shielding tensors employed the GAUSSIAN 98 implementation of the gauge-including atomic orbital (GIAO) and continuous set of gauge transformations (CSGT) by using 6-31G(d,p), 6-31++G(d,p) and 6-311++G(d,p) basis set methods at density functional levels of theories (DFT). The values determined using the GIAO and CSGT were found to give a good agreement with the experimental chemical shielding.

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1. Introduction

Nuclear Magnetic Resonance (NMR) is a useful technique for studying the structure of chemical and biological systems, from small molecules to complicated structures such as nucleic acids and proteins. Chemical shifts and spin–spin coupling serve to recognize the molecular conformation, composition and environment of the moiety. However, the investigation and understanding of the relationships between molecular structure and measured NMR parameters can sometimes be quite difficult, and need the support of theoretical calculations (Doskocz et al., 2009). Theoretical methods for the prediction of the nuclear magnetic resonance (NMR) parameters of molecules have become a useful quantum chemical tool. A number of papers have recently appeared in the literature concerning the calculation of NMR chemical shift by quantum chemistry methods (Atalay et al., 2008; Encheva et al., 2003; Sergeyev and Moyna, 2005; Silly et al., 2004; Alam and Segall, 2004; Johnson et al., 2005; Virtanen et al., 2003; Marshall et al., 2004; Gao et al., 2007). These papers indicate that geometry optimization is a crucial factor in an accurate determination of computed NMR chemical shift. Moreover, it is known that the DFT (B3LYP) method adequately takes into account electron correlation contributions, which are especially important in systems containing extensive electron conjugation and/or electron lone pairs (Atalay et al., 2008). However, considering that as molecular size increases, computing time limitations are introduced for obtaining optimized geometries at the DFT level, it was proposed that the single-point calculation of magnetic shielding by DFT methods was combined with a fast and reliable geometry optimization procedure at the molecular mechanics level (Forsyth and Sebag, 1997). After pervious work (Re-
In this letter we describe the capability of the theoretical method ab initio/GIAO (Ditchfield, 1972) and CSGT (Keith and Bader, 1993) at the B3lyp/6-31G(d,p), B3lyp/6-31+ +G(d,p) and B3lyp/6-311+ +G(d,p) levels by comparing the calculated chemical shift values of $^{17}$O NMR computed for a set of substituted benzyl ethers derivatives containing (methyl, ethyl, isopropyl, i-butyl, brome and lithium) with the data obtained experimentally (Dostal et al., 2006).

2. Computational methods

The entire calculations were performed at density functional (DFT) levels on a Pentium IV/3200 MHz personal computer using Gaussian 98 (Frisch et al., 2001) program package, invoking gradient geometry optimization (Schlegel, 1982). The geometry of the title compounds (A1–A11, in Fig. 1) are fully optimized and $^{17}$O NMR chemical shielding are calculated with GIAO and CSGT approach by applying B3LYP method at the 6-31G (d,p), 6-31++G(d,p) and 6-311++G(d,p) basis sets. The obtained shielding tensors were referenced against an absolute shielding reference $\sigma_{\text{ref}} = 287.5$ ppm (Wasylishen and Bryce, 2002; Wong et al., 2006).

3. Results and discussion

We first focus on substituted benzyl ethers derivatives in order to find out which quantum method is appropriate to describe the NMR chemical shifts in these molecules. For this reason all substituted benzyl ethers derivatives (A1–A11) were optimized with B3lyp/6-31++G(d,p) levels of theory by using the Gaussian 98 program (see Fig. 2a and 2b). After full optimization of all components (A1–A11), we use the Gaussian GIAO and CSGT options to study the effect of basis set on chemical shift. After selection of appropriate basis set such as 6-31G(d,p), 6-31++G(d,p) and 6-311++G(d,p), we calculated the NMR chemical shifts. Typically it is only necessary to report the three principal components (or eigenvalues) of the $^{17}$O shielding tensor ($\sigma_{11}$, $\sigma_{22}$, and $\sigma_{33}$) when discussing the magnitude of the shielding tensor. The $^{17}$O NMR shielding tensor can also be described by three additional parameters:

(a) The isotropic value (or trace), $\sigma_{\text{iso}}$, of the shielding tensor which is defined as (Rezai-Sameti, 2008):

$$\sigma_{\text{iso}} = \frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33})$$

(b) The anisotropy ($\Delta\sigma$) of the tensor,

$$\Delta\sigma = \sigma_{33} - \frac{1}{2} (\sigma_{22} + \sigma_{11})$$

(c) The shielding tensor asymmetry parameter ($\eta$) given by

$$\eta = \left(\frac{\sigma_{22} - \sigma_{11}}{\sigma_{33} - \sigma_{\text{iso}}}\right)$$

The $^{17}$O NMR shielding tensors ($\sigma_{11}$, $\sigma_{22}$, and $\sigma_{33}$) are described within the principal axis system for all components were calculated. The results show that the isotropic chemical shielding ($\sigma_{\text{iso}}$) calculated for all components in GIAO and CSGT with three bases set: {a} 6-31G (d,p), {b} 6-31+ +G(d,p) and {c} 6-311+ +G(d,p) is in the following order:

$$\sigma_{\text{iso}}^{(a)} > \sigma_{\text{iso}}^{(b)} > \sigma_{\text{iso}}^{(c)}$$

The shielding tensor asymmetry parameter ($\eta$) and the anisotropy ($\Delta\sigma$) of tensor for all components do not show trended in all methods and components.

The primary result of any quantum chemical calculation of NMR shifts is the absolute magnetic shielding $\sigma_{\text{cal}}$, i.e., the chemical shift with respect to a naked nucleus. The chemical shift of a substance (S) with respect to a reference compound is then given as:

$$\delta(S) = \sigma_{\text{cal}}(S) - \sigma(S)$$

The absolute isotropic chemical shielding values ($\sigma_{\text{iso}}$) can be converted to chemical shifts ($\delta$) relative to an absolute shielding reference $\sigma_{\text{ref}} = 287.5$ ppm (Wasylishen and Bryce, 2002; Wong et al., 2006). The chemical shifts for the substituted benzyl ethers derivatives (A1–A11) compounds have been calculated with the computational methods described above and the results are summarized in (Tables 1–3). As can be detected from (Tables 1–3), the $\Delta\delta$ values for compound A1 with three base set (a, b, c) and GIAO methods are 7.0, 4.0 and −5.3 ppm and for CSGT −13.1, −11.3 and −18.2 ppm, respectively. For compound A2 the corresponding values are 13.6, 5.3, and −6.7 ppm with GIAO and with CSGT 0.4.

![Figure 1 Scheme benzyl ethers derivatives.](image-url)
In compounds A1 and A2, the GIAO method by 6-31++G (d,p) is a good agreement with experimental. For compound A3, the corresponding values with GIAO are 18.6, 9.7, and −3.5 ppm and with CSGT 12.5, 1.0, and −15.2 ppm, respectively. In this compound, the CSGT method by 6-31++G(d,p) is better than others. For compound A4, the corresponding values with GIAO are 24.8, 13.6, and 1.3 ppm and with CSGT 19.2, 9.5, and −8.8 ppm, respectively. For compound A5, the corresponding values with GIAO are 2.6, −12.1, and −23.8 ppm and with CSGT −5.9, −
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In compounds A4 and A5, the GIAO method by 6-31++G (d,p) and 6-31G(d,p), respectively, are a good agreement with experimental. For compound A6 the corresponding values with GIAO are 10.2, 1.3 and 15.2 ppm and with CSGT 0.5, 11.2 and 25.5 ppm, respectively, in this compound the CSGT method by 6-31G (d,p) is better than others. For compound A7 the corresponding values with GIAO are 3.3, 1.3 and 7.9 ppm and with CSGT 15.3, 14.1 and 21.7 ppm, respectively, in this compound the GIAO method by 6-31++G(d,p) is better than others. For compound A11, the corresponding values with GIAO are $-13.8$, $-18.6$ and $-34.4$ ppm and with CSGT $-19.0$, $-24.4$ and $-42.9$ ppm, respectively, in this compound the GIAO method by 6-31G (d,p) is better than others.

### 4. Conclusion

In this work, we have calculated the geometric parameters, $17^\text{O}$ NMR shielding tensors and chemical shift values of the title compound (A1–A11) by using B3LYP method with 6-
31G(d,p), 6-31++G(d,p) and 6-311++G(d,p) basis sets. The results show that in the compounds A1 and A2, A4 and A7 the GIAO method by 6-31++G(d,p), in compound A3 and A6 the CSGT method by [6-31++G(d,p), 6-31G(d,p)] and in the compounds A5 and A11 the GIAO method by 6-31G(d,p) basis set are a good agreement with experimental.

### References


### Table 3

Theoretical chemical shift and experimental chemical shift of benzyl ethers 17O NMR spectra (ppm), deviation error \( \Delta \delta = \delta_{\text{EXP}} - \delta_{\text{calc}} \) with B3lyp/6-31G(d,p).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>GIAO</th>
<th>CSGT</th>
<th>Exp.</th>
<th>( \Delta \delta_{\text{GIAO}} )</th>
<th>( \Delta \delta_{\text{CSGT}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>−21.0</td>
<td>−0.9</td>
<td>−14.0</td>
<td>7.0</td>
<td>−13.1</td>
</tr>
<tr>
<td>A2</td>
<td>−4.0</td>
<td>9.2</td>
<td>9.6</td>
<td>13.6</td>
<td>0.4</td>
</tr>
<tr>
<td>A3</td>
<td>20.4</td>
<td>26.5</td>
<td>39.0</td>
<td>18.6</td>
<td>12.5</td>
</tr>
<tr>
<td>A4</td>
<td>24.2</td>
<td>29.8</td>
<td>49.0</td>
<td>24.8</td>
<td>19.2</td>
</tr>
<tr>
<td>A5</td>
<td>37.5</td>
<td>46.0</td>
<td>40.1</td>
<td>2.6</td>
<td>−5.9</td>
</tr>
<tr>
<td>A6</td>
<td>22.8</td>
<td>32.5</td>
<td>33.0</td>
<td>10.2</td>
<td>0.5</td>
</tr>
<tr>
<td>A7</td>
<td>−23.3</td>
<td>−4.7</td>
<td>−20.0</td>
<td>3.3</td>
<td>−15.3</td>
</tr>
<tr>
<td>A8</td>
<td>−4.1</td>
<td>7.7</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>A9</td>
<td>11.1</td>
<td>20.7</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>A10</td>
<td>−4.8</td>
<td>15.0</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>A11</td>
<td>47.3</td>
<td>52.5</td>
<td>33.5</td>
<td>−13.8</td>
<td>−19.0</td>
</tr>
</tbody>
</table>

\[ a \text{ Ref = Dostal et al. (2006).} \]