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^{17}O NMR parameters of some substituted benzyl ethers components: *Ab initio* study



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Abstract The ^{17}O 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 ^{17}O 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 nucle-

ar 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-

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zaei-Sameti, 2008) 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 ¹⁷O NMR computed for a set of substituted benzyl ethers derivatives containing (methyl, ethyl, isopropyl, *t*-butyl, bromo 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 ¹⁷O 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), 6-311++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 ¹⁷O shielding tensor (σ_{11} , σ_{22} , and σ_{33}) when discussing the magnitude of the shielding tensor. The ¹⁷O NMR shielding tensor can also be described by three additional parameters:

- (a) The isotropic value (or trace), σ_{iso} , of the shielding tensor which is defined as (Rezaei-Sameti, 2008):

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

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

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

- (c) The shielding tensor asymmetry parameter (η) given by

$$\eta = \frac{(\sigma_{22} - \sigma_{11})}{(\sigma_{33} - \sigma_{\text{iso}})} \quad (3)$$

The ¹⁷O NMR shielding tensors (σ_{11} , σ_{22} , and σ_{33}) are described within the principal axis system for all components were calculated. The results show that the isotropic chemical shielding (σ_{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 (η) 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:

$$\delta(S) = \sigma(\text{ref}) - \sigma(S) \quad (4)$$

The absolute isotropic chemical shielding values (σ_{iso}) can be converted to chemical shifts (δ) 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,

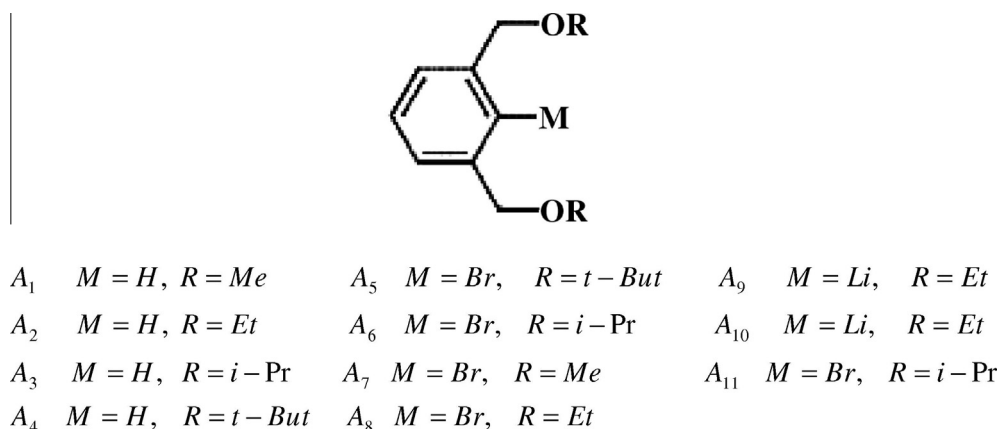


Figure 1 Scheme benzyl ethers derivatives.

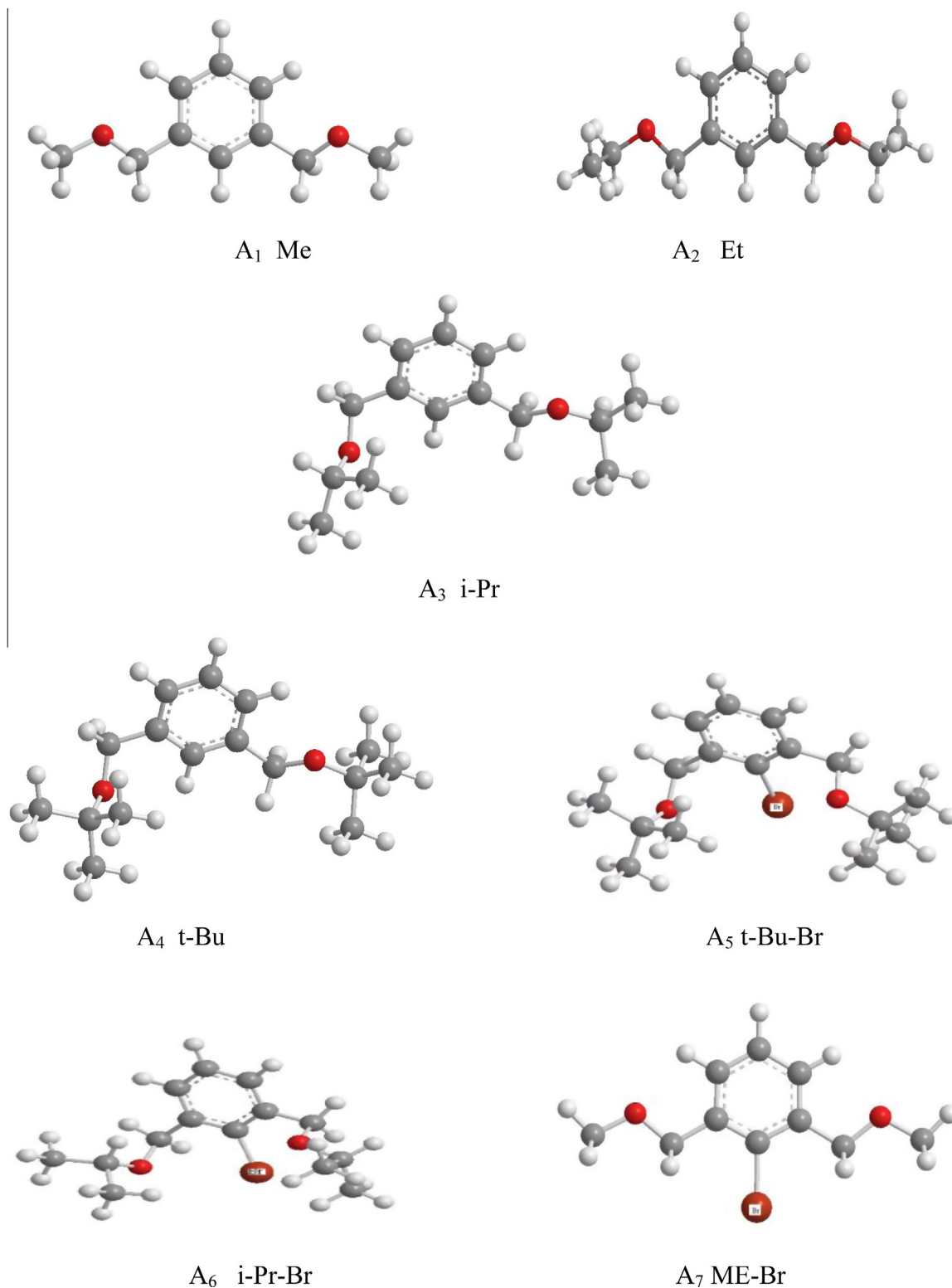


Figure 2a Optimized of structures of benzyl ethers derivatives A₁ Me, A₂ Et, A₃ *i*-Pr, A₄ *t*-Bu, A₅ *t*-Bu-Br, A₆ *i*-Pr-Br and A₇ ME-Br.

−8.1 and −18.4 ppm, respectively. 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,

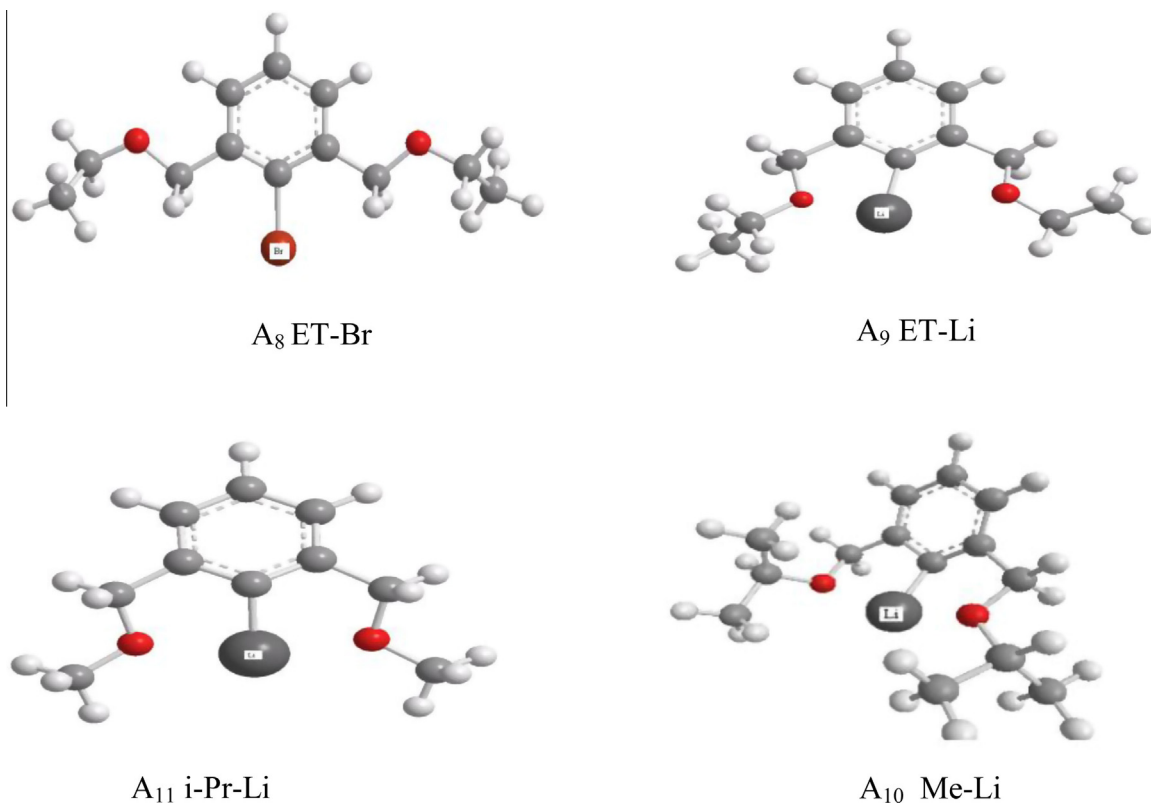


Figure 2b Optimized of structures of benzyl ethers derivatives A₈ ET-Br, A₉ ET-Li, A₁₁ *i*-Pr-Li and A₁₀ Me-Li.

Table 1 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/6-311 + + G (d, p).

Compounds	GIAO	CSGT	Exp. ^a	$\Delta\delta_{\text{GIAO}}$	$\Delta\delta_{\text{CSGT}}$
A1	-8.7	4.2	-14.0	-5.3	-18.2
A2	16.3	28.0	9.6	-6.7	-18.4
A3	42.5	53.2	39.0	-3.5	-14.2
A4	47.7	57.8	49.0	1.3	-8.8
A5	63.9	73.6	40.1	-23.8	-33.5
A6	48.2	58.5	33.0	-15.2	-25.5
A7	-12.1	1.7	-20.0	-7.9	-21.7
A8	16.5	27.2	-	-	-
A9	26.3	35.1	-	-	-
A10	4.8	14.4	-	-	-
A11	67.9	76.4	33.5	-34.4	-42.9

^a Ref = Dostal et al. (2006).

Table 2 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/6-31 + + G(d,p).

Compounds	GIAO	CSGT	Exp. ^a	$\Delta\delta_{\text{GIAO}}$	$\Delta\delta_{\text{CSGT}}$
A1	-18.0	-2.7	-14.0	4.0	-11.3
A2	4.3	17.7	9.6	5.3	-8.1
A3	29.3	38.0	39.0	9.7	1.0
A4	35.4	39.5	49.0	13.6	9.5
A5	52.2	56.5	40.1	-12.1	-16.4
A6	34.3	44.2	33.0	-1.3	-11.2
A7	-21.3	-5.9	-20.0	1.3	-14.1
A8	2.5	16.2	-	-	-
A9	14.1	20.3	-	-	-
A10	52.0	-5.3	-	-	-
A11	52.1	57.9	33.5	-18.6	-24.4

^a Ref = Dostal et al. (2006).

-16.4 and -33.5 ppm, respectively, 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, ¹⁷O NMR shielding tensors and chemical shift values of the title compound (A₁-A₁₁) by using B3LYP method with 6-

Table 3 Theoretical chemical shift and experimental chemical shift of benzyl ethers ^{17}O NMR spectra (ppm), deviation error $\Delta\delta = \delta_{\text{EXP}} - \delta_{\text{calc}}$ with B3lyp/6-31G(d,p).

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

^a Ref = Dostal et al. (2006).

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.

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