

## Correlation Between Experimental and Calculated $^{17}\text{O}$ NMR Chemical Shift Correlations of Polycyclic Compounds

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**Abstract:** *In this work, we describe a systematic and comparative study of  $^{17}\text{O}$ -NMR and related parameters of bicyclic, tricyclic, tetracyclic (endo-endo and endo-exo fusion), pentacyclic (ketone; endo and exo- alcohol/ester), and hexacyclic compounds (alcohol/ester). We report the values and the respective comparisons between experimental  $^{17}\text{O}$ -NMR chemical shifts and calculated chemical shifts. Based on these data, a linear correlation between calculated and experimental  $^{17}\text{O}$  chemical shifts of the alcohols, esters and ketones were observed and equations were generated.*

The main difficulty in studying  $^{17}\text{O}$  lies on the combination of low natural abundance (0.037%) and the existence of an electric quadrupole moment (spin quantum number  $I = 5/2$ ) that has the general effect of broadening the spectral lines due to efficient quadrupolar relaxation. The linewidth of  $^{17}\text{O}$  resonance observed in solution is usually limited by quadrupole relaxation rates. These aspects increase the necessity of theoretical methods capable of predicting  $^{17}\text{O}$  experimental chemical shifts.

It is well known that oxygen plays an important part in the properties of polycyclic compounds and  $^{17}\text{O}$ -NMR is rather sensible to structural alterations. Thus, we describe a systematic and comparative study of  $^{17}\text{O}$ -NMR and related parameters of bicyclic, tricyclic, tetracyclic (*endo-endo* and *endo-exo fusion*), pentacyclic (ketone; *endo* and *exo*-alcohol/ester), and hexacyclic compounds

(alcohol/ester). We report the values and the respective comparisons between experimental  $^{17}\text{O}$  NMR chemical shifts and calculated chemical shifts. All structures studied were fully optimized within the density functional theory (DFT) framework, and the B3LYP method was employed. All the calculations were carried out with the Gaussian 98W package of the molecular orbital program. The Gauge-Independent Atomic Orbital (GIAO) method with the B3LYP functional and the 6-31g (d) basis set, as implemented in Gaussian 98w, was used to obtain absolute isotropic magnetic shielding tensors.

The calculated chemical shift should be determined by comparison with the reference, *i.e.*, the absolute isotropic magnetic shielding tensor of water. Using Karadakov reference<sup>1</sup> to  $[(\text{H}_2\text{O})_5]$ ,  $\sigma_{\text{H}_2\text{O}} = 311.34$ , it is possible to determine the calculated chemical shifts through Equation 1:

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










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$$\delta_{calc} = \sigma_{H_2O} - \sigma_{absoluta} \quad (1)$$

However, this equation cannot be generalized, because, for each functional group, a respective magnetic shielding tensor

is required. This occurs due to the different interactions between solvent - sample molecules.<sup>2</sup> A summary of *ab initio* results for absolute isotropic magnetic shielding tensor ( $\sigma$ ) and the respective <sup>17</sup>O chemical shifts is shown in Table 1.

**Table 1.** Correlation between experimental and calculated  $\delta$ -<sup>17</sup>O of alcohols and esters.

Structure	ALCOHOL (R = H)			ESTER		
	Absolute isotropic magnetic shielding tensor $\sigma$ (alcohol)	$\delta$ - <sup>17</sup> O experimental (ppm)	$\delta$ - <sup>17</sup> O calculated (ppm)	Absolute isotropic magnetic shielding tensor $\sigma$ (ester)	$\delta$ - <sup>17</sup> O experimental (ppm)	$\delta$ - <sup>17</sup> O calculated (ppm)
	250.32	43.5	61.02	COC: 103.35 C=O: - 83.89	COC: 202.5 C=O: 368.9	COC: 207.99 C=O: 395.23
	268.90	22.4	42.44	COC: 122.06 C=O: - 80.95	COC: 184.7 C=O: 368.3	COC: 189.28 C=O: 392.29
	254.80	39.6	56.54	COC: 113.24 C=O: - 79.14	COC: 199.8 C=O: 364.5	COC: 198.10 C=O: 390.48
	271.71	22.4	39.63	COC: 121.94 C=O: - 79.34	COC: 184.8 C=O: 365.1	COC: 189.40 C=O: 390.68
	247.54	45.6	63.80	COC: 106.12 C=O: - 77.50	COC: 207.9 C=O: 367.0	COC: 205.22 C=O: 388.84
	263.37	30.9	47.97	COC: 116.40 C=O: - 79.21	COC: 191.5 C=O: 362.2	COC: 194.94 C=O: 390.55
	253.51	41.3	57.83	COC: 103.93 C=O: - 82.26	COC: 203.5 C=O: 365.1	COC: 207.41 C=O: 393.60
	271.78	21.5	39.56	COC: 122.36 C=O: - 78.41	COC: 186.5 C=O: 365.7	COC: 188.98 C=O: 389.75
	269.39	27.7	41.95	COC: 120.13 C=O: -76.16	COC: 189.4 C=O: 364.5	COC: 191.21 C=O: 387.50
	267.57	27.9	43.77	COC: 120.67 C=O: - 79.02	COC: 184.7 C=O: 364.5	COC: 190.67 C=O: 390.36
	261.51	30.2	49.83	COC: 118.76 C=O: - 91.57	COC: 190.4 C=O: 379.3	COC: 192.58 C=O: 402.91

Based on these data, a linear correlation between calculated and experimental <sup>17</sup>O chemical shifts of the alcohols and esters was observed, and equations 2 and 3 were generated, which allows us to predict other chemical shifts for alcohols and esters with similar structures.

The same methodology was applied to ketones with the same polycyclic systems when good linear correlation was reached (Equation 4). <sup>17</sup>O NMR spectra of the compounds were measured on a VARIAN NMR spectrometer model YH-300 (7.05T) working at 40 MHz.

Alcool:  $\delta_{\text{exp}} = -16.6 + 0.98 \delta_{\text{calc}}$  ( $R = 0.983$ ) (eq. 2)

Ester:  $\text{COC: } \delta_{\text{exp}} = -19.18 + 1.08 \delta_{\text{calc}}$  ( $R = 0.949$ );  $\text{C=O: } \delta_{\text{exp}} = -9.62 + 0.96 \delta_{\text{calc}}$  ( $R = 0.886$ ) (eq. 3)

Ketone:  $\delta_{\text{exp}} = 42.28 + 0.89 \delta_{\text{calc}}$  ( $R = 0.992$ ) (eq. 4)

$^{17}\text{O}$  NMR spectra were obtained with a variable temperature multinuclear probe head in 5 mm diameter NMR tubes containing 5.0 mol.L<sup>-1</sup> acetonitrile at 60 °C. Chemical shifts are expressed as  $\delta$  (parts per million) relative to D<sub>2</sub>O (0.0 ppm) as an external standard. The number of transients (nt) varies in the range 10<sup>4</sup> – 10<sup>6</sup>, depending on the compound.

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#### References

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