^{13}C and ^{1}H NMR Chemical Shifts Prediction Models for *tert*-butyl peroxides

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INTRODUCTION

What

Determining the optimal NMR chemical shift (δ) prediction model of ^{13}C and ^{1}H for the *tert*-butyl peroxides molecules;
other energetic properties can be calculated as well with
computational chemistry.

How

Utilizing Gaussian's DFT level of theory in order to compare CSGT, GIAO and IGAIM NMR models with B3LYP and B3PW91 methods in 6-311+G(2d,p) and cc-pVTZ basis sets; yielding twelve combination models in total per molecule. Comparing experimental and computational values by correlation coefficient (R^2) and mean absolute error (MAE).

RELEVANCE OF STUDY

NMR chemical shift prediction by computational chemistry is of great importance due to the advantage of minimizing instrument setup, sample cost and potential risks. Moreover, acquiring such information for the structural characterization of molecules.

METHOD AND RESULTS

HEM Molecule Selection

Fifteen tert-butyl peroxide molecules, with their experimental ^{13}C and ^{1}H NMR chemical shifts were selected.

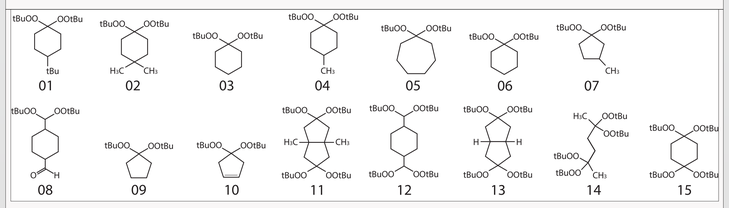

Figure 01: *Tert*-butyl peroxide molecules modeled

Molecules Optimization

DFT level of theory with B3LYP method and 6-311+G(2d,p) was utilized for optimization.

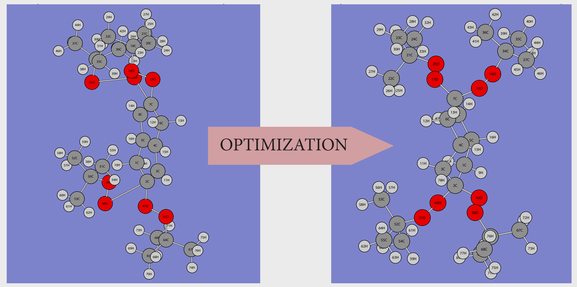

Figure 02: *Tert*-butyl peroxide molecule before and after optimization

NMR Calculation

Calculating NMR chemical shifts for ^{1}H and ^{13}C are averaged and plotted in order to obtain trendline equation for prediction.

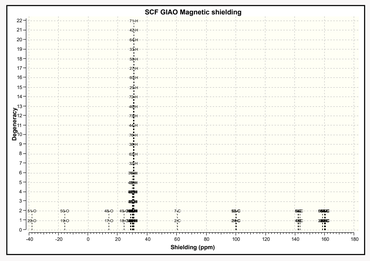

Figure 03: GIAO NMR Graph

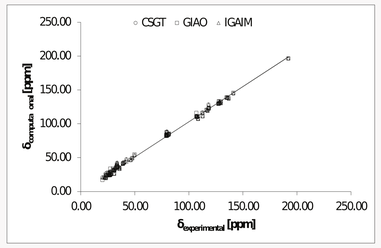

Figure 04: NMR δ computational vs experimental

NMR Models	6-311+G(2d,p) Basis Set				cc-pVTZ Basis Set			
	MAE ^{13}C [ppm]	Slope ^{13}C	Intercept ^{13}C	R^2 ^{13}C	MAE ^{13}C [ppm]	Slope ^{13}C	Intercept ^{13}C	R^2 ^{13}C
CSGT	5.35[a]	1.0453[a]	2.3791[a]	0.9967[a]	5.47[a]	1.0426[a]	2.5827[a]	0.9955[a]
	2.97[b]	1.0387[b]	-0.8932[b]	0.9962[b]	3.00[b]	1.0420[b]	-1.3563[b]	0.9962[b]
GIAO	5.55[a]	1.0471[a]	1.7160[a]	0.9932[a]	5.10[a]	1.0444[a]	2.0536[a]	0.9966[a]
	2.91[b]	1.0416[b]	-1.1958[b]	0.9970[b]	2.65[b]	1.0423[b]	-1.7587[b]	0.9973[b]
IGAIM	5.29[a]	1.0430[a]	2.4677[a]	0.9975[a]	5.46[a]	1.0425[a]	2.5843[a]	0.9955[a]
	2.93[b]	1.0388[b]	-0.9032[b]	0.9992[b]	3.00[b]	1.0420[b]	-1.3679[b]	0.9962[b]

Table 01: ^{13}C NMR δ from diferent models with B3LYP (a) and B3PW91 (b) at 6-311 and cc-pVTZ basis sets

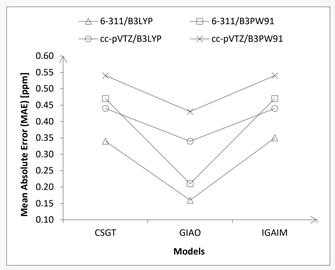

Figure 05: Accuracy of ^{1}H NMR Models

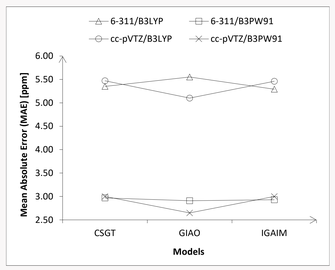

Figure 06: Accuracy of ^{13}C NMR Models

CONCLUSION

Optimal ^{1}H and ^{13}C NMR chemical shifts prediction based on DFT level of theory in *tert*-butyl peroxides was found by comparing CSGT, GIAO and IGAIM models on different basis sets and methods. Results suggest that GIAO with cc-pVTZ/B3PW91 has the highest accuracy for ^{13}C and GIAO with 6-311+G(2d,p)/B3LYP for the ^{1}H isotope. Regarding precision, IGAIM with 6-311+G(2d,p)/B3LYP and CSGT with 6-311+G(2d,p)/B3LYP had the highest for ^{13}C and ^{1}H respectively. As for future endeavors, by means of their thermochemistry, heats of explosion can be acquired and a possible correlation between such and NBO charges can be found as well.

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All opinions expressed in this paper are the author's and do not necessarily reflect the policies and views of DHS, DOE or ORAU/ORISE.

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