COMPARISON OF ^{13}C–NMR CHEMICAL SHIFTS WITH QUANTUM CALCULATIONS

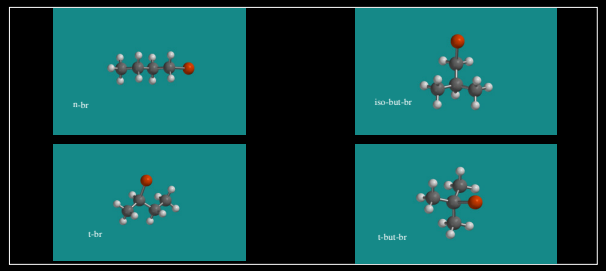
Cardell Givens*, Joseph A. Bentley and Alline P. Somlai

Division of Biological and Physical Sciences, Delta State University, Cleveland, MS 38733

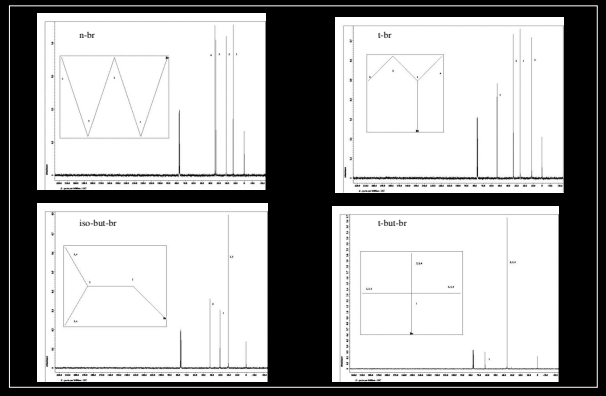
ABSTRACT

The Carbon-13 Nuclear Magnetic Resonance (^{13}C–NMR) spectra were collected on a 300 MHz ECX-JEOL spectrometer for four constitutional isomers: *n*-butyl bromide, isobutyl bromide, *t*-butyl bromide and 2-butyl bromide. The ^{13}C-NMR chemical shifts were calculated by both ChemNMR and the computational chemistry package SPARTAN using the STO-3G, 3-21G(*), 6-31G(D) and 6-31G** basis sets. For the molecules in this study, ChemNMR and SPARTAN give comparable estimates for experimental ^{13}C-NMR chemical shifts. The energies calculated using SPARTAN are also presented.

CONSTITUTIONAL ISOMERS



CARBON NMR SPECTA OF CONSTITUTIONAL ISOMERS IN DEUTERATED CHLOROFORM



PREDICTIONS

With ChemNMR, carbons are given a chemical shift base number determined by molecular mechanics. The chemicals shifts are based on the additive effects of shielding and deshielding groups. Similar work for ^{1}H-NMR Spectroscopy was done by Van Arnum [1].

With SPARTAN, carbon chemical shifts are determined from an *ab initio* calculation. The energies and the wave functions are found in the Hartree-Fock calculation. The wave functions are then used to calculate the chemical shifts [2].

CHEMDRAW AND EXPERIMENTAL PREDICTIONS OF CHEMICAL SHIFTS

n-but-br

	Chem NMR	Experimental
C1	13.0	13.21
C2	21.5	21.35
C3	32.6	33.68
C4	36.3	34.82

t-br

	Chem NMR	Experimental
C1	40.5	53.62
C2	33.8	34.21
C3	23.6	26.05
C4	9.9	12.23

iso-but-br

	Chem NMR	Experimental
C1	32.3	30.75
C2	42.0	42.54
C3	20.7	21.01
C4	20.7	21.01

t-but-br

	Chem NMR	Experimental
C1	39.4	62.80
C2	33.2	36.43
C3	33.2	36.43
C4	33.2	36.43

PREDICTIONS BY SPARTAN FOR CHEMICAL SHIFTS USING VARIOUS BASIS SETS

n-but-br

	STO-3G	3-21G(*)	6-31G(D)	6-31G**	6-31+G*
C1	24.223	13.101	14.865	14.953	14.445
C2	31.119	18.494	20.819	21.481	20.807
C3	35.241	29.036	33.510	34.101	33.594
C4	39.163	31.665	38.510	39.209	37.952

t-br

	STO-3G	3-21G(*)	6-31G(D)	6-31G**	6-31+G*
C1	49.924	46.710	55.582	56.928	55.455
C2	35.104	27.821	31.091	31.776	31.026
C3	23.743	12.280	13.590	13.691	12.731
C4	28.994	24.058	26.665	26.708	25.931

iso-but-br

	STO-3G	3-21G(*)	6-31G(D)	6-31G**	6-31+G*
C1	36.125	22.490	25.702	26.649	26.175
C2	43.706	40.800	46.585	47.503	46.183
C3	26.190	17.081	18.592	18.807	17.600
C4	26.381	17.440	18.592	18.807	17.600

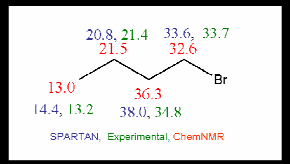
t-but-br

	STO-3G	3-21G(*)	6-31G(D)	6-31G**	6-31+G*
C1	55.484	50.642	63.464	65.022	62.722
C2	32.032	29.968	32.734	33.025	31.892
C3	32.032	30.637	32.734	33.025	31.892
C4	32.032	30.214	32.734	33.025	31.892

HARTREE FOCK ENERGIES IN ATOMIC UNITS BY BASIS SET

	STO-3G	3-21G(*)	6-31G(D)	6-31G**.	6-31+G*
n-but-br	-2699.555586	-2716.124328	-2728.825275	-2728.839307	-2728.826629
t-br	-2699.555666	-2716.127907	-2728.826285	-2728.840431	-2728.827663
iso-but-br	-2699.554543	-2716.126441	-2728.823993	-2728.838172	-2728.825346
t-but-br	-2699.556116	-2716.13154	-2728.828169	-2728.842335	-2728.82969

^{13}C-NMR Shifts for *n*-Bromobutane



CONCLUSION AND FUTURE WORK

- A comparison of experimental NMR chemical shifts with those calculated using SPARTAN is a useful means of introducing computational chemistry to undergraduate students.
- For the molecules in this study, ChemNMR and SPARTAN give comparable estimates for ^{13}C- NMR chemical shifts.
- Using higher quality basis sets in SPARTAN should yield better estimates of the chemical shifts. This will be the subject of future work.
- More complex molecules will be further investigated.

REFERENCES

1. Cheeseman, J. R. and Frisch, Æ. "Predicting Magnetic Properties with ChemDraw and Gaussian," Technical Report, Gaussian, Inc. 2000.
2. Van Arnum,S. D. *J. Chem. Educ.* **2006**, 83, 429-431.

ACKNOWLEDGEMENTS

- Matt Teale and Heather Jo Hilderbrand for running the ^{13}C-NMR spectra.
- National Science Foundation CCLI Grant, NSF# 0310861.
- Division of Biological and Physical Sciences, Delta State University.