Calculating Accurate Proton Chemical Shifts of Organic Molecules with Density Functional Methods and Modest Basis Sets

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Supporting Information

Note:

- A complete Gaussian input to run a set of calculations on the entire test set is provided separately as a text file

- Excel spreadsheets with the raw data and their statistical workup, both for the test set and the probe set, are also provided as a separate part of the Supporting Information

The above files are contained in the zip archive "NMR_Data.zip".

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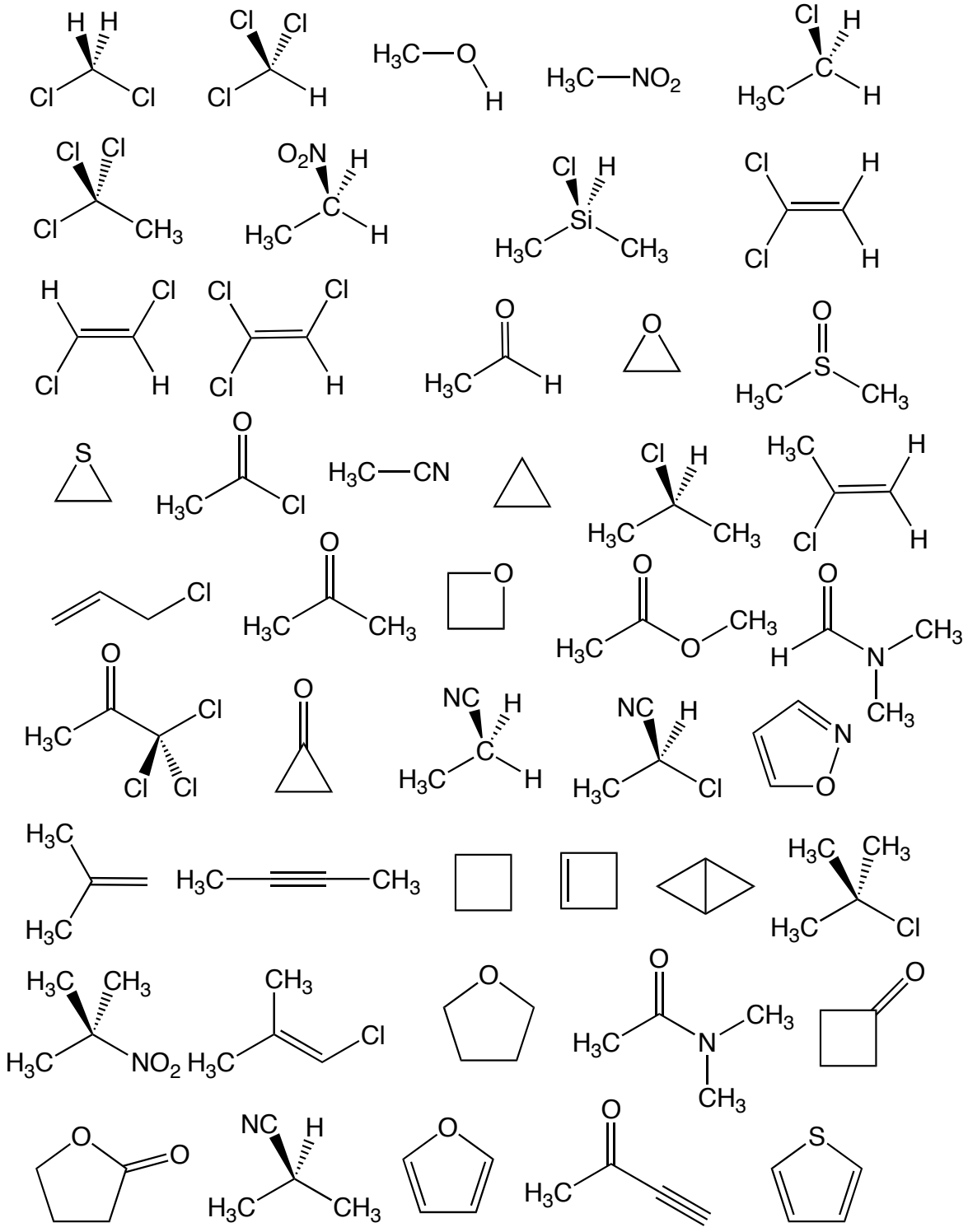
1. *Complete form of Reference 29 (Gaussian program):*

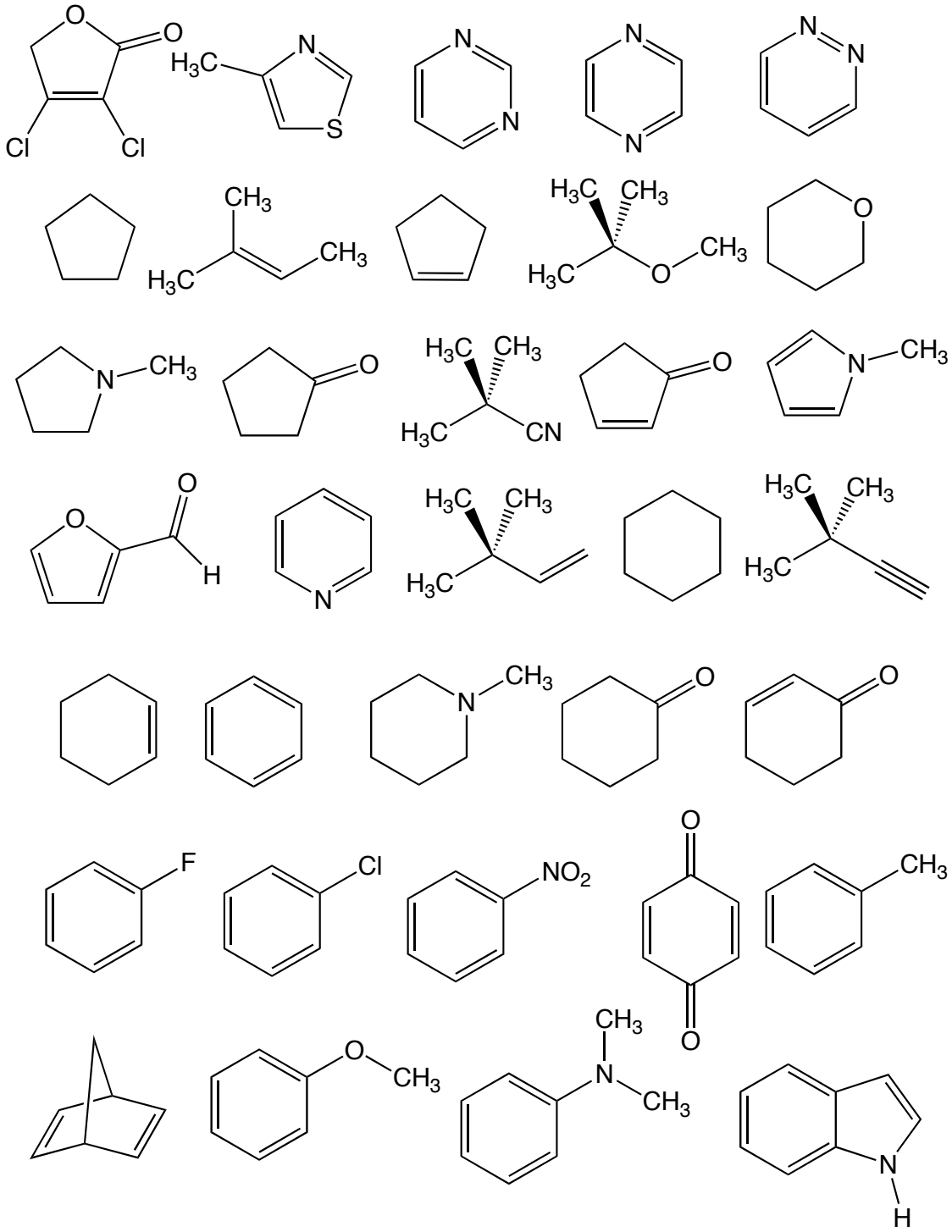
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Rev E.01, Gaussian, Inc., Wallingford CT, 2004.

2. *The 80 Molecules in the test set (cf. Reference 12), in the order in which they appear in the Excel spreadsheets that contain the full set of results (supplied as part of the Supporting Information, cf. p. S1).*



(*continued on next page)*

The 80 Molecules in the test set (cf. Reference 12), continued

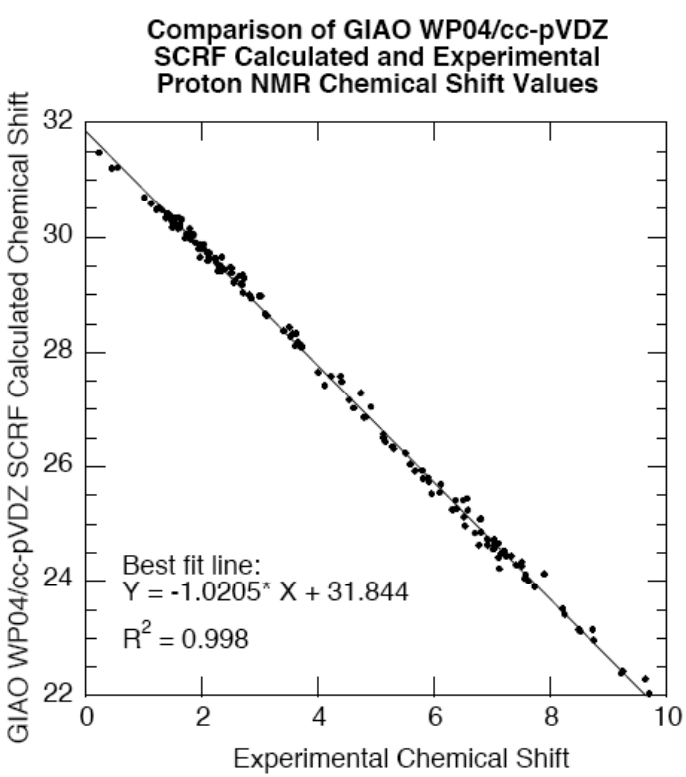


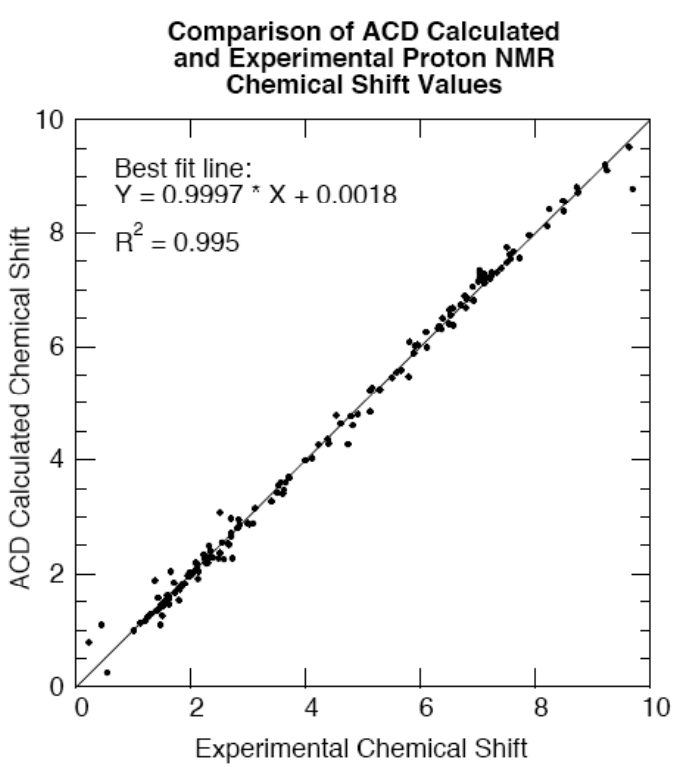
A complete Gaussian input to run a set of calculations on the entire test set is provided as a separate part of the Supporting Information.

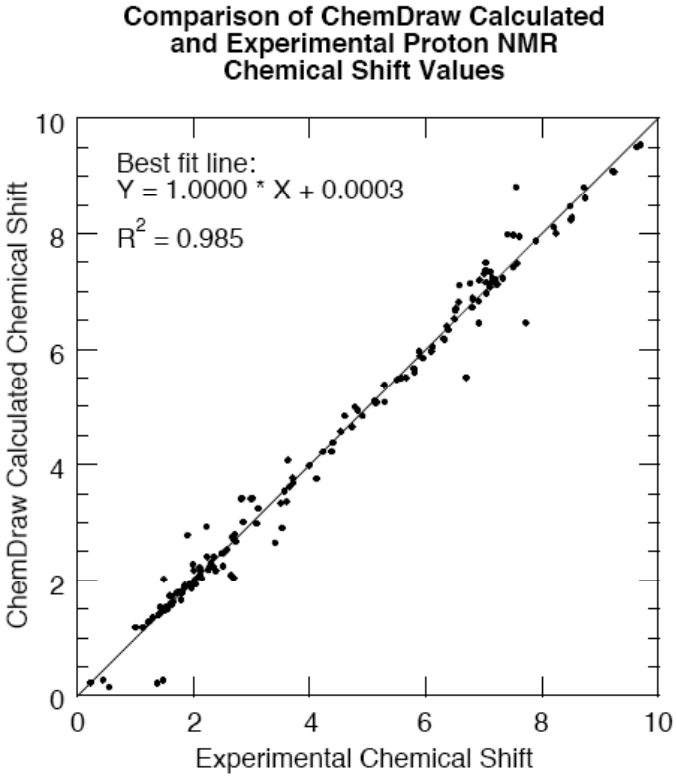
3. Results of calculations of ^{1}H NMR chemical shifts, molecules of the "probe set"

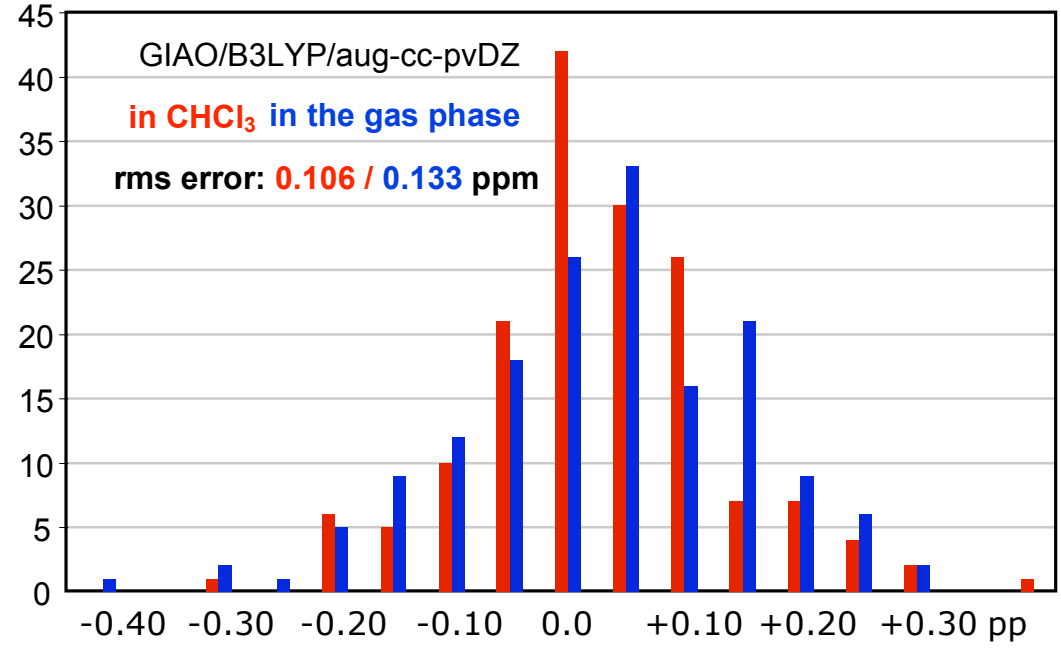
method[a]	functional[b]	basis set[c]	SCRF[d]	rms error (unscaled)	rms error (scaled)[e]	rms error (test set)
GIAO	WP04	cc-pVTZ	yes	0.180	0.134	0.112
GIAO	WP04	aug-cc-pVDZ	yes	0.186	0.113	0.103
GIAO	WP04	cc-pVDZ	yes	0.213	0.113	0.115
GIAO	WP04	6-31++G(d,p)	yes	0.154	0.119	0.121
GIAO	WP04	6-31G(d,p)	yes	0.176	0.100	0.119
GIAO	WP04	6-31G*	yes	0.164	0.079	0.120
GIAO	WP04	cc-pVTZ	no	0.228	0.128	0.124
GIAO	WP04	aug-cc-pVDZ	no	0.175	0.112	0.112
GIAO	WP04	cc-pVDZ	no	0.296	0.118	0.146
GIAO	WP04	6-31++G(d,p)	no	0.194	0.103	0.129
GIAO	WP04	6-31G(d,p)	no	0.234	0.093	0.140
GIAO	WP04	6-31G*	no	0.300	0.093	0.159
GIAO	B3LYP	cc-pVTZ	yes	0.202	0.138	0.118
GIAO	B3LYP	aug-cc-pVDZ	yes	0.239	0.122	0.106
GIAO	B3LYP	cc-pVDZ	yes	0.226	0.118	0.132
GIAO	B3LYP	6-31++G(d,p)	yes	0.190	0.122	0.132
GIAO	B3LYP	6-31G(d,p)	yes	0.199	0.098	0.162
GIAO	B3LYP	cc-pVTZ	no	0.224	0.169	0.143
GIAO	B3LYP	aug-cc-pVDZ	no	0.206	0.133	0.133
GIAO	B3LYP	cc-pVDZ	no	0.292	0.135	0.173
GIAO	B3LYP	6-31++G(d,p)	no	0.189	0.116	0.153
GIAO	B3LYP	6-31G(d,p)	no	0.236	0.107	0.188

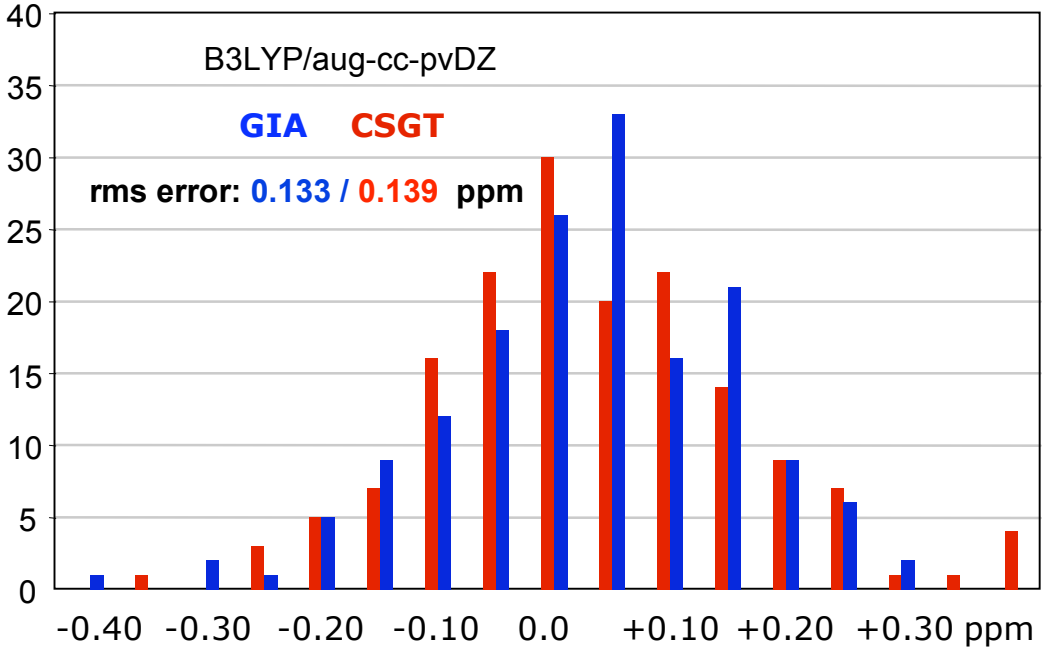
[a] Method for calculating chemical shieldings (see "Methods" section); [b] B3LYP and WP04 are hybrid functional, [c] The basis sets are denoted by their corresponding key-words in Gaussian; pVDZ and 6-31G denote doble zeta, pVTZ a triple-zeta basis sets; [d] "yes" means that chloroform was included as a solvent in a PCM-SCRF calculation, "no" refers to gas-phase calculations; [e] scaled chemical shift δ = (intercept - isotropic magnetic shielding) / slope;

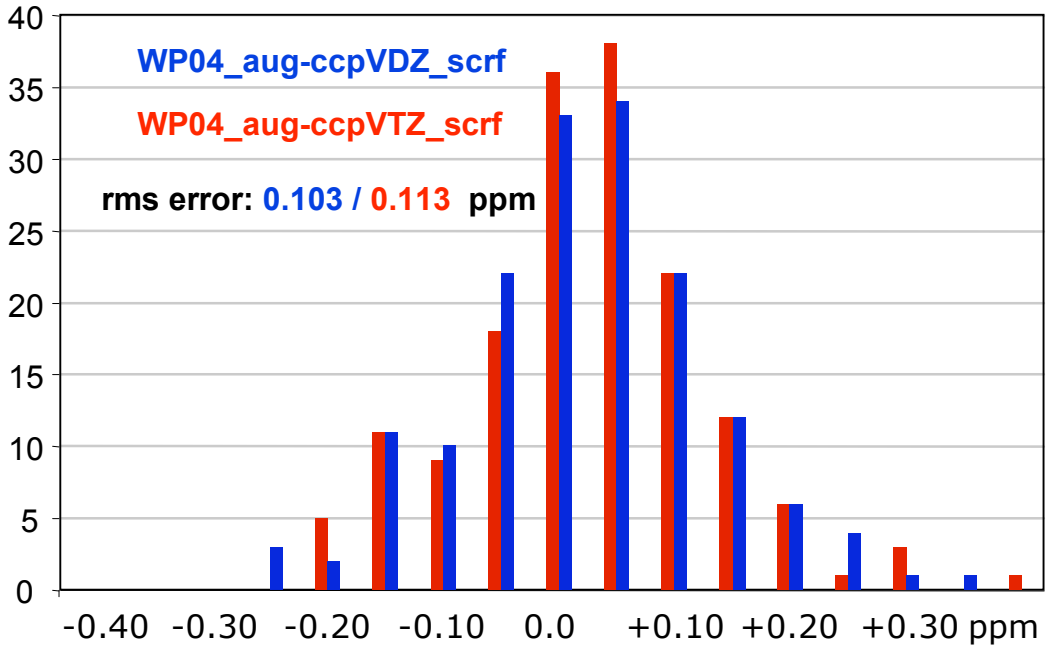

Comparison of GIAO WP04/cc-pVDZ SCRF Calculated and Experimental Proton NMR Chemical Shift Values
GIAO WP04/cc-pVDZ SCRF Calculated Chemical Shift
Experimental Chemical Shift
Best fit line:
Y = -1.0205* X + 31.844
R2 = 0.998
32
30
28
26
24
22
0
2
4
6
8
10


Comparison of ACD Calculated and Experimental Proton NMR Chemical Shift Values
ACD Calculated Chemical Shift
Experimental Chemical Shift
Best fit line:
Y = 0.9997 * X + 0.0018
R2 = 0.995
10
8
6
4
2
0
0
2
4
6
8
10


Comparison of ChemDraw Calculated and Experimental Proton NMR Chemical Shift Values
ChemDraw Calculated Chemical Shift
Experimental Chemical Shift
Best fit line:
Y = 1.0000 * X + 0.0003
R2 = 0.985
10
8
6
4
2
0
0
2
4
6
8
10


GIAO/B3LYP/aug-cc-pvDZ
in CHCl3 in the gas phase
rms error: 0.106 / 0.133 ppm
45
40
35
30
25
20
15
10
5
0
-0.40 -0.30 -0.20 -0.10 0.0 +0.10 +0.20 +0.30 pp


B3LYP/aug-cc-pvDZ
GIA CSGT
rms error: 0.133 / 0.139 ppm
40
35
30
25
20
15
10
5
0
-0.40 -0.30 -0.20 -0.10 0.0 +0.10 +0.20 +0.30 ppm


WP04_aug-ccpVDZ_scrf
WP04_aug-ccpVTZ_scrf
rms error: 0.103 / 0.113 ppm
40
35
30
25
20
15
10
5
0
-0.40 -0.30 -0.20 -0.10 0.0 +0.10 +0.20 +0.30 ppm