^{13}C NMR calculations on azepines and diazepines

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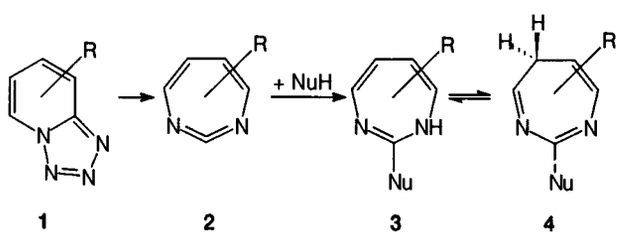
***Ab initio* and DFT calculations of ^{13}C NMR chemical shifts of 1*H*-, 2*H*- and 3*H*-azepines as well as recently synthesised 1*H*- and 5*H*-1,3-diazepines are reported. The reliabilities of the computational methods used for this purpose are evaluated by examining a large number of combinations of basis sets and geometry optimisations. Generally, the Becke3LYP/6-31+G* and HF/6-31G* or HF/6-31+G* single-point calculations based on MP2/6-31G* geometries give the best agreement with experiment (3–4 ppm deviation), better than the corresponding BLYP calculations. Localised orbital methods such as IGLO or LORG do not improve the accuracy. The ^{1}H NMR chemical shifts are also calculated, but the smaller chemical shift range for protons makes the calculated data inherently less precise. Again, Becke3LYP/6-31G* or BLYP/6-31G* with MP2/6-31G* geometries and the HF/6-311+G(3df,2p)//HF/6-31G* combination give the best results. Overall, the ^{13}C NMR calculations in particular are sufficiently precise to be a valuable tool in the identification of novel compounds of this type.**

Introduction

Recently, we reported the first syntheses of stable, monocyclic *N*-unsubstituted 1*H*-1,3-diazepines **3**.[1] It was shown that 1,3-diazacyclohepta-1,2,4,6-tetraenes **2**, which are easily accessible from tetrazoles **1**, can be trapped with nucleophiles NuH to yield the desired products **3** (Scheme 1). However,



Scheme 1

in some cases, these 1*H*-diazepines isomerise to their 5*H*-isomers **4**.

Since the 1,3-diazepines are mostly novel compounds, there is little experimental IR and NMR data available for comparison. Therefore, reliable computational data are desirable. While high level calculations of IR spectra are becoming commonplace, the calculation of chemical shifts is a fairly new method[2] which is, however, becoming more and more important because (*i*) improved computer resources allow the handling of demanding calculations necessary for NMR predictions,[3] and (*ii*) the steady improvement of methods increases the accuracy of the predictions.[4] This has led to a wealth of computational NMR chemical shift data in recent years, as is documented in the literature.[5]

As an adjunct to our experimental work on diazepines, we have evaluated the theoretical methods for calculating chemical shifts of such systems. Simple azepines have also been examined. For large systems where MP2-calculated shieldings are not (yet) feasible, the combination of a density functional method with an extensive basis set is considered to give the best results.[6] Nevertheless, additional calibration work was done to find a reliable method/basis set combination by testing molecular geometries optimised at several levels of theory with a large number of basis sets and different methods for a variety of azepines and diazepines. The basis sets employed herein were chosen to cover a wide spectrum, ranging from 'small' (6-31G*) to 'extensive' [6-311+G(3df,2p)]. The applied levels of theory are selected in the same manner.

Computational methods

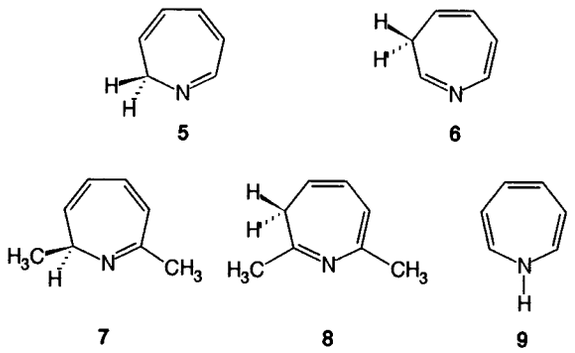
Standard *ab initio* molecular orbital calculations[7] were carried out with the GAUSSIAN 94 system of programs using the (default) GIAO method.[8] Some additional optimizations and chemical shift calculations (IGLO[3a,b] and LORG[9]) using the UniChem package were also performed.[10] Chemical shift calculations give only absolute values, which cannot be compared with the measured relative shifts. Therefore, it is necessary to include the calculation of a reference (tetramethylsilane, TMS). The structures and energies of all compounds were optimised at the HF, the BLYP, and the MP2 levels of the theory using the 6-31G* basis set, and the azepines **5**, **6** and **9** also at the Becke3LYP/6-311+G* and the DGauss–internal BLYP/TZ94AUX and BLYP/DZ94AUX levels. The application of experimental geometries is not feasible because, for the most part, there are no X-ray or other structural data available for the target molecules (except in the case of compound **11**, shown in Fig. 1 and Table 8, where a closely related experimental structure is known, and the agreement with calculated structures is quite good). Furthermore, the use of experimental structures is known usually to give only modest to poor results.[11] Single-point calculations to determine the absolute ^{13}C and ^{1}H shifts were performed using the 6-31G*, 6-31+G** or 6-311+G(3df,2p), and in some cases also the 6-311+G*, TZ94, or DZ94P, basis sets. The frozen-core approximation was employed for all correlated calculations as it is not necessary to include inner-shell orbitals.[12]

Results and discussion

The first task was to find a suitable method which allows a reliable prediction of NMR data for azepines and diazepines. Both ^{13}C and ^{1}H theoretical shifts were evaluated and compared with the available experimental data. The main emphasis is on

the ^{13}C data, as the calculation of these values is considered to be more reliable.[4]

The first molecules investigated here are the simple azepines (**5**, **6** and **9**) and the 2,7-dimethyl-substituted derivatives **7** and **8**.



Steglich *et al*. recently reported the first NMR data for 2*H*-azepine (**5**).[13] Comparison of calculated and experimental relative shifts gives a good indication of the accuracy of the theoretical predictions (Table 1). These data suggest that the best agreement is obtained with the MP2 geometry, making use of HF or Becke3LYP single-point calculations with small or medium basis sets. The same is true for the HF single-point calculations with HF geometry. The average error for the six carbon atoms is around 3–4 ppm. Surprisingly, the error margins for BLYP calculations (employing both BLYP and MP2 geometries) are by far the largest. A very large basis set does not improve the reproduction of the experimental NMR data; increased complexity of the basis set leads to a low-field shift of the calculated values. HF-based calculations (*i.e.* Hartree–Fock single-point NMR calculations for any geometry calculation) do not, however, give the correct ordering of carbon atoms C3, C4 and C6, which all lie within a 4 ppm range.

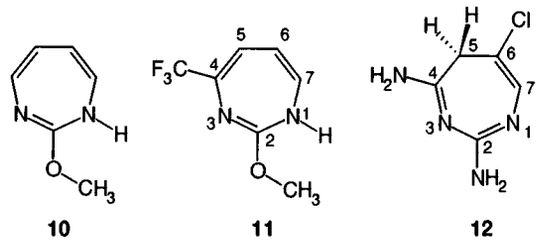
The ^{13}C and ^{1}H NMR spectra of the 3*H*-azepine **6** were reported by Vogel *et al*.[14] However, no assignment of the ^{13}C NMR signals was made. Using the calculated shifts (Table 2), it is possible to assign the experimentally obtained values for the carbon atoms with a high degree of accuracy. Comparison with the relative shifts for another 3*H*-azepine (2,7-dimethyl-3*H*-azepine **8**, see below) eliminates any remaining uncertainties. As in the case of **5**, the HF-based methods with a small to medium basis set give very good results for **6**, with an average error of *ca*. 3 ppm. The best agreement was achieved with a BLYP/6-311+G(3df,2p)//BLYP/6-31G* calculation, giving values almost identical with the experimental ones for all carbon atoms.

Both the 2*H*- and 3*H*-dimethylazepines **7** and **8** have been described by Steglich *et al*., together with their NMR data.[15] In particular the calculated ^{13}C NMR data for the dimethyl-2*H*-azepine **7** (Table 3) are in excellent agreement with the measured values, having again the same variety of methods reproducing the spectrum with an average error of 3 ppm or less. The only minor inconsistency is the ordering of atoms C3 and C5, which are separated by only 0.2 ppm. The theoretical values for these two carbon atoms are also close together, usually within 2 ppm. The ^{13}C NMR spectrum of the 3*H* isomer **8** (Table 4) was also calculated with high accuracy. Despite giving some of the smallest average errors (*ca*. 3 ppm), the HF-based methods sometimes predict an incorrect ordering of carbon atoms. The Becke3LYP/6-31+G**//MP2/6-31G* single-point calculation also turns out to be reliable. The best results for both dimethylazepines **7** and **8** were obtained with the BLYP/6-311+G(3df,2p)//BLYP/6-31G* combination, as in the case of **6**.

The NMR data for 1*H*-azepine (**9**, Table 5) were first reported by Vogel *et al*.[14] It is obvious from the calculated shifts that the prediction of the relative ordering of the carbon atoms in **9** is particularly difficult. With the exception of the data based on the HF/6-31G*-optimised structure, all other methods, especially the density functional methods, give erroneous predictions. For this molecule, the HF single-point calculations (again using both HF and MP2 geometries) give reasonable results, although the average error is still about 7 ppm. One likely explanation is that the structure of 1*H*-azepine in solution is significantly different from that calculated for the gas phase, possibly due to dynamic ring inversion in **9** and/or hydrogen bonding in the liquid phase. Optimization of **9** in a solvent sphere does not lead to any significant geometry change, and hence the shifts are almost identical.[16] The presence of the valence-tautomeric benzene imine can also be ruled out.[17]

Some representatives of the diazepines[1,18] have also been studied. These molecules bear various electronically and sterically demanding substituents and might therefore test the quality of the calculated chemical shifts.

2-Methoxy-1*H*-1,3-diazepine (**10**) is the least substituted



1,3-diazepine synthesised so far.[18] Once again, the computational methods regarded as most reliable (*vide supra*), reproduce the NMR spectrum of **10** the best (Table 6). The average error is 3–4 ppm. It is worth mentioning that only the DFT methods predict the same assignment as made experimentally, whereas HF-based calculations cause an interchange of the values for C5 and C6.

The fully characterised 2-methoxy-4-trifluoromethyl-1*H*-1,3-diazepine **11** (Table 7) was studied next. The data again suggest that the best agreement is found with HF- and Becke3LYP single-point calculations (small and medium basis sets) making use of the MP2 geometry. Disregarding the difficulty of reproducing the value for the trifluoromethyl carbon atom (deviation *ca*. 10 ppm), the average error for the remaining six carbon atoms is under 3 ppm. The error margins for BLYP calculations are much larger.

The only experimental structural data available for the molecules reported herein, the X-ray structure of the 1-benzoyl derivative of **11**, is compared with selected calculated structural data in Table 8 and Fig. 1. These data clearly illustrate the superior performance of MP2 geometry calculations. Hence, it would appear to be legitimate to make use of these calculated structures in predictive chemical shift computations.

For 6-chloro-5*H*-1,3-diazepine-2,4-diamine (**12**), the best method is again Becke3LYP/6-31+G**//MP2/6-31-G* (Table 9). All methods have some difficulties explaining the unusual high-field shift of C7.

One of the reasons for investigating calculated chemical shifts was the difficulty of clearly distinguishing isomers by using common experimental methods. Thus, 2-diisopropylamino(chloro)methoxy-1,3-diazepine could exist as either the 4*H*- (**13**) or the 5*H*-tautomer **14**.

For computational reasons, we neglected the isopropyl substituents on the amine function (R = H, **13′** and **14′**). Table 10 gives the calculated and experimental values for the two plausible isomers in question.

Based on data for other diazepines, the experimental ^{13}C NMR shift values of 39.5, 55.0, 102.8, 135.9, 153.5 and 158.5 ppm can be assigned to the saturated carbon atoms C4 (**13′**) or C5 (**14′**), the methoxy carbon C9, the chlorine-bearing carbons

Table 1 Experimental and calculated chemical shifts of 2*H*-azepine **5**, including error margins for ^{13}C NMR calculations

Method	Geometry	C2	C3	C4	C5	C6	C7	H2	H3	H4	H5	H6	H7	Error[a]	Error[b]
Experiment		50.9	126.7	129.3	136.7	130.8	158.5	3.61	5.69	6.35	6.74	6.60	7.84		
HF/6-31G*	HF/6-31G*	44.3	128.5	122.5	134.7	126.7	152.9	2.74/4.40	5.89	6.18	6.73	6.39	7.84	4.5	24
HF/6-31 + G**		45.6	130.7	124.0	136.1	127.6	154.3	2.69/4.39	6.07	6.35	6.93	6.63	7.85	3.8	17
HF/6-311 + G(3df,2p)		47.1	138.6	131.4	143.9	134.3	163.2	2.76/4.30	5.99	6.25	6.86	6.57	7.76	5.5	41
BLYP/6-31G*	BLYP/6-31G*	53.9	115.9	119.6	126.4	122.7	147.2	3.05/4.76	5.25	6.30	6.45	6.30	7.85	8.9	87
BLYP/6-31 + G**		57.7	119.8	123.5	130.0	125.7	151.8	3.05/4.94	5.62	6.68	6.82	6.72	8.12	6.3	41
BLYP/6-311 + G(3df,2p)		60.4	130.2	134.7	141.2	136.2	164.8	3.03/4.98	5.62	6.68	6.88	6.78	8.19	5.8	37
HF/6-31G*	MP2/6-31G*	49.6	130.8	123.8	139.2	128.6	162.2	2.26/4.61	6.20	6.44	7.15	6.71	8.25	3.7	15
HF/6-31 + G**		48.1	133.1	125.3	140.4	129.4	163.4	2.16/4.58	6.37	6.60	7.34	6.96	8.31	3.9	17
HF/6-311 + G(3df,2p)		49.7	140.9	132.3	148.3	135.8	172.6	2.27/4.47	6.30	6.48	7.25	6.87	8.18	8.2	96
BLYP/6-31G*		54.0	117.2	119.7	126.8	123.5	148.0	2.64/4.82	5.56	6.46	6.72	6.59	7.98	8.3	75
BLYP/6-31 + G**		57.6	121.2	123.6	130.3	126.5	152.7	2.58/4.95	5.90	6.80	7.06	6.99	8.22	5.7	33
BLYP/6-311 + G(3df,2p)		60.3	131.6	134.8	141.5	136.9	165.7	2.57/4.99	5.91	6.80	7.13	7.06	8.29	6.3	42
Becke3LYP/6-31G*		52.7	121.2	121.9	130.6	126.0	152.3	2.52/4.81	5.70	6.49	6.84	6.66	8.04	5.3	32
Becke3LYP/6-31 + G**		55.6	124.5	125.1	133.5	128.4	156.0	2.44/4.88	5.98	6.78	7.14	7.01	8.23	3.2	11
Becke3LYP/6-311 + G(3df,2p)		58.1	134.7	135.8	144.3	138.3	168.3	2.46/4.89	5.97	6.75	7.17	7.05	8.26	7.7	61
Becke3LYP/6-311 + G*	Becke3LYP/ 6-311 + G*	55.8	132.9	134.8	142.5	136.9	164.4	2.94/4.90	5.72	6.57	6.91	6.70	8.13	5.7	33
Becke3LYP/6-311 + G(3df,2p)		57.1	134.1	135.6	143.6	137.8	165.6	2.92/4.87	5.77	6.65	6.99	6.85	8.16	6.8	46
BLYP/TZ94 (IGLO)	BLYP/ TZ94AUX	49.9	120.0	125.1	128.7	126.1	163.1							4.9	28
BLYP/TZ94 (LORG)		57.9	130.2	145.1	144.8	143.1	169.9							9.7	109
BLYP/DZ94P (IGLO)	BLYP/ DZ94AUX	54.0	118.5	123.3	133.9	126.7	153.2							4.9	28
BLYP/DZ94P (LORG)		52.8	119.3	123.4	133.4	126.3	150.8							5.1	31

[a] Average error = [Σ|(calc − exp)|]/*n*, sum of deviation of calculated values from experimental ones, divided by the number of carbon atoms. [b] Average quadratic deviation = (Σ|(calc. − exp.)|^2)/*n*, sum of quadratic deviation of calculated values from experimental ones, divided by the number of carbon atoms.

Table 2 Experimental and calculated chemical shifts of 3*H*-azepine **6**, including error margins for ^{13}C NMR calculations

Method	Geometry	C2	C3	C4	C5	C6	C7	H2	H3	H4	H5	H6	H7	Error[a]	Error[b]
Experiment		136.4	34.3	113.3	127.3	117.5	141.0	6.2–6.7	2.42	5.35	6.2–6.7	6.2–6.7	7.55		
HF/6-31G*	HF/6-31G*	142.8	29.1	113.4	124.2	113.6	139.8	7.01	2.76/1.38	5.28	6.31	5.94	7.57	3.3	16
HF/6-31 + G**		144.9	30.3	115.2	125.9	114.1	141.8	7.01	2.86/1.45	5.42	6.46	6.15	7.71	3.3	18
HF/6-311 + G(3df,2p)		153.4	31.1	122.2	133.8	120.0	149.9	6.99	2.93/1.53	5.34	6.34	6.09	7.55	7.8	84
BLYP/6-31G*	BLYP/6-31G*	121.6	31.5	100.6	113.5	105.9	127.9	5.80	2.62/1.02	4.34	5.74	5.50	6.72	11.5	149
BLYP/6-31 + G**		125.9	34.3	104.4	117.6	108.7	132.3	6.08	2.84/1.15	4.66	6.08	5.87	7.08	7.8	73
BLYP/6-311 + G(3df,2p)		136.3	35.9	113.3	128.5	118.0	143.5	6.14	2.95/1.11	4.64	6.09	5.91	7.14	1.0	2
HF/6-31G*	MP2/6-31G*	135.7	30.5	107.6	127.2	114.6	145.1	6.74	3.29/0.55	5.24	6.73	6.29	8.05	2.9	12
HF/6-31 + G**		137.7	31.7	109.5	128.9	115.0	147.0	6.77	3.37/0.62	5.39	6.87	6.50	8.21	3.0	11
HF/6-311 + G(3df,2p)		145.7	32.6	115.8	136.8	120.7	155.1	6.75	3.41/0.70	5.32	6.73	6.41	8.03	6.8	66
BLYP/6-31G*		114.2	37.0	97.4	118.6	108.5	132.5	5.84	3.65/0.66	4.79	6.59	6.22	7.49	11.2	163
BLYP/6-31 + G**		118.5	39.7	101.3	122.7	111.3	137.2	6.11	3.82/0.77	5.10	6.89	6.44	7.84	8.3	95
BLYP/6-311 + G(3df,2p)		127.9	41.5	109.5	133.9	120.7	148.6	6.17	3.92/0.74	5.09	6.89	6.58	7.91	6.2	42
Becke3LYP/6-31G*		119.8	35.9	100.8	121.5	111.3	136.7	6.03	3.60/0.61	4.90	6.64	6.29	7.66	7.9	88
Becke3LYP/6-31 + G**		123.4	38.0	104.1	124.9	113.4	140.5	6.23	3.74/0.70	5.16	6.89	6.57	7.95	5.5	49
Becke3LYP/6-311 + G(3df,2p)		132.9	39.7	112.3	135.8	122.3	151.6	6.27	3.82/0.69	5.14	6.86	6.59	7.97	5.6	41
Becke3LYP/6-311 + G*	Becke3LYP/ 6-311 + G*	133.1	38.7	113.4	134.5	121.2	148.3	6.30	3.68/1.12	5.05	6.68	6.31	7.77	4.3	25
Becke3LYP/6-311 + G(3df,2p)		134.3	39.5	114.2	135.3	121.9	149.7	6.27	3.72/1.08	5.06	6.76	6.44	7.84	4.9	32
BLYP/TZ94 (IGLO)	BLYP/ TZ94AUX	130.7	32.0	99.6	123.6	103.4	137.0							7.2	75
BLYP/TZ94 (LORG)		141.7	45.8	110.6	144.1	122.0	150.1							8.4	93
BLYP/DZ94P (IGLO)	BLYP/ DZ94AUX	119.4	36.1	100.4	123.6	112.6	142.0							6.9	83
BLYP/DZ94P (LORG)		119.1	35.9	100.6	123.6	112.0	139.3							7.1	85

[a,b] Footnotes as for Table 1.

Table 3 Experimental and calculated chemical shifts of 2,7-dimethyl-2*H*-azepine **7**, including error margins for ^{13}C NMR calculations

Method	Geometry	C2	C3	C4	C5	C6	C7	2-CH_3	7-CH_3	H2	H3	H4	H5	H6	2-CH_3	7-CH_3	Error[a]	Error[b]
Experiment		54.8	135.5	126.2	135.7	133.2	163.1	21.8	24.1	2.81	5.59	6.17	6.68	6.77	1.58	2.10		
HF/6-31G*	HF/6-31G*	47.4	136.3	120.1	134.3	128.1	158.4	22.6	24.6	2.72	5.87	6.01	6.70	6.51	1.54	1.97	3.3	18
HF/6-31 + G**		48.6	138.6	121.4	135.5	128.7	160.6	23.0	25.3	2.53	5.94	6.14	6.85	6.71	1.51	2.02	3.0	13
HF/6-311 + G(3df,2p)		50.3	147.0	128.6	143.3	135.7	169.4	24.3	26.9	2.65	5.88	6.06	6.77	6.66	1.46	1.97	5.0	34
BLYP/6-31G*	BLYP/6-31G*	52.2	123.0	112.4	121.9	121.3	144.5	19.4	20.5	2.83	4.93	5.52	5.93	6.15	0.89	1.36	9.9	131
BLYP/6-31 + G**		55.9	127.3	116.2	125.1	123.8	149.3	21.2	23.2	2.66	5.15	5.84	6.28	6.53	0.92	1.49	6.8	70
BLYP/6-311 + G(3df,2p)		58.2	138.4	126.6	135.9	134.1	161.5	21.2	24.0	2.62	5.13	5.83	6.32	6.59	0.95	1.52	1.3	3
HF/6-31G*	MP2/6-31G*	49.6	139.3	121.3	139.3	130.2	168.2	22.1	24.1	2.26	6.21	6.26	7.12	6.83	1.63	2.15	3.2	14
HF/6-31 + G**		50.8	141.8	122.4	140.4	130.6	170.4	22.4	24.8	2.05	6.27	6.39	7.27	7.04	1.62	2.20	3.7	19
HF/6-311 + G(3df,2p)		52.6	150.0	129.5	148.2	137.4	179.5	23.6	26.1	2.18	6.21	6.28	7.16	6.96	1.53	2.14	7.1	85
BLYP/6-31G*		58.4	126.3	116.9	127.0	125.4	153.8	22.9	23.7	2.72	5.61	6.28	6.70	6.86	1.54	2.07	6.2	51
BLYP/6-31 + G**		62.1	130.8	120.6	130.2	128.0	158.7	24.1	26.3	2.53	5.81	6.56	7.00	7.21	1.54	2.18	4.7	24
BLYP/6-311 + G(3df,2p)		64.8	141.9	131.3	141.3	138.4	171.7	24.7	27.3	2.52	5.81	6.55	7.05	7.28	1.56	2.22	5.9	40
Becke3LYP/6-31G*		56.9	130.1	119.3	130.8	127.9	158.0	22.7	24.0	2.60	5.74	6.31	6.81	6.87	1.58	2.10	3.9	20
Becke3LYP/6-31 + G**		59.8	134.0	122.2	133.4	129.9	162.1	23.6	26.0	2.40	5.90	6.55	7.07	7.19	1.56	2.18	2.6	8
Becke3LYP/6-311 + G(3df,2p)		62.5	144.8	132.5	144.2	139.9	174.7	24.4	27.2	2.41	5.88	6.52	7.09	7.22	1.56	2.20	6.9	56

[a,b] Footnotes as for Table 1.

Table 4 Experimental and calculated chemical shifts of 2,7-dimethyl-3*H*-azepine **8**, including error margins for ^{13}C NMR calculations

Method	Geometry	C2	C3	C4	C5	C6	C7	2-CH_3	7-CH_3	H3	H4	H5	H6	2-CH_3	7-CH_3	Error[a]	Error[b]
Experiment		147.1	37.8	112.8	127.3	113.2	149.3	26.1	24.2	2.15	5.13	6.19	5.96	2.14	2.12		
HF/6-31G*	HF/6-31G*	153.0	31.7	112.0	125.7	108.6	148.4	26.6	24.9	1.51/2.69	5.21	6.21	5.62	1.99	2.00	2.6	12
HF/6-31 + G**		155.9	32.4	113.5	127.3	197.8	152.3	26.8	25.3	1.59/2.78	5.34	6.33	5.79	2.05	2.08	3.1	18
HF/6-311 + G(3df,2p)		164.8	33.3	120.5	135.4	113.1	160.6	28.7	26.4	1.68/2.82	5.26	6.22	5.77	2.04	2.01	6.8	74
BLYP/6-31G*	BLYP/6-31G*	132.0	33.2	100.5	113.5	102.6	136.4	23.1	22.1	1.18/2.60	4.40	5.56	5.31	1.35	1.36	9.3	110
BLYP/6-31 + G**		137.1	35.7	103.8	117.7	104.2	142.5	25.1	23.7	1.29/2.78	4.66	5.87	5.65	1.52	1.51	6.0	51
BLYP/6-311 + G(3df,2p)		147.6	37.2	112.7	128.4	112.7	153.7	26.9	24.8	1.28/2.89	4.64	5.87	5.72	1.56	1.56	1.1	3
HF/6-31G*	MP2/6-31G*	150.1	33.4	109.0	129.0	110.2	154.2	24.9	24.7	0.93/3.18	5.22	6.59	5.90	2.09	2.17	2.8	10
HF/6-31 + G**		153.6	34.2	110.7	130.5	109.3	158.0	25.0	25.1	1.03/3.25	5.31	6.71	6.07	2.17	2.27	3.8	20
HF/6-311 + G(3df,2p)		162.2	35.3	117.2	138.7	114.4	166.5	26.7	26.0	1.14/3.26	5.23	6.56	6.02	2.16	2.19	6.8	86
BLYP/6-31G*		128.9	39.3	100.5	118.7	106.6	141.7	25.3	25.4	1.07/3.57	4.88	6.37	5.99	1.95	2.02	7.1	83
BLYP/6-31 + G**		134.2	41.8	104.1	122.9	108.3	147.9	27.2	27.1	1.17/3.70	5.10	6.64	6.29	2.11	2.16	5.0	39
BLYP/6-311 + G(3df,2p)		144.3	43.6	112.6	133.9	117.0	159.3	29.0	28.3	1.19/3.79	5.10	6.63	6.35	2.16	2.22	4.5	28
Becke3LYP/6-31G*		134.4	38.4	103.6	121.9	109.0	145.7	25.5	25.5	1.01/3.51	4.97	6.44	6.01	1.99	2.07	4.7	39
Becke3LYP/6-31 + G**		139.0	40.4	106.6	125.4	109.9	151.1	26.9	26.7	1.10/3.62	5.14	6.66	6.28	2.12	2.19	3.4	17
Becke3LYP/6-311 + G(3df,2p)		149.2	42.1	115.0	136.2	118.2	162.4	28.7	27.9	1.13/3.69	5.13	6.62	6.31	2.15	2.21	5.2	40.0

[a,b] Footnotes as for Table 1.

Table 5 Experimental and calculated chemical shifts of 1*H*-azepine **9**, including error margins for ^{13}C NMR calculations

Method	Geometry	C2,7	C3,6	C4,5	H2,7	H3,6	H4,5	Error[a]	Error[b]
Experiment		138.0	113.0	132.3	5.22	4.69	5.57		
HF/6-31G*	HF/6-31G*	127.9	122.3	127.7	5.85	6.00	6.50	8.0	70
HF/6-31 + G**		129.6	123.3	129.0	5.97	6.20	6.72	7.4	63
HF/6-311 + G(3df,2p)		137.6	130.7	136.5	5.84	6.15	6.65	7.4	110
BLYP/6-31G*	BLYP/6-31G*	109.3	117.7	120.6	5.32	6.32	6.45	15.3	328
BLYP/6-31 + G**		113.3	121.1	124.3	5.69	6.69	6.83	12.6	247
BLYP/6-311 + G(3df,2p)		123.5	132.1	135.2	5.64	6.74	6.89	12.2	194
HF/6-31G*	MP2/6-31G*	121.2	121.0	130.2	5.98	6.40	6.98	9.0	117
HF/6-31 + G**		123.0	122.1	131.3	6.14	6.59	7.19	8.4	103
HF/6-311 + G(3df,2p)		130.5	129.2	138.7	6.01	6.52	7.10	10.0	120
BLYP/6-31G*		108.4	117.0	120.4	5.53	6.46	6.66	15.2	344
BLYP/6-31 + G**		112.5	120.4	124.1	5.89	6.79	7.02	13.7	257
BLYP/6-311 + G(3df,2p)		122.3	131.2	134.9	5.89	6.84	7.09	12.2	195
Becke3LYP/6-31G*		112.1	119.2	123.8	5.62	6.48	6.78	13.5	261
Becke3LYP/6-31 + G**		115.5	121.9	126.8	5.91	6.76	7.08	12.3	205
Becke3LYP/6-311 + G(3df,2p)		125.2	132.3	137.2	5.85	6.79	7.12	12.3	186
Becke3LYP/6-311 + G*	Becke3LYP/6-311 + G*	128.5	133.6	136.5	5.83	6.51	6.83	11.4	177
Becke3LYP/6-311 + G(3df,2p)		129.5	134.2	137.6	5.75	6.68	6.95	11.7	183
BLYP/TZ94 (IGLO)	BLYP/TZ94AUX	126.7	128.2	122.9				12.0	149
BLYP/TZ94 (LORG)		138.4	147.9	138.7				13.9	421
BLYP/DZ94P (IGLO)	BLYP/DZ94AUX	126.7	128.2	122.9				9.3	101
BLYP/DZ94P (LORG)		138.4	147.9	138.7				13.7	206

[a,b] Footnotes as for Table 1.

Table 6 Experimental and calculated chemical shifts of 2-methoxy-1*H*-1,3-diazepine **10**, including error margins for ^{13}C NMR calculations

Method	Geometry	C2	C4	C5	C6	C7	C9	H4	H5	H6	H7	CH_3	Error[a]	Error[b]
Experiment		155.2	139.1	116.7	112.7	130.1	55.5	6.20	5.33	5.04	5.40	3.70		
HF/6-31G*	HF/6-31G*	151.3	138.9	110.1	110.6	124.7	49.5	6.31	4.88	4.82	5.21	3.46	4.0	21
HF/6-31 + G**		153.8	140.4	110.4	111.7	126.5	49.7	6.46	5.16	5.10	5.39	3.49	3.3	16
HF/6-311 + G(3df,2p)		163.4	148.6	116.1	118.3	134.2	51.9	6.31	5.11	5.07	5.36	3.39	5.3	36
BLYP/6-31G*	BLYP/6-31G*	140.2	132.9	110.0	106.5	117.5	55.6	5.93	4.79	4.57	4.65	3.49	7.8	84
BLYP/6-31 + G**		146.3	137.1	112.6	110.1	122.3	58.1	6.42	5.28	5.04	5.11	3.76	4.7	29
BLYP/6-311 + G(3df,2p)		158.8	148.3	121.7	119.8	132.9	61.4	6.45	5.35	5.13	5.21	3.76	5.6	37
HF/6-31G*	MP2/6-31G*	155.3	143.7	113.5	116.4	126.2	52.9	6.91	5.45	5.45	5.60	3.70	3.0	11
HF/6-31 + G**		157.9	145.2	113.6	117.7	128.3	53.1	7.12	5.72	5.69	5.79	3.74	3.5	15
HF/6-311 + G(3df,2p)		167.3	153.1	119.3	124.4	135.9	55.5	6.89	5.63	5.62	5.73	3.63	7.7	87
BLYP/6-31G*		140.2	134.4	110.4	108.3	118.0	55.6	6.40	5.29	5.06	5.13	3.58	7.1	75
BLYP/6-31 + G**		146.3	138.6	112.9	112.1	122.8	58.1	6.86	5.72	5.47	5.56	3.81	3.4	26
BLYP/6-311 + G(3df,2p)		158.9	149.8	122.1	122.0	133.3	61.3	6.89	5.79	5.54	5.65	3.82	6.3	48
Becke3LYP/6-31G*		144.9	137.9	112.7	111.3	121.3	55.4	6.53	5.37	5.17	5.22	3.60	4.3	34
Becke3LYP/6-31 + G**		150.0	141.2	114.5	114.4	125.3	57.3	6.91	5.75	5.52	5.57	3.81	3.0	11
Becke3LYP/6-311 + G(3df,2p)		162.4	152.1	123.2	123.9	135.6	60.3	6.89	5.79	5.57	5.57	3.76	8.0	73

[a,b] Footnotes as for Table 1.

Table 7 Experimental and calculated chemical shifts of 2-methoxy-4-trifluoromethyl-1*H*-1,3-diazepine **11**, including error margins for ^{13}C NMR calculations

Method	Geometry	C2	C4	C5	C6	C7	C9	C10	H1	H5	H6	H7	CH_3	Error[a]	Error[b]
Experiment		158.0	138.4	117.3	109.8	132.9	56.1	121.2	4.80	5.84	4.94	5.45	3.73		
HF/6-31G*	HF/6-31G*	153.0	138.1	113.9	106.8	128.5	50.2	106.4	2.91	5.68	4.81	5.41	3.57	5.2	45
HF/6-31 + G**		155.5	139.7	114.1	107.5	130.3	50.5	107.5	3.67	5.96	5.04	5.58	3.60	4.4	32
HF/6-311 + G(3df,2p)		165.1	146.9	119.4	113.9	138.0	52.6	110.5	3.74	5.93	5.02	5.53	3.49	5.9	42
BLYP/6-31G*	BLYP/6-31G*	142.9	135.0	112.0	104.3	121.4	56.2	130.1	3.23	5.25	4.49	4.75	3.55	7.1	73
BLYP/6-31 + G**		149.1	138.8	114.8	107.6	126.5	59.1	134.9	4.20	5.90	4.95	5.24	3.84	5.3	46
BLYP/6-311 + G(3df,2p)		161.6	149.4	123.3	116.6	137.2	62.2	142.2	4.30	6.02	5.06	5.33	3.83	8.4	102
HF/6-31G*	MP2/6-31G*	158.9	142.3	118.7	113.4	131.1	50.8	111.3	3.63	6.35	5.47	5.84	3.83	3.8	23
HF/6-31 + G**		161.2	143.7	118.9	114.3	133.2	54.0	113.3	4.32	6.62	5.68	6.01	3.86	3.5	18
HF/6-311 + G(3df,2p)		170.7	150.7	124.3	120.7	140.8	56.4	115.4	4.31	6.56	5.61	5.93	3.74	8.1	83
BLYP/6-31G*		144.0	137.1	111.5	107.5	121.0	56.3	127.3	3.60	5.79	5.06	5.22	3.66	5.9	59
BLYP/6-31 + G**		150.1	140.7	114.3	111.0	126.0	59.2	131.7	4.50	6.38	5.45	5.67	3.91	5.0	35
BLYP/6-311 + G(3df,2p)		162.9	151.5	122.7	120.4	136.7	62.2	138.9	4.56	6.51	5.56	5.75	3.90	8.8	100
Becke3LYP/6-31G*		148.8	139.6	114.8	110.1	124.8	56.1	124.8	3.63	5.95	5.18	5.34	3.70	3.6	25
Becke3LYP/6-31 + G**		152.9	142.5	116.9	112.9	129.0	58.3	128.6	4.46	6.45	5.51	5.71	3.88	3.6	17
Becke3LYP/6-311 + G(3df,2p)		166.4	152.8	125.0	121.9	139.4	61.2	134.7	4.50	5.59	6.54	5.76	3.85	9.7	104
BLYP/TZ94 (IGLO)	BLYP/TZ94AUX	108.8	99.4	100.3	97.0	114.8	83.7	54.3						32.9	1421
BLYP/TZ94 (LORG)		111.2	102.6	125.2	122.9	137.3	98.2	95.6						25.1	879
BLYP/DZ94P (IGLO)	BLYP/DZ94AUX	101.5	109.6	102.1	98.3	126.0	78.1	88.3						24.8	857
BLYP/DZ94P (LORG)		104.6	111.6	106.3	102.6	124.5	82.2	90.1						23.4	780

[a,b] Footnotes as for Table 1.

Table 8 Selected geometrical data for 2-methoxy-4-trifluoromethyl-1*H*-1,3-diazepine **11**[a]

	Experimental[b]	HF/6-31G*	MP2/6-31G*	BLYP/6-31G*
Bond lengths				
N1–C2	142.2	138.5	140.9	142.6
C2–N3	126.8	125.6	128.2	128.5
N3–C4	138.8	139.6	139.8	140.8
C4–C5	134.8	132.5	135.5	136.3
C5–C6	143.2	146.7	145.1	146.2
C6–C7	131.4	132.0	134.7	135.5
C7–N1	142.6	141.2	142.5	143.4
C2–O8	132.8	132.0	134.6	136.0
O8–C9	143.7	141.9	144.3	145.6
C4–C10	148.8	150.7	150.1	151.9
Bond angles				
N1–C2–N3	125.2	128.3	126.7	128.0
C2–N3–C4	120.5	123.0	119.8	128.1
N3–C4–C5	127.2	129.1	128.1	128.5
C4–C5–C6	124.5	124.2	123.3	124.7
C5–C6–C7	123.9	124.1	123.1	124.9
C6–C7–N1	121.2	124.7	122.1	124.1
C7–N1–C2	113.4	119.5	113.1	116.6

[a] Bond lengths in pm, bond angles in degrees. [b] Experimental X-ray data for the 1-benzoyl derivative of **11** (ref. 1).

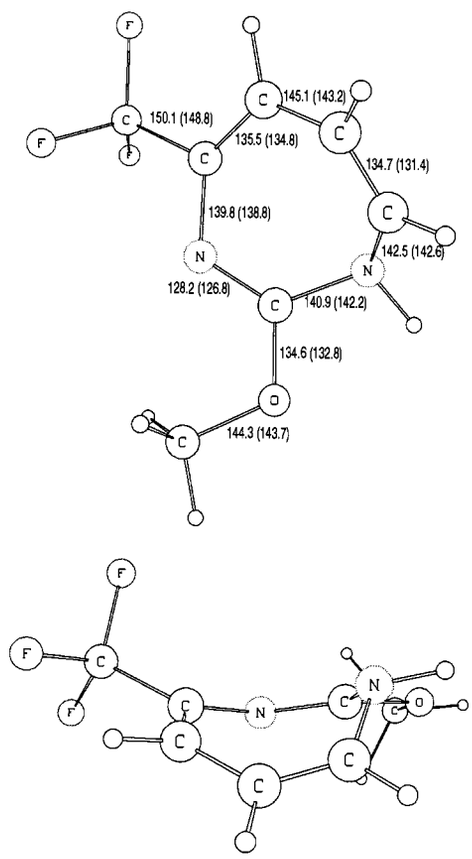
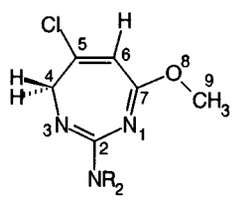


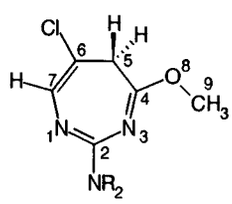
Fig. 1 Calculated structure of **11** (MP2/6-31G*//MP2/6-31G*). Experimental bond lengths (in ppm) for the 1-benzoyl derivative are given in parentheses. For bond angles, see Table 8.

C5 (**13′**) or C6 (**14′**), C6 (**13′**) or C7 (**14′**), the methoxy-bearing carbon C7 (**13′**) or C4 (**14′**) and the guanidine carbon C2, respectively.

From the results in Table 10, it is obvious that the calculated spectrum of **14′** agrees very well with the above assignment. Examination of the calculated data for **13′**, including two values at *ca.* 50 ppm and three around 160 ppm, reveals that it is impossible to correlate the experimental and calculated data for



13 (R = Pr^i)
13' (R = H)



14 (R = Pr^i)
14' (R = H)

this compound. Hence, the structure **13** can be ruled out, and tautomer **14** is in fact the true structure. This conclusion was subsequently confirmed by means of long-range NMR coupling experiments.

We have so far neglected to comment on the performance of calculations of ^{1}H NMR data, the reason being the unreliability of these predictions.[4] Again, 1*H*-azepine (**9**) is the most problematical. The situation is clearly better for the other compounds studied here. It seems that proton NMR data are even more sensitive to structural changes than are ^{13}C NMR shifts. Again, increased complexity of the basis set usually leads to higher values (downfield shifts). The following methods appear to be the most accurate for azepines and diazepines: Becke3LYP/6-31G* and BLYP/6-31G*, both based on MP2 geometries, as well as HF/6-311+G(3df,2p)//HF/6-31G* combination. From the data investigated in this context, however, it is evident that calculated ^{1}H chemical shifts should be treated with caution; they can at best be used as an indication when supported by ^{13}C NMR data.

Conclusions

Becke3LYP/ and HF/6-31G* and /6-31+G** single-point calculations based on MP2 geometries give the lowest average errors, the former usually reproducing the correct relative ordering of the carbon chemical shifts. The combination of Hartree–Fock NMR calculations with HF geometries is also reasonably accurate. In some cases, e.g. 2*H*- and 3*H*-azepines, the BLYP/6-311+G(3df,2p)//BLYP/6-31G* calculations gave astonishingly good results. However, we believe that this is simply a coincidence, as the overall performance of this basis set/method combination is not consistent enough for general use on these molecules. Further conclusions are summarised as fol-

Table 9 Experimental and calculated chemical shifts of 6-chloro-5*H*-1,3-diazepine-2,4-diamine **12**, including error margins for ^{13}C NMR calculations

Method	Geometry	C2	C4	C5	C6	C7	H5	H7	Error[a]	Error[b]
Experiment		155.0	151.4	37.8	109.0	126.0	3.30	6.90		
HF/6-31G*	HF/6-31G*	156.8	157.9	36.5	99.0	140.2	2.06/2.53	6.80	6.8	70
HF/6-31 + G**		159.2	160.8	37.0	102.3	140.7	2.19/2.74	6.92	7.2	73
HF/6-311 + G(3df,2p)		167.9	169.8	38.5	107.8	149.1	2.33/2.87	6.80	11.2	207
BLYP/6-31G*	BLYP/6-31G*	146.3	136.3	38.3	100.6	130.9	2.45/2.52	6.57	7.5	80
BLYP/6-31 + G**		149.7	138.4	45.2	108.3	133.3	2.77/2.88	6.92	6.7	61
BLYP/6-311 + G(3df,2p)		162.2	150.6	47.4	114.4	145.5	2.98/3.00	7.01	8.5	111
HF/6-31G*	MP2/6-31G*	164.7	161.5	36.9	99.0	145.4	2.31/2.44	7.10	10.0	134
HF/6-31 + G**		167.0	164.3	37.5	102.4	145.7	2.49/2.56	7.22	10.3	148
HF/6-311 + G(3df,2p)		175.6	173.1	38.9	107.7	154.2	2.63/2.64	7.08	14.6	340
BLYP/6-31G*		143.8	133.9	41.5	99.8	130.8	2.47/2.47	6.57	9.3	110
BLYP/6-31 + G**		149.8	139.9	43.9	105.3	133.9	2.65/2.68	6.95	6.9	54
BLYP/6-311 + G(3df,2p)		162.2	152.1	46.0	111.2	146.2	2.80/2.90	7.05	7.7	106
Becke3LYP/6-31G*		149.8	141.2	40.9	101.2	135.0	2.40/2.49	6.69	7.1	57
Becke3LYP/6-31 + G**		154.7	146.2	42.8	106.1	137.4	2.57/2.66	7.00	4.8	38
Becke3LYP/6-311 + G(3df,2p)		166.8	158.3	44.9	112.1	149.3	2.72/2.85	7.05	10.4	157

[a,b] Footnotes as for Table 1.

Table 10 Experimental and calculated chemical shifts of 5-chloro-7-methoxy-4*H*-1,3-diazepin-2-amine **13′** and 6-chloro-4-methoxy-5*H*-1,3-diazepin-2-amine **14′** including error margins for ^{13}C NMR calculations

Method	Geometry	C2	C4	C5	C6	C7	C9	H4	H6	CH_3	Error[a]	Error[b]
5-Chloro-7-methoxy-4*H*-1,3-diazepin-2-amine **13′**												
Experiment		158.5	39.5	102.8	135.9	153.5	55.0	2.99	6.69	3.73		
HF/6-31G*	HF/6-31G*	156.1	47.4	160.2	110.2	160.2	49.2	3.27/3.86	5.65	3.38	17.7	684
HF/6-31 + G**		158.8	48.5	163.1	110.2	162.2	49.2	3.32/3.78	5.95	3.41	18.3	747
HF/6-311 + G(3df,2p)		167.8	50.4	171.4	116.2	171.3	51.3	3.49/3.66	5.93	3.42	21.7	937
BLYP/6-31G*	BLYP/6-31G*	147.8	56.0	153.0	105.3	153.5	53.8	3.65/3.99	5.43	3.56	18.2	641
BLYP/6-31 + G**		154.2	59.3	157.6	107.4	158.1	56.0	3.89/4.11	5.96	3.78	18.8	708
BLYP/6-311 + G(3df,2p)		167.2	62.4	168.9	116.8	172.5	59.2	3.88/4.20	6.14	3.87	23.3	952
HF/6-31G*	MP2/6-31G*	166.3	48.6	164.6	110.7	170.3	51.9	3.17/3.95	5.81	3.50	20.6	815
HF/6-31 + G**		168.6	49.6	167.5	110.6	172.1	51.8	3.19/3.87	6.11	3.53	22.0	897
HF/6-311 + G(3df,2p)		177.7	51.5	175.9	116.4	181.3	54.0	3.39/3.73	6.06	3.53	25.4	1170
BLYP/6-31G*		148.3	55.7	148.8	104.7	153.9	54.1	1.46/2.64	6.78	3.39	17.5	576
BLYP/6-31 + G**		154.6	58.9	153.5	106.8	158.6	56.3	3.82/3.90	6.01	3.78	18.3	648
BLYP/6-311 + G(3df,2p)		167.8	62.0	164.3	116.1	172.1	59.4	3.91/3.94	6.18	3.88	22.7	855
Becke3LYP/6-31G*		153.5	54.4	153.3	107.8	158.8	54.0	3.57/3.71	5.62	3.60	17.5	602
Becke3LYP/6-31 + G**		158.7	57.0	157.5	109.3	162.7	55.6	3.62/3.88	6.06	3.71	18.1	682
Becke3LYP/6-311 + G(3df,2p)		171.6	59.9	168.3	118.2	175.7	58.6	3.76/3.87	6.19	3.79	23.8	948
6-Chloro-4-methoxy-5*H*-1,3-diazepin-2-amine **14′**												
								H5	H7			
Experiment		158.5	153.5	39.5	102.8	135.9	55.0	2.99	6.69	3.73		
HF/6-31G*	HF/6-31G*	155.4	159.3	31.2	97.9	140.1	50.0	2.11/2.66	6.92	3.41	5.2	30
HF/6-31 + G**		157.9	161.6	31.2	100.7	140.8	50.0	2.31/2.84	7.03	3.66	4.9	32
HF/6-311 + G(3df,2p)		166.3	170.8	32.2	106.2	149.3	52.2	2.50/2.99	6.89	3.69	8.7	102
BLYP/6-31G*	BLYP/6-31G*	141.4	140.2	37.7	100.7	130.7	55.1	2.15/3.28	6.66	3.53	6.6	84
BLYP/6-31 + G**		147.4	145.6	39.2	105.0	134.3	57.2	2.43/3.63	7.09	3.95	4.2	33
BLYP/6-311 + G(3df,2p)		159.6	157.5	41.0	110.8	146.4	60.5	2.59/3.92	7.15	4.03	5.1	37
HF/6-31G*	MP2/6-31G*	163.1	163.5	32.5	96.9	145.8	52.6	1.90/3.10	7.24	3.68	6.6	51
HF/6-31 + G**		165.4	165.7	32.6	99.8	146.3	52.6	2.11/3.27	7.36	3.93	7.0	61
HF/6-311 + G(3df,2p)		173.8	174.8	33.5	105.0	154.9	55.0	2.31/3.40	7.18	3.95	10.6	182
BLYP/6-31G*		141.7	141.5	36.7	97.5	131.3	55.1	2.03/3.32	6.73	3.82	6.9	80
BLYP/6-31 + G**		147.6	146.9	38.1	102.2	134.8	57.2	2.25/3.62	7.12	4.01	3.8	28
BLYP/6-311 + G(3df,2p)		159.8	158.8	39.8	107.7	147.1	60.3	2.44/3.92	7.18	4.10	4.7	35
Becke3LYP/6-31G*		147.7	147.4	36.2	98.9	135.5	54.9	1.97/3.29	6.85	3.84	4.1	30
Becke3LYP/6-31 + G**		152.6	152.0	37.3	103.0	138.2	56.4	2.17/3.54	7.16	3.94	2.3	8
Becke3LYP/6-311 + G(3df,2p)		164.5	163.8	38.9	108.8	150.1	59.5	2.36/3.82	7.18	4.07	6.9	66

[a,b] Footnotes as for Table 1.

lows: (*i*) Hartree–Fock and Becke3LYP NMR calculations are preferred over BLYP density functional methods; (*ii*) Becke-3LYP calculations are better at predicting the correct order of chemical shifts; (*iii*) medium-sized basis sets (*e.g.* 6-31+G**) give better results than extensive ones, with the latter generally leading to downfield shifts of the relative values; (*iv*) HF single-point calculations both on HF and MP2 geometries give the lowest average errors, but Becke3LYP single points employing an MP2 geometry seem to be consistently more reliable; (*v*) localised orbital methods such as IGLO or LORG do not improve the quality of the results (at least not for BLYP). Judging from these calculations, it seems important to include polarisation functions, as in the DZ94P basis set.

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