PERKIN 2

Predictions of ^{13}C chemical shifts in carbocations. The use of scaled chemical shifts calculated using GIAO DFT methods†

Valerije Vrček,[a] Olga Kronja *[a] and Hans-Ullrich Siehl *[b]

[a] *Faculty of Pharmacy and Biochemistry, University of Zagreb, 10000 Zagreb, Croatia*
[b] *Division of Organic Chemistry I, University of Ulm, D-89069 Ulm, Germany*

Received (in Cambridge) 19th March 1999, Accepted 29th April 1999

Accurate prediction of ^{13}C chemical shifts (δ_{pred}) for the C$^+$ and the α- and β-carbon atoms in alkyl and cycloalkyl carbocations is achieved through scaling. *Ab initio* calculated chemical shifts (δ_{calc}) at the GIAO-B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level of theory for 16 different carbocations are scaled using a linear correlation equation ($\delta_{\text{pred}} = a\delta_{\text{calc}} + b$). The slope and intercept a and b were determined separately for C$^+$ and the α- and β-carbon positions, and were found to be different for cation structures preferentially stabilized by β-C–H and β-C–C hyperconjugation. A very good correlation of all predicted and experimental chemical shifts is obtained ($a = 0.999 \pm 0.002$, $b = 0.231 \pm 0.320$). Preliminary results indicate that scaling using linear correlations can also be applied to the C$^+$ carbon chemical shift in benzyl type carbocations.

Introduction

The combination of quantum chemical *ab initio* calculation of molecular structures and NMR chemical shifts provides a new tool for the assignment of experimental NMR spectra which can be applied to the elucidation of carbocation structures. Accurate geometries, calculated at high levels of theory including electron correlation are required to obtain reliable chemical shift data.[1] For neutral molecules with various functional groups Forsyth and Sebag[2] reported a computationally inexpensive approach in which empirical scaling factors are used to scale *ab initio* calculated ^{13}C NMR chemical shifts for MM3 forcefield optimized geometries.

Carbocations are electron deficient and have an electron distribution quite different from neutral molecules resulting in geometries which are not adequately reproduced by molecular mechanic calculations. High-level *ab initio* calculations including electron correlations such as the Møller–Plesset second order perturbation method (MP2/6-31G(d)) and more recently DFT-SCF hybrid methods are standard levels for the geometry optimization of carbocations.[3] For *ab initio* NMR chemical shift calculations of carbocations at least DFT and DFT-SCF hybrid methods are required. Often inclusion of electron correlation using the GIAO-MP2 method is required and in difficult cases only coupled cluster methods such as CCSD(T) provide approximately quantitative agreement.[4]

These methods are computationally demanding and thus not generally applicable. We present here an approach interfacing experimental and calculated NMR data of carbocations, which is based on scaling of chemical shifts calculated using DFT-hybrid methods both for the structures and the chemical shifts.[5]

Results and discussion

^{13}C NMR chemical shifts were calculated for a set of alkyl and cycloalkyl carbocations **1**–**16** (Fig. 1). The structures were optimized at the B3LYP/6-31G(d) level and for comparison purposes also at the MP2/6-31G(d) level. Frequency calculations at the same levels give no imaginary frequencies (NImag = 0), thus confirming that all structures are minima. Chemical shift calculations were done using the GIAO approach with the DFT-hybrid method B3LYP and the 6-311G(d,p) basis set. No significant changes for the calculated shifts were observed with a diffuse function (6-311+) added to the basis set. All quantum chemical calculations were carried out with the GAUSSIAN94 program suite.[6]

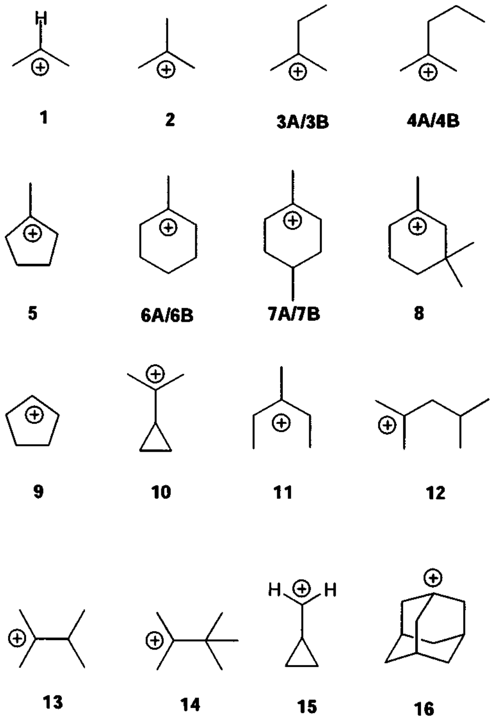

Fig. 1 Carbocations **1**–**16**.

The comparison of calculated and experimental NMR chemical shift data is reported here for the formally positively charged carbon (C$^+$) and the α- and β-carbons which are in close proximity to the carbocation center. The shifts of these carbons are expected to show the largest effects from the posi-

---

† Experimental and calculated ^{13}C NMR shifts from GIAO-B3LYP/6-311G(d,p)//B3LYP/6-31G(d) and GIAO-B3LYP/6-311G(d,p)//MP2/6-31G(d) and optimized structures of carbocations **1**–**16** in Gaussian z-matrix format are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/1999/1317, otherwise available from BLDSC (SUPPL. NO. 57548, pp. 78) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http:www.rsc.org/authors).

Table 1 Experimental, calculated and predicted ^{13}C NMR shifts for C–H hyperconjugative isomers of carbocations (group **A**)

carbocation	carbon atom	δ_{exp}(ppm)[a]	δ_{calc}(ppm)[b]	$\delta_{exp}/\delta_{calc}$	δ_{pred}(ppm)[c]
1	C^+	320.6	339.10	0.95	321.83
	α-CH_3	51.5	57.40	0.90	51.59
2	C^+	335	351.73	0.95	333.79
	α-CH_3	47.5	52.12	0.91	47.24
3A	C^+	335.4	353.59	0.95	335.54
	α-CH_3	44.6	49.37	0.90	44.97
	α-CH_2	57.5	65.87	0.87	58.58
	β-CH_3	9.3	12.00	0.78	9.02
4A	C^+	333.4	350.88	0.95	332.98
	α-CH_3	45.0	49.28	0.91	44.90
	α-CH_2	64.4	74.30	0.91	65.53
	β-CH_2	20.9	25.20	0.83	20.67
5	C^+	336.9	354.35	0.95	336.27
	α-CH_3	36.7	41.54	0.88	38.51
	α-CH_2	63.3	70.15	0.90	62.11
	β-CH_2	26.4	31.62	0.83	26.33
6A	C^+	332.7	350.92	0.95	333.02
	α-CH_3	44.2	50.76	0.87	46.11
	α-CH_2	58.2	64.69	0.90	57.61
	β-CH_2	26.9	32.98	0.82	27.52
7A	C^+	328.7	348.97	0.94	331.17
	α-CH_3	43.6	49.57	0.88	45.13
	α-CH_2	56.4	63.84	0.88	56.90
	β-CH_2	35.8	46.86	0.76	39.77
8	C^+	329.0	346.89	0.95	329.20
	α-CH_3	46.2	48.50	0.94	44.25
	α-CH_2	69.7	80.40	0.87	70.57
	α-CH_2	58.6	65.55	0.89	58.32
	β-CH_2	26.1	31.86	0.82	26.54
9	C^+	320.0	336.15	0.95	319.03
	α-CH_2	71.0	76.46	0.92	67.32
	β-CH_2	28.0	31.39	0.89	26.13
10	C^+	279.3	294.19	0.95	279.30
	α-CH_3	34.1	37.73	0.90	35.36
	α-CH	57.3	61.87	0.94	55.28
	β-CH_2	54.15	60.51	0.89	51.81

[a] Experimental chemical shifts are taken from ref. 11*a* (**1**, **2**, **3A** and **4A**), ref. 14 (**5**), ref. 15 (**6A**), ref. 16 (**7A**, **8**), ref. 17 (**9**) and ref. 18 (**10**). [b] Calculated using GIAO B3LYP/6-311G(d,p) for B3LYP/6-31G(d) optimized structures. [c] Obtained using the scaling equation $\delta_{pred} = a\delta_{calc} + b$ and parameters from Table 4.

tive charge. The more remote carbons are expected to follow a regular pattern much as in neutral compounds carrying an electron withdrawing substituent unless special effects such as transannular interactions are operative.

The calculated (δ_{calc}) and the experimental (δ_{exp}) chemical shifts for the carbon carrying the positive charge, and for the adjacent α-C and β-C carbons are given (relative to TMS[7]) in Table 1 and Table 2, respectively, along with the ratio between the experimental and calculated shifts ($\delta_{exp}/\delta_{calc}$).

The data in Tables 1 and 2 show that all chemical shifts calculated from B3LYP/6-31G(d) geometries using the GIAO-B3LYP/6-311G(d,p) method are overestimated. The chemical shifts are calculated more downfield than the experimental shifts. The ratio $\delta_{exp}/\delta_{calc}$ for the C^+ carbon chemical shift was found to be related to the mode of hyperconjugative charge delocalization in the particular carbocation structure. Carbocation structures with a geometry favorable for β-C–H hyperconjugation are summarized in Table 1 as group **A** type cations. They show a ratio $\delta_{exp}/\delta_{calc} = 0.95$ for the C^+ carbon shift. The carbocation structures which have a suitable geometry for β-C–C hyperconjugation are summarized as group **B** type carbocations. They have a different scaling ratio $\delta_{exp}/\delta_{calc} = 0.97$–$0.98$ for the C^+ carbon shift (Table 2).

The carbocations **3**, **4**, **6** and **7** have two conformational isomers **A** and **B**, resulting from favored β-C–H-σ-bond (**3A**, **4A**, **6A** and **7A**) or β-C–C-σ-bond (**3B**, **4B**, **6B** and **7B**) hyperconjugative stabilization of the positive charge. Both isomeric structures type **A** and **B** are calculated to be energy minima at the B3LYP/6-31G(d) and MP2/6-31G(d) levels of theory. The C–C hyperconjugative isomers **B** are found to be slightly lower in energy than structures **A** (Table 3). It is possible however that solvation plays a role in the energy difference between type **A** and **B** structures in solution.[8]

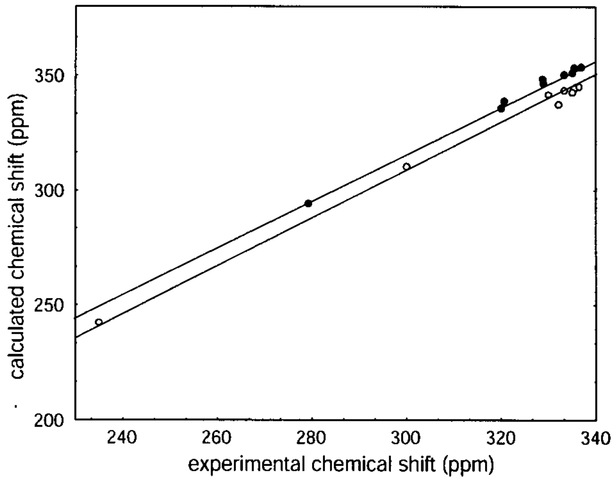

Fig. 2 Plots of theoretical ^{13}C chemical shifts (δ_{calc}) *vs.* experimental values (δ_{exp}) for C^+ in carbocations both in C–C (open circles) and in C–H (closed circles) hyperconjugative isomers.

The regression analysis for the experimental *vs.* calculated chemical shifts for the C^+ carbons of cations **1**–**16** was carried out separately for group **A** and **B** structures (Fig. 2). The values of δ_{exp} plotted against δ_{calc} exhibit excellent linearity. The predicted chemical shifts (δ_{pred}) can be determined with high accuracy ($|\Delta\delta|_{av} = 0.75$ ppm; rms = 1.35 ppm) according to eqn. (1).

$$\delta_{pred} = a\delta_{calc} + b \qquad (1)$$

Table 2 Experimental, calculated and predicted ^{13}C NMR shifts for C–C hyperconjugative isomers of carbocations (group **B**)

carbocation	carbon atom	$\delta_{\rm exp}$(ppm)[a]	$\delta_{\rm calc}$(ppm)[b]	$\delta_{\rm exp}/\delta_{\rm calc}$	$\delta_{\rm pred}$(ppm)[c]
3B	C$^+$	335.4	344.90	0.97	335.55
	α-CH$_3$	44.6	48.17	0.93	43.98
	α-CH$_2$	57.5	63.05	0.91	56.26
	β-CH$_3$	9.3	25.99	0.36	13.13
4B	C$^+$	333.4	343.98	0.97	334.65
	α-CH$_3$	45.0	46.92	0.95	42.95
	α-CH$_2$	64.4	73.52	0.88	64.89
	β-CH$_2$	20.9	47.47	0.53	22.15
6B	C$^+$	329.4	335.38	0.98	326.20
	α-CH$_3$	44.2	46.39	0.95	42.51
	α-CH$_2$	58.2	66.04	0.88	58.72
	β-CH$_2$	26.9	68.72	0.40	31.08
7B	C$^+$	328.7	337.31	0.97	328.10
	α-CH$_3$	43.6	46.80	0.93	42.85
	α-CH$_2$	56.4	65.33	0.86	58.13
	β-CH$_3$	35.8	73.13	0.49	32.93
11	C$^+$	336.4	345.51	0.97	336.16
	α-CH$_3$	41.9	45.24	0.92	41.56
	α-CH$_2$	54.5	59.51	0.91	53.34
	β-CH$_3$	8.9	13.79	0.65	8.01
12	C$^+$	332.1	337.8	0.98	328.58
	α-CH$_3$	45.4	48.07	0.94	43.90
	α-CH$_2$	70.1	80.04	0.88	70.27
	β-CH	31.4	67.54	0.47	30.59
13	C$^+$	335	343.12	0.97	333.81
	α-CH$_3$	43	45.78	0.94	42.01
	α-CH	59	66.67	0.89	59.24
	β-CH$_3$	17	27.16	0.63	13.63
14	C$^+$	330	342.00	0.97	332.70
	α-CH$_3$	41	45.17	0.91	41.50
	α-C	56	68.45	0.82	60.71
	β-CH$_3$	n.a.	32.41	—	—
15	C$^+$	235	242.69	0.97	235.08
	α-CH	n.a.	80.35	—	—
	β-CH$_2$	n.a.	84.49	—	—
16	C$^+$	300	310.60	0.97	301.84
	α-CH$_2$	65.7	72.54	0.91	64.09
	β-CH	86.8	102.63	0.85	45.33

[a] Experimental chemical shifts are taken from ref. 11*a* (**3B**, **4B**, **7B** and **11**), ref. 15 (**6B**), ref. 17 (**13**, **14**), ref. 19 (**15**) and ref. 20 (**16**). [b] Calculated ^{13}C NMR shifts using GIAO-B3LYP/6-311G(d,p) for B3LYP/6-31G(d) optimized structures. [c] Obtained using scaling equation $\delta_{\rm pred} = a\delta_{\rm calc} + b$ and parameters from Table 4.

For example, the correlation for the chemical shift of the C$^+$ carbons in cations of group **A** is characterized by the correlation coefficient $r = 0.998$, the value of the slope is $a = 0.947$ and the intercept is $b = 0.700$. The slope (a) and intercept (b) values for correlation of the C$^+$, α-C and β-C carbon shifts are presented in Table 4.

The statistical Ψ test[9] was used to verify the classification of carbocations into groups **A** and **B**. The values obtained for the C$^+$ carbon shifts, correlated separately for group **A** and group **B** type of carbocations, are $\psi_{\rm A} = 0.064$ and $\psi_{\rm B} = 0.063$, respectively.[10] The correlation was poor ($\psi_{\rm A+B} = 0.18$) when all the C$^+$ shifts were treated together. For the α-carbon shift in all carbocations a correlation coefficient $r = 0.990$ is obtained. Treating carbocations from group **A** and **B** separately did not significantly improve the correlation. The chemical shift for the α-carbons in all carbocations ($|\Delta\delta|_{\rm av} = 1.15$ ppm, rms = 1.91 ppm) is obtained according to eqn. (1) with the slope and intercept presented in Table 4.

The regression analysis for the shifts for β-carbons was carried out separately for group **A** ($r = 0.998$) and **B** ($r = 0.970$) type carbocations. Slopes and intercepts are presented in Table 4. The worst correlation ($r = 0.970$) between calculated and experimental chemical shifts was obtained for the β-carbons in group **B**. However the scaling generally gives a reasonable agreement with experiment and the only significant deviation from the experimental value is found for the predicted shift for the β-carbon of the 1-adamantyl cation (**16**, Table 2).

The relatively large error for the prediction of the chemical

Table 3 Calculated absolute energies, including zero point vibrational energy (ZPE) and relative energies for isomeric carbocations, C–H hyperconjugative isomers: **3A**, **4A**, **6A**, **7A** and the C–C hyperconjugative isomers: **3B**, **4B**, **6B**, **7B**

cation	B3LYP/ 6-31G(d)/ Hartree	B3LYP/ 6-31G(d) + ZPE/Hartree	ΔE/kcal mol^{-1}	MP2/ 6-31G(d)/ Hartree	MP2/ 6-31G(d) + ZPE/Hartree	ΔE/kcal mol^{-1}
3A	−196.8715415	−196.7244915	0.72	−196.1098661	−195.9606701	0.22
3B	−196.8716621	−19.67256411	0	−196.111144	−195.9610270	0
4A	−236.1867547	−236.0121297	0.73	−235.2771649	−235.0986889	1.37
4B	−236.1890571	−236.0132941	0	−235.2806244	−235.1008714	0
6A	−274.3000610	−274.1137065	1.62	−273.2812865	−273.0929835	3.04
6B	−274.3023439	−274.1162919	0	−273.2861339	−273.0978309	0
7A	−313.6161671	−313.4036861	1.13	−312.4515095	−312.2346215	1.20
7B	−313.6179664	−313.4054869	0	−312.4559264	−312.2365338	0

Table 4 Parameters for the equation $\delta_{pred} = a\delta_{calc} + b$ for the linear regression between experimental ^{13}C NMR chemical shifts and calculated ^{13}C chemical shifts (GIAO B3LYP/6-311G**// B3LYP/6-31G(d)) for the C^+, α-C and β-C carbons in carbocations **1**–**16**

carbon atom[a]	a	b	r
C^+ (group **A**)	0.947 ± 0.021	0.70 ± 7.30	0.998
C^+ (group **B**)	0.983 ± 0.029	−3.48 ± 7.57	0.998
α-C	0.825 ± 0.024	4.24 ± 1.45	0.998
β-C (group **A**)	0.882 ± 0.054	−1.56 ± 1.98	0.998
β-C (group **B**)	0.420 ± 0.070	2.22 ± 3.00	0.970

[a] α-C and β-C are carbons one or two bonds remote from the C^+ carbon. Group **A** type of carbocations are stabilized by β-C–H hyperconjugation, group **B** type of carbocations are stabilized by β-C–C hyperconjugation.

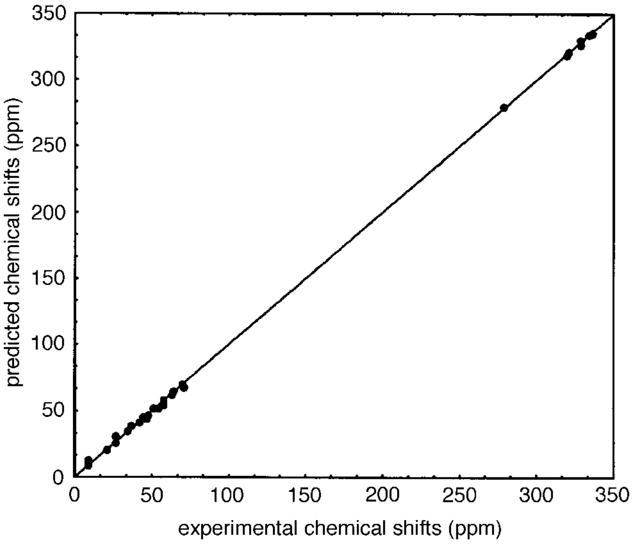

Fig. 3 Plot of predicted ^{13}C chemical shifts (δ_{pred}) *vs.* experimental values (δ_{exp}) for C^+, α-and β-C atoms in carbocations **1**–**16**.

shifts of the β-carbons for the carbocations in group **B** is not due to an inadequate level for the calculation of the geometry but is a consequence of the limitations in the quantum chemical model used for the calculation of NMR chemical shifts. It has been demonstrated that the structural distortions accompanying hyperconjugation in simple tertiary alkyl carbocations are adequately described using the MP2 correlation for the geometry optimization.[8] The chemical shifts calculated at the B3LYP/6-311G(d,p) level for cation structures **1**–**16** optimized with the MP2 electron correlation show similar deviations from experiment. Thus B3LYP/6-31G(d) and MP2/6-31G(d) optimized geometries give similar results. Preliminary data for chemical shift calculations for cation structure **3A** using the GIAO-MP2 method, although closer to the experimental data, still show significant deviations in particular for the shift of the β-carbon. We have shown that β-C–C-σ-bond hyperconjugatively stabilized carbocations such as the 1-cyclopropylcyclopropylidenemethyl cation may require methods beyond DFT and MP2 electron correlation methods, *i.e.* CCSD and CCSD(T) methods for the adequate calculation of chemical shifts.[4] At least for this case the congruence of calculated and observed ^{13}C chemical shifts suggested that the geometry of carbocations in superacid solution is similar to the gas phase prediction and that there is no specific perturbation of geometrical and/or electronic structure in superacid solution.

A linear regression of all scaled shifts (δ_{pred}) with the experimental shifts (δ_{exp}) (Fig. 3) gives an excellent correlation coefficient $r = 0.999$, the slope is unity ($a = 0.999 \pm 0.002$) and the value of the intercept is close to zero ($b = 0.231 \pm 0.320$).

Table 5 Experimental and calculated ^{13}C NMR shifts for the C^+ atom in substituted 2-phenyl-2-propyl cations

substituent	δ_{exp}(ppm)[a]	δ_{calc}(ppm)[b]	$\delta_{exp}/\delta_{calc}$
p-OCH_3	223.2	230.99	0.966
p-CH_3	247.2	243.43	1.015
H	259.2	253.78	1.021
m-F	265.2	257.75	1.029
p-CF_3	273.2	258.84	1.055

[a] Experimental chemical shifts are taken from ref. 21. [b] Calculated by the GIAO B3LYP/6-311G(d,p)//B3LYP/6-31G(d) method.

Carbocations often have low energy barriers and can undergo rapid degenerate rearrangements leading to time averaged chemical shifts of the exchanging sites even at the lowest temperatures accessible for high resolution NMR spectroscopy in solution. The experimental chemical shifts of the "frozen-out" static structures are often not accessible. Experimental ^{13}C NMR chemical shifts of static structures determined at very low temperatures by solid state MAS-NMR techniques are available for the cyclopentyl cation (**9**, Table 1), 2,3-dimethylbutyl cation (**13**, Table 2), 2,3,3-trimethyl-2-butyl cation (**14**, Table 2) and the cyclopropylmethyl cation (**15**, Table 2).[11] Scaling of the GIAO-B3LYP/6-311g(d,p) calculated NMR chemical shift for B3LYP/6-31g(d) optimized structures of these cations leads to satisfactory agreement (*e.g.* for C^+ of cation **13**: $\delta_{calc} = 343$ ppm, $\delta_{exp} = 335$ ppm, $\delta_{pred} = 334$ ppm). Thus the chemical shifts for the "frozen out" structures of fast equilibrating carbocations can be predicted with the same reliability as for static carbocations.

The chemical shifts calculated using the GIAO-B3LYP/6-311G(d,p) method for MP2/6-31G(d) optimized structures are generally somewhat closer to the experimental values, *i.e.* the ratio $\delta_{exp}/\delta_{calc}$ is closer to unity.[12] Structure optimization at B3LYP/6-31G(d) level[13] leads however to satisfactory results at a reduced computational cost compared to the MP2/6-31G(d) method. Some preliminary calculations (GIAO-B3LYP/6-311G(d,p)//B3LYP/6-31G(d)) were carried out for carbocations that are stabilized by resonance effects. The results obtained for *p*-OCH_3, *p*-CH_3, *p*-H, *m*-F and *p*-CF_3 substituted 2-phenyl-2-propyl cations (Table 5) show that almost all values of the chemical shifts for C^+ atoms are underestimated. The exception is the 2-phenyl-2-propyl cation substituted with a *p*-methoxy group which is a strong electron-donating group. The ratio between the experimental and calculated chemical shifts ($\delta_{exp}/\delta_{calc}$) decreases with the electron-donating ability of the substituent (Table 5). A reasonably good linear correlation of δ_{exp} with δ_{calc} was obtained ($r = 0.990$). The slope is 1.64 (±0.14) and the intercept $b = -154.60$ (±35.02). These results suggest that the calculated ^{13}C chemical shifts for benzyl-type carbocations could be also corrected by scaling to obtain accurate chemical shifts.

Acknowledgements

We gratefully acknowledge financial support by the Deutsche Forschungs Gemeinschaft (DFG), the Fond der Chemischen Industrie and the Ministry of Science and Technology of the Republic of Croatia (Grant No. 006151). We also acknowledge support for V. V. and O. K. from the Deutscher Akademischer Austauschdienst (DAAD) during their stay at Ulm University. We thank Thomas Nau, Computer Center, University of Ulm, Germany, for software adaptations.

References

1 (*a*) T. Helgaker, M. Jaszunki and K. Ruud, *Chem. Rev.*, 1999, **99**, 293; (*b*) J. R. Cheeseman, G. W. Trucks, T. A. Keith and M. J. Frisch, *J. Chem. Phys.*, 1996, **104**, 5497.

2 D. A. Forsyth and A. B. Sebag, *J. Am. Chem. Soc.*, 1997, **119**, 9483.

3 (*a*) M. Bühl, J. Gauss, M. Hofmann and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1993, **115**, 12385; (*b*) G. A. Olah, M. Diaz and

M. Barfield, *J. Am. Chem. Soc.*, 1995, **117**, 1403; (*c*) A. Rauk, T. S. Sorensen, C. Maerker, J. W. de M. Carneiro, S. Sieber and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1996, **118**, 3761; (*d*) P. v. R. Schleyer, C. Maerker, P. Buzek and S. Sieber, in *Stable Carbocation Chemistry*, Ed. G. K. S. Prakash and P. v. R. Schleyer, John Wiley & Sons, 1997, ch. 2.

4 (*a*) J. Gauss, *J. Chem. Phys.*, 1993, **99**, 3629; (*b*) J. Gauss and J. F. Stanton, *J. Chem. Phys.*, 1995, **103**, 3561; (*c*) J. Gauss and J. F. Stanton, *J. Chem. Phys.*, 1996, **104**, 2574; (*d*) H.-U. Siehl, T. Müller, J. Gauss, P. Buzek and P. v. R. Schleyer, *J. Am. Chem Soc.*, 1994, **116**, 6384; (*e*) J. F. Stanton, J. Gauss and H.-U. Siehl, *Chem. Phys. Lett.*, 1996, **262**, 183; (*f*) J. Gauss and J. F. Stanton, *J. Mol. Struct.* (*THEOCHEM*), 1996, **73**, 398; (*g*) H.-U. Siehl, abstracts from the International Conference on Quantum Chemical Calculations of NMR and EPR Parameters (NMR-EPR-98) Smolenice-Bratislava, Slovakia, September, 1998.

5 H.-U. Siehl, V. Vrcek, O. Kronja and M. Knez, presented in part at the French–German NMR Conference II, Obernai, France, September, 1998.

6 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, GAUSSIAN94, Revision E.1, Gaussian, Inc., Pittsburgh PA, 1995.

7 The absolute shielding values for tetramethylsilane (TMS) both for the B3LYP/6-31G(d) optimized structure (^{13}C: 183.8564; ^{1}H: 31.9168; ^{29}Si 339.9423) and for the MP2/6-31G(d) optimized structure (^{13}C: 184.4497; H: 31.9997, ^{29}Si 340.9428) were obtained using the GIAO-B3LYP/6-311G(d,p) method. Optimized structures are minima according to frequency calculations (NImag = 0).

8 (*a*) P. v. R. Schleyer, J. W. M. Carneiro, W. Koch, D. A. Forsyth, *J. Am. Chem. Soc.*, 1991, **113**, 3990; (*b*) P. R. Schreiner, D. L. Severance, W. L. Jorgensen, P. v. R. Schleyer and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1995, **117**, 2663.

9 O. Exner, *Collect. Czech. Chem. Commun.*, 1966, **31**, 3222.

10 Statistical test $\psi = [n(1 - r^2)/n - 2]^{1/2}$, where n is a number of data points and r is a correlation coefficient. A correlation is considered good if $\psi \leqslant 0.1$.

11 (*a*) G. A. Olah and D. J. Donovan, *J. Am. Chem. Soc.*, 1977, **99**, 5026; (*b*) P. v. R. Schleyer, D. Lenoir, P. Mison, G. Laing, G. K. S. Prakash and G. A Olah, *J. Am. Chem. Soc.*, 1980, **102**, 683; (*c*) C. P. Myhre and C. S. Yannoni, in *Stable Carbocation Chemistry*, Eds. G. K. S. Prakash and P. v. R. Schleyer, John Wiley & Sons, New York, 1997, ch. 12.

12 For example, chemical shifts obtained using GIAO-B3LYP/6-311G(d,p)//MP2/6-31G(d) method for **3A**: δ (C^+) = 350.46, δ (α-CH_3) = 51.78, δ (α-CH_2) = 65.67, δ (β-$CH._2$) = 12.26; for **12**: δ (C^+) = 336.51, δ (α-CH_3) = 48.24, δ (α-CH_2) = 78.94, δ (β-CH_2) =66.67.

13 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) T. Ziegler, *Chem. Rev.*, 1991, **91**, 651.

14 J. H. Botkin, D. A. Forsyth and D. J. Sardella, *J. Am. Chem. Soc.*, 1986, **108**, 2797.

15 R. P. Kirchen and T. S. Sorensen, *J. Am. Chem. Soc.*, 1978, **100**, 1487.

16 R. P. Kirchen, K. Ranganayakulu and T. S. Sorensen, *J. Am. Chem. Soc.*, 1987, **109**, 7811.

17 P. C. Myhre, J. D. Kruger, B. L. Hammond, S. M. Lok, C. S. Yannoni, V. Macho, H. H. Limbach and H. M. Vieth, *J. Am. Chem. Soc.*, 1984, **106**, 6079.

18 G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, 1973, **95**, 3792.

19 P. C. Myhre, G. G. Webb and C. S. Yannoni, *J. Am. Chem. Soc.*, 1990, **112**, 8992.

20 G. A. Olah, G. K. S. Prakash, J. G. Shih, V. V. Krishnamurthy, G. D. Mateescu, G. Liang, G. Sipos, V. Buss, T. M. Gund and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1985, **107**, 2764.

21 G. A. Olah, R. D. Porter, C. L. Jeuell and A. M. White, *J. Am. Chem. Soc.*, 1972, **94**, 2044.

Paper 9/02184A