

The Magnetic Shielding Polarizabilities of Some Tetrahedral Molecules

Martin Grayson and Paul Chittenden

Department of Chemistry, The University, Sheffield S3 7HF, UK
Tel.: +44 114 222 9527, E-mail: M.Grayson@sheffield.ac.uk,
URL: <http://www.shef.ac.uk/misc/personal/ch1mg/>

Received: 25 May 2000 / Accepted: 23 August 2000 / Published: 9 September 2000

Abstract: TMS is the commonest standard reference for both protons and ^{13}C NMR spectroscopy. The Magnetic Shielding and its Polarizabilities, plus the static polarizability have been calculated for TMS, tetramethyl ammonium cation and 2,2-dimethylpropane. An investigation of continuum solvation effects on these highly symmetrical molecules, whose first surviving electric moment is the octopole, showed interaction with solvent makes little change to these magnetic properties. This small change is however consistent with both the high symmetry of the molecules and the available extensive experimental data for TMS. A rationalization of the signs and magnitudes of A in a sequence of related molecules has been suggested.

Keywords: Magnetic, Shielding, Buckingham and TDMS.

Introduction

There is surprisingly extensive solvent shift data for TMS [1, 2], so a calculation of the Buckingham A parameters is the first step to allow researchers to investigate models of these solvent shifts. A knowledge of the A s for these molecules is also useful for building up the data set of A s in different chemical environments. These are the largest molecules for which an *abinitio* A has been calculated to date.

In the molecules considered here the 4 $-\text{CH}_3$ groups can be placed in an orientation such that all 12 hydrogens are precisely equivalent. and the molecular symmetry is T_d . Both the 4 equivalent Cs and the 12 protons are used as references in NMR spectroscopy. The local site symmetry [3] at the 4 equivalent carbons is C_{3v} so they are in a cylindrical environment with one Buckingham A and two B s.

The Buckingham equation [4] for the shielding of a nucleus in a uniform electric field F is:

$$\sigma = \sigma_0 - AF_{\parallel bond} - BF^2 \quad (1)$$

where the sign of A is defined by a standard orientation of the functional group being considered.

The A and B parameters in the Buckingham equation behave like dipole moments and polarizabilities respectively.

$$\frac{\partial \sigma_{iso}}{\partial F} \quad \text{is like} \quad \frac{\partial E}{\partial F} \quad \text{and} \quad -\frac{1}{2} \frac{\partial^2 \sigma_{iso}}{\partial F^2} \quad \text{is like} \quad \frac{\partial^2 E}{\partial F^2}$$

This means even more care must be taken over the vector direction of A than of μ because there are no simple electronegativity based visualizations to reveal an error in the sign.

Augsburger and Dykstra [5] use a formulation differing by a sign and a factor of two, so care must be taken when comparing data. Their equation is:

$$\sigma = \sigma_0 + AF_{\parallel bond} + \frac{1}{2!}BF^2 \quad (2)$$

The conversion factor between atomic (ppm au⁻¹) and SI units for A is

$$\frac{10^{-6}}{e/4\pi\epsilon_0 a_0^2} = 1.94469 \times 10^{-18} \text{mV}^{-1}$$

and correspondingly the conversion factor for the second derivatives, (B), ppm au⁻², is

$$\frac{10^{-6}}{(e/4\pi\epsilon_0 a_0^2)^2} = 3.78182 \times 10^{-30} \text{m}^2 \text{V}^{-2}$$

2. Computational

Geometries for the molecules under consideration were obtained by geometry optimisation using an SCF wavefunction at the 6-31G** level, (Table 1). The shieldings were calculated using London Orbitals [6, 7]. All calculations used the Dalton [8] program.

The solvation calculations were calculated using the Self-Consistent Reaction Field Model [9, 10], as implemented in Dalton.

3. Results

In previous papers concerned with small molecules it has been the custom to report separately diamagnetic and paramagnetic parts of the shieldings and their derivatives. On these larger molecules this has not been reported because this separation does not correspond to any observable. In a full relativistic calculation this separation disappears and there is only the one physically observable component. However it must be noted that in terms of basis set convergence of the property and magnitude of the derivatives the paramagnetic part is the most volatile. The separation is therefore sometimes mentioned.

In the previous work by Grayson and Raynes the proton shieldings are on average 74% paramagnetic, with a standard deviation of 4.8% in a range of C-H environments. The paramagnetic contributions to the ^{13}C shielding are large in the multiple bonded situation, anomalously so in the carbonyl group where there is a strongly allowed magnetic dipole transition.

The basis set used is not ideally large enough and the impracticality of using a correlated wavefunction is also a source of error. However the authors have thought it is timely to make the numbers and the estimation formula available so that revisiting with a stronger wavefunction can be done when more computer power is available. One of the problems with a correlated calculation is that for an aliphatic system MCSCF does not give a good balance of correlation effects. The preferred method of calculation would be perturbation theory but with the SOPPA [11, 12] method London Orbitals cannot be used. Without London Orbitals a very large basis would be required. However a referee has kindly pointed out that Møller-Plesset perturbation theory from orders 2 to 4 and also CCSD is now available in the Aces2 [13] program and a MP2 code is in Gaussian98 [14].

The shieldings, polarizability and solvent shifts are in Table 2. Baldrige and Siegel [15] have a set of values for the proton shielding in TMS with different basis sets. Our value is in the middle of these. The absolute experimental shielding is difficult to determine. Jameson [16] gives proton shieldings for related molecules as CH_4 30.80, CH_3F 28.27 and SiH_4 27.52 ppm respectively. The calculated value for TMS, 32.34, is probably a little too high.

The polarizability in brackets is estimated by the MolWeb algorithm [17]. It suggests that the basis is too small to reproduce the Hartree-Fock limit but this is expected.

Unfortunately this will be expected to have a similar effect on the accuracy of B which is equivalent to a polarizability.

The solvation calculations have the molecule in a spherical cavity with a radius of the central atom to proton distance plus the hydrogen van der Waals radius (120 picometres). The dielectric constant used is as for water, (78.5). A multipole expansion up to $L = 10$ was used for the reaction field method.

The solvation calculations were performed to see if there would be a shift to high frequency, (smaller in ppm), of the TMS carbons as 203ppm is too large. What is felt to be the best number for TMS, (the absolute shieldings of nuclei are rather difficult to obtain experimentally, the experiment gives only relative chemical shifts), is 184.1 ppm [16]. Jiao *et al.* [18] use the higher number of 201ppm, which is comparable to this SCF calculation. As the first surviving electric moment is the octopole one should not expect much interaction. Even solvation in the strong dielectric of water does not reduce the shielding significantly. However the greatest shift is the -0.13 of the carbon in TMS. This is qualitatively in agreement with the experimental data [1, 2] but is too small a shift. The shift might be expected to increase considerably with an enhancement to the basis set.

Interestingly though the cation interacts strongly with the solvent to the extent of about half a chemical bond, the shieldings are not appreciably changed. The positive charge to some extent protects the electrons from distortion and most of the energy of solvation comes from a spherical Coulomb interaction.

Cammi *et al.* [19] have calculated the solvation shift for some small molecules with dipole moments. They see small effects for C and H but significant shifts for N and O. They have a division into *direct* effects caused by an unrelaxed geometry interacting and *indirect* effects where the geometry is relaxed, corresponding to incorporating some partial derivatives of nuclear displacement.

Tables 3 and 4 show the shielding polarizabilities. The axis system used, where A corresponds to A_z , has the the z -axis as the principal axis of the functional group, with the attached protons at $+z$. For C_{3v} site symmetry there are independent values for

B_{\parallel} and B_{\perp} but here the spherical average is quoted because the low accuracy of SCF B s does not justify the complex tensor algebra and extra perturbations required to use the full tensor. The new B s here have low accuracy due to the numerical differentiation procedure. The accuracy is only 2 significant figures. They can also be expected to have large correlation contributions and severe basis set dependence. This is demonstrated by the much larger variation of B in the data from the references cited here than in the values of A . An average working B for $-\text{CH}_3$ from this data is 928.

The B for the positively charged nitrogen is high at 3200 but this is very believable as B for N in $-\text{CN}$ is around 6000 [21].

In C-H bonds A has so far always been positive [22], which corresponds to what you expect in this orientation if electrons were to flow towards the field and deshield the nucleus in question. In general B s are positive, as are all B s quoted here, corresponding to anticipation of deshielding when the Buckingham equation was first set up. There are some examples where B is negative. In these cases there are always π -systems or the strong magnetic dipole transitions of the carbonyl group, making simple predictions based on inductive effects unreliable.

Cybulski and Bishop [23] have calculated some A s for small molecules with a more accurate wavefunction, getting for the C-H bond in methane 76.8 as compared with the SCF value of 80.2 used here for fitting with the other SCF calculations. This is encouraging that basis and correlation effects may be acceptably small.

The average proton B for $\text{C}(\text{sp}^3)\text{-H}$ is 74 but this is too much influenced by the outlier value 33 for the cation $\text{N}(\text{CH}_3)_4^{(+)}$. 80 has been the recommended working value. Cybulski and Bishop, with their better coupled cluster calculation get 64.2 for methane.

Notice the smaller value of B for $\text{N}(\text{CH}_3)_4^{(+)}$, this is caused by the positive charge pulling in the electrons tighter, reducing the polarizability and analogously B .

4. Electronegativity and the computations

It is clear from a casual glance at the tables that there is some relation between the value of A and electronegativity. However we would not expect it to be too clear or quantitative because in the SCF formalism the paramagnetic part of the shielding can vary widely with changes in electronic structure which are not pure inductive effects. Nevertheless there is

some pattern here so an attempt is made to make it quantitative.

For analysis of the inductive effects group electronegativities have to be calculated or obtained [24]. Different authors have varying values for these group electronegativities as despite the advances in density functional theory which have quantified electronegativity, hardness and softness there is still a lack of practical numerical definition.

The formula for estimating these from atomic electronegativities according to Bratsch [25] is:

$$\chi_G = \sum_{i=1}^n a_i/n + \left(\sum_{i=1}^n b_i/n^2 \right) \delta_G \quad (3)$$

where a and b are the electronegativity and hardness parameters, n is the number of atoms in the group and δ is the partial charge. We have applied this to calculating the group values for $-\text{Si}(\text{CH}_3)_3$ and $-\text{N}(\text{CH}_3)_3^{(+)}$. It gives numbers which are too similar to the methyl group to give a good expression of the differential inductive effects. This is because the electronegativities of C and H are close and do not allow for the effects of hyperconjugation [26, 27, 28]. Mo and Peyerimhoff [29] have recently produced a methodology for *abinitio* calculation of hyperconjugation energetics using *Block Localised Wavefunctions* (BLW) or Weinhold's *Natural Bond Orbital* (NBO) [30]. The data of Sen *et al.* [31] does give a good differentiation between $-\text{CH}_3$ and $-\text{tbut}$. Using this data, (Table 5), and our calculations gives a new value for χ $-\text{N}(\text{CH}_3)_3^{(+)}$ but the value for $-\text{Si}(\text{CH}_3)_3$ is uncertain. The recalibration and the decision to use the data of Sen *et al.* where available gives the inductive effect from electronegativity in the order: $-\text{Si}(\text{CH}_3)_3 = 4$, $-\text{C}(\text{CH}_3)_3 = 4.61$, $-\text{CH}_3 = 6.32$ and $-\text{N}(\text{CH}_3)_3^{(+)} = 8.16$. This follows chemical intuition.

The use of electronegativity data to analyse such a complex property is equivalent to frontier orbital theory [33, 34, 35] using only two states, in this case an attachment state and an ionization state. This is really truncating the expansion required to match reality far too short and so will only give *rule of thumb estimations* if used in a predictive capacity. This explains the failure of the simplest picture where the Silicon atom is involved.

The estimation formula for a proton-X A is:

$$A = 85.47 - 1.932\chi \quad (4)$$

where χ is in electron volts, ($1\text{eV} = 96.49 \text{ kJ / mol}$). It was generated using the data of Sen *et al.* for group electronegativities and the calculated A s for CH_3 - connected to

F, Cl, -CH₃ and -C(CH₃)₃. This gives a good straight line with a σ of only 0.96ppm/au, (good considering the general accuracy of A_s). With our calculated TMS A this implies an unreasonably electropositive -Si(CH₃)₃ with a χ of -1.67.

The estimation formula for a sp³-carbon A , by using the same procedure is:

$$A = 50.67\chi - 344.83 \quad (5)$$

This is a considerably worse fit than for the proton, but this might be expected to be nonlinear because the atom and group concerned are directly bonded. This implies a group electronegativity of 5.48 for -Si(CH₃)₃. One feels on grounds of chemical intuition it ought to be about 4.

All the data follows a rational monotonic series apart from the X-C(sp³) A where the -Si(CH₃)₃ and -C(CH₃)₃ groups are interchanged. The actual σ_s rather than the A_s for both proton and ¹³C follow chemical intuition in the order -Si(CH₃)₃ > -C(CH₃)₃ > -N(CH₃)₃⁽⁺⁾. The proton chemical shifts imply a group electronegativity of 3.04 for -Si(CH₃)₃, about the same as Lithium or Calcium, once again unreasonably low.

5. Tables

Table 1 - Bond Lengths and angles of tetrahedral molecules / pm

	r(Cen-C)	r(C-H)	θ (Cen,C,H)	Solvent cavity radius
N(CH ₃) ₄ ⁽⁺⁾	149.28	107.97	109° 3' 34"	416.5
C(CH ₃) ₄	153.52	108.67	111° 7' 49"	425.5
Si(CH ₃) ₄	189.25	108.74	111° 22' 15"	443.5

Table 2 - Shieldings and polarizability of tetrahedral molecules

	σ_H / ppm	σ_C / ppm	σ (Central atom)	α x 10 ⁴¹ / C ² m ² J ⁻¹	ΔH solvation / kJ per mole
N(CH ₃) ₄ ⁽⁺⁾	29.40	154.06	244.21	74.62 (99.36)	-164.93
	0.0001	0.0013	-0.0233		(†)
C(CH ₃) ₄	31.44	174.39	179.88	86.73 (102.24)	-0.16
	0.0014	-0.0697	0.0254		(†)
Si(CH ₃) ₄	32.34	203.30	448.65	100.48 (139.72)	-0.83
	0.0014	-0.1292	-0.0490		(†)

(†) - these are $\Delta = \sigma_{gas} - \sigma_{solv.}$ from the solvation calculations.

Table 3 - Carbon shielding polarizabilities

	A / ppm au ⁻¹	B_{iso} / ppm au ⁻²	Source
CH ₄	0	134.8	(1)
C(CH ₃) ₄	-125.0	737.5	(†)
Central Carbon	(0)	1650.0	(†)
Si(CH ₃) ₄	-67.2	558.3	(†)
Central Si	(0)	2175.0	(†)
C ₂ H ₆	-49.2	1361.8	(1)
N(CH ₃) ₄ ⁽⁺⁾	33.7	754.2	(†)
Central N	(0)	3200.0	(†)
CH ₃ Cl	219.1	1290.2	(1)
CH ₃ F	222.0	853.4	(1)

(1) Reference [20], (†) - this work.

Table 4 - Proton shielding polarizabilities / au. For orientations see the text

	A_{\parallel}	A_{\perp}	B_{iso}	source
CH ₃ F	62.0	5.6	65.0	(1)
CH ₃ Cl	67.8	17.7	80.0	(1)
N(CH ₃) ₄ ⁽⁺⁾	69.7	(0)	33.3	(†)
CH ₃ CN	71.6	3.5	74.8	(1)
C ₂ H ₆	71.7	4.0	91.6	(1)
C(CH ₃) ₄	77.6	(0)	75.0	(†)
CH ₄	80.2	(0)	80.5	(1)
	76.8	(0)	64.2	(2)
Si(CH ₃) ₄	88.7	(0)	94.2	(†)

(0) zero by symmetry, (1) SCF calculation reference [22]. (2) is a more accurate coupled cluster calculation [23]. (†) - this work.

Table 5 - Group Electronegativities

	Bratsch [32]	Sen <i>et al.</i> [31]	recalibrated χ
-CH ₃	7.45	6.32(*)	
-C(CH ₃) ₃	(†)7.41	4.61(*)	
-Si(CH ₃) ₃	(†)7.37		4
-N(CH ₃) ₃ ⁽⁺⁾	(†)8.59		8.16

(†) - calculated from Bratsch's formula, (*) - values used to make extrapolation formula.

Conclusions

These are some of the largest molecules in which A has been calculated and there is some transferability between the A s of smaller molecules and the environment in the larger molecule. The A s of both the CH_3 carbons and the protons have some systematic dependence on the inductive effect of the remaining portion of the molecule. The results are comparable with previous calculations on CH_3F , CH_3Cl and $\text{CH}_3\text{-CH}_3$ *etc* which also touch experiment *via* their good agreement with Zürcher's experimental data [36] and the use of other A s in the prediction of macromolecular NMR spectra [37].

This would allow a way of estimating A from the above formulae relating A to group electronegativities. This would not be expected to be too accurate because of the paramagnetic effects at the central atom but is a useful aid to rationalization of the meaning and magnitude of these derivatives.

The behaviour of the $-\text{Si}(\text{CH}_3)_3$ functional group cannot be simply rationalised by a pure electronegativity argument, though it almost fits into a linear logic. The availability of low lying d-orbitals can be invoked to explain the nonlinearity and the failure of a simple two state ionisation / attachment picture.

Both the problem of quantifying the inductive effect of common functional groups using density functional theory and a higher quality calculation on TMS including correlation and a more complete basis remain to be done, but this paper points out what can be demonstrated with modest SCF level calculations.

References and Notes

1. Bacon, M.; Maciel, G. E. *J. Amer. Chem. Soc.* **1973**, *95*, 2413.
2. Bacon, M.; Maciel, G. E.; Musker, W. K.; Scholl, R. *J. Amer. Chem. Soc.* **1971**, *93*, 2537.
3. Raynes, W. T.; Ratcliffe, R. *Molec. Phys.* **1979**, *37*, 571.
4. Buckingham, A. D. *Can. J. Chem.* **1960**, *38*, 300.
5. Augspurger, J. D.; Dykstra, C. E. *J. Phys. Chem.* **1991**, *95*, 9230.
6. Pulay, P.; Hinton, J. F. in *The Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K.; Wiley: Chichester, 1996; 7, pp 4334-4339.
7. Ruud, K.; Helgaker, T.; Kobayashi, R.; Jørgensen, P.; Bak, K. L.; Jensen, H. J. Aa. *J. Chem. Phys.* **1994**, *100*, 8178.
8. Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Andersen, T.; Bak, K. L.; Bakken, V.; Christiansen, O.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Fernandez, B.; Heiberg, H.; Hetttema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Saue, T.; Taylor, P. R.; Vahtras, O. *DALTON, an electronic structure program, Release 1.0* (<http://www.kjemi.uio.no/software/dalton/dalton.html>, 1997).
9. Mikkelsen, K. V.; Dalgaard, E.; Swanstrøm, P. *J. Phys. Chem.* **1987**, *91*, 3081.
10. Mikkelsen, K. V.; Ågren, H.; Jensen, H. J. Aa.; Helgaker, T. *J. Chem. Phys.* **1988**, *89*, 3086.
11. Nielsen, E. S.; Jørgensen, P.; Oddershede, J. *J. Chem. Phys.* **1980**, *73*, 6238.
12. Enevoldsen, T.; Oddershede, J.; Sauer, S. P. A. *Theor. Chem. Acc.* **1998**, *100*, 275.
13. Web address, <http://www.qtp.ufl.edu/Aces2/>.
14. Web address, <http://www.gaussian.com/>.
15. Baldrige, K. K.; Siegel, J. S. *J. Phys. Chem. A* **1999**, *103*, 4038.
16. Jameson, C. in *The Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K.; Wiley: Chichester, 1986; 2, p 1273.
17. Grayson, M. *J. Comput. Chem.* **2000**, (submitted).
18. Jiao, D.; Barfield, M.; Hruba, V. *J. Magn. Reson. Chem.* **1993**, *31*, 75.
19. Cammi, R.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1999**, *110*, 7627.
20. Grayson, M.; Raynes, W. T. *Molec. Phys.* **1994**, *81*, 533.
21. Grayson, M.; Raynes, W. T. *Chem. Phys. Lett.* **1993**, *214*, 473.
22. Grayson, M.; Raynes, W. T. *Magn. Reson. Chem.* **1995**, *33*, 138.
23. Cybulski, S. M.; Bishop, D. M. *Molec. Phys.* **1998**, *93*, 739.
24. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic chemistry: principles of structure and reactivity*; Harper Collins: 1993.
25. Bratsch, S. G. *J. Chem. Educ.* **1985**, *62*, 101.
26. Rablen, P. R.; Hoffmann, R. W.; Hrovat, D. A.; Borden, W. T. *J. Chem. Soc. Perkin Trans., 2* **1999**, 1719.
27. Beamson, G.; Pickup, B. T. *J. Phys. Chem. B* **2000**, *104*, 2656.
28. Dewar, M. J. S. *Hyperconjugation*; Ronald Press: New York, 1962.
29. Mo, Y. R.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687.
30. Reed, A. E.; Curtiss, C. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
31. Sen, K. D.; Böhm, M. C.; Schmidt, P. C. *Electronegativity, Structure and Bonding*; Sen, K. D., Jørgensen, C. K.; Springer: Berlin & Heidelberg, 1987; 66, p 99.

32. Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 223.
33. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.
34. Dewar, M. J. S. *Science* **1975**, *187*, 1037.
35. Fukui, K. *Science* **1982**, *218*, 747.
36. Zürcher, R. F. *Progr. NMR Spectrosc.* **1967**, *2*, 205.
37. Williamson, M. P.; Asakura, T. *J. Magn. Reson., Series B* **1993**, *101*, 63.