

Calculation of Proton Chemical Shifts in Hydrocarbons

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A novel simple computational scheme based on partial atomic charges and involving an orientational dependence of electronegative substituents plus a steric contribution gives calculated proton chemical shifts for a variety of hydrocarbons in excellent agreement with the observed values.

The most important single experimental parameter in NMR spectroscopy is the chemical shift, and proton chemical shifts have been compiled and interpreted for many years.¹ Despite this considerable effort there is still no calculation of proton chemical shifts sufficiently accurate to be of use to the practising chemist. This is generally explained as due to the complex interactions contributing to proton chemical shifts. The magnetic anisotropy, electric field and Van-der-Waals effects of the substituents have all been implicated as well as the charge on the proton.²

These explanations become questionable when applied to saturated hydrocarbons. The range of proton chemical shifts of simple hydrocarbons is >2 ppm, which is 20% of the usual range of proton chemical shifts, yet these molecules possess neither magnetically anisotropic nor polar substituents. Clearly there are other important factors determining proton chemical shifts.

Recent studies have begun to provide an insight into these factors. Li and Allinger³ calculated proton shifts in cyclohexanes from their steric interactions using MM2, but this was only partially successful. Danneels and Anteunis⁴ noted that the influence of a vicinal methyl group on the proton chemical shift was a function of the C-C-C-H dihedral angle. In a *gauche* orientation the methyl is shielding, whereas in the *trans* orientation the methyl group is deshielding and this was approximated by a $\cos \phi$ dependence. Recent studies on methyl norbornanes,⁵ *trans*-decalin⁶ and *trans*-perhydrophenanthrene⁷ have confirmed this orientation dependence.



In contrast to quantum mechanical calculations,⁸ semi-empirical calculations of partial atomic charges in molecules have given good correlations with proton chemical shifts.⁹⁻¹¹ We present here a simple extension to the CHARGE3 routine¹¹ which allows the prediction to almost experimental accuracy of the proton chemical shifts of a variety of saturated hydrocarbons. The modifications may be summarised as follows. In all previous investigations^{10,11} the calculated proton chemical shift for methane was anomalous. We show that this is simply due to an incorrect value for the electronegativity of hydrogen. A value of 6.80 (Mulliken scale), *i.e.* 2.20 (Pauling scale), removes this anomaly. We use a $\cos \phi \times \cos |\phi|$ dependence of the γ effect of a carbon atom, which gives somewhat better agreement with the experimental shifts


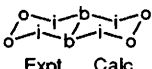
than a $\cos \phi$ dependence and has a sounder theoretical basis. On this basis the vicinal C-C-C-H through bond interaction is zero at 90° and also the derivative with respect to the dihedral angle is zero, exactly analogous to the well-known Karplus equation for the $^3J_{\text{HH}}$ coupling. The repulsion exchange forces between two hydrogen atoms at closer distances than the sum of their Van-der-Waals radii produce a shielding effect proportional to this steric repulsion. Intriguingly this shielding effect for $\text{CH}_3 < \text{CH}_2 < \text{CH}$ is possibly due to the increased positive charge on the proton as the number of attached carbon atoms increases, giving increased sensitivity to external perturbations. The steric repulsion of a hydrogen atom and a carbon atom, again at distances closer than the sum of their Van-der-Waals radii, produces a much larger deshielding effect on the hydrogen atom, rather analogous to the site-factor term used in the calculations of intermolecular effects on proton chemical shifts.¹² These simple modifications, when included into the CHARGE3 scheme together with eqn. (1) relating the proton chemical shift (δ_{H}) to the partial atomic charge (q_{H}) on the proton, gives good agreement between the observed and calculated chemical shifts for a variety of hydrocarbons (Fig. 1).

$$\delta_{\text{H}} = 153.1q_{\text{H}} - 8.64 \quad (1)$$

The chemical shifts of the simple alkanes¹³ are well reproduced; the decrease in shielding on going from $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2 \rightarrow \text{CH}$ is simply due to the increased electronegativity of carbon *vs.* hydrogen. The much smaller decrease in shielding of a methyl group on increasing β substitution, $\text{CH}_3 \cdot \text{CH}_3 \rightarrow \text{CH}_3 \cdot \text{Et} \rightarrow \text{CH}_3 \cdot \text{Pr}^i \rightarrow \text{CH}_3 \cdot \text{Bu}^t$ is due to the near cancellation of the deshielding inductive effect of the carbon atom and the shielding effect due to increasing steric repulsion.

The chemical shift difference of the axial and equatorial protons in cyclohexane,¹⁴ is now given a simple interpretation as due to the orientation dependence of the carbon γ effect, the equatorial hydrogen having two carbon γ substituents in an *anti* (*trans*) orientation is deshielded, whereas the *gauche* orientation of these carbon atoms with respect to the equivalent axial proton, gives a shielding contribution. The observed proton chemical shifts for cyclopentane,^{13b} for all

	Expt.	Calc.		Expt.	Calc.
CH ₄	0.27	0.39		ax. 1.19	1.16
CH ₃ CH ₃	0.86	0.88		eq. 1.68	1.68
CH ₃ CH ₂ CH ₃	0.90	0.90			
CH ₃ CH ₂ CH ₃	1.33	1.35			
(CH ₃) ₃ CH	0.89	0.91		Expt.	Calc.
(CH ₃) ₃ CH	1.72	1.81		CH ₂ 1.51	1.46
(CH ₃) ₄ C	0.93	0.92			

	Expt.	Calc.		Expt.	Calc.
	1.18	1.49		ba 0.88	0.85
Bridge	1.18	1.49		ia 0.93	0.96
B. head	2.19	2.27		oa 1.25	1.18
exo	1.47	1.49		ie 1.54	1.52
endo	1.16	1.21		oe 1.67	1.68


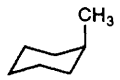
	Expt.	Calc.		Expt.	Calc.
	1a 1.32	1.37		1a 1.00	1.12
1a	1.32	1.37		1e 2.01	2.13
1e	0.86	0.90		2,6a 1.40	1.32
2,6a	0.88	1.01		2,6e 1.48	1.48
2,6e	1.68	1.53		3,5a 1.32	1.28
3,5a	1.20	1.15		3,5e 1.53	1.68
3,5e	1.68	1.68		4a 1.19	1.15
4a	1.11	1.14		4e 1.68	1.68
4e	1.68	1.68			

Fig. 1 Observed and calculated proton chemical shifts (δ_{H}) in hydrocarbons

the protons in *trans*-decalin and for the unique bridge proton of *trans*-perhydrophenanthrene^{7,8} are well reproduced, the latter illustrating the combined shielding effects of a number of *gauche* oriented carbon atoms plus steric interactions. The observed proton chemical shifts for norbornane¹⁴ are also well reproduced, particularly the *exo/endo* protons, with the exception of the bridging protons. This is not surprising, as the C-C-C angle of the bridge is 95.3°, and thus hybridisation effects, which are not considered in the present scheme, could influence these protons. Finally, the methyl substituent chemical shifts in cyclohexane^{4,15} are also reasonably well reproduced. Most of the 'experimental' values for axial

methylcyclohexane were obtained from SCS data,⁴ and are therefore not as definitive as the other shifts in Fig. 1.

In all cases the geometry used was that obtained from molecular modelling calculations. This was only of importance for axial methylcyclohexane, in which a 'standard' geometry, *i.e.*, adding a methyl group to an unstrained cyclohexane ring gave much poorer agreement, due to the vastly increased steric shifts.

In summary, we show that a simple extension of the CHARGE3 scheme can give an accurate prediction of the proton chemical shifts of a variety of hydrocarbons, and this suggests that an extension of such methodology could provide a simple method of predicting the proton chemical shifts of a wide variety of organic compounds.

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