Proton Chemical Shift and Localization in Aliphatic Open-chain Hydrocarbons

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Summary A relationship between proton chemical shift and hybridization at carbon has been established in open-chain alkanes, suggesting that, in these compounds, proton shielding depends miainly on C–H bond electrons.

THE proton shielding constant is commonly partitioned into several terms which account for effects arising from molecular charge distribution, electric field, magnetic anisotropy, dispersion forces, ring-currents, and hybridization.[1] These terms are closely interdependent, which often invalidates the reliability of such partitioning from a theoretical point of view.[2] On the other hand, correlations between chemical shift and a calculated[3] or experimental[4] molecular property were found to hold in related series of molecules where other superimposing effects are presumably constant.

In a recent paper by Allinger and his co-workers,[5] the shielding constant of proton in hydrocarbons is considered as being made up from two contributions σ_{loc} and σ' [equation (1)] where σ_{loc} is the shielding arising from the

$$\sigma = \sigma_{\mathrm{loc}} + \sigma' \qquad (1)$$

hydrogen electron cloud, assumed constant for different protons in a hydrocarbon, and σ' is due to the magnetic properties of neighbouring atoms and/or bonds. The conclusion of these authors[5] is that their interpolating equations, which include several types of effects contributing to σ', and incomplete and a specific effect is omitted in the calculation.

Our results were obtained with a view to checking the local polarization of the C–H bond in saturated hydrocarbons starting from localized molecular orbitals (LMOs).

TABLE

s-Character for C–H *hybrids and proton chemical shift* σ_H *in open-chain alkanes*

		MLC		INDO-LMO		
		X_s	σ_H^a(calc.)	Y_s	σ_H^b(calc.)	σ_H(exp.)
Methane[c]	.. ..	0·2500	0·2493	0·2725	0·3404	0·23[d]
Ethane[c]	.. ..	0·2362	0·8345	0·2580	0·7529	0·856[e]
Propane[c]	$(-CH_2)$	0·2247	1·3221	0·2405	1·2507	1·343[e]
	$(-CH_3)$	0·2365	0·8218	0·2590	0·7244	0·906[e]
Isobutane[c]	$(-CH)$	0·2143	1·7631	0·2203	1·8254	1·740[e]
	$(-CH_3)$	0·2366	0·8175	0·2601	0·6931	0·890[e]
Neopentane	.. ..	0·2367	0·8133	0·2611	0·6647	0·927[e]
Isopentane	$(-CH_3)_2$	0·2366	0·8175	0·2602	0·6903	0·940[f]
	$(-CH_3)$	0·2365	0·8218	0·2590	0·7244	0·860[f]
	$(-CH_2)$	0·2248	1·3179	0·2420	1·2080	—
	$(-CH)$	0·2144	1·7589	0·2207	1·8140	—

[a] $\sigma_H = -42{\cdot}4042\ X_s + 10{\cdot}8503$ (standard deviation 0·0212). [b] $\sigma_H = -28{\cdot}4484\ Y_s + 8{\cdot}0925$ (standard deviation 0·0983). [c] Points fitted in equations in footnotes (a) and (b). [d] L. M. Jackman and S. Sternhell, 'Applications of NMR Spectroscopy in Organic Chemistry,' Pergamon Press, Oxford, 1968, p. 164. [e] A. G. Moritz and N. Sheppard, *Mol. Phys.*, 1963, **6**, 489. [f] H. Conroy, *Adv. Org. Chem.*, 1960, **2**, 265.

The approach will be especially useful if it is successful in representing covalent bonds (like C–C and C–H) with strictly localized orbitals and it is found that there are local properties on the proton or on other parts within the molecule which will largely explain the observed trends. To overcome the questionable assumption of nearly identical atomic charge densities for all protons in a hydrocarbon[5] we examined the hybridization at the carbon atom to which the proton is bonded, bearing in mind that, when localization is perfect, hybridization and charge density are two strictly related quantities.

In a perfectly localized orthonormal MO associated to a C_A–H_B bond, there are non-zero coefficients only for AOs belonging to the atoms C_A and H_B so that, if the MO j is normalized to 1, the charge density for the atom H_B is given by equation (2). Following Trindle and Sinanoglu,[6]

$$q_{H_B} = 2\,a^2_{jH_B} = 2(1 - \sum_{i\in C_A} a^2_{ji}) \qquad (2)$$

we can define s-character, X_s, for the hybrid pointing from C_A to H_B as in equation (3). We can thus use the s-character of hybrids in place of charge densities for

$$X_s(C_A\text{–}H_B) = a^2_{jC_A(28)}/\sum_{i\in C_A} a^2_{ji} \qquad (3)$$

correlations against proton chemical shift, since q_{H_B} clearly depends only on the AOs of the atom C_A.

The canonical orbitals obtained by INDO calculations[7] on alkanes were therefore localized[8] and the s-character of C–H hybrid orbitals calculated from LMOs. Since the localization is not completely fulfilled, the term Y_s is to be considered a quantity related to the real s-character X_s.

The results, collected in the Table together with the X_s values computed following a Maximum Localization Criterion[9] show that the experimental trends of chemical shifts are well reproduced passing from methane to methinic hydrogen in isobutane. For these protons, the localized contribution to the screening constant is clearly the dominant term, the neighbouring atoms or bonds causing only minor contributions to the total σ: for the protons of methyl groups we calculate a practically constant s-character and the experimental chemical shifts range from 0·86 to 0·94 p.p.m.

The most interesting feature of this correlation is that, for the above compounds, the commonly called C–C bond effect which refers to the decrease in proton shielding with the progressive substitution of a C–H with a C–C bond,[10,11] *i.e.* on going from CH_3– to C–CH_2– and $(C\text{–})_2$–CH–, is fully accounted for by changes in a local property of the C–H bond without invoking contributions due to distant atoms or bonds.

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