

ORBITAL HYBRIDIZATION AND PROTON CHEMICAL SHIFTS IN SUBSTITUTED METHANES

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(Received in UK 21 February 1972; accepted for publication 2 March 1972)

It is commonly held that the proton chemical shift of alkyl-substituted compounds is affected by several factors,¹ namely, charge density on the proton and the adjacent carbon atom and electric and magnetic field effects. Previously^{2,3} we reported an investigation into the contribution of σ MO charge densities to the proton chemical shifts of substituted methanes, showing that the former quantities are a dominating factor in determining experimental shifts. In the past it has been suggested⁴⁻⁷ that the hybridization of bonds, as well as their polarization due to substituent electronegativity,^{8,9} plays an important role in determining proton chemical shifts.

The present study sets out to ascertain to what extent bond-hybridization contributes to modify the experimental quantities and to find out whether our previous correlations^{2,3} between charge densities and proton shieldings are contradicted. In this approximate treatment a series of substituted methanes with known geometry are considered, and the parameter a , which gives the s character of carbon hybrids directed toward the hydrogen atoms, was derived by the orthogonality condition:¹⁰

$$a_i a_j - (z_i z_j + x_i x_j + y_i y_j) \cos \Phi_{ij} = 0$$

It has been assumed that the hybrids are directed along the bonds, that is to say that no bent bonds are present in our molecules, and $\cos \Phi_{ij} = \cos \Phi_{HH}$ or $\cos \Phi_{XX}$. Calculation shows that an increase of s character in the hybrid orbital lying along the C-H bond parallels a decrease of shielding (low field shift). The results are collected in the Table together with experimental chemical shifts. The plot of the Figure shows that a linear correlation exists between δ_H and a^2 which is restricted to monosubstituted methanes where the first atom of the substituent belongs to the same row or group of the periodic system. This agrees with previous results showing the periodic character of spectroscopic, NMR and IR, properties of alkyl derivatives.^{2,3,8,9,26,27} A possible explanation of the linear proportionality between δ_H and a^2 within the rows of the periodic system is that hybridization and substituent electronegativity might be strictly

connected quantities. In this respect, the higher electronegativity of one substituent X should cause an increase of the p character of the hybrid at carbon lying along the C-H bond.^{13,28-30} In this context, the parallel periodic behaviour of electronegativity and per cent s character of carbon hybrids can be justified, as can the fact that in the case of heavier elements which possess more diffuse orbitals, as shown by the greater C-X bond distance, for a most efficient orbital overlap the carbon hybrid directed toward X should acquire more p character. This could explain for example why chlorine and nitrogen, which have almost equal electronegativity, cause different proton chemical shifts in substituted methanes. When polysubstituted derivatives are examined, the problem arises of obtaining orthonormalized hybrids that reproduce the experimental interbond angles.^{30,31}

The results of our calculation show that for CH_2F_2 and CHF_3 , polysubstitution increases the s character of C-H bonds with a parallel increase of proton chemical shift, so we may conclude that the strong electronegativity of fluorine and its relative small size should favour the overlap of carbon orbitals with higher p content. When other elements such as chlorine or even more bromine and iodine are involved, significant deviations can be found as results from a preliminary inspection. Steric interactions and bent bonds can be invoked to explain the deviations occurring.^{30,31}

It can thus be concluded that carbon hybridization can also be a variable which influences the proton chemical shift of substituted methanes, even if on account of the small changes occurring even for polysubstituted compounds, it clearly represents a second order effect which can be masked by more important perturbations, such as the change of electron charge density around the proton due to electrostatic effects which are undoubtedly related to the electronegativity of the substituents.

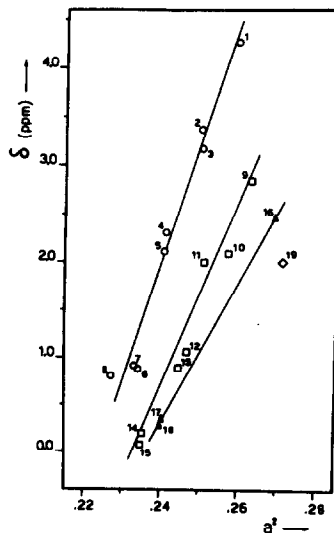


Figure
Proton chemical shift for monosubstituted methanes vs. per cent s character in the C-H bonds. Numbering refers to the values reported in the Table.

TABLE

Per cent s character (a^2)* and proton chemical shifts δ_H (ppm from TMS) for substituted methanes.

n°	Molecule	a^2	δ_H	n°	Molecule	a^2	δ_H
1	CH ₃ F	25.91 ^a	4.26 ⁱ	12	(CH ₃) ₂ PH	24.69 ^g	1.06 ⁱ
2	CH ₃ OH	24.99 ^a	3.37 ^l	13	(CH ₃) ₃ P	24.67 ^j	0.89 ⁱ
3	(CH ₃) ₂ O	25.03 ^a	3.17 ^m	14	CH ₃ SiH ₃	23.54 ^h	0.19 ^q
4	(CH ₃) ₂ NH	24.09 ^b	2.31 ^m	15	(CH ₃) ₃ SiH	23.50 ^h	0.08 ⁿ
5	(CH ₃) ₃ N	24.08 ^a	2.11 ^m	16	CH ₃ Br	26.92 ^a	2.47 ^m
6	CH ₃ CH ₃	23.41 ^c	0.88 ^m	17	CH ₃ GeH ₃	24.05 ^a	0.35 ^q
7	(CH ₃) ₂ CH ₂	23.31 ^d	0.91 ^m	18	(CH ₃) ₂ GeH ₂	24.01 ^k	0.29 ^q
8	(CH ₃) ₃ B	22.72 ^e	0.80 ⁿ	19	CH ₃ I	27.13 ^a	2.00 ^m
9	CH ₃ Cl	26.29 ^a	2.85 ^m	20	CH ₂ F ₂	27.17 ^a	5.62 ⁱ
10	CH ₃ SH	25.73 ^a	2.09 ^p	21	CHF ₃	26.88 ^a	6.38 ⁱ
11	(CH ₃) ₂ S	25.09 ^f	2.00 ^m				

* References relative to this value refer to the molecular geometry of the compounds.

^a Ref. 11; ^b Ref. 12; ^c Ref. 13; ^d Ref. 14; ^e Ref. 15; ^f Ref. 16; ^g Ref. 17; ^h Ref. 18;

^k Ref. 19; ^j Ref. 20; ⁱ Ref. 21; ^l Ref. 22; ^m Ref. 2; ⁿ Ref. 23; ^p Ref. 24; ^q Ref. 25.

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