

Tentative Interpretation of ^{13}C and ^1H Nuclear Magnetic Resonance Chemical Shifts in Simple Methyl and Ethyl Derivatives

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Abstract: Chemical shifts of ^{13}C and ^1H in $(\text{CH}_3)_n\text{M}$ and $(\text{CH}_3\text{CH}_2)_n\text{M}$ compounds are correlated with electronegativity and number of lone pairs present in M. The effect of the electrostatic field on hydrogen atoms agrees with the correlation parameters for the number of lone pairs. Correlation formulas capable of predicting unknown shifts are given.

Several authors¹⁻⁵ have attempted to correlate ^{13}C and ^1H chemical shifts in simple methyl and ethyl derivatives in the vapor state with the electronegativity of the substituent. The results show that, even though a correlation is evident, other factors are important. We have now tried to correlate ^{13}C and ^1H chemical shifts of methyl and methylene groups directly bonded to a substituent of the two series of compounds of general formulas $(\text{CH}_3)_n\text{M}$ and $(\text{CH}_3\text{CH}_2)_n\text{M}$, in which M is an element of valence n . In Figures 1 and 2 the ^{13}C chemical shift is plotted against the chemical shift of the protons of the same group for methyl in $(^{13}\text{CH}_3)_n\text{M}$ and for methylene groups in $(\text{CH}_3^{13}\text{CH}_2)_n\text{M}$. It is easily seen that the position of the points in both diagrams is correlated with the position of the element M in the periodic system. Now the two linear correlations found thus far hold for the elements of the first row (C, N, O, F) or of the seventh group (F, Cl, Br, I) of the periodic system. We think that the major difference between two elements having the same electronegativity is the number of lone pairs that they possess in the valence shell when bonded in a molecule. One can also assume, on the basis of localized orbitals obtained by the most accurate SCF *ab initio* calculations,^{6,7} that, because of electronic repulsion, atoms tend to form tetrahedral bonds and tetrahedral lone pairs. From some triatomic and tetraatomic molecules (OF_2 , H_2O_2 , FNO , H_2O , and others), Scrocco and coworkers⁷ have shown that, whatever the method of localization of the electrons (*i.e.*, Ruedenberg or Boys method), quasi-tetrahedral lone pairs with a near-constant electric dipole moment are always found. It should be pointed out that all calculations thus far performed concern elements belonging to the first row of the periodic system. The value of the electric dipole moment of each lone pair is $\sim 3\text{ D}$.

Empirical Correlation

We can now try to correlate the values of both ^{13}C and ^1H chemical shifts in terms of two variables: (1) electronegativity and (2) number of lone pairs. We have

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(2) P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958).

(3) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1089 (1961).

(4) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 722 (1961).

(5) E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *ibid.*, **36**, 129 (1962).

(6) C. Edmiston and K. Ruedenberg, *ibid.*, **43**, 597 (1965).

(7) E. Scrocco, private communications.

searched for a series of relations of the form

$$\delta = \delta_0 + aE + bm$$

where E is Pauling's electronegativity, m is the number of lone pairs on M, δ_0 , a , and b are adjustable parameters, different in principle for ^{13}C and ^1H and also for each of two kind of groups ($(\text{CH}_3)_n\text{M}$ or $(\text{CH}_3\text{CH}_2)_n\text{M}$). We have not taken into account the shifts of the methyl groups in ethyl derivatives because of their very small chemical shift changes that may be strongly affected by experimental uncertainty, different experimental conditions, and also second-order effects. At present, an explanation of these having physical meaning is very difficult. The correlations obtained are shown in Figures 3 and 4 for ^{13}C and ^1H chemical shifts, respectively. (Chemical shifts from benzene as internal reference for ^{13}C and from TMS taken as 10.0 for ^1H .)⁴ The empirical formulas are the following.

^{13}C

$$(1) \delta_{\text{CH}_3\text{M}} = 234 - 55E + 13m$$

$$(2) \delta_{\text{CH}_3\text{CH}_2\text{M}} = 208 - 45E + 7m$$

^1H

$$(3) \tau_{\text{CH}_3\text{M}} = 12.3 - 1.3E - 0.4m$$

$$(4) \tau_{\text{CH}_3\text{CH}_2\text{M}} = 11.0 - 1.0E - 0.5m$$

Discussion

Figures 3 and 4 show that the correlations are good, and the values of the parameters should therefore have physical meaning. It is interesting to note that the sign of b is opposite for ^{13}C and ^1H . This is difficult to explain on the basis of magnetic anisotropic shielding effects as pointed out by Buckingham.⁵ It seems more reasonable to us that this can be caused by the electric field generated by the electric dipole moment of the lone pairs. If we take, for instance, the two compounds CH_3F and $(\text{CH}_3)_2\text{O}$, two influences would affect the chemical shift of the methyl nuclei, *i.e.*, the change in electronegativity and the substitution of a M-CH₃ bond to a lone pair, the latter causing a drastic decrease or even a change of the sign of the local electric dipole moment.

Owing to the rapid rotation around the C-M bond, the effective dipole moment seen by a C-H bond is one-third of the dipole moment of each lone pair and is directed along the bond axis. For the first-row element of the periodic system, for which accurate *ab initio* calculations are available, and the C-M bond lengths are well known, a value of $\sim 1.8 \times 10^5$ esu cm^{-2} at the H nucleus for the electric field directed along C-H bond is obtained. For the other elements two coun-

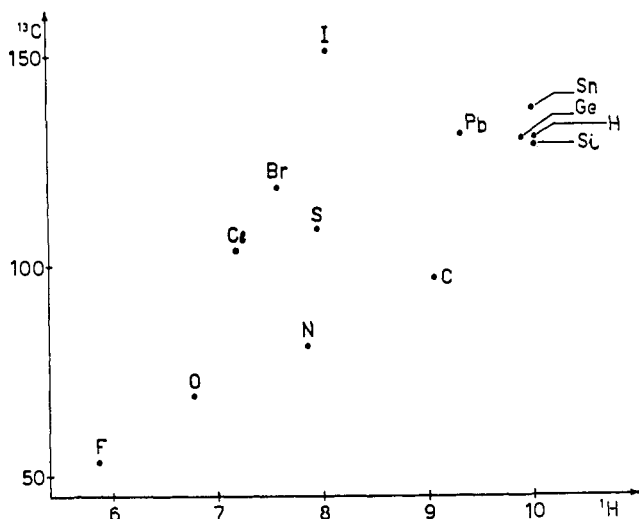


Figure 1. ^{13}C vs. ^1H chemical shifts in $(\text{CH}_3)_n\text{M}$ compounds.

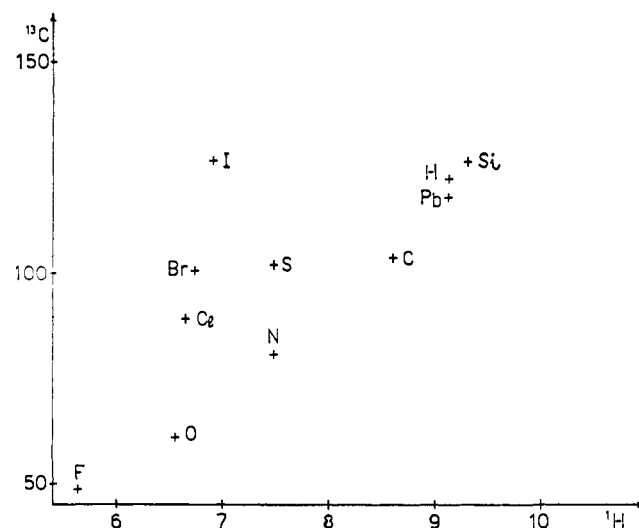


Figure 2. ^{13}C vs. ^1H chemical shifts in $(\text{CH}_3\text{CH}_2)_n\text{M}$ compounds.

teracting effects should play a significant role in varying this result. First, a decrease in field is associated with the increase in the C-M bond length. This effect is opposite that of the increase in field, which will result from the greater expansion of the lone pairs to give larger electric dipole moments. A compensation of these two effects may perhaps justify the simplifying assumption that each lone pair have the same effect for all compounds considered. This assumption is justified by the good correlations obtained. That the electric field so calculated may produce the shifts experimentally observed is shown qualitatively by the calculations of Buckingham.⁸ This author estimated the effect of an electrostatic field on the shielding constant of a ^1H atom polarized by an external charge. He obtained the following formula

$$\delta = 2 \times 10^{-5} - 2 \times 10^{-12} E_z - 10^{-18} E_z^2$$

where E_z is the component of the electrostatic field along the line from the external charge to the H nucleus. This is the simplest model for an H-X bond, in which the external charge simulates the X atom or group. With this formula and the previously evaluated electric field component, an effect of 0.36 ppm per lone pair in the right sense is estimated. This is in surprisingly good agreement with the empirical coefficients 0.4 and 0.5

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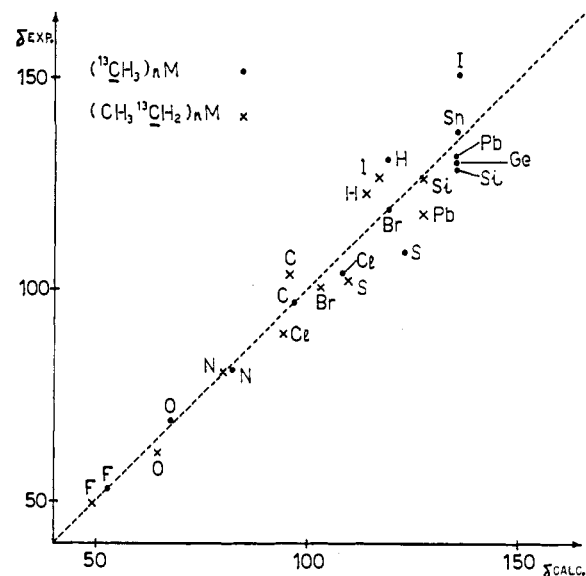


Figure 3. Experimental ^{13}C chemical shifts vs. that calculated with (1) and (2) correlation formulas.

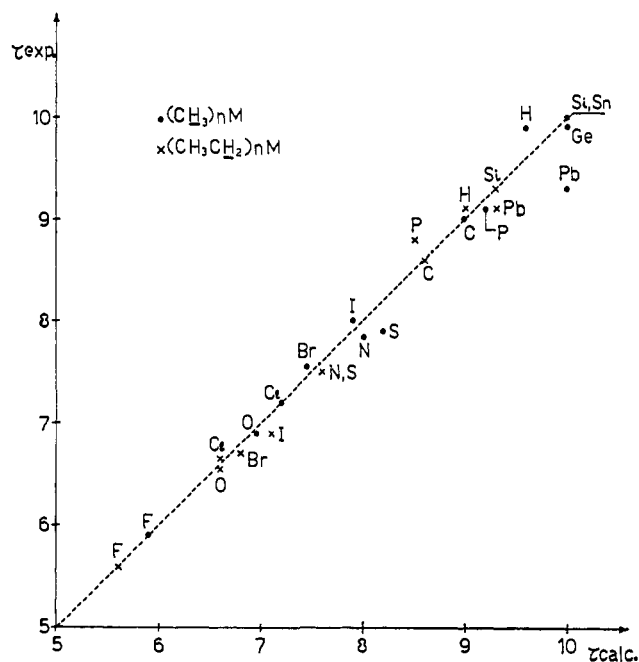


Figure 4. Experimental ^1H chemical shifts vs. that calculated with (3) and (4) correlation formulas.

obtained in the correlations for ^1H chemical shifts. No direct information on the effect of an electrostatic field on a bonded C atom is presently available. Simple considerations about charge shifts in the C-H bond are in agreement with the proposed mechanism. Namely, the electric field of a lone pair tends to displace the charge of a C-H bond from H to C, producing opposite shielding changes. Moreover, the fact that the order of magnitude of the b factors for ^{13}C is 20 times that of the b factors for ^1H agrees with the greater charge dependence of ^{13}C shifts observed by several authors.^{9,10}

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