A New Approach to ^{13}C Chemical Shift Additivity Parameters

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Empirical ^{13}C chemical shift additivity parameters having some theoretical significance are derived. The parameters are of two types: the first categorises the type of the carbon and the second takes the proton interactions into consideration and is formulated in terms of the number of protons in α-, β-, γ-, and δ-positions relative to the carbon under study. With eight parameters the difference between calculated and observed chemical shifts lies within the range obtained by older sets of parameters. It is hoped that this approach will aid better understanding of the factors determining ^{13}C chemical shifts.

The ^{13}C n.m.r. additivity parameters of Grant and Paul[1] and their modifications[2–4] play a major role in the assignment of ^{13}C n.m.r. abosrptions in low-molecular-weight compounds[5] and macromolecules.[6,7] However, despite their practical importance, no effort has been applied to give these parameters meaning in terms of the theory of ^{13}C n.m.r. spectroscopy. Moreover, their magnitudes cannot be explained in a self-consistent manner; there is no explanation for the nearly equal increments for α- and β-carbons, and the effect of proton interactions is limited to the γ-position, which is difficult to justify. If proton interactions exert any real effect on ^{13}C chemical shifts, then it is reasonable to treat the subject in a more general way. Indeed, the effect of proton interactions at the α-position should be more pronounced owing to the proximity of the interacting protons.

Beierbeck and Saunders[8] derived additivity parameters based on the experimental chemical shifts of ethane (for primary carbon), propane (for secondary carbon) isobutane (for tertiary carbon), and neopentane (for quaternary carbon). Further parameters include an interaction between an α-hydrogen and a β-carbon, an exocyclic carbon-carbon interaction in the gauche conformation, and the known proton–proton γ-interaction. Apparently the parameters are applicable only to polycycloalkanes, and even for this class of compounds deviation between observed and calculated chemical shifts amounts in some cases to 3—6 p.p.m. In subsequent communcations[9,10] the authors stressed the importance of 1,3-diaxial interactions (β-effect) for ^{13}C chemical shifts. A similar approach has been adopted by Boaz,[11] who studied the subject in connection with the mutual polarisation of vertically oriented CH and CC dipoles.

We attempt in this work to develop ^{13}C chemical shifts based on two factors: (1) the contribution of H(1*s*) electrons to the molecular valence orbitals of carbons; (2) proton interactions.

The first factor originates from theoretical considerations, and takes into account the share of *p*-electrons which constitute the valence orbitals of carbons. It was recognised at an early stage of the development of n.m.r. that the deshielding paramagnetic term is dominant,[12] and that only *p* and higher orbitals contribute to this term. The valence orbitals of a paraffinic carbon atom are formed out of sp^3 electrons delivered by carbons and a *s* electrons donated by hydrogens. Greater participation of sp^3 electrons leads to more *p*-character for the respective carbon and in consequence to more deshielding. Thus, the *p*-character of a paraffinic carbon decreases in the order: tertiary > secondary > primary. This may explain the experimental fact that in general deshielding of carbons shows the same trend. Remote carbons at β, γ, and positions further away may also contribute to determining the *p*-character of other carbons in the molecule, since every ultimate carbon reduces the number of hydrogens attached to its penultimate neighbour and hence increases its *p*-character. But it is likely that the contribution of distant carbons attenuates rapidly with increase in the number of intervening bonds. In methane, the valence orbitals of carbon are composed of four C(sp^3) electrons and four H(1*s*) electrons; in ethane five C(sp^3) electrons and three H(1*s*) electrons contribute to the valence orbitals of each carbon. Therefore, we expect deshielding of the ethane carbon relative to methane on the grounds of an increase in the *p*-character of the former carbon. Proceeding further with this reasoning, C-1 of propane should have more *p*-character than a carbon of ethane because it is bonded to a secondary carbon with higher *p*-character. It is evident that the secondary carbon of propane has the highest *p*-character among all carbons considered, and therefore it is the most deshielded.

Proton interactions affect the electronic energy and in turn the chemical shift in a manner not yet definitely understood. But it can be inferred experimentally that proton interactions give rise in most cases to upfield shifts and only few observations have been reported of downfield shifts.[13,14]

Additivity Parameters.—The chemical shifts of alkane carbons have been calculated with equation (1) where $\delta C(k)$

$$\delta C(k) = A + B + \Sigma\, n_l H_l \qquad (1)$$

is the ^{13}C chemical shifts value of the *k*th carbon, *A* is a scaling constant which is reference dependent, *B* is a parameter referring to the type of carbon (primary, secondary, or tertiary), H_l is a parameter belonging to a proton in the *l*th position with respect to the *k*th carbon, and n_l is the number of protons at that position.

Calculations

The experimental results obtained by Carman[4] and his co-workers were used to calculate the additivity parameters applying a regression analysis program.† The Table shows the values of the parameters.

Discussion

A proper way to treat the subject is to find a quantum mechanical method for calculating the *p*-character of valence electrons of carbons, and to treat proton interactions in relation to through-space distances. The difficulties of this type of treatment are apparent and work is progressing along this line in our laboratory. In the meantime and in order to test the merit of the method and to evaluate some effects of help to the theoretical

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† Multiple linear regression program, written by R. W. Kopitzke for a Hewlett–Packard 4830 A calculator.

Results of regression analysis

Parameter	No. of observations	Value (p.p.m.)
Primary carbon	13	7.98
Secondary carbon	30	13.62
Tertiary carbon	16	12.91
α-Proton	59	1.36
β-Proton	59	2.91
γ-Proton	58	0.19
δ-Proton	54	0.13
ε-Proton	46	0.03
No. of total observations	59	
No. of independent variables	8	
Multiple correlation coefficient	0.9985	
Standard deviation (p.p.m.)	±0.27	
Constant term (p.p.m.)	−1.94	

treatment, the present empirical approach is adopted as a first step.

The weakness in the significance of the parameters as introduced here lies in the fact that the two factors (the *p*-character of valence electrons of carbons and the proton interactions) are not completely separated. The value of each of the eight parameters is the result of the interplay between the two effects. The increase in branching which increases the *p*-character (deshielding effect) of tertiary carbons relative to secondary and primary carbons is accompanied at the same time by proton congestion and stronger proton interactions (shielding effect). On the other hand, the term representing the effect of a proton in a definite position (shielding effect) also includes a contribution to the *p*-character provided by the carbon to which the proton is attached (deshielding effect). The consequence of this interplay in determining the values of the individual additivity parameters is clearly reflected in the Table. The deshielding effect increases from methyl to methylene by 5.64 p.p.m. in accord with increased *p*-character, and then slightly decreases for methine relative to methylene due to counterbalancing increase in the shielding interaction term induced by proton congestion at the branching sites. Similar reasoning applies to the interpretation of the unexpected positive values of the terms characterizing proton interactions. It is obvious that the increase in the deshielding paramagnetic term resulting from the addition of a definite carbon to a certain position has more weight than the shielding interaction effect caused by its protons.

The result of the application of these additivity parameters to cycloalkanes was unsatisfactory. These compounds introduce problems of geometrical and conformation isomerism, and any successful approach has to take these factors into account. This has been excellently achieved through the work of Grant and his co-workers[15] which remains the best treatment of the subject to date.

The parameters introduced in this work are able to predict ^{13}C chemical shifts with a standard deviation of ±0.27 p.p.m. using only eight variables. The highest individual deviation arises in a highly branched alkane (C-3 of 2,4,6-trimethylheptane) and amounts to 0.82 p.p.m. The results suggest that this new approach possesses certain promising aspects.

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Received 1*st August* 1986; *Paper* 6/1567