

Short communication

The relation of directly bonded C–H coupling constants to s -characters revisited

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Summary. Following earlier theoretical studies of orbital delocalization effects on one-bond ^{13}C –H coupling constants ($^1J_{\text{CH}}$) an approximate proportionality of $^1J_{\text{CH}}$ to $\rho^{3/2}$, where ρ is the s -character of the carbon hybrid orbital appropriate to the construction of the best localized molecular orbitals, is predicted and verified by using published data. It is proposed that this proportionality should replace the previous linear correlations of $^1J_{\text{CH}}$ with ρ , which involve large additive constants.

Key words: NMR — C–H coupling — s -Character — Delocalization effects

The almost exact proportionality of the one-bond ^{13}C –H coupling constants in the simple hydrocarbons to the s -character of the formal sp^3 , sp^2 and sp hybrid orbitals provides one of the rare examples of excellent agreement between experiment and theory in the field of nuclear spin coupling constants, especially when the theoretical calculation is carried out at a very simple and crude level, as is usually the case [1, 2]. These circumstances have made the above relationship an important landmark in the subject of NMR spectroscopy, with more or less successful applications and extensions to other systems and other one-bond coupling constants. For hydrocarbons in general, linear relationships have been established between ^{13}C –H coupling constants 1J and the s -character ρ of the corresponding carbon hybrid orbital appropriate to a localized description of the C–H bond [3–5]. For substituted hydrocarbons, other factors are known to operate, namely changes in the density of the carbon s orbital at the nucleus (which is a function of the total electron charge on the carbon atom) [6], and electron lone-pair effects (which have an orientational dependence) [7].

The linear relationships between $^1J_{\text{CH}}$ and ρ established by using some criterion for constructing almost localized electron functions all have two things

in common. Firstly, they are based on the assumption that the residual orbital delocalization, which is essential in the interpretation of two-bond and longer range couplings, has a negligible effect on ${}^1J_{\text{CH}}$. Secondly, they all include a large additive constant; the empirical relationship established for hydrocarbons is

$${}^1J_{\text{CH}} = \frac{1079}{1 + S^2} \rho - 54.9 \text{ Hz} \quad (1)$$

when the maximum overlap method is used to define localized valence-bond functions (S is the orbital overlap integral between the hydrogen $1s$ orbital and the carbon hybrid orbital in the C–H bond) [3],

$${}^1J_{\text{CH}} = 570\rho - 18.4 \text{ Hz} \quad (\text{SD}^1 = 5.7 \text{ Hz}) \quad (2)$$

when the Edmiston–Ruedenberg localization procedure is used on INDO molecular orbitals [4], and

$${}^1J_{\text{CH}} = 691\rho - 72.4 \text{ Hz} \quad (\text{SD} = 5.0 \text{ Hz}) \quad (3)$$

when modified (with optimized atomic orbital exponents) INDO molecular orbitals are transformed according to the localization method of von Niessen [5]. Equation (3) becomes

$${}^1J_{\text{CH}} = 709\rho - 80.8 \text{ Hz} \quad (\text{SD} = 6.7 \text{ Hz}) \quad (4)$$

when heteroatomic molecules are also included [5].

It has been suggested that these two points are not independent: to a large extent the size of the additive constant may be an artifact of the neglect of residual delocalization [8]. That residual delocalization can be important for directly bonded C–H coupling has been shown in calculations on symmetrical CH_n systems (tetrahedral CH_4 , trigonal planar CH_3 , linear CH_2) [9], for which it was found that delocalization made the excitation energy in the denominator of the ${}^1J_{\text{CH}}$ theoretical expression dependent on $n - \Delta E$ increasing with \sqrt{n} —contrary to what is assumed in the initial theoretical models; accordingly, for those systems we have

$${}^1J_{\text{CH}} \propto \rho^{3/2} \quad (5)$$

with $\rho = 1/n$ corresponding to a starting localized bond description in terms of sp^{n-1} carbon hybrid orbitals.

On going from CH_n to the hydrocarbons C_2H_6 , C_2H_4 and C_2H_2 , the symmetrical arrangement of the orbitals around the carbon atom is lost and changes are expected, mainly due to the replacement of hydrogen by carbon orbitals. One way of accounting for these alterations, and which still considers the C–H bonds to be described in terms of carbon sp^{n-1} orbitals (where n is again the carbon coordination number), requires changes in the ΔE values. The fact that ${}^1J_{\text{CH}}$ for the simple hydrocarbons is found to be proportional to $\rho = 1/n$ means that ΔE becomes (accidentally) almost independent of the carbon coordination number.

¹ SD, standard deviation

An alternative method is to describe the C–H bonds in terms of new carbon hybrid orbitals in such a way that residual delocalization is kept to a minimum when an H atom in CH_n is replaced by a C atom (or CH_{n-1} fragment). In such cases, less significant changes in ΔE are required than was the case for CH_n . Our hypothesis is that to a good approximation, ΔE continues to increase with $\sqrt{n} \simeq \sqrt{1/\rho}$. Accordingly, ${}^1J_{\text{CH}}$ cannot be expected to be proportional to the newly defined ρ values, and this is confirmed by Eqs. (1)–(4). Instead, the \sqrt{n} dependence of ΔE (in the denominator of ${}^1J_{\text{CH}}$ theoretical expressions) should imply that ${}^1J_{\text{CH}}$ is approximately proportional to $\rho^{3/2}$. This is what is found when we replot the data of [5], including heteroatomic molecules:

$${}^1J_{\text{CH}} = 769\rho^{3/2} + 6.5 \text{ Hz} \quad (\text{SD} = 5.9 \text{ Hz}). \quad (6)$$

It is noted that the effect of electron lone-pairs is largely reflected in the computed ρ values, and that no changes in the *s*-orbital densities have been invoked in the approximation used.

In conclusion, as a result of orbital delocalization effects which make excitation energies approximately depend on \sqrt{n} , n being the C coordination number, linear relationships of ${}^1J_{\text{CH}}$ with *s*-characters, ρ , defined by an acceptable localization procedure of good molecular orbitals, should be replaced by an approximate proportionality to $\rho^{3/2}$.

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