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Non-neighbour effects on hyperfine coupling constants in alternant hydrocarbon radicals

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An improvement of the McConnell formula for the correlation of hydrogen coupling constants in alternant hydrocarbon ions is derived.

The new formula is analogous to the one recently proposed by COLPA and BOLTON and is obtained without introducing any charge effect but only considering, in the first order perturbation expansion, terms arising from hydrogen next nearest neighbour carbon p orbitals.

Die McConnell-Formel für die Wasserstoff-Kopplungskonstante in alternierenden Kohlenwasserstoffionen wird verbessert. Die neue Formel ist ein Analogon der kürzlich von COLPA und BOLTON vorgeschlagenen, wird aber ohne Einführung von Ladungseffekten erhalten. Sie ergibt sich vielmehr durch Hinzunahme der Glieder, die die der *CH*-Bindung benachbarten Kohlenstoff-p-Eigenfunktionen in erster Näherung berücksichtigen.

La formule de McConnell pour les constantes de couplage hyperfin protonique dans les ions des hydrocarbures alternants est améliorée.

La nouvelle formule est analogue à une autre proposée récemment par COLPA et BOLTON; on l'obtient, sans introduire des effets de charge, seulement par inclusion des termes perturbateurs de premier ordre, dérivant des orbitales p des carbones adjacent à la liaison *C-H* considérée.

Introduction

As is well known a very simple formula due to McCONNELL [4] is generally used for the rationalisation of the hyperfine coupling constants for the hydrogen atoms attached to the carbon atoms of conjugated radicals.

The formula is

$$a_H = Q\varrho \tag{1}$$

where a_H is the coupling constant, ϱ is the π electron spin density on the adjacent carbon atom and Q is a semi-empirical constant characteristic of the aromatic *C-H* bond.

There are however some important discrepancies with experiment in this correlation even in the simplest cases of alternant hydrocarbon ions.

In these systems the simple Hückel spin density, which is equivalent to the square of the m. o. coefficient in the singly occupied orbital, is probably a good approximation to the true density and it is the one most used in testing equation (1). While for a comprehensive discussion one should also consider spin densities as given by more elaborate treatments such as SCF and CI calculations, we shall stick in the following to the Hückel theoretical scheme of the π electron systems with the purpose of seing how much of the discrepancies is due to the neglect of important terms within this scheme and leaving to subsequent papers, dealing also with non alternant and non hydrocarbon systems, other possible improvements.

The two major discrepancies within the series under investigation are:

1. the Q for the first member of the series, benzene, is almost 30 per cent lower than the best Q for the higher members. In fact the experimental a_H for benzene negative ion is 3.75 gauss giving a Q value of 22.5 gauss while all other hydrocarbons require Q values around 30 gauss.

2. The positive and the negative ions of the same hydrocarbon, which according to (1) should have the same coupling constants within the Hückel π electron scheme, have in fact significantly different ones, the positive ions having in general higher c.c. 's than the negative.

The latter point has been recently discussed by Colpa and Bolton [3] (cited in the following as C.B.) who propose an explanation for this behaviour based on the fact that the σ electrons of the CH bond, which are the ultimate responsible of the isotropic c.c. of the proton, "feel" the influence of the charge on the C atom and that the σ orbitals in the case of a positive charge will be different from those in the case of a negative charge.

We propose in this paper an alternative explanation of the disagreement, based on the fact that formula (1) is only a crude approximation which can be improved in a very simple way by the introduction of a second semi-empirical constant, as done by C. B. but on quite different physical grounds in particular avoiding the consideration of a distortion of the σ bond.

Our approach gives essentially the same result as the one by C. B. for point 2 but has the advantage of disposing also of point 1 by fitting perfectly in the correlation also the benzene coupling constant.

Theoretical

The theoretical justification of (1) lies essentially in the consideration of a π-σ interaction between the aromatic π system and the C-H bond electrons. The interaction is described by adding to the usual ground state wave function configuration wave functions obtained by exciting one electron from the bonding CH orbital (σ) to the corresponding antibonding orbital (σ^*). First order perturbation theory gives the result

$$a_H \propto \frac{(\sigma\pi_0 \mid \sigma^*\pi_0)}{\Delta E_{\sigma\sigma}{}^*} \qquad [4] \qquad (2)$$

where the quantity at the numerator is a short hand for

$$\iint \sigma(1)\,\pi_0(1)\,\frac{e^2}{r_{12}}\,\sigma^*(2)\,\pi_0(2)\,d\tau_1\,d\tau_2.$$

π_0 is the singly occupied π orbital and $\Delta E_{\sigma\sigma}{}^*$ is the difference in energy between the two CH σ orbitals.

If we expand π_0 according to:

$$\pi_0 = \sum_i c_{0i}\,\chi_i \qquad (3)$$

where the χ_i are the p orbitals on the carbon atoms, we obtain from (2):

$$a_H \propto \frac{\sum_{ij} c_{0i}\,c_{0j}\,(\sigma\,\chi_i \mid \sigma^*\,\chi_j)}{\Delta E_{\sigma\sigma}{}^*}\,. \qquad (4)$$

Now, if H is attached to the i-th carbon atom, the approximation is made of neglecting all integrals except $(\sigma\,\chi_i \mid \sigma^*\,\chi_i)$, hence:

$$a_{H_i} \propto \frac{c_{0i}^2\,(\sigma\,\chi_i \mid \sigma^*\,\chi_i)}{\Delta\,E_{\sigma\sigma^*}}. \tag{5}$$

For all aromatic hydrocarbon ions the assumption is now made that the atomic orbitals involved are always essentially the same and (5) becomes eqn. (1).

If we are prepared to fit the experimental results by using a second empirical constant as done by C.B., we may investigate the effect of the terms in (4) containing integrals of the type: $(\sigma_i\,\chi_i \mid \sigma_i^*\,\chi_{i\pm1})$ involving only nearest neighbour atomic orbitals of χ_i.

It is qualitatively apparent that such an inclusion will produce an effect on a_H of opposite sign for positive and negative ions, owing to the different symmetry of the singly occupied m.o. 's in the two cases, for in the case of alternant hydrocarbons the product $c_{0i}\,c_{0j}$ for the positive and respectively negative ions are equal in magnitude but of opposite sign.

It follows that eqn. (4) can be approximated to:

$$a_{H_i} \propto \frac{c_{0i}^2\,(\sigma\,\chi_i \mid \sigma^*\,\chi_i)}{\Delta\,E_{\sigma\sigma^*}} \pm \frac{\left|\Sigma_j{}^{\dagger}\,c_{0i}\,c_{0j}\right|\left[(\sigma\,\chi_i \mid \sigma^*\,\chi_j) + (\sigma\,\chi_j \mid \sigma^*\,\chi_i)\right]}{\Delta\,E_{\sigma\sigma^*}} \tag{6}$$

the $+$ and $-$ signs being used for positive and negative ions respectively and the summation being extended only to orbitals adjacent to the i-th one.

On the usual hypothesis that the atomic orbitals remain the same in all hydrocarbons we can write:

$$a_{H_i} = Q_1\,c_{0i}^2 \pm Q_2 \Big|\sum_j{}^{\dagger}\,c_{0i}\,c_{0j}\Big|. \tag{7}$$

This formula is very similar to the one obtained by C. B. but the second term has obviously quite a different meaning.

Results and discussion

The correlation for the proton coupling constants of alternant hydrocarbon ions expressed by (7) has been tested for all the ions listed in the Table where the results are compared with the experimental ones and with the values given by the C. B. correlation.

The constants Q_1 and Q_2 were obtained by a best fit procedure. The values obtained by using Hückel coefficients are $Q_1 = 31.5$ gauss, $Q_2 = 7.0$ gauss. The correlation holds equally well if coefficients including nearest neighbours' overlap $(S = 0.248)$ are used in the equation

$$a_{Hi} = \overline{Q}_1 \overline{c}_{ki}^2 + \overline{Q}_2 \sum_j{}^{\dagger} \overline{c}_{ki}\,\overline{c}_{kj}. \tag{7'}$$

In this case the two constants are $\overline{Q}_1 = 32$ gauss and $\overline{Q}_2 = 15$ gauss.

This fact is easily understood from the well known relations existing between the two series of coefficients in the case of hydrocarbon systems (see for example [5]), namely:

$$\overline{c}_{ki} = \frac{c_{ki}}{(1 + S m_k)^{1/2}} \tag{8}$$

where $\bar{c}_{ki}$ is the coefficient of the i-th atomic orbital in the k-th molecular orbital including overlap, c_{ki} is the corresponding coefficient neglecting overlap, S ist the overlap integral and m_k is the k'th eigenvalue of the topological matrix.

Table

	Without overlap $Q_1 = 31.5$ $Q_2 = 7$	With overlap $\bar{Q}_1 = 32$ $\bar{Q}_2 = 15$	Exp.	C. B.
Benzene$^-$	4.08	3.77	3.75	[4.73]
Naphtalene$^-$	1.87	1.85	1.83^a	2.08
	4.91	4.86	4.90^a	5.09
Anthracene$^+$	1.66	1.67	1.40^a	1.54
	3.32	3.35	3.11^a	3.18
	6.65	6.69	6.65^a	6,67
Anthracene$^-$	1.38	1.39	1.57^a	1.46
	2.76	2.77	2.74^a	2.86
	5.53	5.55	5.56^a	5,40
Tetracene$^+$	1.13	1.14	1.03^a	1.07
	1.89	1.91	1.74^a	1.81
	4.94	5.00	5.17^a	4.97
Tetracene$^-$	0.99	1.06	1.17^a	1.03
	1.66	1.67	1.49^a	1.70
	4.34	4.39	4.25^a	4.23
Pentacene$^-$	0.71	0.72	0.88^b	0.78
	1.06	1.07	0.88^b	1.10
	3.17	3.21	3.01^b	3.11
	4.23	4.28	4.27^b	4.07
Perylene$^+$	0.44	0.44	0.46^a	0.41
	2.82	2.84	3.09^a	2.72
	3.66	3.69	4.11^a	3.56
Perylene$^-$	0.38	0.38	0.46^a	0.40
	2.42	2.45	3.09^a	2.48
	3.13	3.16	3.53^a	3.17
Phenanthrene$^-$	0.05	0.05	0.43^b	0.06
	1.47	1.46	0.63^b	1.64
	2.70	2.67	2.88^b	2.92
	3.15	3.12	3.71^b	3.38
	4.69	4,64	4.43^b	4.87
Diphenylene$^+$	0.93	0.94	0.21^c	[0.85]
	3.02	3.04	3.96^c	[2.85]
Diphenylene$^-$	0.76	0.76	0.21^c	[0.83]
	2.48	2.48	2.86^c	[2.59]

^{a} see ref. [*1*] ^{b} see ref. [*3*] ^{c} see ref. [*2*]

For diphenylene ions SCF calculations give evidence of negative spin densities at the positions of smaller coupling constants.

Keeping in mind the „pairing properties" of the aromatic ions we can write equation (7′) in terms of the c's:

$$a_{H_i}^{(\pm)} = \frac{\bar{Q}_1 c_{0i}^2 \pm \bar{Q}_2 \left| \sum_j{}^* c_{0i} c_{0j} \right|}{1 \pm |m_0| S} \tag{9}$$

where the + and — signs hold for positive and negative ions respectively.

By summing and subtracting (9) for the positive and negative ions of the same compound we obtain:

$$\begin{aligned} a^{+}_{H_i} + a^{-}_{H_i} &= 2\,\bar{Q}_1\, x - |\, m_0 \,|\, S\, (a^{+}_{H_i} - a^{-}_{H_i}) \\ a^{+}_{H_i} - a^{-}_{H_i} &= 2\,\bar{Q}_2\, y - |\, m_0 \,|\, S\, (a^{+}_{H_i} + a^{-}_{H_i}) \end{aligned} \tag{10}$$

where

$$x = c^2_{0i} \text{ and } y = \Big|\sum_{j}{}^{*}\, c_{0i}\, c_{0j}\Big| .$$

If we now neglect the second term on the right of the first of eqns. (10) which is in all cases at most 2—3 per cent of the first term, and use the obvious fact that $y/x = |\, m_0 \,|$, we obtain:

$$\begin{aligned} \frac{a^{+}_{H_i} + a^{-}_{H_i}}{2} &= \bar{Q}_1\, x \\ \frac{a^{+}_{H_i} - a^{-}_{H_i}}{2} &= (\bar{Q}_2 - S\bar{Q}_1)\, y \end{aligned} \tag{11}$$

or:

$$a^{(\pm)}_{H_i} = \bar{Q}_1\, x \pm (\bar{Q}_2 - S\bar{Q}_1)\, y \tag{12}$$

Q_2 should then be equal to $(\bar{Q}_2 - S\bar{Q}_1)$ whose value is 7.05 gauss in agreement with the value obtained from the fit.

The non complete agreement is due to the neglection of the second term of the first of eqns. (10). The disagreement is felt most in the case of benzene for which $|\, m_0 \,| = 1$ while in all other cases $|\, m_0 \,|$ is always less than one. The inclusion of overlap in Hückel spin densities is in this way shown to be essentially non important in the case of alternant hydrocarbon ions and in all cases in which the topological matrix has the same eigenvectors as the overlap matrix. It could however be of some importance in other cases.

If one however desires to discuss the absolute value of the Q constants the necessity seems obvious of considering the correlation equation including overlap. From (6) we can try to get an estimate of the ratio $\bar{Q}_1/\bar{Q}_2$ to be expected in the correlation. It should be:

$$\frac{\bar{Q}_1}{\bar{Q}_2} = \frac{(\sigma_i\, \chi_i \,|\, \sigma^*_i\, \chi_i)}{(\sigma_i\, \chi_i \,|\, \sigma^*_i\, \chi_j) + (\sigma_i\, \chi_j \,|\, \sigma^*_i\, \chi_i)} .$$

If we assume:

$$\sigma_i = \frac{1}{\sqrt{2 + 2S}}\,(t_i + h_i) \qquad \sigma^*_i = \frac{1}{\sqrt{2 - 2S}}\,(t_i - h_i)$$

in which t_i is a carbon sp^2 orbital on atom i and h_i the attached hydrogen orbital we obtain:

$$\frac{\bar{Q}_1}{\bar{Q}_2} = \frac{(t_i\, \chi_i \,|\, t_i\, \chi_i) - (h_i\, \chi_i \,|\, h_i\, \chi_i)}{2\,[(t_i\, \chi_i \,|\, t_i\, \chi_j) - (h_i\, \chi_i \,|\, h_i\, \chi_j)]} .$$

By using theoretical values of the integrals* over Slater a. o.'s for the usual geometry of the hydrocarbon systems we obtain: $\bar{Q}_1/\bar{Q}_2 \simeq 2$ which is the value obtained in the correlation including overlap.

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* The three center integral $(h_i\, \chi_i | h_i\, \chi_j)$ has been taken as the average between $(h_i\, \chi_i | h_i\, \chi_i)$ and $(h_i\, \chi_j | h_i\, \chi_j)$.

From the success of the correlation here proposed we conclude that the charge effect considered by the C. B. equation, while probably existing as a second order effect, is too much overestimated. In support of this conclusion, beside the obvious existence of the nearest neighbours' effect, we note also that our correlation is distinctly superior to the one by C. B. for the larger coupling constants where two effects which can be of importance in upsetting the correlation are certainly smaller: the effect, when present, of negative spin densities and that of different solvent environment due to the very different media in which negative and respectively positive ions are prepared.

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