Theoretical Study of the Variations in the β-Protons Hyperfine Splitting Parameter of Hydrocarbon Radicals

Marina Brustolon, Carlo Corvaja, and Giovanni Giacometti

Institute of Physical Chemistry, University of Padua, Padua, Italy

The β proton hyperfine splitting constants of a large number of positive, negative, and neutral π radicals, have been examined in term of the Heller-McConnell relation $a_H = B \varrho_c \cos^2 \vartheta$ whose validity is discussed. B is taken as a function of the energy of the singly occupied orbital and values are calculated by first order perturbation theory for the cases of a methyl, methylene, and dimethylene group attached to the π system. Substantial agreement is found between theory and experiment indicating the correctness of the postulated cause of the B behaviour.

Die Konstante der Hyperfeinaufspaltung für β-Protonen einer großen Anzahl positiver, negativer und neutraler π-Radikale wurde mit der Beziehung von Heller und McConnell als Grundlage untersucht; die Gültigkeit dieser Beziehung wird diskutiert. B wird als von der Energie des einfach besetzten Orbitals abhängig angenommen und seine Werte mit Hilfe der Störungstheorie erster Ordnung für die Fälle von Methyl-, Methylen- und Dimethylengruppe am π-System berechnet. Aus der guten Übereinstimmung zwischen Theorie und Experiment wird auf die Richtigkeit der postulierten Ursachen für das Verhalten von B geschlossen.

Introduction

In the past ten years, thanks to ESR spectroscopy, the knowledge of the electronic structure of organic π radicals is greatly enhanced [1]. The distribution of the electron spin over the molecule in negative, positive or neutral conjugated radicals has been calculated by means of quantum theories and the results have been compared with "experimental" distributions.

The latter were obtained from the well known McConnell equation [2]

$$a_H = Q \varrho_c , \tag{1}$$

which relates the hyperfine splitting constant of a proton to the π spin density on the conjugated carbon atom to which the proton is directly bonded.

In some cases corrections to (1) have proved to be necessary; for instance Colpa and Bolton [3] have modified it by introducing a corrective term dependent on the electrical charge on the carbon atom in order to account for the different hyperfine splittings measured in positive and negative alternant hydrocarbon radicals. The same difference has been explained in another way by Giacometti, Nordio and Pavan, who took into account the bond spin density ϱ_{ij} [4]. However in most cases the simple McConnell equation seems to be sufficiently accurate for the correlation of α proton hyperfine splittings with π spin densities [5].

In the ESR spectrum of alkyl substituted π radicals, in addition to the hyperfine structure due to the α-protons, a rich structure due to the alkyl protons in

the β position is observed. There are good evidences that the mechanism by which the unpaired electron interacts with the β protons is hyperconjugation [6–8]. It follows that the hyperfine splitting constant of a β proton shows an angular dependence, being given by an equation of the form [9]:

$$a_H^\beta = B \varrho_c \cos^2 \vartheta \,. \tag{2}$$

ϑ is the dihedral angle formed by the direction of the π_c orbital and the C^β–H bond. An additional term B_0 which is assigned to a "spin polarization" effect is generally neglected.

It should be noted that if the β proton belongs to a freely rotating methyl group the dependence on ϑ is averaged by the rapid motion and Eq. (2) is immediately suitable for a test of the spin density [10, 11].

Eq. (2) is widely accepted by ESR spectroscopists and it is extensively used in investigations of free radical conformations [12]. However, in spite of the extense use of (2), several values of B are reported in the literature for different series of compounds without a satisfactory explanation for their variation. For example the β proton splittings in the ESR spectra of neutral aliphatic type radicals are described with a B value of 58 Gauss [11, 13] while for a very large number of semidione radical anions a value of $B = 40$ Gauss seems to be more adequate in order to fit the experimental data [14].

The purpose of this work is to examine the reasons of the variation of B by comparing the experimental B values taken from a large number of literature data with those which are predicted on the basis of a simple model.

Theory

In this section we examine the mechanism by which the unpaired electron of a π radical is brought into contact with the protons of an attached methyl group.

Except for the case where the methyl substitution lifts the degeneracy of the orbital occupied by the unpaired electron [15], the spin distribution in a free radical is not changed in a significant way by the presence of the methyl. Furthermore, the observed coupling constants are consistent with a spin population on the $1s$ orbitals of the methyl hydrogens, of only a few percent. This means that one can adequately describe the interaction between a methyl group and the π system in the framework of first order perturbation theory.

The usual description of the –CH_3 group interacting with the π-system is made through two π orbitals. They are the π bonding and antibonding orbitals formed with a $2p_z$ atomic orbital centered on the methyl carbon (ϕ_c) and a linear combination of $1s$ hydrogen orbitals on the three hydrogens, having π symmetry (ϕ_x) [16].

We assume in the following this model and we shall call the two orbitals π_b and π_a

$$\pi_b = S_x \phi_x + S_c \phi_c \,, \tag{3}$$

$$\pi_a = S_c \phi_x - S_x \phi_c \,. \tag{3'}$$

π_a and π_b may be both mixed with the singly occupied molecular orbital π_0 with mixing coefficients b and a, which may be calculated according to first order perturbation theory.

$$b = \frac{\langle \pi_b |H'| \pi_0 \rangle}{\Delta E_{0b}}, \tag{4}$$

$$a = \frac{\langle \pi_a |H'| \pi_0 \rangle}{\Delta E_{0a}}. \tag{4'}$$

In (4) and (4') H' is the Hamiltonian describing the interaction between CH_3 group and π system. In the simple Hückel MO approximation the two matrix elements of H' are given by

$$\langle \pi_b |H'| \pi_0 \rangle = C_{c'}^{\circ} S_c \beta_{cc'} ; \tag{5}$$

$$\langle \pi_a |H'| \pi_0 \rangle = - C_{c'}^{\circ} S_x \beta_{cc'} , \tag{5'}$$

where $\beta_{cc'}$ is the resonance integral between the $2p_z$ orbital of the methyl model and that centered on the carbon atom C' to which the methyl is bonded, and $C_{c'}^{\circ}$ is the Hückel molecular orbital coefficient of π_0 relative to C' carbon atom.

Within this approximation the coupling constant of the proton whose C–H bond makes a dihedral angle ϑ with the p_z orbital of the C_α carbon is:

$$a_H^\beta = B(C_c^{\circ})^2 \cos^2 \vartheta , \tag{6}$$

$$B = \frac{(a_H)^{1s}}{[\psi_{1s}(0)]^2} \beta_{cc'}^2 \left[2 \frac{\langle \phi_c |\hat{\varrho}_H| \phi_x \rangle}{\cos^2 \vartheta} (LS_x^2 - LS_c^2 + MS_c^2 - NS_x^2) \right. \tag{7}$$
$$\left. + \frac{\langle \phi_x |\hat{\varrho}_H| \phi_x \rangle}{\cos^2 \vartheta} (-2LS_cS_x + MS_cS_x + NS_cS_x) \right],$$

where

$$L = \frac{S_c S_x}{\Delta E_{0a} \Delta E_{0b}} ; \quad M = \frac{S_c S_x}{(\Delta E_{0b})^2} ; \quad N = \frac{S_c S_x}{(\Delta E_{0a})^2} ,$$

$(a_H)^{1s}$ is the splitting constant of the hydrogen atom in the ground state and $\hat{\varrho}_H$ is the spin density operator.

For the free rotating methyl group $\cos^2 \vartheta$ is $\frac{1}{2}$ and the (6) may be written as

$$a_H^\beta = \frac{B}{2} (C_c^{\circ})^2 . \tag{6'}$$

As Eqs. (6) and (7) show, the coupling constant a_H is proportional to $(C_c^{\circ})^2$ and the proportionality constant depends on the energy differences ΔE_{0b} and ΔE_{0a} [17].

In the case of a methylene group the same arguments hold with little modifications. If the $-CH_2$-group is bonded to two carbon atoms k and l of the conjugated system, the mixing coefficient is dependent on the coefficients of both carbon orbitals and the spin density is proportional to $(C_k^{\circ} + C_l^{\circ})^2$ [18].

Another different case is that of the $-CH_2-CH_2$-group present in free radicals such as pyracene and acenaphthene ions. The $-CH_2-CH_2$-group should be considered as a system containing 4π orbitals, two of which are symmetric and two

antisymmetric with respect to a plane σ perpendicular to the carbon carbon bond. When the substituted molecule possesses a plane of symmetry coinciding with σ, only one of the two sets of orbitals can be mixed with the singly occupied orbital π°: the one having the same symmetry properties of π°. In these cases one must take into account the appropriate value of the ϑ angle for relating B with the methylene protons coupling constant.

Some other comments are necessary since the equation which is generally used is not exactly the same as (6). We shall discuss this point referring to the case of the methyl group.

The use of Eq. (6) implies the many electrons wave function of the π system be described by a single Slater determinant. On the contrary we know that electron correlation gives rise to a mixing of determinant wave functions obtained by a formal excitation of one electron from a doubly occupied orbital 'i' to a vacant one 'j'. In agreement with this is the experimental observation of the occurrence of negative spin densities which leads to the necessity of using a multideterminant wave function of the form:

$$\Psi = \Psi_0 + \sum_{i,j} \lambda_{ij} \Psi_{ij}. \tag{8}$$

As a consequence the spin density on the hydrogen pseudo π orbital consists of contributions from ϱ_0 together with contributions from the ϱ_{ij}'s. It is only the first contribution which is given by (6). The other contributions depend on the product $C^i C^j$ as well as on the energy of the two π molecular orbitals 'i' and 'j'. Taking into account these contributions the hyperfine coupling of the methyl protons may be written in the form:

$$a_H^\beta = \frac{B}{2} (C_{c'}^\circ)^2 + \sum_{i,j} \frac{1}{2} B_{ij} \lambda_{ij} (C_{c'}^i, C_{c'}^j). \tag{9}$$

The B_{ij}'s are given in the Appendix. Since the spin density ϱ_c on the carbon C is given by

$$\varrho_c = (C_c^\circ)^2 + \sum_{ij} \lambda_{ij} (C_c^i C_c^j) \, (4/\sqrt{6}). \tag{10}$$

Eq. (9) shows that Eqs. (2) and (6) are incorrect.

The exact calculation of the methyl proton hyperfine coupling should be performed by including the methyl π orbitals in a complete MO + CI calculation, as it has been done with success by many authors [16, 19].

However, Eq. (2) may be used with a rather good confidence in most cases, particularly when the methyl group is attached to a carbon atom bearing a quite high spin density, the contributions from the ϱ_{ij} being small. Moreover it is more convenient to use Eq. (2) rather than Eq. (6) (see Appendix).

Evaluation of ϱ

In order to get B values from Eq. (2) we need, beside the experimental β-proton coupling constants, the spin density $\varrho_{c'}$ on the carbon atom to which the methyl is bonded. In the case of radicals with more than one methyl group, we need only the sum of the corresponding ϱ's.

Among the several ways to get ϱ we choose the following one, which uses as much as possible experimental data: namely the α-proton hyperfine splitting constants of the radical and of its unsubstituted parent.

The sum of the spin densities over all the π centers being unity, we have

$$\sum_{c'} \varrho_{c'} = 1 - \sum_{k \neq c'} \varrho_k. \tag{11}$$

In calculating the sum over k, we have to distinguish between carbons to which a proton is attached and carbons in "blind" position. Only for the former the spin density can be obtained from the McConnell equation. For the others we can take the ϱ's calculated according to some theoretical procedure.

The error we introduce in this way is generally small because in most cases the spin density in the "blind" positions is quite small.

Eq. (11) becomes

$$\sum_{c'} \varrho_{c'} = 1 - \sum_{i} \frac{a_{Hi}^{\alpha}}{Q} - \sum_{blind} \varrho_{theoretical}. \tag{12}$$

The Q we use is obtained from the hyperfine splittings of the unmethylated radical:

$$Q = \frac{\sum_{i} a_{Hi}^{\alpha'}}{1 - \sum_{blind} \varrho_{theoretical}}. \tag{13}$$

It is assumed that its value does not change with methyl substitution.

It should be noted that in this way one takes into account also the small variations of spin distribution due to the methyls.

For cases in which the necessary experimental data are lacking we shall rely on purely theoretical calculations of the ϱ's.

Results and Discussion

The calculated B values depend on four parameters: α_c, α_x and β_{cx} which determine the coefficients and the energies of the molecular orbitals π_b and π_a of the C–X group (X = H_3, H_2), and $\beta_{c-c'}$, the resonance integral governing the interaction between the C–X group and the π system.

Several values of the MO parameters have been used by different authors [44, 16, 17] in treating the C–X fragment. We have not performed a systematic search of the best parameters because of their number and the rough approximations involved. Moreover, their variation inside the range of values found in the literature has little effect on the results. For this reason we only looked for a reasonable set showing the correlation of the B values according to Eq. (7). The set we used is the following:

$$\beta_{cc'} = 0.92 \quad \beta_{cx} = 2.5 \quad \alpha_x = -0.5 \quad \alpha_c = 0.$$

The resonance integral β_{c-c} between the two methylene carbons of the –CH_2–CH_2-group is assumed equal to $\beta_{cc'}$.

The table lists all the compounds for which we have found the necessary data in the literature. We should mention however that cases for which $\varrho_{c'}$ is
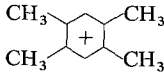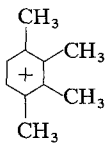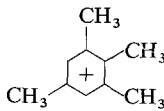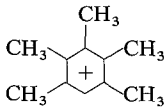
Table
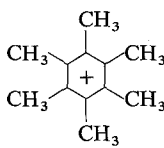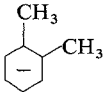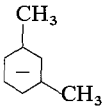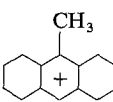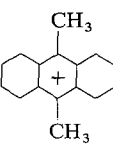
	Radical		a_H^h	Q^a	B_H	B^+	E_0 (β units)	Ref.
1	(cyclohexadienyl cation, tetramethyl)		10.7	26.64 [38]	85.5	85.5[b]	+1	[20]
2	(cyclohexadienyl cation, tetramethyl)	1, 4 \ 2, 3	15.13 \ 2.78	26.64 [38]	79[c]	85	+1	[20]
3	(cyclohexadienyl cation, tetramethyl)	1, 3 \ 2 \ 5	2.96 \ 16.82 \ 14.36	26.64 [38]	[h]	85.5	+1	[20]
4	(cyclohexadienyl cation, pentamethyl)	1 < 0.3 \ 2, 3, 5, 6	10.05	26.64 [38]	80.5	80.5	+1	[20]
5	(cyclohexadienyl cation, hexamethyl)		6.45	26.64 [38]	77.5	77.5	+1	[20]
6	(cyclohexadienyl anion, dimethyl)		6.53	22.5 [39]	48	36	−1	[21]
7	(cyclohexadienyl anion, dimethyl)		2.00	22.5 [39]	54	41	−1	[22]
8	(decalin anion)		—	—	—	43.5[e]	−0.618	[23]
9	(octahydroanthracene cation, methyl)		7.79	27.7[s] [40]	81	60	+0.414	[7]
10	(octahydroanthracene cation, dimethyl)		8.00	27.7[s] [40]	83	56	+0.414	[7]

Table (continued)
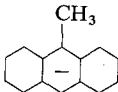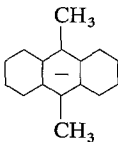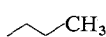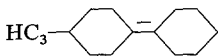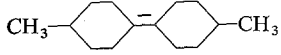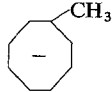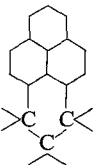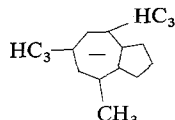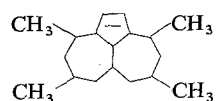
	Radical		a_H^β	Q	B_H		B^+		E_0 (β units)	Ref.
11	(9-methyl octahydroanthracene anion)		4.27	24.9[s] [40]	44		44		-0.414	[7]
12	(9,10-dimethyl octahydroanthracene anion)		3.88	24.9[s] [40]	40		39		-0.414	[7]
13	(CH3 substituted)		3.42	20.8 [43]	50		43		-0.618	[24]
14	(CH3, CH3 substituted)		1.2	20.8 [43]	17		15		-0.618	[24]
15	$\sim\sim$CH3	α-CH$_3$ β-CH$_3$	14.01 16.43	24.65	α-CH$_3$ 56 β-CH$_3$ 66		α-CH$_3$ 48.5 β-CH$_3$ 57		0	[25]
16	H_3C—(bicyclohexylidene)		5.43	26.5[f]	69		53		-0.704	[26]
17	CH_3—(bicyclohexylidene)—CH_3		5.63	26.5[f]	71		54		-0.704	[26]
18	(methyl cyclooctane)		5.1	25.7	55		53.5		0	[27]
19	(tricyclic structure)	ax eq	2.99 11.97	28.6 [45]	72[p]		52[p]		0	[28]
20	(tetramethyl hydrindane anion)	1, 5 3	6.56 9.32	—	67[c]		48[g]		-0.400	[29]
21	(tetramethyl azulene anion)	1, 8 3, 5	5.44 5.12	—	69[c]		46[g]		-0.320	[30]

Table (continued)

	Radical	a_H^h	Q	B_H	B^+	E_0 (β units)	Ref.
22	CH₃ substituted O–[ring]–O	2.045	27.8[h]	44	42	0.343[h]	[31]
23	CH₃ substituted O–[ring]–O, CH₃	2.248	27.8[h]	49	43	0.343[h]	[31]
24	O–[ring]–O, CH₃ / CH₃	2.125	27.8[h]	46	41	0.343[h]	[31]
25	CH₃ CH₃ / O–[ring]–O	1.714	27.8[h]	37	44	0.343[h]	[31]
26	CH₃ CH₃ / O–[ring]–O / CH₃	—	27.8[h]	—	43	0.343[h]	[31]
27	CH₃ CH₃ / O–[ring]–O / CH₃ CH₃	1.897	27.8[h]	41	44[g]	0.343[h]	[31]
28	CH₃ CH₃ / HO–[ring]–OH / CH₃ CH₃	2.1	—	47[i]	47[i]	0.511[i]	[32]
29	O ⋯ CH₃ / C–C / H C	—	—	—	40[j]	−0.369[j]	[14]
30	CH₃–N–CH₃ / [ring] / N	2.04	—	36[k]	37[l]	−0.545[k]	[33]
31	N–CH₃ / [ring] / CH₃–N	1.13	—	39[k]	36[l]	−0.545[k]	[33]
32	CH₃–N–CH₃ / [ring] / CH₃–N–CH₃	1.73	—	30[k]	31[l]	−0.545[k]	[36]
33	H–N / [ring]–CH₃ / +N / H	2.54	29.6[m]	38[n]	51[m]	−0.318[n]	[34]

Table (continued)
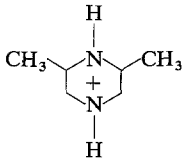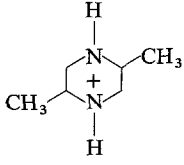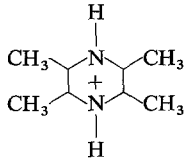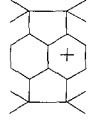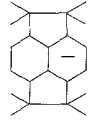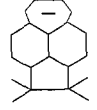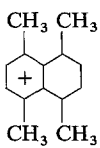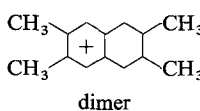
	Radical	a_H^h	Q	B_H	B^+	E_0 (β units)	Ref.
34		2.83	29.6[m]	42[n]	50[m]	−0.318[n]	[34]
35		1.96	29.6[m]	29[n]	48[m]	−0.318[n]	[34]
36		2.53	29.6[m]	38[n]	41[m]	−0.318[n]	[34]
37		11.114	20.8 [43]	41[q]	37[q]	−0.618	[24]
38		5.3	22.5 [39]	85[q]	61[q]	−1	[35]
39		12.8	28.2[o,r] [41, 48]	94[q]	86[q]	+0.618	[16]
40		7.53	25.2 [42]	55[q]	43[q]	−0.618	[16]
41		6.58	25.2 [42]	48[q]	43[q]	−0.618	[16]
42		10.06	—	88[q]	67[g,q]	0.241	[30]
43		3.02	—	109[q]	105[g,q]	−0.457	[30]

Table (continued)

	Radical	a_H^h	Q	B_H	B^+	E_0 (β units)	Ref.
44	CH₃ CH₃ [structure] CH₃ CH₃	7.84	28.2^{o,r} [41, 48]	87	76.5	+0.618	[48]
45	CH₃ CH₃ [structure] CH₃ CH₃ dimer	2.288	28.2° [41, 48]	66	65	+0.618	[48]

[a] The numbers in parenthesis are the references for the experimental data used in the calculation of the Q value.

[b] Assumed equal to Hückel B for uncertainty about the sign of α-coupling constant.

[c] An average value.

[d] Not evaluable; the unpaired electron orbital is a mixing of the two degenerate orbitals of benzene.

[e] For the methylated naphthalenes we assume the B evaluated by Fraenkel et al. (see Ref. [23]).

[f] ϱ-McLachlan from Allred, A. L., Bush, L. W.: J. physic. Chem. 72, 2238 (1968).

[g] Obtained from $B = \dfrac{a_H^\beta}{\cos^2 \vartheta \, \varrho\text{-McLachlan}}$.

[h] ϱ-McLachlan and E_0 from Das, M. R., Fraenkel, G. K.: J. chem. Physics 42, 1350 (1965). Obtained for ethanol-water medium, and for integral values $\alpha_0 = 1.6$, $\beta_{c-o} = 1.2$.

[i] ϱ-Hückel and E_0 obtained with integral values $\alpha_0 = 2.0$, $\beta_{c-o} = 1.1$.

[j] For the semidiones we assume the B evaluated by G. A. Russell. The E_0 value is calculated with $\alpha_0 = 1.5$, $\beta_{co} = 1.6$ [14].

[k] ϱ-Hückel and E_0 calculated with $\alpha_N = 0.75$, $\beta_{CN} = 1$ (Carrington, A., Dos Santos-Veiga, J.: Molecular Physics 5, 21 (1962)).

[l] $\sum\limits_{c'} \varrho_{c'}$ (see text) calculated by using the equation $a_N = Q_N^N \varrho_N + 2 Q_c^N \varrho_C$. The Q^N parameters have been evaluated from the a_N of two compounds, pyrazine⁻ and 2,6 dimethylpyrazine⁻. In this latter, equidistribution of spin density between the two half-rings it is assumed. The ϱ_c, ϱ_N are determined by using $Q_H = -27$ g. The values obtained for Q_N^N and Q_c^N are respectively 23.13 and −1.07.

[m] $\varrho_{N_1} + \varrho_{N_2}$ evaluated from $a_H^{N-H} = -27.5 \, \varrho_N$ [37].

[n] ϱ-Hückel and E_0 obtained with $\alpha_N = 1.2$ $K_{CN} = 1$ [34].

[o] ϱ-McLachlan from L. Salem Molecular orbital theory of conjugated molecules.

[p] $\vartheta_{ax} = 0°$, $\vartheta_{eq} = 60°$. A methylene group, belonging to case (a) in Fig. 1.

[q] $\vartheta = 30°$.

[r] The dimer naphthalene cation Q value.

[s] Calculated with ϱ-McLachlan of the 'blind' positions.

[t] $B_H = \dfrac{a_H^\beta}{(c_{c'}^o)^2 \cos^2 \vartheta}$ where $c_{c'}^o$ is the Hückel coefficient of MO carrying the unpaired electron,

and $B^+ = \dfrac{a_H^\beta}{\varrho_{c'} \cos^2 \vartheta}$ where $\varrho_{c'}$ is evaluated by semiempirical methods (see text and notes). The β-hyperfine coupling constants, the Hückel energy level E_0 of the unpaired electron orbital of the unmethylated parent compound and the Q values are also included. The Q values are evaluated from Eq. (13). The B and Q values are in gauss.

7*

known or expected to be very small or negative have been omitted from been considered.

The Table compares the B values obtained from Eq. (2) (best B, B^+) and Eq. (6) (Hückel B, B_H).

The results for the best B are shown in Fig. 1 where B is plotted against the Hückel energy of the singly occupied orbital, and the "experimental" points have been averaged for the cases of the same parent compounds with one or more methyl group. The two full curves represent the theoretical behaviour as predicted by Eq. (7) for the cases of a methyl group attached to a π center (a), and a dimethylene group attached to two π centers and interacting with an antisymmetric π orbital (b).

The experimental B's seem to fit the correlation even if a certain scatter of the points is present.

This is not too surprising if one realizes that, in the calculation of the molecular orbital energy we used Hückel theory, which is a quite crude approximation. It is interesting to note at this regard that the larger deviations are presented by the quinone radicals (22 to 28 in the table) and by the pyrazine radicals, due to the difficulty to take into proper account the presence of the heteroatoms in the energy calculations. If only hydrocarbon radicals are considered (as in Fig. 1b) the fit is better.

For the radicals containing a large number of methyl groups (4 and 5), there is also an appreciable deviation from the theoretical curve. Also in this case the reason may be ascribed to an error in the calculated energies due to the inductive effect of the methyls.

The methyl proton hyperfine splittings of the 1, 4, 5, 8 tetramethylnaphthalene cation and of the 2, 3, 6, 7 tetramethylnaphthalene dimer cation have been very recently published by Howarth and Fraenkel [48]. The calculated B's of the monomer and dimer radicals fit rather well the correlation.

The experimental B of biphenyl (16 and 17) seems to be too high. It must be noted that in this radical the spin density in the blind positions is quite appreciable and this fact may cause an error in the calculated spin density on the carbon where the methyl is bonded. In this case a change in the energy of the molecular orbital π_0 due to a twist of the benzene rings has little effect on the B since the curve is quite flat in the range of energies involved.

Two radicals are completely outside the correlation: they are the 2,3-dimethyl-butadiene and acepleiadiene ions (14 and 43) and we do not attempt any explanation for this fact.

As to the case of a dimethylene group attached to two π-centers and interacting with a symmetric π_0 orbital, the available experimental data are not enough in order to give a pictorial idea of the fit. The only data we have are those relative to radicals 37 and 38, which show a trend in agreement with the theory.

In conclusion we can say that the β proton hyperfine splitting constants are quite well described by Eq. (2) if the variation of B with the energy of the mono-occupied molecular orbital is taken into account.

An effect of the charge density on the B value is not necessary to explain the results. This is in contrast with the view recently proposed by Underwood and
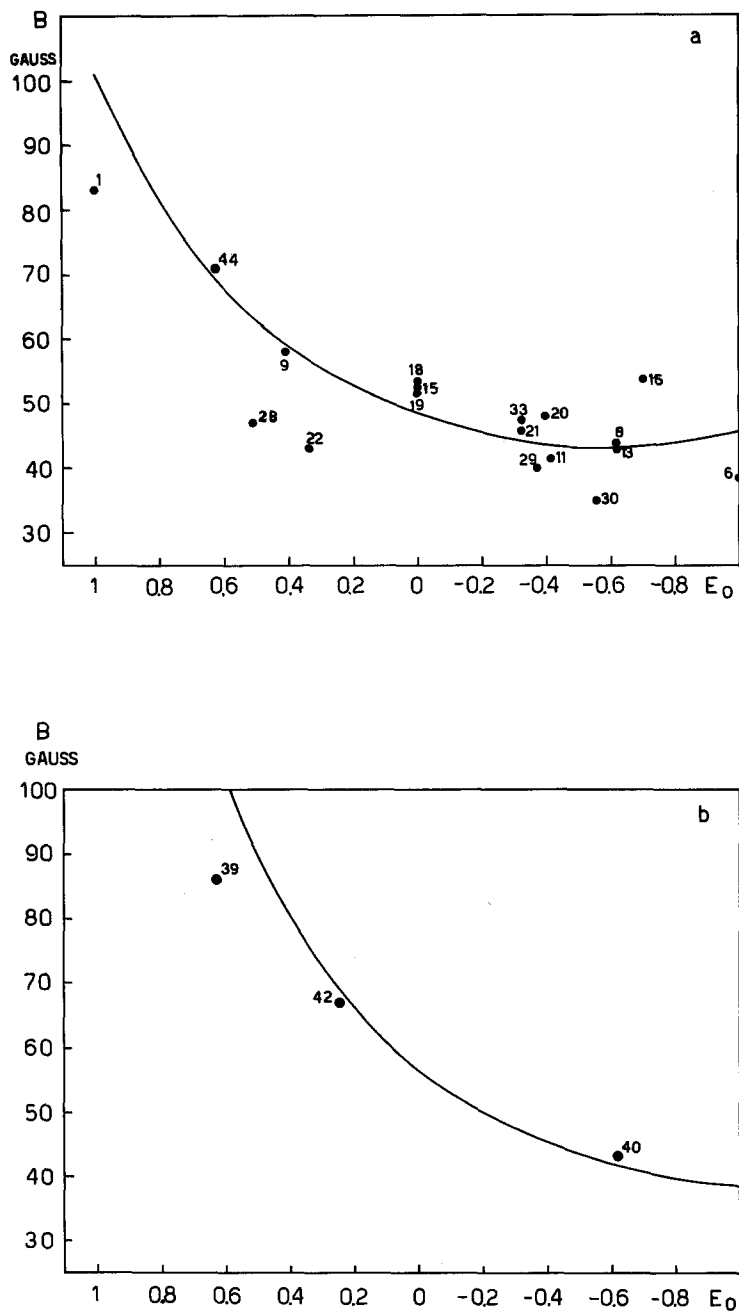
Fig. 1. Curve *a* and *b* show the *B* values predicted by Eq. (7) for: a) a methyl group, b) a $-CH_2-CH_2-$ group, twice bonded to a π system with π_0 antisymmetric with respect to a σ plane perpendicular to the C–C bond. E_0 is the Hückel energy of the singly occupied π orbital. Experimental points are the averaged B^+ values for any serie of homologous compounds. The numbers correspond to the first compound of any series in the Table

Vogel [46]. These authors, on the basis of McLachlan spin densities and experimental splittings, calculated B values whose variations were accounted for by a charge effect. They neglected however the important contributions of the energy of the monooccupied molecular orbital.

Appendix

The electronic state of a methyl substituted free radical is described by a multideterminant wave function of the form:

$$\Psi = \Psi_0 + \sum_{i,j} \lambda_{ij} \Psi_{ij}, \tag{A 1}$$

where

$$\Psi_0 = |1\,\bar{1}\,2\,\bar{2} \ldots i\,\bar{i} \ldots m|, \tag{A 2}$$

$$\Psi_{i \to j} = |1\,1\,2\,\bar{2} \ldots i\,j \ldots m| \frac{1}{\sqrt{6}} (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha). \tag{A 3}$$

Other determinants are omitted because they give no contribution to the spin density. In (A 2) and (A 3) the i molecular orbitals are a mixture of π orbitals and π_b and π_a bonding and antibonding CH_3 orbitals of π symmetry. For the k-th molecular orbital

$$k = \phi_k^\pi + \frac{\langle \phi_k^\pi | \mathcal{H}' | \pi_b \rangle}{\Delta E_{kb}} \pi_b + \frac{\langle \phi_k^\pi | \mathcal{H}' | \pi_a \rangle}{\Delta E_{ka}} \pi_a, \tag{A 4}$$

where ΔE_{kb} and ΔE_{ka} are the energies differences between the ϕ_k^π orbital and respectively the π_b and π_a orbitals; $\mathcal{H}'$ is the hamiltonian describing the interaction between the CH_3 group and the π system. If k is a bonding orbital ΔE_{ka} is large and the mixing of π_a is negligible; for the same reason we can neglect the mixing of π_b in an antibonding orbital.

We shall consider now the effect on the methyl spin density of the configuration $\Psi_{i \to j}$.

The spin density on the methyl protons is given by

$$\langle \Psi | \hat{\varrho}_H | \Psi \rangle = \langle \Psi_0 | \hat{\varrho}_H | \Psi_0 \rangle + 2 \sum_{ij} \lambda_{ij} \langle \Psi_0 | \hat{\varrho}_H | \Psi_{ij} \rangle \tag{A 5}$$

where second order terms in λ_{ij}^2 are neglected.

The hyperfine splitting of a methyl proton thus becomes

$$\begin{aligned}
a_H^\beta &= \langle \Psi | \hat{\varrho}_H | \Psi \rangle \frac{(a_H)^{1s}}{[\psi_{1s}(0)]^2} \\
&= \frac{(a_H)^{1s}}{[\psi_{1s}(0)]^2} \left[\langle m | \hat{\varrho}_H | m \rangle + 2 \sum_{ij} \lambda_{ij} \frac{2}{\sqrt{6}} \langle i | \hat{\varrho}_H | j \rangle \right] \\
&= B C^{02} \cos^2 \vartheta + \sum_{ij} B_{ij} \left(\frac{4}{\sqrt{6}} \lambda_{ij} C^i C^j \right) \cos^2 \vartheta,
\end{aligned} \tag{A 6}$$

where B is defined in (7) and

$$B_{ij} = \frac{(a_H)^{1s}}{[\psi_{1s}(0)]^2} \frac{S_c S_x \beta_{cc'}^2}{\Delta E_{ib} \Delta E_{ja}} \left[(S_x^2 - S_c^2) \frac{\langle \phi_c | \hat{\varrho}_H | \phi_x \rangle}{\cos^2 \vartheta} + S_c S_x \frac{\langle \phi_x | \hat{\varrho}_H | \phi_x \rangle}{\cos^2 \vartheta} \right]. \qquad (A\,7)$$

The spin density on a carbon atom C after first order CI is given by

$$\varrho_c = \varrho_c^0 + \sum_{ij} \lambda_{ij} \varrho_c^{ij} \qquad (A\,8)$$

with

$$\varrho_c^0 = C^{02} \qquad \varrho_c^{ij} = \lambda_{ij} C^i C^j. \qquad (A\,9)$$

ϱ_c^{ij} is the contribution to ϱ_c due to the configuration obtained by the promotion of one electron from i to j.

According to (A 8) and (A 9) Eq. (A 6) may be written as

$$a_H^\beta = B\varrho_c^0 + \sum B_{ij} \varrho_c^{ij}. \qquad (A\,10)$$

Calculations of B_{ij} for a number of different E_i and E_j values show that in most cases the B_{ij} values are close to B, so that the use of Eq. (2) introduces a small error with respect to a complete MO + CI calculation. Moreover this fact points to the advantage of (2) over (6) because (2) takes into account the contributions to the hyperfine coupling arising from the inner electron polarization.

Finally it should be noted that Eq. (2) allows one to use properly empirical data. It should be pointed out also that the contribution from the B_{ij} may still operate when the C^{02} vanishes and there is no contribution from the B term. In such cases the occurrence of a hyperfine splitting by the β protons was attributed to a spin polarization effect [47], but its cause may still be considered of hyperconjugative nature.

References

1. Ayscough, P. B.: Electron spin resonance in chemistry, London: Methuen and Co. LTD. 1967.
2. McConnell, H. M.: J. chem. Physics **24**, 632, 764 (1956).
3. Colpa, J. P., Bolton, J. R.: Molecular Physics **6**, 273 (1963).
4. Giacometti, G., Nordio, P. L., Pavan, M. V.: Theoret. chim. Acta (Berl.) **1**, 404 (1963).
5. Vincow, G.: J. chem. Physics **47**, 2774 (1967).
6. Symons, M. C. R.: Tetrahedron **18**, 333 (1962).
7. Bolton, J. R., Carrington, A., McLachlan, A. D.: Molecular Physics **5**, 31 (1962).
8. Nordio, P. L., Pavan, M. V., Giacometti, G.: Theoret. chim. Acta (Berl.) **1**, 302 (1963).
9. Heller, C., McConnell, H. M.: J. chem. Physics **32**, 1535 (1960).
10. Fessenden, R. W., Schuler, R. H.: J. chem. Physics **39**, 2147 (1963).
11. Fischer, H.: Z. Naturforsch. **19**a, 866 (1964).
12. Geske, D. H.: In: Streitwieser, A., Jr., Taft, R. W., Eds.: Progress in physical organic chemistry, Vol. 4, p. 125. New York: Interscience 1967.
13a. Corvaja, C., Fischer, H., Giacometti, G.: Z. Physik. Chem. (Frankfurt) **45**, 1 (1965).
13b. — Brustolon, M., Giacometti, G.: Z. Physik. Chem. (Frankfurt) **66**, 279 (1969).
14. Russell, G. A.: In: Kaiser, E. T., Kevan, L., Eds.: Radical Ions, p. 87. New York: J. Wiley 1968.
15. Bowers, K. W.: In: Kaiser, E. T., Kevan, L., Eds.: Radical Ions, p. 211. New York: J. Wiley 1968; and references cited therein.

16. Colpa, J. P., de Boer, E.: Molecular Physics **7**, 333 (1964).
17. Bersohn, R.: J. chem. Physics **24**, 1066 (1956).
18. Whiffen, D. H.: Molecular Physics **6**, 223 (1963).
19. Nordio, P. L., Pavan, M. V., Giacometti, G.: Theoret. chim. Acta (Berl.) **1**, 302 (1963).
20. Dessau, R. M., Shih, S., Heiba, E. I.: J. Amer. chem. Soc. **92**, 412 (1970).
21. Bolton, J. R.: J. chem. Physics **41**, 2455 (1964).
22. — Carrington, A.: Molecular Physics **4**, 497 (1961).
23. Moss, R. E., Ashford, N. A., Lawler, R. G., Fraenkel, G. K.: J. chem. Physics **51**, 1765 (1969).
24. Levy, D. H., Myers, R. J.: J. chem. Physics **44**, 4177 (1966).
25. Kochi, J. K., Krusic, P. J.: J. Amer. chem. Soc. **90**, 7157 (1968).
26. Ishizu, K.: Bull. chem. Soc. Japan **37**, 1093 (1964).
27. Carrington, A., Todd, P. F.: Molecular Physics **7**, 533 (1964).
28. Gerson, F., Heilbronner, E., Reddoch, H. A., Paskovich, D. H., Das, N. C.: Helv. chim. Acta **50**, 813 (1967).
29. Bernal, I., Rieger, P. H., Fraenkel, G. K.: J. chem. Physics **37**, 1489 (1962).
30. Gerson, F., Heinzer, J.: Helv. chim. Acta **50**, 1852 (1967).
31. Venkataraman, B., Segal, B. G., Fraenkel, G. K.: J. chem. Physics **30**, 1006 (1959).
32. Bolton, J. R., Carrington, A.: Molecular Physics **5**, 161 (1962).
33. McDowell, C. A., Paulus, K. F. G.: Molecular Physics **7**, 542 (1964).
34. Barton, B. L., Fraenkel, G. K.: J. chem. Physics **41**, 1455 (1964).
35. Rieke, R. D., Bales, S. E., Hudnall, P. M., Meares, C. F.: J. Amer. chem. Soc. **92**, 1418 (1970).
36. McDowell, C. A., Paulus, K. F. G.: Canad. J. Chem. **43**, 224 (1965).
37. Corre, F., Odiot, S.: J. Chim. Physique **62**, 1202 (1965).
38. Carter, M. K., Vincow, G.: J. chem. Physics **47**, 292 (1967).
39. Tuttle, T. R., Weissman, S. I.: J. Amer. chem. Soc. **80**, 5342 (1958).
40. Bolton, J. R., Fraenkel, G. K.: J. chem. Physics **40**, 3307 (1964).
41. Lewis, I. C., Singer, L. S.: J. chem. Physics **43**, 2712 (1965).
42. Lawler, R. G., Bolton, J. R., Karplus, M., Fraenkel, G. K.: J. chem. Physics **47**, 2149 (1967).
43. Levy, D. H., Myers, R. J.: J. chem. Physics **41**, 1062 (1964).
44. Coulson, C. A., Crawford, V. A.: J. chem. Soc. (London) **1953**, 2052.
45. Gerson, F.: Helv. chim. Acta **49**, 1463 (1966).
46. Underwood, G. R., Vogel, V. L.: J. chem. Physics **51**, 4323 (1969).
47. Levy, D. H., Myers, R. J.: J. chem. Physics **43**, 3063 (1965).
48. Howarth, O. W., Fraenkel, G. K.: J. chem. Physics **52**, 6258 (1970).

Dr. Giovanni Giacometti
Institute of Physical Chemistry
University of Padua
Padua, Italy