On the Relations between ESR-Hyperfine Splittings and Spin Densities in Simple Substituted Alkyl Radicals

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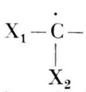
(Z. Naturforschg. **20 a**, 428—432 [1965]; eingegangen am 24. Dezember 1964)

A simple treatment of spin densities and ESR-coupling constants of substituted alkylradicals  $X_1-\dot{C}(X_2)-X_3$ is developed. It is shown that the spin densities ϱ_α in the α-carbon 2 p_z-functions may be calculated by use of a product rule from substituent parameters $\Delta(X_i)$. Furtheron it is found, that the parameters Q in the well known relations $a=Q\cdot\varrho_\alpha$ are unique constants for rotating methylgroups, whereas for α-protons they depend on the electron withdrawing forces of the substituents.

Values of $\Delta(X_i)$ and $Q_{\mathrm{H}}^{\mathrm{CH}}$ are tabulated and discussed. The ESR-coupling constants of four new transient alkyl radicals are also given.

The treatment of isotropic proton hyperfine splittings in the ESR-spectra of π-electronic organic free radicals is normally based on the two following assumptions:

(1) The coupling constants $a_{\mathrm{H}}^{\mathrm{CH}}$ of the nuclei of hydrogen atoms, and

(2) the coupling constants $a_{\mathrm{H}}^{\mathrm{CH_3}}$ of the protons of rotating methylgroups are both proportional to the spin density ϱ_α in the 2 p_z-eigenfunction of that trigonal carbon atom C_α to which the hydrogen atoms or methylgroups are bonded. The corresponding equations

$$a_{\mathrm{H}}^{\mathrm{CH}}=Q_{\mathrm{H}}^{\mathrm{CH}}\cdot\varrho_\alpha\,,\quad a_{\mathrm{H}}^{\mathrm{CH_3}}=Q_{\mathrm{H}}^{\mathrm{CH_3}}\cdot\varrho_\alpha \qquad (1),\ (2)$$

were derived at first by MCCONNELL [1] and MCLACHLAN [2], and they have since received wide spread application [3] and considerable discussion [4–7].

Theoretical values for the parameters Q are [4, 2]

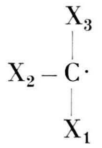
$$Q_{\mathrm{H}}^{\mathrm{CH}}=-23.61\ \mathrm{Oe}\,,\qquad Q_{\mathrm{H}}^{\mathrm{CH_3}}=+28\ \mathrm{Oe}$$

whereas from the experimental data so far only the ranges

$$19\ \mathrm{Oe}\leqq|Q_{\mathrm{H}}^{\mathrm{CH}}|\leqq 26\ \mathrm{Oe}\,,$$
$$25\ \mathrm{Oe}\leqq|Q_{\mathrm{H}}^{\mathrm{CH_3}}|\leqq 30\ \mathrm{Oe}$$

may be stated. Thus, though relations (1) and (2) always explain the observed isotropic proton splittings to the first order, more exact and reliable values of the parameters Q have not yet been unambiguously fixed. Furthermore, recent observations on coupling constants $a_{\mathrm{H}}^{\mathrm{CH}}$ and $a_{\mathrm{H}}^{\mathrm{CH_3}}$ of simple carbon radicals with only one trigonal carbon atom give rise to the question wether $Q_{\mathrm{H}}^{\mathrm{CH}}$ and $Q_{\mathrm{H}}^{\mathrm{CH_3}}$ may at all be considered as unique constants, valid for all types of π-electronic free radicals [8, 9].

To clarify this question, we discuss the coupling constants $a_{\mathrm{H}}^{\mathrm{CH}}$ and $a_{\mathrm{H}}^{\mathrm{CH_3}}$ of simple substituted carbon radicals



$$X_2-\dot{C}(X_3)(X_1)$$

where one or the other of the substituents X_i are hydrogens or rotating methylgroups. The coupling constants of a large number of such radicals are known with high accuracy from the papers of FESSENDEN and SCHULER [8], DIXON and NORMAN [10, 11] and of the author [9], some further data being given also in section IV of this paper.

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[1] H. M. MCCONNELL, J. Chem. Phys. **24**, 764 [1956].

[2] A. D. MCLACHLAN, Mol. Phys. **1**, 233 [1959].

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[6] P. V. SHASTNEV and G. M. SHIDOMIROV, Dokl. Akad. Nauk SSSR **153**, 151 [1963].

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[8] R. W. FESSENDEN and R. H. SCHULER, J. Chem. Phys. **39**, 2147 [1963].

[9] H. FISCHER, Z. Naturforschg. **19 a**, 866 [1964].

With the restriction to the type of free radicals mentioned, we wish to avoid complications from strong non-neighbor effects [12] and from charge effects [13], but we think, that our conclusions may well be valid for other uncharged free radicals also.

I. Experimental Relations

Some experimental refinements of equs. (1) and (2) have already been introduced in the literature.

FESSENDEN and SCHULER [8] discuss the α-hydrogen and the methylproton coupling constants of the free radicals series $\cdot CH_3$, $\cdot CH_2-CH_3$, $\cdot CH(CH_3)_2$, and $\cdot C-(CH_3)_3$. They conclude that for these radicals $Q_H^{CH_3}$ is a unique constant

$$Q_H^{CH_3} = (29.30 \pm 0.05)\ \text{Oe} \qquad (3)$$

and they express the spin density in the $2p_z$-function of C_a as

$$\varrho_\alpha = (1-0.081)^n \qquad (4)$$

where n is the number of methylgroups in the radical. Eq. (4) implies that a methylgroup draws 8.1% of the spin density from the central carbon. FESSENDEN and SCHULER's treatment agrees with CHESNUT's MO-calculations [14] on this same radical series.

In our previous papers [9, 15] we have adopted their eq. (3) for free radicals with polar substituents and have applied a more general relation

$$\varrho_a = \prod_{i=1}^{3} (1-\Delta(X_i)) \qquad (5)$$

for the description of the spin densities. $\Delta(X_i)$ is an empirical parameter which expresses the influence of the substituent X_i. With eq. (3) and (5) a consistent treatment of CH_3-splittings of simple alkyl radicals was possible. A table of $\Delta(X)$-values was derived, from which CH_3-splittings of free radicals so far unknown can be predicted. For instance, with $\Delta(CN) = 0.145$ and $\Delta(CH_3) = 0.081$[9] and eqs. (3), (5) we predict for the free radical $CN-\dot{C}-(CH_3)_2$ a CH_3-coupling constant of $a_H^{CH_3} = (21.20 \pm 0.40)$ Oe. Experimentally $a_H^{CH_3} = (21.5 \pm 0.5)$ Oe was obtained quite recently [16]. Since the same consistency between calculated and observed couplings was found also for other radicals [9], eq. (3) and (5) seem to be reasonable.

However, if these equs. are accepted, one has to admit, that the parameters Q_H^{CH} of α-protons vary from one radical to the other. In the radical series studied by FESSENDEN [8] Q_H^{CH} varies from 23.04 to 26.20, and in our previous paper [9] similar variations were stated.

On the other hand, if Q_H^{CH} is considered as a unique constant, the same difficulty occurs with $Q_H^{CH_3}$. It is possible in this case, to introduce relations analogeous to (3) and (5) and to achieve a consistent treatment of α-proton couplings, but then $Q_H^{CH_3}$ varies considerably.

Obviously, from the experimental data alone, a justification of either treatment cannot be obtained. Therefore, we discuss $Q_H^{CH_3}$, Q_H^{CH} and eq. (5) from a theoretical standpoint in the next sections.

II. Theoretical Considerations

From the developments of various authors [7, 14, 17, 18] it is understood that coupling of CH_3-protons arises almost exclusively through a hyperconjugative mechanism. By interaction of the pseudo-π-system of the methylgroup with the carbon-$2p_z$-function spin density is transfered to the methyl hydrogen 1s-functions. On the other hand, the coupling of α-protons arises through a spin polarisation of the CH-σ-bond.

Thus, $Q_H^{CH_3}$ seems to be to the first order a property alone of the π-system, whereas Q_H^{CH} reflects features of π- and σ-systems as well. It may be assumed, therefore, that Q_H^{CH} depends on changes in the σ-system introduced by substituents, as on inductive polarizations or on variations of bond angles between σ-bonds, the latter having already been shown by LENK [19]. Since such effects may be thought to be only of minor importance for $Q_H^{CH_3}$, we may suppose this quantity to be a rather unique constant.

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[10] W. T. DIXON and R. O. C. NORMAN, J. Chem. Soc., London **1963**, 3119.

[11] W. T. DIXON, R. O. C. NORMAN, and A. L. BULEY, J. Chem. Soc., London **1964**, 3625.

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This is also shown by the following semiquantitative treatment of $Q_{\mathrm{H}}^{\mathrm{CH}_3}$ and ϱ_α. In this discussion of hyperconjugation we apply simple HMO theory [20] neglecting overlap, since a more detailed calculation on spin densities in the ethyl radical $^{\cdot}\mathrm{CH}_2-\mathrm{CH}_3$ has shown [17] that negative spin densities are low, and since HMO theory is known to be well applicable when this is the case.

As usual [20], the methylgroup is replaced by the two center pseudo-π-system $\mathrm{C}_1-\mathrm{H}$. This is added at the position C_α to the other π-system, which contains the unpaired electron (in the unsubstituted case). The electron exchange between π- and pseudo-π-systems is treated as perturbation and the small inductive effect [20] of the methylgroup on the π-system is neglected.

Then, regarding only the unpaired electron, we have the zero order wave function

$$\psi_0 = a_\alpha \varphi_\alpha + \sum_k a_k \varphi_k \tag{6}$$

for the unsubstituted molecule, where φ_α and φ_k belong to the various π-centers, and similarly we have

$$\begin{aligned} \psi_{\mathrm{B}} &= a_{1\mathrm{B}} \varphi_1 + a_{\mathrm{HB}} \varphi_{\mathrm{H}}\,, \\ \psi_{\mathrm{A}} &= a_{1\mathrm{A}} \varphi_1 + a_{\mathrm{HA}} \varphi_{\mathrm{H}} \end{aligned} \tag{7}$$

for the bonding and antibonding eigenfunctions of the pseudo-π-system. Under the influence of the perturbation (6) and (7) are mixed, and the first order wave function of the unpaired electron becomes

$$\psi = \left(1 - \tfrac{1}{2} a_\alpha^2 (\delta_{\mathrm{A}}^2 + \delta_{\mathrm{B}}^2)\right) \{\psi_0 + a_\alpha \delta_{\mathrm{B}} \psi_{\mathrm{B}} + a_\alpha \delta_{\mathrm{A}} \psi_{\mathrm{A}}\} \tag{8}$$

where the $\delta_{\mathrm{A,B}}$ are the abbreviations

$$\delta_{\mathrm{A,B}} = a_{1\mathrm{A,B}}\, k_{1\alpha} \beta / (E\,\psi_0 - E\,\psi_{\mathrm{A,B}}) \tag{9}$$

and $k_{1\alpha}\beta$ is the exchange integral [20] between C_α and C_1. In (8) higher powers than δ^2 have been neglected, as will be done also in the following. Thus, we have the spin densities

$$\varrho_\alpha = \left(1 - a_\alpha^2 (\delta_{\mathrm{A}}^2 + \delta_{\mathrm{B}}^2)\right) a_\alpha^2, \tag{10 a}$$

$$\varrho_{\mathrm{H}} = \left(1 - a_\alpha^2 (\delta_{\mathrm{A}}^2 + \delta_{\mathrm{B}}^2)\right) a_\alpha^2 \cdot (\delta_{\mathrm{B}}\, a_{\mathrm{HB}} + \delta_{\mathrm{A}}\, a_{\mathrm{HA}})^2 \tag{10 b}$$

from which we see

$$\varrho_{\mathrm{H}} \sim \varrho_\alpha$$

or, since $a_{\mathrm{H}}^{\mathrm{CH}_3} \sim \varrho_{\mathrm{H}}$, we have

$$a_{\mathrm{H}}^{\mathrm{CH}_3} = Q_{\mathrm{H}}^{\mathrm{CH}_3} \cdot \varrho_\alpha \tag{11}$$

where $Q_{\mathrm{H}}^{\mathrm{CH}_3} = 330$. $(\delta_{\mathrm{B}}\, a_{\mathrm{HB}} + \delta_{\mathrm{A}}\, a_{\mathrm{HA}})^2$ is a constant, not depending on the further structure of π- and σ-systems. Thus it may indeed be considered as a unique parameter.

Furthermore, if the methylgroup is attached to an unsubstituted radical with $a_\alpha = 1$, we have from (10 a) that the methylgroup draws $\delta^2 = (\delta_{\mathrm{A}}^2 + \delta_{\mathrm{B}}^2)$ percent of the original spin density. Likewise, if we attach three "weak" substituents X_i, which show only small inductive effects on the π-system and have π-orbitals similar to a methylgroup, one after the other to a trigonal carbon atom in steps 1, 2, 3, we obtain from (10 a), since $a_\alpha^2(1) = \varrho_\alpha(1)$ and so on,

$$\varrho_\alpha = \prod_i \left(1 - \delta^2(\mathrm{X}_i)\right)$$

or with $\delta^2 = \Delta$

$$\varrho_\alpha = \prod_i \left(1 - \Delta(\mathrm{X}_i)\right) \tag{12}$$

when again higher powers than δ^2 are neglected. Thus we have derived a formula which is exactly the experimental relation (5). It holds as long as the substituents are in fact "weak", and it may be envisaged to break down for "strong" substituents like $-\mathrm{OH}$ or $-\mathrm{CN}$.

With eqs. (11) and (12) the general discussion of the splitting parameters by use of eqs. (3) and (5) is justified. An explanation of the magnitude of $\Delta(\mathrm{X}_i)$ and of the variations of $Q_{\mathrm{H}}^{\mathrm{CH}}$ is given in the next sections.

At this point we should like to recall the quite similar calculations on CH_3-coupling constants in aromatic radical ions by Bolton et al. [18]. From their formulae and our eq. (9) it may be seen that $Q_{\mathrm{H}}^{\mathrm{CH}_3}$ is only a unique constant for uncharged free radicals $(E\,\psi_0 = \alpha)$. In charged species $(E\psi_0 = \alpha \pm m\,\beta)$ specific variations occur.

The author should like to state, that the general concept of these calculations was obtained independently by G. Giacometti (personal communication and ref. [15]). The differentiation between "strong" and "weak" substituents also follows his suggestions.

III. The Parameters $\Delta(\mathrm{X}_i)$

In table 1 the parameters $\Delta(\mathrm{X}_i)$ of various substituents are given. Eight of these are taken from previous work [8, 9, 15], four are calculated by applica-

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[20] A. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemists, J. Wiley, New York 1961.

tion of eqs. (3) and (5) to the coupling constants of the free radicals listed in section IV, though as mentioned above, eq. (5) may in the correct sense not be applicable in all of these cases.

Substituent X	Δ(X)	ref.
H	0.000	[8, 9]
CH_3	0.081	[8, 9]
CH_2CH_2OH	0.092	[15]
CH_2OH	0.079	[9]
CH_2NH_2	0.034	[15]
CH(OH)COOH	0.041	[9]
COOR	0.072	[9]
CN	0.148	[9]
$CO-CH_2CH_3$	0.162	this work
$O-CHO$	0.136	this work
OH	0.160	this work
$O-CH_2CH_3$	0.172	this work

Table 1. $\Delta(X_i)$ values of various substituents X_i.

From these values it is easily seen that Δ(X) increases with increasing mesomeric effect[21] of the substituent X, as is expected from the treatment given above [eq. (9)].

In the application of eq. (5)

$$\Delta(CH_3) = 0.081$$

occurs quite often. To this parameter some more discussion should be given, therefore.

From (9) and the HMO-parameters[14, 20]

$$h_{C1} = -0.1;\; h_H = -0.5;$$
$$k_{1\alpha} = 0.93;\; 3.0 \geqq k_{1H} \geqq 2.5$$

we obtain by solving the secular equation for the pseudo-π-system

$$0.096 \leqq \Delta(CH_3) \leqq 0.152 .$$

Furthermore, applying eq. (5) to the theoretical results of CHESNUT[14] and GIACOMETTI et al.[17] we get

$$0.084 \leqq \Delta(CH_3) \leqq 0.133 \text{ and } \Delta(CH_3) = 0.07$$

respectively. Thus, the experimental value aggrees reasonably with those expected from theory.

With the better fit of $k_{1H} = 3.0$ we finally obtain $Q_H^{CH_3} = 31.2$ Oe, which is to be compared with the value $Q_H^{CH_3} = 29.30$ Oe stated above [eq. (3)].

IV. The Parameters Q_H^{CH}

In sections II and III of this paper eqs. (3) and (5) have been proven theoretically. They are assumed to be valid throughout the following. So we have to explain the effects of substituents on Q_H^{CH}, which was pointed out already in section I. To show the magnitude of the variations, Table 2 gives the α- and the methylproton coupling constants a_H^{CH} and $a_H^{CH_3}$ of eight free radicals of the type $CH_3-\dot{C}H-X$ together with the parameters Q_H^{CH} as calculated from the couplings. Part of the data was taken from the literature. Partly they were obtained in this laboratory from the ESR-spectra of the free radicals

$$CH_3-CH_2^{\cdot},\quad CH_3-\dot{C}H-OH,$$
$$CH_3-\dot{C}H-O-CH_2-CH_3,$$
$$CH_3-\dot{C}H-CO-CH_2-CH_3 \text{ and } CH_3-\dot{C}H-COOH .$$

The free radicals were produced by the reaction of $HO^{\cdot}$ with propionaldehyde[22] ethanol, diethylether, diethylketone and ethylformiate applying the flow method described earlier[9].

X	a_H^{CH}	$a_H^{CH_3}$	Q_H^{CH}	T(°K)	references
CH_2CH_3	21.8	24.5	26.1	175	[8]
CH_3	21.11	24.68	26.2	188	[8]
H	22.38	26.87	24.4	93	[8]
	22.04	27.06	23.9	300	this work[22]
$CO-CH_2CH_3$	18.45	22.59	23.9	300	this work
COOH	20.18	24.98	23.7	300	[9]
OH	15.04	22.61	19.5	300	this work
	15.0	22.0	20.0	300	[10]
$O-CHO$	14.80	23.22	18.7	300	this work
$O-CH_2CH_3$	13.96	22.28	18.3	300	this work
	13.8	21.9	18.5	300	[11]

Table 2. Variations of Q_H^{CH} with the substituents X in the free radicals $CH_3-\dot{C}H-X$

The considerable variation of Q_H^{CH} with the substituents X as shown in the Table cannot be explained in the frame of any of the theoretical treatments published so far. It may of course be due to variations in bond angles[19], but it is hard to see why then the effect should have the order found. Therefore we suggest the following explanation:

We think that the changes in Q_H^{CH} are due to the different electron withdrawing forces of the substituents (−I-effect). The higher this force, the lower the total electron density in the $C-H-\sigma$-bond, and consequently the lower the spin polarization of the α-hydrogen 1s-function. Indeed, if we list the substituents according to increasing −I-effect and compare this arrangement with the corresponding arrangements of the Q_H^{CH} values,

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[21] H. A. STAAB, Einführung in die theoretische Chemie, Verlag Chemie, Weinheim 1959, p. 557 ff.

[22] The features of the reaction of $HO^{\cdot}$ with propionaldehyde will be published separately.

alkyl	H	$\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{R}$	COOH	OH	OR
26.1	24.4	23.9	23.7	19.5	18.4

we have excellent agreement. The validity of our assumption is demonstrated further in Fig. 1. Here we plot $Q_{\mathrm{H}}^{\mathrm{CH}}$ of the free radicals $CH_3-\dot{C}H-X$ versus the chemical shift $\sigma(CH_2)$ of the CH_2-group of the corresponding molecules CH_3-CH_2-X as measured by NMR[23, 24] (reference: benzene). A perfectly straight line is obtained. This is easily explained, since the chemical shifts are likewise known to depend on the electron withdrawing forces of the substituents[23]. With the variations of $Q_{\mathrm{H}}^{\mathrm{CH}}$ thus interpreted, our whole treatment seems to be justified.

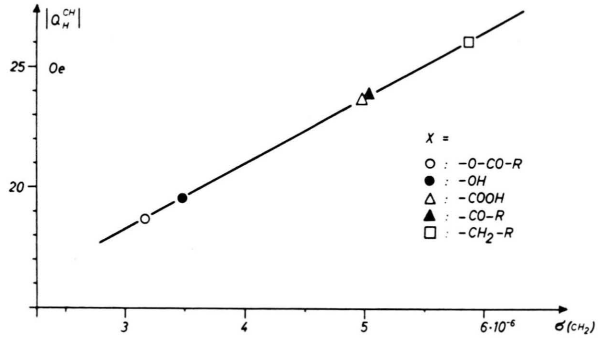

Fig. 1. $|Q_{\mathrm{H}}^{\mathrm{CH}}|$ of the free radicals CH_3-CH-X versus the chemical shifts $\sigma(CH_2)$ of the molecules CH_3-CH_2-X.

V. Conclusions

In section II . . . IV of this paper a treatment of proton coupling constants of simple substituted alkyl radicals was verified. Its basic facts are:

1. The parameter $Q_{\mathrm{H}}^{\mathrm{CH_3}}$ of rotating methylgroups is a unique constant for all uncharged radicals.
2. The spin density ϱ_a is a product type function of parameters $\Delta(X_i)$ characteristic for the substituents X_i.
3. The parameter $Q_{\mathrm{H}}^{\mathrm{CH}}$ depends specificly on the electron withdrawing forces of the substituents.

In the calculations it was assumed that $\Delta(X_i)$ depends on the mesomeric effect of the substituents almost exclusively, whereas $Q_{\mathrm{H}}^{\mathrm{CH}}$ shows the importance of inductive effects. Though both effects may affect Δ and $Q_{\mathrm{H}}^{\mathrm{CH}}$ as well, it may be thought, that the mesomeric effect dominates in the π-system and the inductive effect in the σ-system.

The treatment given above is thus of course only of first order, and the success should not be overestimated. However, it can be a reasonable help for the discussion of coupling constants regarding the large amount of data available so far on transient free radicals in the solid and liquid phase.

Acknowledgements

It is a pleasure to acknowledge a most valuable correspondence with Prof. G. Giacometti, Padova, Italy, many clarifying discussions with Dr. U. Johnsen and the stimulating interest of Prof. K.-H. Hellwege, both of this institute.

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[23] J. A. Pople, W. G. Schneider, and H. J. Bernstein, High-resolution Nuclear Magnetic Resonance, McGraw-Hill, New York 1959, p. 277.

[24] B. P. Dailey and J. N. Shoolery, J. Amer. Chem. Soc. **77**, 3977 [1955].