A Relationship between Coupling Constants in E.s.r. and N.m.r. Spectra

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FROM a relatively simple viewpoint the C–H* bond in an organic molecule R–H* is approximately localised and may be described by means of a linear combination of the orbitals containing odd electrons in the H· and R· fragments.[1] The geometry of R· is as in the molecule and not, of course, the same as that of the free radical which has the same formula.

Using this way of describing the bond, it can be shown that the scalar coupling of the proton H* with other nuclei in the molecule RH* should be approximately proportional[2] to the spin densities at those nuclei in the fragment R·, provided certain conditions are fulfilled. For example, the hyperfine splittings observed in the e.s.r. spectrum of α-methylvinyl are in a constant ratio to the corresponding proton spin–spin coupling constants in propene (in this case the fragment and the free radical are almost identical).

Now both in the free radical and in the hypothetical fragment formed by abstraction of a hydrogen atom from a substituted ethane, the odd electron is largely confined to a single atomic orbital on the α-carbon atom, as long as the

substituents are not unsaturated. If the attached groups do not interact appreciably with each other then their effects are approximately additive, i.e., each substituent absorbs a certain proportion of the spin density on the α-carbon atom. Suppose that the ratio of the spin density on the methyl hydrogen atoms in RR'ĊMe to that on the α-carbon atom is λ_r for the free radical and λ_f for the fragment. The ratio of the hyperfine coupling of the methyl protons with the odd electron in these two odd-electron systems will be:

$$\frac{\lambda_r}{\lambda_f}\left(\frac{1 + \lambda_f}{1 + \lambda_r}\right) \text{ for ethyl,} \quad \frac{\lambda_r}{\lambda_f}\left(\frac{1 + 2\lambda_f}{1 + 2\lambda_r}\right) \text{ for isopropyl,}$$

$$\text{and} \quad \frac{\lambda_r}{\lambda_f}\left(\frac{1 + \lambda_f + \lambda_f'}{1 + \lambda_r + \lambda_r'}\right) \text{ for R\overset{\cdot}{C}HMe}$$

where λ_r', λ_f' pertain to the substituent R. Provided that the differences $\lambda_r - \lambda_f$, $\lambda_r' - \lambda_f'$ etc., are small, then these ratios will have almost the same value for different molecules. We

TABLE

Coupling constants of methyl protons

R¹	R²	(a) N.m.r. (c./sec.)[3]	(b) E.s.r. (gauss)[4]	Ratio [gauss/(c./sec.)]
H	H	8·0	26·87	3·4
Me	H	7·3	24·68	3·4
Me	Me	6·8	22·72	3·3
OH	H	6·97	22·0	3·2
OEt	H	6·96	21·9	3·1
OH	Me	6·05	20·0	3·3
OPr	Me	5·98	20·0	3·3
CO_2H	Me	7·41	26·6	3·6

(a) with the odd electron in the radicals $R^1R^2\dot{C}Me$ and
(b) with H* in the molecules $R^1R^2CH^*Me$.

might therefore expect the methyl proton splittings, observed in the e.s.r. spectra of α-substituted ethyl radicals, to be proportional to the corresponding proton spin–spin coupling constants obtained from the proton magnetic resonance spectra of similarly substituted ethanes. From the Table it would appear that this expectation is realised.

(*Received, October 21st, 1966; Com. 804.*)

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