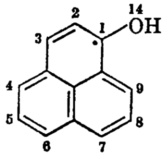
# Paramagnetic Hyperfine Splitting by Hydroxylic Hydrogen

By G. P. RABOLD, K. H. BAR-ELI, and K. WEISS

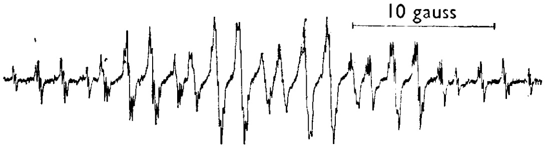
(*Department of Chemistry, Northeastern University, Boston,* 15, *Mass., U.S.A.*)

HYPERFINE interaction between an electron spin and the nuclear spin of a proton attached to oxygen in an organic radical has been observed in only a few instances.[1] We now report the high resolution electron spin resonance spectrum of the 1-hydroxyphenalen-1-yl radical (I) and its interpretation on the basis of McLachlan MO-SCF theory,[2] which allow an estimate to be made of $Q_{OH}$, the spin density transmission parameter for the OH $\sigma$-bond.

The irradiation of phenalen-1-one in propan-2-ol gives rise to a dark green solution which is paramagnetic.[3] At moderate modulation amplitude the spectrum consists of six quartets with splitting constants (6·21 and 1·68 gauss) and intensities which clearly show them to arise from groups of protons at positions 3, 4, 6, 7, and 9 and at positions 2, 5, and 8, respectively, of radical (I). Under optimized irradiation and resolution conditions, the spectrum is further resolved into 100 lines (see Figure). Splitting by hydrogen on oxygen is reflected in the terminal doublets of equal intensity. The inner multiplets are due to small differences within the two groups of ring protons which are satisfactorily predicted by the McLachlan calculation (see Table), but not by Hückel MO theory. The spin density distribution is compatible with a six-constant model with CH splittings of 6·40, 6·26, 6·12, 1·73, and 1·58 gauss, and an OH splitting of 0·14 gauss, which accurately reproduce the spectrum. If McConnell's equation[4] is applicable in the form $a_{OH} = Q_{OH}\rho_{OH}$, the results furnish $Q_{OH}/Q_{CH} = 0·29$. With $|Q_{CH}| = 24·2$ gauss,[2] this gives $|Q_{OH}| \approx 7$ gauss. Actually better agreement between the observed and calculated spin densities is obtained with $|Q_{CH}| = 27$ gauss, which raises $|Q_{OH}|$ to about 8 gauss.



(I)



*E.s.r. spectrum of radical* (*I*) *from the photolysis of* 1 × $10^{-3}$M-*phenalen*-1-*one in propan*-2-*ol.*

*Spin densities in radical* (*I*)

| Position | 2 | 5 | 8 | 6 | 4 | 7 | 3 | 9 | 14 |
|---|---|---|---|---|---|---|---|---|---|
| $\rho_i$ (calc.)* .. | −0·058 | −0·068 | −0·067 | 0·240 | 0·230 | 0·230 | 0·217 | 0·219 | 0·018 |
| $\rho_i$ (obs.)† .. | 0·058 | 0·064 |  | 0·237 | 0·231 |  | 0·226 |  | 0·017 |

* $\lambda = 1·2$, cf. ref. 2. MO parameters $h = 2·0$, $k = 1·0$ in $\alpha_O = \alpha + h\beta$ and $\beta_{OC} = k\beta$ ($\alpha$'s coulomb integrals, $\beta$'s exchange integrals) give best fit within narrow limits.

† $\rho_i = a_i/27$ for positions 2—9; $\rho_{14} = a_{OH}/8$.

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[1] W. T. Dixon and R. O. C. Norman, *J.*, 1963, 3119; J. R. Bolton, A. Carrington, and J. dos Santos-Veiga, *Mol. Phys.*, 1962, 5, 465; L. H. Piette, G. Bulow, and K. Loeffler, Preprints, Symposium on the Use of e.s.r. in the Elucidation of Reaction Mechanisms, 1964, 9, No. 2C, p. C-9.

[2] A. D. McLachlan, *Mol. Phys.*, 1960, 3, 233.

[3] H. Köller, G. P. Rabold, K. Weiss, and T. K. Mukherjee, *Proc. Chem. Soc.*, 1964, 332.

The configuration interaction model developed by McConnell[4,5] can be used to provide an independent estimate of $Q_{\mathrm{OH}}$. If it is assumed that an odd electron localized on the oxygen atom can be represented by a neutral hydroxyl radical, this approach leads to the equation

$$\frac{Q_{\mathrm{OH}}}{Q_{\mathrm{CH}}} - \frac{(J_{p_z p_x} - J_{p_z s})_{\mathrm{OH}}\,(1 - S_{\mathrm{C}}{}^4)\,\Delta E_{21}^{\mathrm{CH}}}{(J_{p_x h} - J_{p_x s})_{\mathrm{CH}}\,(1 - S_{\mathrm{O}}{}^4)\,\Delta E_{21}^{\mathrm{OH}}}$$

Values for the exchange integrals, $J$, between the indicated orbitals ($h = sp^2$), and for the overlap integrals $S_{\mathrm{O}}$ and $S_{\mathrm{C}}$ ($<p/s>$ and $<h/s>$ for OH and CH, respectively) were obtained from published data. The ratio of the energy differences ($\Delta E_{21}$) between the doublet ground and excited states was taken as equal to the ratio of the lowest transitions of CH and OH radicals. The calculation[6] yields $Q_{\mathrm{OH}}|Q_{\mathrm{CH}} \approx 0{\cdot}3$ and, with $|Q_{\mathrm{CH}}| =$ 24—27 gauss, $|Q_{\mathrm{OH}}| \approx$ 7—8 gauss, which supports the experimentally derived assignment.

The presence of non-bonding electrons on oxygen and its greater electronegativity may cause hydroxylic proton splitting to be more sensitive to the medium than CH proton splitting. It remains to be established with further experimental examples whether $Q_{\mathrm{OH}}$ is as independent of the environment as $Q_{\mathrm{CH}}$ appears to be.[7]

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[4] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 632, 764.

[5] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, 1958, **28**, 107.

[6] For details cf. G. P. Rabold, K. H. Bar-Eli, E. Reid, and K. Weiss, *J. Chem. Phys.*, to be published.

[7] Cf. J. Gendell, F. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2832.