

AFCU - 774
Hyperfine Structure and Exchange Narrowing^a
of Paramagnetic Resonance

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The free radical α , α -diphenyl β -picryl hydrazyl, $(C_6H_5)_2N-NC_6H_4(NO_2)_3$, shows the strongest and narrowest electronic paramagnetic resonance absorption so far reported. This resonance was observed by its effect on the transmission of microwaves (frequency approximately 24,000 m.c.) through a TE_{01} cavity with a small amount of the free radical placed approximately on the axis of the cavity. The microwave frequency was tuned to give maximum transmission through the cavity while the cavity was in place between the pole pieces of an electromagnet. With an amount of the free radical as small as 2 mg. the transmitted power was reduced by a factor of three when the magnetic field was of the proper value (approximately 8600 oersteds) to give resonance. The half-width of this resonance at half maximum absorption was 1.45 oersteds. Because of its sharpness and intensity, this resonance may be of value for stabilizing or measuring magnetic fields in cases where the signal produced by the proton resonance is not sufficiently strong.

The electronic g-value was obtained by measuring the electron's resonant frequency and the proton frequency in the same magnetic field. The ratio of proton to electron frequencies obtained was 15.178×10^{-4} which, combined with results of Taub and Kusch⁽¹⁾, gives a g-value of $2.0042 \pm .0004$. The g-value and line width obtained are in fair agree-

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ment with the results of Holden, Kittel, Merritt, and Yager⁽²⁾, who have made measurements parallel to those presented here and with whom we have enjoyed very helpful discussions.

The unusually narrow line-width observed is evidently due to exchange narrowing⁽³⁾ since spin-spin interactions alone would lead one to expect a half-width of approximately 50 oersteds. The free radical was dissolved in concentrations of 3.0 and 1.5 weight percent in benzene and the resonance width examined. With these dilutions exchange effects should be negligible, and indeed the resonance half-widths (half-width at half maximum) were greater than in the solid, being 7.5 and 5 oersteds respectively for the two solutions. These latter widths are, as closely as can be calculated, just those to be expected from spin-spin interactions. Motion of the molecules in solution gives no appreciable narrowing of the line at the frequencies used since the relaxation time is 10^{-10} sec. or larger.

Gaseous NO has been examined by Beringer and Castle⁽⁴⁾ with a somewhat similar technique. They find associated with the electronic resonance a hyperfine structure due to coupling between the N^{14} and electronic magnetic moments. If the odd electron in NO is considered to be on the nitrogen atom in an essentially atomic 2 p state, the expected interaction is approximately $75 \frac{I \cdot J}{r^3}$ megacycles/sec. Here the average inverse cube of the electron's distance from the nucleus has been taken from a previous estimate for nuclear quadrupole effects⁽⁵⁾. The experimental results give an interaction of $31 \frac{I \cdot J}{r^3}$ m.c., indicating that the probability of finding the odd electron on the nitrogen atom is approximately 1/2. This is what may be expected if the electron participates in a 3-electron band⁽⁶⁾.

The free radical examined here is in a $^2\Sigma$ electronic state and the odd electron might be assumed to be in a 2 p orbit on the nitrogen atom which has only two bonds. In this case hyperfine structure consisting of three equally spaced, equal intensity lines separated by 125 m.c. or 45 gauss may be expected. If exchange interactions between the electrons in adjacent molecules are as large as the electron-nuclear coupling, this hyperfine structure may be considerably modified or eliminated. Since exchange effects are evidently important in the solid material, failure to find hyperfine structure is perhaps not surprising. However, in the diluted solutions of the free radical hyperfine structure of the type described was expected, but not found. What hyperfine splitting is present must be less than the line width, hence the probability of finding the odd electron on the nitrogen which formally has only two valence bonds must be less than 0.15. In order to produce such a small hyperfine structure, this electron must either have considerable probability of being found on nuclei of zero spin such as oxygen, or perhaps circulate over a considerable region of the molecule and hence average out a large number of small interactions with nuclei.

Study of the hyperfine structure in other molecules with magnetic moments of electronic origin should give considerable information about the electron distributions. *Handwritten mark*

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