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Spin Exchange in Biradicals*

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The electron spin resonance spectra of four isotopically labeled biradicals have been observed. The hyperfine splittings demonstrate independence of the halves.

MOST paramagnetic organic molecules contain an odd number of electrons. Their magnetic properties are well accounted for by the contributions from a single electronic spin, i.e., their ground electronic states are almost pure doublets. The small number of even electron paramagnetic molecules have not, on the other hand, been so sharply classified. The even electron paramagnetic molecules are, for the most part, formed by joining together two odd electron molecules in such a way that the features of the structure responsible for the stability of the orginial odd electron molecules are preserved. Studies have been made of the static magnetic susceptibilities of such biradical molecules and of the catalysis of the interconversion of ortho and para hydrogen.

Since the development of the method of magnetic resonance, new information not accessible to the older methods has been obtained for several biradicals. Hutchison and co-workers¹ demonstrated that the intensity of the resonance absorption of hydrocarbon I at room temperature corresponded to about 4% of the molecules being paramagnetic. Sloan, Jarrett, and Vaughan² showed that the magnetic resonance spectra of liquid solutions of a series of biradicals exhibit proton hyperfine splittings, and that the spectra suggest strongly that the two halves of these biradicals are "uncoupled." A simple explanation of the small magnetism is that the paramagnetic state is a thermally excited triplet. However, classification as a triplet state implies a degree of coupling between halves not compatible with the hyperfine splittings.

Our investigations include measurements of C^{13} hyperfine splittings, determination of variation of spectra with temperature, and estimates of the absolute intensity of the absorption.

We consider first how the hyperfine splittings and the coupling between the halves of a biradical are related. As a particularly simple example we may think of a pair of one-electron atoms with nuclei of spin $\frac{1}{2}$ maintained at various fixed distances from each other. In the extreme case where the atoms are close together,

the system will be in either a singlet or a triplet electronic state. The former has no resonance absorption. This latter would yield a symmetrical hyperfine spectrum of three lines with intensity ratio 1:2:1. When the atoms are far apart the hyperfine spectrum is simply a pair of lines—the spectrum of isolated atoms.

The set of states appropriate for coupled two-electron systems may be used for the description of the separated atoms. The states in which both electron spins of the separated atom are in the same spin state are pure triplet, but the two states in which one spin is up and the other down are the sum and difference of the corresponding singlet and triplet functions. While such mixtures are not good stationary state functions for a system consisting of only two electron spins, they are appropriate in the separated atom limit where the electron-nuclear hyperfine interactions dominate in determining the spin configuration.

We now give a simplified account of the magnetic resonance spectrum of a pair of electrons coupled to a pair of nuclei of equal charges.

The orbital interaction of the electron may be expressed in the familiar way as a spin interaction; only the isotropic part of the hyperfine interaction will be considered. Designate σ_1 and σ_2 as the Pauli spin operators for the two electrons; I_A and I_B the spin operators for the two nuclei. Let H_0 be the spin-independent part of the Hamiltonian, with solutions

 $\alpha \phi_A, \beta \phi_B; \qquad \beta \phi_A, \alpha \phi_B; \qquad \alpha \phi_A, \alpha \phi_B; \qquad \beta \phi_A, \beta \phi_B.$

 ϕ_A is a space function associated with nucleus A, ϕ_B is an equivalent function for nucleus B, and α and β are the two spin functions. The functions are normalized and antisymmetrized with respect to exchange of the labels of the electrons. Each represents a particular orientation of electron spin in the neighborhood of each nucleus.

Now consider the effects of electron exchange and of hyperfine interactions. The former may be represented as $J\sigma_1 \cdot \sigma_2$. For our purposes it is convenient to use the operator $\sigma_A \cdot \sigma_B$ in which σ_A and σ_B are the spin operators for the occupants of ϕ_A and ϕ_B , respectively.

The hyperfine interaction is

$$-(8\pi/3)\left\{\sigma_{1}\cdot\left[I_{A}\delta(\mathbf{r}_{1}-\mathbf{r}_{A})+I_{B}\delta(\mathbf{r}_{1}-\mathbf{r}_{B})\right]\right\}$$

$$+\sigma_2\cdot [I_A\delta(\mathbf{r}_2-\mathbf{r}_A)+I_B\delta(\mathbf{r}_2-\mathbf{r}_B)]\}.$$

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^{*} This work was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract. Reproduction in whole or in part is permitted for any purpose of the U. S. Government. ¹ C. A. Hutchison, Jr., A. Kowalsky, R. C. Pastor, and G. W. Wheland, J. Chem. Phys. **20**, 1485 (1952). ² H S. Jarrett G. L. Slear, and W. P. Vaughe, J. Chem. Phys.

² H. S. Jarrett, G. J. Sloan, and W. R. Vaughn, J. Chem. Phys. 25, 697 (1956).



FIG. 1. Splittings for two electrons coupled to one nucleus with $I = \frac{1}{2}$ and one with I = 0.

In the approximation in which ϕ_A vanishes at r_B and ϕ_B vanishes at r_A and the overlap between ϕ_A and ϕ_B is neglected, the hyperfine term becomes

where

$$a = -\left(\frac{8\pi}{3}\right)\mu_e\mu_n \mid \phi_A(r_A) \mid^2$$

 $a(\sigma_A \cdot I_A + \sigma_B \cdot I_B)$

and μ_e and μ_n are the magnetic moments of electron and nucleus, respectively.

The total Hamiltonian is now

$$\mathfrak{K}_0 + J\sigma_A \cdot \sigma_B + a(\sigma_A \cdot I_A + \sigma_B \cdot I_B).$$

We consider three cases: (a) Neither nucleus has spin. (b) Nucleus A has spin $\frac{1}{2}$ and nucleus B has spin zero. (c) Nuclei A and B have identical moments and spin $\frac{1}{2}$. The solutions for case (a) are obvious. They are the familiar singlet and triplet functions.

The triplet states are split in an external field and yield a single line (anisotropic spin-spin interactions are neglected). The solution for case (b) when $J \ll a$. i.e., for spin-exchange rate small compared with hyper-

FIG. 2. Splittings for two electrons coupled to two nuclei each with $I = \frac{1}{2}$.

fine frequency, lead to a spectrum consisting of a symmetrical triplet with intensity ratios 1:2:1. The central line arises from spin transitions on the side of the molecule which does not have a nuclear spin; the two outside lines from the spin transitions on the side which contains a nuclear spin. As the exchange rate increases the lines split (with splitting of order J), and finally when $J \gg a$ the spectrum becomes a doublet of half the splitting of the original spectrum. Each spin spends half its time on the side of the molecule which contains the nuclear spin. The details of the change from one spectrum to another are given in Fig. 1.

For the case when each side of the molecule contains a nucleus of spin $\frac{1}{2}$, the spectrum consists of two lines for slow exchange (each electron remains in the vicinity of one nucleus) and of three lines with intensities 1:2:1 when the spin migrates rapidly from one side of the molecule to the other. Details of the changes in the spectrum are given in Fig. 2.

EXPERIMENTAL PROCEDURES AND RESULTS

The radicals here discussed are:



I, II, and III were labeled at both methyl carbons with C¹³. The procedure (to be described below) yielded a mixture containing 16% of unlabeled material (case a), 48% with one C¹³ (case b) and 36% with two C¹³ (case c). The spectrum for such a mixture should have consisted of five lines with intensity ratio

9:24:34:24:9 in the limit of rapid exchange and of three lines with ratio 3:4:3 for slow exchange. IV was labeled in only one position so that 40% of the mole-cules contained no C¹³ and 60% contained one C¹³. The expected spectra are one of three lines with half the usual C¹³ splitting in ratio 3:4:3 for fast exchange

J=0

J≫a

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FIG. 4. Spectrum of II at 263°K (top); 215°K (bottom).

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and one of three lines with the usual C^{13} splitting in ratio 3:14:3 for slow exchange.

Preparation of Labeled Biradicals

Compound I was prepared by the following sequence of reactions:



II and III were prepared by analogous reactions through the benzoylation of diphenylether and diphenylethane, respectively.

Compound IV was labeled with C^{13} at only one of the methyl positions. It was prepared as follows:



In the case of compounds I, II, and III, the intermediate diketones were isolated and crystallized; for IV the diester was isolated and crystallized. The dihalogen derivatives were not isolated as crystalline solids in the preparation of the labeled compounds. Preparation of the biradicals from unlabeled compounds by a procedure identical with those used for the labeled compounds resulted in biradicals with the same magnetic resonance spectra as those which were obtained from large scale preparation with isolation and purification of the intermediate dihalides. Our unlabeled biradicals were identical in their magnetic and optical properties with those described by Jarrett, Soan, and Vaughn.²

Conversion of the dihalides to biradicals was carried out under high vacuum conditions by the techniques described by Lewis, Lipkin, and Magel.³ The radicals produced by such techniques are far more stable than those prepared by the more conventional methods. A sample of I, stored in the dark, has been stable for one year.

Magnetic Measurements

Magnetic resonance spectra of dilute liquid solutions under conditions of the highest resolutions available to us were recorded. The solvent in each case was either toluene, dimethoxyethane, or tetrahydrofuran. The spectra were the same in all solvents. Most of the measurements were made in a small magnet with magnetic field inhomogeneity of about 0.3 oe over the sample. Repetition of the measurements with an improved instrument which permitted resolution of about 0.03 oe revealed a complex hyperfine structure, each radical possessing its distinctive spectrum. At 0.3 oe resolution the resonances of I, II, III, and IV are hardly distinguishable from each other.

Figures 3 and 4 show the resonances of I and II (normal isotopic abundance) in toluene at several different temperatures. The sharpening of lines with decreasing temperature is more marked than for most other radicals. Figure 5 shows the resonance of III with 60% C¹³ in the methyl position.

Crude measurements were made of the variation in intensity of the resonances with temperature, of the absolute spin susceptibility of I and III, and of the variation of spin susceptibility with concentration at constant temperature.

Relative to C¹³ splitting, the spectra in each case corresponded to independence of the two spins: J < A = 7×10^7 sec⁻¹. Since the proton splittings have not been analyzed it is not impossible that J may be in the range of the proton splittings, i.e., J could be as high as a few megacycles per second.

All resonance diminished in intensity with decreasing temperature. Because of the rapid decrease in line breadth with decreasing temperature (Figs. 3 and 4) accurate measurements of dependence of susceptibility on temperature are difficult. The variation of intensity with temperature corresponds to an energy interval of 2 to 3 kcal/mole between the magnetic state and the normal paramagnetic state. The estimates of total spin

³ G. N. Lewis, D. Lipkin, and T. T. Magel, J. Am. Chem. Soc. **66**, 1579 (1944).

susceptibility correspond to energy intervals in the same range.

Absolute susceptibilities were measured by comparison of the integrated absorptions of solutions of biradical and peroxylamine disulphonate of known concentrations. Cavity Q, filling factor, microwave power, and modulation amplitudes were made equal for the biradical solution and the standard samples. Microwave power levels were sufficiently low so that no appreciable saturation was observed.

DISCUSSION OF THE RESULTS

Our results require for each of the molecules described here an energy level scheme consisting of a singlet normal state and a singlet and triplet effectively degenerate with each other about 10¹³ cps above the normal state. The situation is markedly different from the one existing in single crystals of cupric acetate where an excited triplet state exhibits a tight spin coupling compatible with the singlet-triplet separation.4

Since the results for the biradicals are unexpected and not easily explained, we have had some suspicions concerning the chemical identity of the substances whose resonances we have studied. In order to eliminate the possibility that a small percentage of the dihalides from which the hydrocarbons are made were only half reduced, we carried out the reduction of IV with an excess of sodium to produce a diamagnetic solution of dinegative ions. The biradical was regenerated by removal of the sodium with mercury. The spectra obtained by this treatment were identical with those obtained by normal reduction with silver amalgam.

The correspondence of the intensities of the hyperfine components in each case to the abundance of C13 in the $C^{13}O_2$ used in the preparation supports but does not conclusively prove that the synthesis proceeded according to the sequences indicated in the section on the preparations. For compounds I, II, and III both methyl carbons originate in the carbon dioxide with which a Grignard intermediate is treated. In compound IV, one of the methyl carbons originates in the CH₃ group of *meta*-bromotoluene while the other comes from carbon dioxide. Nevertheless, the intensities of the hyperfine components indicated that the two methyl carbons originating from the two different sources have identical roles in the biradicals.

A polymerization process which leads to large molecules with spins effectively at the ends or a dissociation which leads to an ordinary radical is not excluded.

We should note that the hyperfine splittings from the biradical porphyrindine indicates independence of the two halves,⁵ while the temperature dependence of susceptibility of the crystalline material shows that the magnetic state is 0.6 kcal above the normal state.⁶

A satisfactory explanation (if we have not made a chemical blunder) of the phenomena must account not only for the position of the magnetic state of the biradicals some 2013 kcal above the normal state but for the mixing of the singlets and triplets. We have no explanation which is completely acceptable to us or to the many people with whom we have discussed the problem. We note a few of the suggestions which have arisen. One is that the normal diamagnetic state should be represented as a resonance hybrid between the two ionic states in which one-half of the molecule is a carbanion, the other a carbonium ion. Because of the approximate equality between ionization potential and electron affinity of odd alternant radicals, no great loss in stability results on formation of the ionic species. Resonance between the forms $R_3C^+R_3C^-$ and $R_3C^-R_3C^+$ could lead to stabilization. This assignment of the structure of the normal state fails to explain the close degeneracy between singlet and triplet of the excited state, but at least it does not preempt the states necessary for forming the degenerate set.

Another suggestion has been that the excited magnetic states should be identified with Pariser's⁷ $^{3}\Omega^{-}$ and Ω^{-} states. Pariser has shown that within the approximations of his treatment of alternant systems a degeneracy between certain triplets and singlets exists. It has not been demonstrated, however, that for the molecule here described these should lie only 2 or 3 kcal above the normal state.

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⁵ K. H. Hauser, Z. Naturforsch. 14a, 425 (1959).
⁶ E. Muller and I. Muller-Rodloff, Ann. 521, 81 (1935).
⁷ R. Pariser, J. Chem. Phys. 24, 250 (1956).