[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, BALTIMORE 18, MARYLAND]

An Electron Spin Resonance Study of Copper Etioporphyrin II[1]

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From the electron spin resonance (e.s.r.) spectrum of a benzene solution of copper etioporphyrin II, a g_0 value of 2.097_5 was obtained. The spectrum of a castor oil solution of CuEtio II gave $g_{\|} = 2.169_3$ and $g_{\perp} = 2.061_6$. The spectrum of the benzene solution is composed of four absorptions separated by 91.2 gauss. A hyperfine structure due to the four-ring nitrogens is observed. The four-nitrogen nuclei cause each of the four copper-hyperfine absorptions to be split into a number of lines. Ideally the latter number should be nine. Actually, all nine lines are not seen but this can be explained by the relative intensities of the nitrogen lines being 1:4:10:16:19:16:10:4:1 as calculated by a multinomial distribution. The spacing in the nitrogen hyperfine structure (14.6 gauss) shows that the odd electron can be found in the copper $d_{x^2-y^2}$ orbital about 74% of the time.

Introduction

The porphyrins constitute a very interesting and much studied class of molecules. Their biological importance is well known and the determinations of their structural configurations and chemical properties have long been problems of great interest.

Several of the metallo porphyrins are interesting for their magnetic properties. It is the purpose of this work to study the electron spin resonance of copper etioporphyrin II (hereafter known simply as Cu Etio II) and draw some conclusions concerning the bonding properties of the odd electron. The general procedure used in this paper follows that of Stevens[3] and Owen.[4]

Discussion

The symmetry of Cu Etio II (Fig. 1) is D_{2h}. It will be assumed, however, that the electric field at the copper atom has D_{4h} symmetry. It may be mentioned that previous magnetic measurements are in agreement with a planar configuration.[5]

The notation for atomic orbitals is summarized as

$$\begin{aligned} N_i(2s) &= \rho_i \\ N_i(2p_z) &= \pi_i \quad i = 21, 22, 23, 24 \\ N_i(2p_y) &= \omega_i \\ N_i(2p_x) &= \tau_i \end{aligned}$$

$$\mathrm{Cu(3d)} = \begin{cases} d_{z^2} \\ d_{xy} \\ d_{xz} \\ d_{yz} \\ d_{x^2-y^2} \end{cases}$$

$$\mathrm{Cu(4s)} = s$$

In building the molecular orbitals only atomic orbitals centered on the nitrogen atoms and the copper atom are used. Application of group theory leads to the symmetrized molecular orbital states

$$|B_{1g}> = \alpha|d_{x^2-y^2}> \pm \frac{\alpha'}{2}[|h_{21}> - |h_{22}> - |h_{23}> + |h_{24}>]$$

$$|B_{2g}> = \beta|d_{xy}> \pm \frac{(1-\beta^2)^{1/2}}{2}[|\tau_{21}> + |\omega_{22}> - |\tau_{23}> - |\omega_{24}>]$$

$$|A_{1g}> = \gamma[|s> + \delta|d_{z^2}>] \pm \frac{\gamma'}{2}[|h_{21}> + |h_{22}> - |h_{23}> - |h_{24}>] \quad (1)$$

$$|E_g> = \beta_1|d_{xz}> \pm \frac{(1-\beta_1^2)^{1/2}}{\sqrt{2}}[|\pi_{22}> - |\pi_{24}>]$$

$$|E_g'> = \beta_1|d_{yz}> \pm \frac{(1-\beta_1^2)^{1/2}}{\sqrt{2}}[|\pi_{21}> - |\pi_{23}>]$$

In the above states the $|h_i>$ are hybrids given by

$$\begin{aligned} |h_{21}> &= a|\omega_{21}> + \sqrt{1-a^2}|\rho_{21}> \\ |h_{22}> &= a|\tau_{22}> + \sqrt{1-a^2}|\rho_{22}> \\ |h_{23}> &= a|\omega_{23}> - \sqrt{1-a^2}|\rho_{23}> \\ |h_{24}> &= a|\tau_{24}> - \sqrt{1-a^2}|\rho_{24}> \end{aligned} \quad (2)$$

The theory of hybrid orbitals leads to the choice of $(^2/_3)^{1/2}$ for a. Overlap has been included in the B_{1g} and A_{1g} orbitals since overlap is the greatest in these two. α' is given by

$$\alpha' = {}^1/_2\alpha S + \sqrt{1-\alpha^2} \quad (3)$$

$$S = <d_{x^2-y^2}|\{|h_{21}> - |h_{22}> - |h_{23}> + |h_{24}>\} \quad (4)$$

Bonding orbitals are obtained by taking the positive sign in equations 1 and antibonding orbitals are obtained by taking the negative sign. Figure 2 shows the approximate relative positions of the molecular orbitals. The energy levels are not drawn to scale. The electronic configuration used in this paper is as follows. The eight sigma electrons from the ring and eight 3d electrons from the copper fill the bonding molecular orbitals shown in Fig. 2. The odd electron responsible for the paramagnetism is placed in the antibonding $|B_{1g}>$ in the ground state. The B_{1g} state has no orbital degeneracy. Placing the odd electron in the antibonding $|B_{1g}>$ (hereafter simply $|B_{1g}>$) conforms to modern ligand field theory.[6] In fact McGarvey[7] has shown that placing the odd electron in the $4p_z$ copper orbital predicts results in disagreement with his paramagnetic resonance data on the copper(II) acetylacetonate. Recent papers by McGarvey and Maki[8,9] further confirm the theory that the paramagnetic properties of copper(II) acetylacetonate are best explained with the odd electron being placed, in the ground state, partly in the $|d_{x^2-y^2}>$ copper orbital.

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(1) This investigation was supported in part by research grant RG-5144 from the Division of General Medical Sciences, Public Health Service.

(2) Kennecott Copper Corporation Fellow for the year 1958–1959.

(3) K. W. H. Stevens, *Proc. Roy. Soc.* (*London*), **A219**, 542 (1953).

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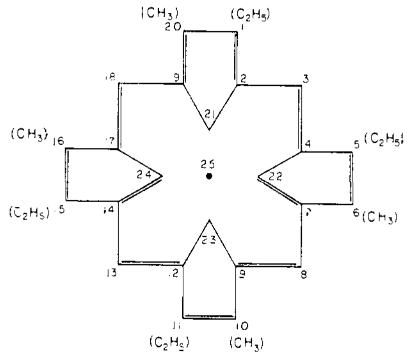

Although the crystal structure of Cu Etio II has been examined in some detail,[10] the orientation of the molecule in the crystal lattice is not known. It is thus necessary to study the e.s.r. in solution.

The spin Hamiltonian for an electron in a tetragonal electric field is

$$H_s = \beta_e g_{\parallel} H_3 S_3 + \beta_e g_{\perp}(H_1 S_1 + H_2 S_2) + A S_3 I_3^{\mathrm{Cu}} + B(S_1 I_1^{\mathrm{Cu}} + S_2 I_2) + \frac{4\pi\gamma_N\beta_e\beta_n}{9}(\alpha')^2|\rho_N(0)|^2 S_i I_i^N + \ldots \text{(smaller terms)} \quad (5)$$

In equation 5 the direction indicated by the subscript 3 is the symmetry axis of the molecule. The 1 and 2 axes pass through atoms 22 and 21, respectively. β_e, β_n and γ_N are the Bohr magneton, nuclear magneton and the nuclear gyromagnetic ratio of the nitrogen nucleus. $\rho_N(0)$ is the value of a nitrogen 2s atomic orbital evaluated at the nitrogen nucleus. The "smaller terms" of equation 5 include the nuclear quadrupole interaction and the interaction of the nuclear moment with the applied field H.

By transforming H_s of equation 5 into a coordinate system fixed in the laboratory we obtain[11]

$$\mathcal{H}_s = g_0\beta_e H S_z + a' S I^{\mathrm{Cu}} + \frac{4\pi\gamma_N\beta_e\beta_n}{9}(\alpha')^2|\rho_N(0)|^2 S I^N + \mathcal{H}_t \quad (6)$$

where the space fixed Z axis is determined by the homogeneous magnetic field. $\mathcal{H}_t$ is defined in reference 9. g_0 and a' are related to $g_{\parallel}$ and $g_{\perp}$.

$$g_0 = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$$

$$a' = \frac{1}{3}(A + 2B)$$

In solvents of low viscosity we may replace the time average of $\mathcal{H}_t$ by the spatial average which vanishes.[12] Hence for solvents of low viscosity we have as the spin Hamiltonian

$$\mathcal{H}_s = \mathcal{H}_0 = g_0\beta_e H S_z + a' \vec{S}\cdot\vec{I}^{\mathrm{Cu}} + \frac{4\pi\gamma_N\beta_e\beta_n}{9}(\alpha')^2|\rho_N(0)|^2 \vec{S}\cdot\vec{I}^N \quad (7)$$

The copper nucleus has a spin of 3/2 and the nitrogen nuclei have spins of 1. The e.s.r. spectrum of Cu Etio II would then be expected to be composed of four copper hyperfine lines with nine nitrogen hyperfine lines superimposed on each of the four copper hyperfine lines. If the strong field approximation is made the spacings in the nitrogen hyperfine structure (h.f.s.) and copper h.f.s. are, respectively

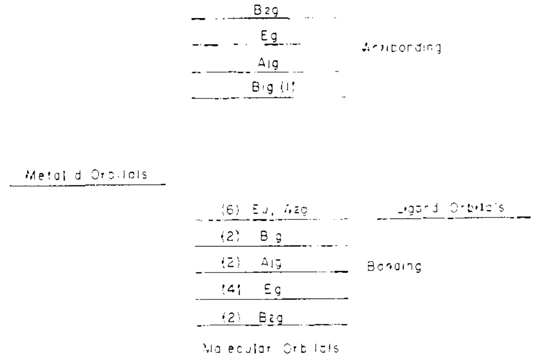

Fig. 2.—Energy level scheme for copper etioporphyrin II. Here the assumption has been made that $\beta^2 = 2\beta_1^2 - 1$ and that $\Delta_2 = 18{,}950$ cm.^{1}.

$$\Delta\nu_N = \frac{4\pi\gamma_N\beta_e\beta_n}{9h}(\alpha')^2|\rho_N(0)|^2 \quad (8a)$$

$$\Delta\nu_{\mathrm{Cu}} = a'/h \quad (8b)$$

In solvents of high viscosity the rotational interaction between solute and solvent molecules is small and the e.s.r. spectrum of such a solution consists of two sets of $2I + 1$ lines.[13,14] One set of lines will be centered at a field strength $H_{\parallel}$ and the other at $H_{\perp}$ where

$$H_{\parallel} = \frac{h\nu}{g_{\parallel}\beta_e} \quad (9)$$

$$H_{\perp} = \frac{h\nu}{g_{\perp}\beta_e}$$

The spacings in the spectrum of the high viscosity solution yield the hyperfine structure constants A and B.

The parameters $g_{\parallel}$, $g_{\perp}$, A and B will depend on the electronic state of the unpaired electron. Abragam and Pryce[15] have derived general formulas for the latter parameters. They are

$$g_{\parallel} = 2.0023\,\{1 - \lambda\Lambda_{33}\} \quad (10)$$

$$g_{\perp} = 2.0023\,\{1 - \lambda\Lambda_{11}\}$$

$$A = -P\,\{K + 3\xi m_{33} + 2\lambda\Lambda_{33} - 3\xi\lambda U_{33}\}$$

$$B = -P\,\{K + 3\xi m_{11} + 2\lambda\Lambda_{11} - 3\xi\lambda U_{11}\}$$

Here λ is the spin orbit coupling constant (-828 cm.$^{-1}$ for the free copper (II) ion); ξ is a constant whose value depends on the electronic configuration of the free ion ($\xi = 2/21$ for d electrons); the product $-PK$ is the contribution to A and B from the well-known Fermi contact interaction. Λ_{ii}, m_{ii} and u_{ii} are defined as

$$\Lambda_{ii} = \sum_{n \neq o} \frac{<0|L_i|n><n|L_i|0>}{E_n - E_0}$$

$$m_{ii} = <0|L_i^2|0> - \frac{1}{3}L(L+1)\alpha^2 \quad (11)$$

$$U_{ij} = -\frac{i}{2}\epsilon_{ikl} \sum_{n \neq o} \frac{<0|L_i|n><n|L_j L_k + L_k L_j|0>}{E_n - E_0}$$

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In 11, $|0>$ is the ground state of the unpaired electron and the $|n>$ the excited states; α is the coefficient in the first of equations 1.

Using equations 1 with hydrogen-like wave functions, equations 10 and 11 and the previously discussed electronic configuration we obtain

$$g_{\parallel} = 2.0023 \left\{1 - \frac{\lambda}{\Delta_1}\left[2\alpha\beta - \alpha'(1-\beta^2)^{1/2}\left(a + \sqrt{1-a^2}\,R\mathcal{R}\right)\right]^2\right\} \quad (12a)$$

$$g_{\perp} = 2.0023 \left\{1 - \frac{\lambda}{\Delta_2}\left[\alpha^2\beta^2{}_1 - \frac{2a\alpha\alpha'\beta_1(1-\beta_1{}^2)^{1/2}}{\sqrt{2}} + \frac{a^2\alpha^{12}(1-\beta_1{}^2)}{2} + \frac{\alpha'^2(1-\beta_1{}^2)(1-a^2)}{2}R^2\mathcal{R}^2\right]\right\} \quad (12b)$$

$$A = P\left\{-\frac{4}{7}\alpha^2 - K + (g_{\parallel} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) - \frac{2}{7}\alpha'^2\left(a + \sqrt{1-a^2}R\mathcal{R}\right) + F_1(\beta_1)\right\} \quad (12c)$$

$$B = P\left\{\frac{2}{7}\alpha^2 + \frac{11}{14}(g_{\perp} - 2.0023) - K - \frac{a^2\alpha^{12}}{7} + F_2(\beta_1)\right\} \quad (12d)$$

R is the copper–nitrogen distance and

$$\mathcal{R} = -<\tau_1\left|\frac{\partial}{\partial x}\right|\rho_1> = -<\omega_1\left|\frac{\partial}{\partial y}\right|\rho_1>$$

$F_1(\beta_1)$ and $F_2(\beta_1)$ are given by

$$F_1(\beta_1) = \frac{6\lambda}{7\Delta_2}(1-\beta_1{}^2)^{1/2}\left\{\frac{a\alpha\alpha'\beta_1}{\sqrt{2}} + \frac{a^2\alpha'^2}{\sqrt{2}} - \frac{\alpha'^2(1-\beta_1{}^2)(1-a^2)}{2}R^2\mathcal{R}^2\right\}$$

and

$$F_2(\beta_1) = \frac{3\lambda}{7\Delta_2}(1-\beta_1{}^2)^{1/2}\left\{\frac{a^2\alpha'^2}{\sqrt{2}} - \frac{\alpha'^2(1-\beta_1{}^2)(1-a^2)}{2}R^2\mathcal{R}^2 + \frac{2a\alpha\alpha'\beta_1(1-\beta_1{}^2)^{1/2}}{\sqrt{2}} - \frac{a\alpha\alpha'\beta_1}{\sqrt{2}} + \left(a + \sqrt{1-a^2}\right)R\mathcal{R}\left(\frac{a\alpha'^2(1-\beta_1{}^2)^{1/2}}{6} - \frac{\alpha\alpha'}{3\sqrt{2}}\right)\right\}$$

Δ_1 and Δ_2 are given by

$$\Delta_1 = E(B_{2g}) - E(B_{1g})$$
$$\Delta_2 = E(E_g) - E(B_{1g})$$

In the above calculations all overlaps between atomic orbitals whose maxima were not along a copper nitrogen bond were neglected. All terms quadratic in overlap also were neglected.

The expression for $\mathcal{R}$ is integrated easily and the result is

$$\mathcal{R} = \frac{8(Z_N{}^s)(Z_N{}^p)^{5/2}(Z_N{}^p - Z_N{}^s)}{(Z_N{}')^s\,a_0}$$

where $Z_N{}^s$ and $Z_N{}^p$ are the effective atomic numbers of 2s and 2p nitrogen electrons respectively and $Z_N{}' = Z_N{}^s + Z_N{}^p$. If Slater's rule for $Z_N{}^s$ and $Z_N{}^p$ is used $\mathcal{R}$ vanishes. We have chosen to use Hartree's values which are[16]

$$Z_N{}^p = 3.54$$
$$Z_N{}^s = 4.50$$

These numbers yield

$$\mathcal{R} = -0.23a_0{}^{-1}$$

The central atom to ligand distance R is 1.84 ± 0.03Å. in the nickel compound[17] and is probably the same in the copper compound.

The ground state, $|B_{1g}>$, has a node at the copper atom. Thus in a low viscosity solvent where the anisotropic hyperfine interactions average to zero we might expect to see little hyperfine structure due to the copper nucleus; however, the spectra of most copper complexes is made conspicuous by the presence of the hyperfine structure in which the spacings are usually rather large. Abragam, Horowitz and Pryce[18] have explained this anomalous hyperfine structure in free ions by including in their ground state wave function a configuration obtained by promoting a 3s electron to the 4s orbital. We may make a similar explanation by promoting an electron from the bonding A_{1g} molecular orbital to the antibonding A_{1g} molecular orbital. The problem then becomes at least a three electron one.

Let $\Phi_1(x) = <x|A_{1g}>$, bonding
$\Phi_2(x) = <x|B_{1g}>$, antibonding
$\Phi_3(x) = <x|A_{1g}>$, antibonding

where x stands for a set of coördinates fixed in the molecule. Keeping the eigenvalue of the Z component of the total spin as 1/2 we may approximate the ground state wave function by

$$\Psi_0{}^{m,M} = \psi_1{}^{m,M} + f\psi_2{}^{m,M} \quad (13)$$

where m and M denote electron and nuclear spin components along the axis. For m we have two values denoted by + and − and M may take on four values. $\psi_1{}^+$ and $\psi_2{}^+$ are

$$\psi_1{}^+ = \frac{1}{\sqrt{3!}}\begin{pmatrix}\Phi_1 & \Phi_1 & \Phi_2\\ \alpha & \beta & \alpha\end{pmatrix}$$

$$\psi_2{}^+ = \frac{1}{\sqrt{36}}\left\{2\begin{pmatrix}\Phi_1 & \Phi_2 & \Phi_3\\ \alpha & \alpha & \beta\end{pmatrix} - \begin{pmatrix}\Phi_1 & \Phi_2 & \Phi_3\\ \alpha & \beta & \alpha\end{pmatrix} - \begin{pmatrix}\Phi_1 & \Phi_2 & \Phi_3\\ \beta & \alpha & \alpha\end{pmatrix}\right\}$$

and

$$f = \frac{\mathcal{H}_{21}}{E_1 - E_2}$$

where $\mathcal{H}$ is the three electron Hamiltonian excluding quantal type interactions.

The electron contact interaction has the form

$$\mathfrak{F} = \frac{16\pi\beta_e\beta_n\gamma_{Cu}}{3}\sum_{e=1}^{3}\delta(\vec{r_e})\vec{S}^e\cdot\vec{I}$$

where $\vec{\nu}_e$ is the distance from the central atom to the eth electron. The general expression for matrix elements of $\mathfrak{F}$ in the ground manifold shows that

$$-PK = \frac{32\pi\beta_e\beta_n\gamma_{Cu}}{3}\left(\frac{2}{3}\right)^{1/2} f\Phi_1(0)\Phi_3(0) \quad (14)$$

where $\Phi_1(0)$ is $\Phi_1(x)$ evaluated at the copper nucleus.

Instrumental

A Varian Associates model V 4500 e.p.r. spectrometer was used to obtain the spectra of Cu Etio II in benzene and castor oil solutions. The magnetic field was monitored with a Harvey–Well Electronic Inc. Model G-501 gaussmeter. Each spectrum was preceded by a spectrum of a benzene solution of DPPH for which the g_0 value is accurately known to be 2.0036.

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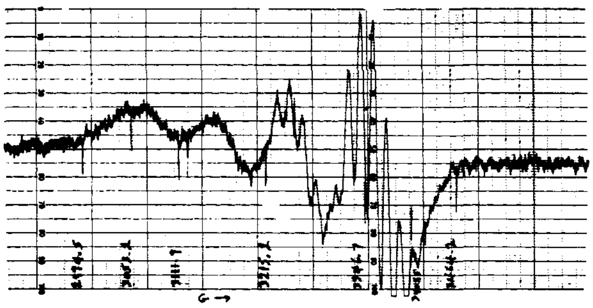

Fig. 3.—The electron spin resonance (derivative) spectrum of CuEtio II in benzene.

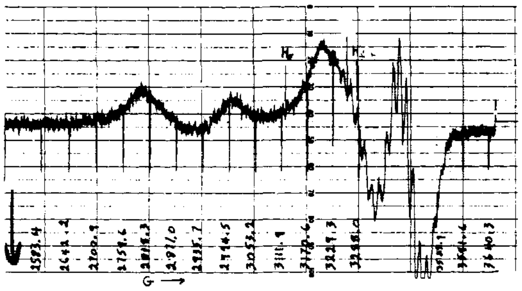

Fig. 4.—The electron spin resonance (derivative) spectrum of CuEtio II in castor oil.

Results

The spectrum of a benzene solution of Cu Etio II (Fig. 3) consists of four almost equally spaced, but not of equal width, lines. These four lines may be attributed to the copper atom which has a nuclear spin of 3/2. Superimposed on each copper hyperfine absorption there should be nine absorptions due to the four nitrogen nuclei, each of spin 1. Observed are seven nitrogen h. f. absorptions on the narrowest copper h. f., five on the next narrowest, three on the next and no discernible nitrogen h. f. absorptions on the broadest copper h. f. The relative intensities of the nine nitrogen h. f. absorptions are, according to a multinomial distribution, 1:4:10:16:19:16:10:4:1. On the basis of these numbers the actual number of nitrogen h. f. observed can be explained.

The spacing of the nitrogen hyperfine structure is 14.6 gauss and that of copper is 91.2 gauss. The approximate half-widths at half maxima for the copper h.f.s. are, as they appear for increasing magnetic field, 39, 27, 13 and 7 gauss. The asymmetry of the copper hyperfine structure may be partly explained by the contribution of the anisotropic nuclear hyperfine interactions to the line width. The theory,[12] as presented by McConnell, shows that the width of the line depends on the value of I_z and the dependence is in qualitative agreement with experiment.

The value for the spin Hamiltonian parameter a' is 0.0089 cm.$^{-1}$. The value of α' can be obtained from the nitrogen h.f.s. spacing of 14.6 gauss. With $\gamma_N = 0.4036$ and $|\rho_N(0)|^2 = 33.4 \times 10^{24}$ cm.$^{-3}$,[9] α' becomes

$$\alpha' = 0.55$$

To obtain α the overlap S must be known. By using hydrogen-like wave functions and atomic numbers from Hartree's book[16] the value of S is approximately 0.1. The value of α then becomes

$$\alpha = 0.86$$

With this the obvious statement can be made that the odd electron can be found in the copper $d_{x^2-y^2}$ orbital about 74% of the time. Thus the B_{1g} molecular orbital is fairly covalent in nature.

The spectrum of Cu Etio II has its center corresponding to a g_0 value of

$$g_0 = 2.097_5$$

The e.s.r. spectrum of Cu Etio II in castor oil (Fig. 4) consists of five lines. Ideally there should be eight lines but there is evidently overlapping of three of the lines from each set. There is enough resolution, however, to calculate the values $g_{\|}$ and $g_{\perp}$. The points corresponding to the centers of the two sets of lines are shown in Fig. 4. The observed values of $g_{\|}$ and $g_{\perp}$ are

$$g_{\|} = 2.169_3$$
$$g_{\perp} = 2.061_6$$

If Δ_1 and Δ_2 were known, β and β_1 could be found from the theoretical expressions for $g_{\|}$

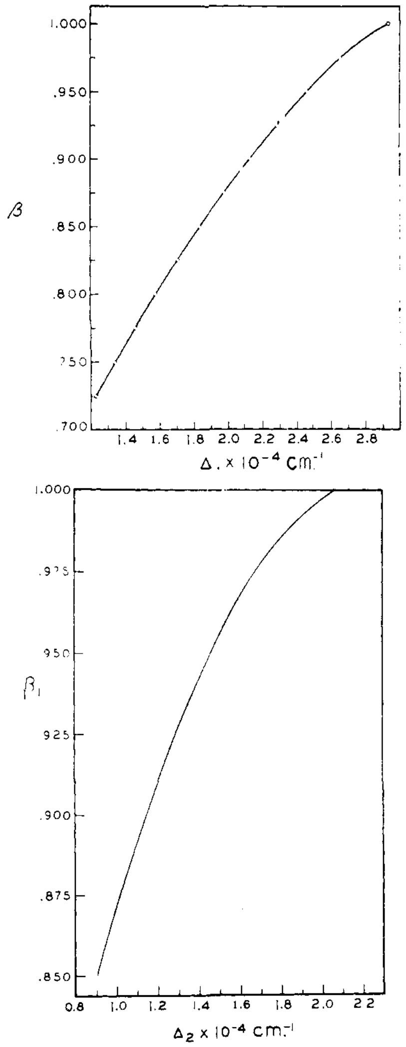

Fig. 5.—Plots of bonding parameters β and β_1 *versus* energy level differences Δ_1 and Δ_2 (a, above and b, below).

and $g_\perp$. Unfortunately Δ_1 and Δ_2 are not known since the optical absorption spectra of the ring pi electrons probably masks the Δ_1 and Δ_2 transitions. A transition corresponding to Δ_2 would be weak in any case. However graphs of β *vs.* Δ_1 and β_1 *vs.* Δ_2 are given in Figs. 5a and 5b.

The values obtained for A and B are, using the value obtained for a′

$$A = \pm 1.88 \times 10^{-2} \text{ cm.}^{-1}$$
$$B = \pm 0.39 \times 10^{-2} \text{ cm.}^{-1}$$

The sign of A is taken as negative; apparently all copper compounds studied so far have negative A's. For $\beta_1 = 1$, equations 13 solve to give $P = 0.030$ cm.$^{-1}$ and $K = 0.36$.

If, in equation 14, we replace $\Phi_1(0)\Phi_3(0)$ by $\gamma^2|S(0)|^2$ and take

$$|S(0)|^2 = 23 \times 10^{24} \text{ cm.}^{-3}$$

along with $\gamma_{Cu} = 1.53$, $K = 0.36$ and $P = 0.030$ cm.$^{-1}$ we obtain the result that

$$f\gamma^2 = -0.048$$

This shows that only a small admixture of Ψ_2 is necessary to explain the copper hyperfine structure. The negative sign obtained for f is due to the promotion of an electron from a bonding orbital to an antibonding orbital.

Conclusions

Some insight has been gained on the nature of the molecular orbital which involves the odd electron. Since this bond has a fair amount of covalent character it is expected that the other sigma orbitals involving electrons from lower copper d orbitals are also appreciably covalent in character. This is in agreement with the fact that Cu Etio II, as well as other metallo etioporphyrins, is very stable toward acids.[19]

Although knowledge of β and β_1 cannot be obtained without prior knowledge of Δ_1 and Δ_2, we can do some speculating. As is pointed out by Gouterman[20] the similarity of the pi spectra of the metal porphyrins seems to indicate that d orbitals do not appreciably affect the pi spectrum. This is equivalent to saying that the d orbitals of π symmetry do not interact with the ring π orbitals. It seems then that the conclusion that $\beta_1 \approx 1$ can be drawn. For $\beta_1 = 1$ the expression for $g_\perp$ is satisfied if Δ_2 is taken to be 20,700 cm.$^{-1}$. The optical spectrum of Cu Etio II[19] suggests taking 18,950 cm.$^{-1}$ for Δ_2 which leads to $\beta_1 = 0.99$. If we further suppose that the probability of an electron being found near the nitrogens is the same for the excited B_{2g} and E_g states then

$$\beta^2 = 2\beta_1^2 - 1$$

For $\beta_1 = 0.99$ we obtain the results that $\beta = 0.98$ and $\Delta_1 = 27{,}000$ cm.$^{-1}$.[21,22]

The authors are indebted to Professor A. H. Corwin for the high purity sample of copper etioporphyrin II.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY, ATLANTA, GEORGIA]

Proton Magnetic Resonance in Substituted Propenes. I. 2-Substituted Propenes

BY E. B. WHIPPLE, J. H. GOLDSTEIN AND LEON MANDELL

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The 40-megacycle n.m.r. spectrum of 2-chloropropene is described in detail, medium effects being used to effect a complete analysis including the vinyl proton assignments. Chemical shifts and spin-coupling constants are then reported and discussed for a series of ten 2-substituted propenes in dilute tetramethylsilane solutions.

In earlier work we have studied the effects of chemical substitution on the proton magnetic resonance shifts and couplings in the propargylic system H–C≡C–CH$_2$X, and the allenic system $H_2C{=}C{=}CHX$.[1-3] In these studies, the chemical shifts were measured in dilute cyclohexane (CH) or tetramethylsilane (TMS) solutions in order to minimize differences in environmental "medium effects," and the results were standardized in terms of the former solvent with respect to an external H_2O (liq.) reference.[1] The present work extends these methods to the substituted propenyl system, beginning with the 2-substituted propenes, $H_2C{=}CY{-}CH_3$.

Analysis of Spectra

Assuming effective averaging of the methyl group protons by internal motions, the appropriate general class[4] of the spectra is ABX_3 since negligible mixing occurs between the spin states for the vinyl (AB) and methyl (X_3) hydrogens. To these approximations, the 32×32 secular equation for the 5-spin systems can be factorized into blocks no larger than 2×2^5 and general solutions for the observed spectrum written in terms of the usual trigonometric parameters.[4] The essential results are summarized in Table I. In the limit where mixing between the vinyl states is also small ($\Delta\omega_{AB} >> J_{AB}$), the analysis may proceed

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(1) E. B. Whipple, J. H. Goldstein, Leon Mandell, G. S. Reddy and G. R. McClure, THIS JOURNAL, **81**, 1321 (1959).

(2) E. B. Whipple, J. H. Goldstein and Leon Mandell, *J. Chem. Phys.*, **30**, 1109 (1959).

(3) E. B. Whipple, J. H. Goldstein and W. E. Stewart, THIS JOURNAL, **81**, 4761 (1959).

(4) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, Ch. 6.

(5) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **30**, 944 (1949).