Free Radicals with Large Negative Spin Densities

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Abstract: We have taken the nmr spectra of a series of nitronyl nitroxide radicals with aromatic substituent in order to measure the sign and magnitude of the hyperfine coupling constants and spin densities. These radicals are unusual in that the ortho and para positions of the aromatic rings are found to have negative spin densities. The spin density at the meta position is smaller and positive. A series of molecular orbital calculations were carried out in order to theoretically determine the spin distribution in these radicals. A second-order perturbation calculation was undertaken to analyze the mode of spin propagation from the nitronyl nitroxide ring to the aromatic ring. This calculation yielded a qualitative technique for predicting the sign and relative magnitude of the spin densities in radicals of this type.

Hyperfine coupling constants of organic free radicals are generally measured by analysis of electron spin resonance spectra. This technique yields the magnitude of the coupling constant, but the sign cannot be determined directly. The signs of π electron spin densities determined from these couplings are generally assigned by molecular orbital (MO) calculations. Hückel MO calculations predict positive or zero spin density, whereas McLachlan calculations yield both positive and negative spin densities. In most of the radicals which have been reported, these calculations predict large positive spin densities and relatively small negative spin densities. In this paper we wish to report a series of radicals containing aromatic rings in which the negative spin densities are larger than the positive spin densities. The sign and magnitude of the hyperfine couplings from these radicals were determined directly from their nmr spectra. A theoretical explanation is presented which allows one to qualitatively predict the sign and relative magnitude of these couplings.

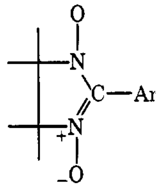
The nuclear magnetic resonance spectra of organic radicals can, in some instances, be used to determine both the sign and magnitude of electron–nuclei coupling constants. In concentrated solutions in which spin exchange is very rapid, one observes a single shifted nmr line from each set of equivalent nuclei.[2] The shift of a given line (ΔH) is related to the hyperfine coupling constant (A) by

$$\Delta H = -A(\gamma_e/\gamma_N)(g\beta H/4kT) \qquad (1)$$

Nuclei with lines shifted to low field have positive couplings, while those with lines shifted to high field have negative couplings.

We have examined the proton nuclear resonance spectra of the group of radicals shown in Chart I. The coupling constants determined by these experiments show that the spin density at the ortho and para positions is negative and larger than the positive spin of the meta position. The only previous example of this type of spin distribution which we are aware of was found in one of the phenyl rings of the triphenylverdazyl radicals.[3] In order to obtain a better understanding of the mode of spin delocalization in these radicals, we have carried out a series of Hückel, McLachlan, and INDO calculations. We have also carried out a second-order perturbation calculation which gives a qualitative explanation of the mechanism for propagation of the spin from the nitronyl nitroxide ring to the aromatic ring.

Chart I



I, Ar = phenyl
II, Ar = 2-pyridyl
III, Ar = 4-pyridyl
IV, Ar = 3-pyridyl

Experimental Section

The radicals were made by Ullman's technique.[4] Compound I has previously been reported. The melting points of the pyridyl radicals are II, 121–122°; III, 127°; and IV, 109°. The nmr spectra were taken on a Jeolco 4H-100 100-MHz spectrometer. A Princeton Applied Research Model HR-8 lock-in amplifier employing 35-Hz field modulation was used in conjunction with this spectrometer.

Results

The nitronyl nitroxide radicals are very soluble in chloroform-*d*, and the nmr spectra of concentrated solutions could be observed without addition of a paramagnetic solvent. The shifts and coupling constants of the four radicals are listed in Table I. The shifts of the lines of the aromatic protons are referenced to benzene, while the shift of the line of the methyl protons is referenced to the methyl line of tetramethylpiperidinol. Internal references were used to account for susceptibility shifts. The spectra of radical I show two lines shifted to low field and two lines shifted to high field. The peaks shifted to low field are assigned to the ortho and para protons of the aromatic ring, while those shifted to high field are assigned to the meta protons and the methyl protons. The assignment is based on the relative areas and the effect of substitution of the various pyridyl rings for the phenyl ring.

The lines from the pyridyl nitronyl nitroxides were slightly broader and a single low-field line was observed

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(1) Alfred P. Sloan Foundation Fellows.

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(3) P. Kopf, K. Morokuma, and R. Kreilick, *J. Chem. Phys.*, 54, 105 (1971).

(4) J. Osiecki and E. F. Ullman, *J. Amer. Chem. Soc.*, 90, 1078 (1968).

Table I. Shifts[a] (ΔH) and Coupling Constants[b] (A)

Compd	Ortho ΔH	Ortho A	Meta ΔH	Meta A	Para ΔH	Para A	Methyl ΔH	Methyl A
I	−3.31	+0.446	+1.31	−0.177	−2.83	+0.382	+1.485	−0.201
II	−2.20	+0.296	+1.00 +0.80	−0.135 −0.108	−2.20	+0.296	+1.450	−0.196
III	−3.63	+0.490	+0.92	−0.125			+1.415	−0.191
IV	−3.21	+0.435	+1.40	−0.189	−3.21	+0.435	+1.440	−0.194

[a] Shifts are in kHz. [b] Coupling constants are in gauss.

Table II. INDO and McLachlan Spin Densities of Model Nitroxides

		Exptl[g]	INDO		McLachlan[c]				Hückel
						Second-order perturbation			
ϕ	Position	ρ_C^{π}	ρ_C^{π} [a]	$-\pi_{\xi\nu}$ [b]	ρ_C^{π} [d]	$B \times 10^{e}$	$C \times 10^{e}$	$\rho_C^{\pi} \times 10^{e}$	$-\pi_{\xi\nu}$ [f]
Phenyl	o	−0.0198	−0.112	−0.506	−0.0169	−0.0041	−0.0148	−0.0188	−0.157
	m	+0.0079	+0.069	+0.020	+0.0005	−0.0041	+0.0048	+0.0007	+0.009
	p	−0.0169	−0.103	−0.287	−0.0143	−0.0129	−0.0028	−0.0156	−0.102
o-Pyridyl	o	−0.0132	−0.143	−0.528	−0.0172	−0.0081	−0.0112	−0.0193	−0.163
	m	+0.0060	−0.123	−0.011	−0.0030	−0.0101	+0.0069	−0.0032	−0.017
	m (far)	+0.0048	+0.113	+0.025	−0.0017	−0.0055	+0.0037	−0.0018	−0.003
	p	−0.0130	−0.131	−0.269	−0.0136	−0.0081	−0.0070	−0.0151	−0.097
p-Pyridyl	o	−0.0218	−0.138	−0.490	−0.0162	−0.0045	−0.0138	−0.0183	−0.153
	m	+0.0055	+0.119	+0.025	−0.0017	−0.0055	+0.0037	−0.0018	−0.003
m-Pyridyl	o	−0.0193	−0.145	−0.528	−0.0172	−0.0081	−0.0112	−0.0193	−0.163
	o (far)	−0.0193	−0.134	−0.490	−0.0164	−0.0045	−0.0138	−0.0183	−0.153
	m	+0.0084	+0.084	+0.021	+0.0006	−0.0088	+0.0095	+0.0007	+0.010
	p	−0.0193	−0.130	−0.269	−0.0139	−0.0081	−0.0070	−0.0151	−0.097

[a] Before projection onto doublet. [b] As defined by eq 16. In units of (eV)$^{-1}$. [c] Energy parameters used: $\alpha_N = \alpha + \beta$, $\alpha_o = \alpha + 2\beta$, $\beta_{ON} = 1.4\beta$, $\beta_{CN} = \beta$. [d] In terms of McLachlan parameter λ. [e] In terms of the perturbation parameter γ^2. $\lambda = 0.1$ is used. [f] In units of $|\beta|^{-1}$. [g] Calculated assuming $Q = -22.5$ G.

from the ortho and para hydrogens. The peak from the meta protons in the *o*-pyridyl radical (compound II) was split into a doublet, indicating nonequivalent spin density at the two meta protons in this compound.

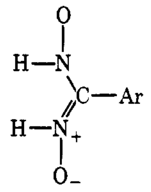
The low-field shift of the lines from the ortho and para hydrogens shows that these hydrogens have positive couplings and indicates negative spin densities for adjacent carbon atoms. The coupling of the meta protons is negative and the spin density of the meta carbon positive. The spin densities of the ortho and para carbons were found to be larger than that of the meta carbon in each case. Our molecular orbital calculations indicate that the sign of the spin densities at various positions in the aromatic ring should be related to the sign of the spin density at the bridging carbon atom in the nitronyl nitroxide ring. An earlier nmr study of nitronyl nitroxide radicals with aliphatic substituents indicates that the spin density at this position is negative.[5]

Theoretical

We have carried out a series of molecular orbital calculations in order to obtain a better understanding of the spin distribution in these radicals. These calculations attempt to account for the relatively large negative spin densities at the ortho and para positions of the aromatic ring and the small positive spin density at the meta position. The spin densities have been calculated directly with INDO[6] and McLachlan[7] treatments. We have also carried out a perturbation calculation which gives some insight into the mechanism of spin propagation from the nitronyl nitroxide ring to the aromatic ring.

An INDO unrestricted Hartree-Fock calculation for the model nitroxides shown in Chart II (assuming planar structures) gives the π electron spin density (ρ_C^{π}) listed in column 4 of Table II. The replacement of the cyclic structure with two hydrogen atoms should not cause a significant change in the spin distribution in the aromatic ring. The sign and relative magnitudes of the spin densities obtained from this calculation are in reasonable agreement with our experimental results. A McLachlan MO calculation (column 6 of Table II) also yields a qualitatively correct picture of the spin densities except for the meta position of the *o*- and *m*-pyridyl radicals where the incorrect sign is calculated. The absolute magnitudes of the INDO spin densities are about a factor of 10 larger than the experimental values. This difference might be accounted for partly by nonplanarity of the NOCNO group and the aromatic ring. The McLachlan calculations also assume planar structures and in this case the ortho and para spin densities are of the correct order of magnitude. The discrepancy between the two methods in predicting absolute magnitudes of spin densities would be of some concern if one wished to compare these calculations

Chart II



Ar = phenyl, 2-, 4-, 3-pyridyl

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(5) R. W. Kreilick, J. Becher, and E. F. Ullman, *J. Amer. Chem. Soc.*, **91**, 5121 (1969).

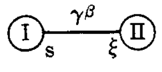
(6) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(7) A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).

with experimental results. The two sets of calculations are, however, adequate for a prediction of the signs and relative magnitudes of the spin densities.

Although these calculations are in accord with our experimental results, a more analytical approach would be helpful in clarifying the "mechanism" for spin delocalization in these compounds. We have carried out a second-order perturbation calculation in the framework of a McLachlan procedure in order to investigate this question.

The model which we have used (A) consists of two



A

conjugated systems, I and II, which are connected by a weak resonance integral $\gamma\beta$. (β is the standard resonance integral of the Hückel method and γ is a small parameter.) System I contains an odd electron, while system II is closed shell. The two systems are connected at atom s of I and atom ξ of II. The McLachlan procedure can be used to obtain a set of zero-order MO's (ψ_q^α) for the α electrons and a different set of zero-order MO's (ψ_q^β) for the β electrons for system I. The β MO's are normal Hückel MO's, while the α MO's are determined by solving the modified secular equation used in the McLachlan procedure (the last sentence of section 6 of ref 7). These MO's are given by

$$\psi_q^\beta = \sum_r (c_r^q)_\beta \chi_r \qquad \psi_q^\alpha = \sum_r (c_r^q)_\alpha \chi_r \qquad (2)$$
$$\text{energy } E_q^\beta \qquad\qquad \text{energy } E_q^\alpha$$

The spin density in a given AO, say t, is then given by

$$\rho_t = \langle \psi_n^\beta | \Delta_t | \psi_n^\beta \rangle + \sum_q^{\mathrm{occ}} \langle \psi_q | \Delta_t | \psi_q \rangle_{\alpha-\beta} \qquad (3)$$

where Δ_t is the spin density operator, ψ_n^β is the half occupied MO, and the summation covers all of the doubly occupied MO's in I. The first term is the Hückel spin density (ρ_t^0) and the second term is the McLachlan correction (ρ_t^1). This term reflects the difference between α and β electron distributions in the doubly occupied MO's and is defined by

$$\langle \psi_q | \Delta_t | \psi_q \rangle_{\alpha-\beta} = \langle \psi_q^\alpha | \Delta_t | \psi_q^\alpha \rangle - \langle \psi_q^\beta | \Delta_t | \psi_q^\beta \rangle \qquad (4)$$

The unperturbed system II has a set of Hückel MO's

$$\phi_j = \sum_\eta^{\mathrm{II}} d_\eta^j \chi_\eta \quad \text{energy } E_j \qquad (5)$$

Since this is a closed shell, we need not distinguish α and β MO's in the zero order. The spin density in system II is zero before the perturbation is introduced.

When the resonance integral $\gamma\beta$ between AO's and ξ

$$\gamma\beta = \langle \chi_\mathrm{s} | h | \chi_\xi \rangle \qquad (6)$$

is introduced, the MO's in I become ψ_q^α and ψ_q^β, while the MO's in II are now split into two MO's, Φ_j^α and Φ_j^β

$$\Psi_q^\Gamma = \psi_q^\Gamma + \sum_j^{\mathrm{II}} \frac{V_{qj}^\Gamma \phi_j}{\Delta E_{qj}^\Gamma} + 0\left(\sum_p^{\mathrm{I}} \gamma^2 \psi_p^\Gamma \right) \qquad (7a)$$

$$\Phi_j^\Gamma = \phi_j + 0\left(\sum_p^{\mathrm{I}} \gamma \psi_p^\Gamma \right) + \sum_q^{\mathrm{I}} \sum_{k(\neq j)}^{\mathrm{II}} \frac{V_{qk}^\Gamma V_{qj}^\Gamma \phi_k}{\Delta E_{jq}^\Gamma \Delta E_{jk}} - \frac{1}{2} \sum_q^{\mathrm{I}} \frac{(V_{qj}^\Gamma)^2 \phi_j}{(\Delta E_{jq}^\Gamma)^2} \qquad (7b)$$

where ($\Gamma = \alpha, \beta$)

$$V_{qj}^\Gamma = \langle \psi_q^\Gamma | h | \phi_j \rangle = (c_\mathrm{s}^q)_\Gamma d_\xi^j \gamma\beta \qquad (8)$$

is the Hamiltonian matrix element between MO ψ_q^Γ of I and MO ϕ_j of II, and ΔE_{qj}^Γ is the energy difference between MO's q and j. The summation covers all of the MO's in I or II as specified.

We want to calculate the spin density ρ_ν at atomic orbital ν in system II. Using the perturbed wave functions (eq 7) in a spin density equation similar to eq 3, we obtain

$$\rho_\nu = A + B + C \qquad (9a)$$

$$A = \sum_j^{\mathrm{II}} \sum_k^{\mathrm{II}} \frac{V_{nj}^\beta}{\Delta E_{nj}^\beta} \frac{V_{nk}^\beta}{\Delta E_{nk}^\beta} \langle \phi_j | \Delta_\nu | \phi_k \rangle = \left(\sum_j^{\mathrm{II}} \frac{d_\xi^j d_\nu^j}{\Delta E_{nj}^\beta} \right)^2 (c_\mathrm{s}^n)^2 = \left(\sum_j^{\mathrm{II}} \frac{d_\xi^j d_\nu^j}{\Delta E_{nj}^\beta} \right)^2 \rho_\mathrm{s}^0 \rangle \geqq 0 \qquad (9b)$$

$$B = \left(\sum_q^{\mathrm{Iocc}} \sum_j^{\mathrm{IIun}} - \sum_q^{\mathrm{Iun}} \sum_j^{\mathrm{IIocc}} \right) \left\{ \frac{(V_{qj})^2}{(\Delta E_{qj})^2} \right\}_{\alpha-\beta} \langle \phi_j | \Delta_\nu | \phi_j \rangle \qquad (9c)$$

$$C = 2\left(\sum_q^{\mathrm{Iocc}} \sum_j^{\mathrm{IIun}} - \sum_q^{\mathrm{Iun}} \sum_j^{\mathrm{IIocc}} \right) \sum_{k(\neq j)}^{\mathrm{II}} \left\{ \frac{V_{qj} V_{qk}}{\Delta E_{qj} \Delta E_{jk}} \right\}_{\alpha-\beta} \times \langle \phi_j | \Delta_\nu | \phi_k \rangle \qquad (9d)$$

where V_{qj}^Γ ($\Gamma = \alpha, \beta$) is evaluated with eq 8 and one uses eq 10 to evaluate the matrix elements of Δ_ν.

$$\langle \phi_j | \Delta_\nu | \phi_k \rangle = \sum_\mu \sum_\lambda d_\mu^j d_\lambda^k \langle \chi_\mu | \Delta_\nu | \chi_\lambda \rangle = d_\nu^j d_\nu^k \qquad (10)$$

In eq 9 the summations cover only the indices specified. For example, $\mathrm{I_{occ}}$ covers all of the doubly occupied MO's of I, while $\mathrm{I_{un}}$ should cover all unoccupied and half-occupied MO's of I. Term A comes from direct delocalization of the half-occupied MO ψ_n^β into segment II through the bridge $\gamma\beta$. This term is always positive because it is a pure Hückel contribution. This term is zero if the Hückel spin density ρ_s^0 at the connecting point s of the unperturbed free radical (I) is zero. Terms B and C arise from differences between α and β electron distributions in the combined system. The subscript α–β in eq 9c and 9d indicates that the difference between terms involving α MO's (ψ_q^α) and terms involving β MO's (ψ_q^β) should be taken. Term B is the sum of two contributions. The first of these comes from the second term in eq 7a and describes delocalization of MO's ψ_q^Γ of I into segment II through $\gamma\beta$. The second contribution comes from the last term of eq 7b and describes the renormalization of MO's ϕ_j due to their delocalization into segment I. Term C is the contribution of the third term in eq 7b (*i.e.*, changes in the MO's ϕ_j of II due to the interaction $\gamma\beta$).

Equation 9 was used for our calculations on the model nitroxides shown in Chart II by considering the $(\mathrm{HNO})_2\mathrm{C}\cdot$ fragment as segment I and the phenyl or pyridyl ring as segment II. The results are shown in columns 7–9 of Table II in units of the perturbation parameter γ^2. The contribution of term A is zero as the unperturbed Hückel spin density at the central carbon atom of $(\mathrm{HNO})_2\mathrm{C}$ is zero. The perturbation results are in good agreement with the results obtained from a direct calculation on the entire system (column 6). Term B is found to make a negative contribution to all of the positions. Term C is large and negative for the ortho and para positions, while it is smaller and positive for the meta positions. Terms B and C add to yield the large negative spin densities at the ortho and para positions, while they subtract to yield the smaller density at the meta position.

Although eq 9c and 9d yield the correct type of spin distribution for these radicals, they are too complicated to give qualitative insight into the mode of spin propagation from system I to system II. We were especially interested in relating the spin distribution in system I in the unperturbed state to the final spin distribution in the aromatic rings. In order to obtain this insight, we have used a series of approximations to simplify eq 9a.

We have simplified term A by assuming that segment II is an alternate hydrocarbon (AH).[8] In addition, we assumed that the energy of the half-occupied MO, E_n^{β}, of I is given by the Coulomb integral of the carbon atom, α. The pairing theorem for AH[8] predicts the following relationship for the jth MO and the $(2m-j)$th MO ($2m$ is defined as the total number of MO's for the system II)

$$E_{2m-j} - \alpha = \alpha - E_j \tag{11}$$

$$d_{\xi}^{2m-j} d_{\nu}^{2m-j} = \pm d_{\xi}^{j} d_{\nu}^{j}$$

(+ when ξ and ν are in the same class, − when ξ and ν are in different classes). With these assumptions one obtains the following expression for A

$$A = 4\left(\sum_{j}^{\mathrm{IIocc}} d_{\xi}^{j} d_{\nu}^{j}/(\alpha - E_j)\right)^2 \rho_{\mathrm{s}}^{0} \tag{12}$$

for ξ and ν in different classes and $A = 0$ for ξ and ν in the same class. Although this expression is correct only for alternate hydrocarbons, one might expect qualitatively similar results for molecules with heteroatoms.

To simplify B and C we consider the double summation $\Sigma_q^{\mathrm{Iocc}}\ \Sigma_j^{\mathrm{IIun}}$, which we call X.

$$\begin{aligned} X &= \sum_{q}^{\mathrm{Iocc}} \sum_{j}^{\mathrm{IIun}} \left\{ \frac{V_{qj}\langle\phi_j|\Delta_\nu|}{\Delta E_{qj}} \left(2 \sum_{k(\neq j)}^{\mathrm{II}} \frac{V_{qk}\phi_k\rangle}{\Delta E_{jk}} + \frac{V_{qj}\phi_j\rangle}{\Delta E_{qj}} \right) \right\}_{\alpha-\beta} \\ &= \sum_{q}^{\mathrm{Iocc}} \sum_{j}^{\mathrm{IIun}} \left\{ \frac{V_{qj}\langle\phi_j|\Delta_\nu|}{\Delta E_{qj}} \left(2 \sum_{k}^{\mathrm{IIocc}} \frac{V_{qk}\phi_k\rangle}{\Delta E_{jk}} + \right.\right. \\ &\qquad\qquad \left.\left. \sum_{k}^{\mathrm{IIun}} \frac{V_{qk}\phi_k\rangle}{\Delta E_{qk}} \right) \right\}_{\alpha-\beta} \end{aligned} \tag{13}$$

The contribution of the first term in eq 13 can be simplified if one assumes that ΔE_{qj} can be replaced by an average energy $-\Delta$ (<0) which is independent of q and j.

$$\begin{aligned} X1 &= 2 \sum_{k}^{\mathrm{IIocc}} \sum_{j}^{\mathrm{IIun}} \frac{\langle\phi_j|\Delta_\nu|\phi_k\rangle}{\Delta E_{jk}} \left\{ \sum_{q}^{\mathrm{Iocc}} \frac{V_{qj}V_{qk}}{\Delta E_{qj}} \right\}_{\alpha-\beta} \simeq \\ &\quad -\frac{2}{\Delta} \sum_{k}^{\mathrm{IIocc}} \sum_{j}^{\mathrm{IIun}} \frac{d_{\nu}^{j} d_{\nu}^{k} d_{\xi}^{j} d_{\xi}^{k}}{\Delta E_{jk}} \sum_{q}^{\mathrm{Iocc}} (c_{\mathrm{s}}^{q})^2{}_{\alpha-\beta} (\gamma\beta)^2 \end{aligned} \tag{14}$$

Here one finds

$$\sum_{q}^{\mathrm{Iocc}} (c_{\mathrm{s}}^{q})^2{}_{\alpha-\beta} = \sum_{q}^{\mathrm{Iocc}} (c_{\mathrm{s}}^{q})^2{}_{\alpha} - \sum_{q}^{\mathrm{Iocc}} (c_{\mathrm{s}}^{q})^2{}_{\beta} = \rho_{\mathrm{s}}^{1} \tag{15}$$

which is the McLachlan correction to the spin density at atom s in unperturbed system I. One also notes that the Hückel polarizability of II is defined by[9]

$$\pi_{\xi\nu} = 4 \sum_{k}^{\mathrm{IIocc}} \sum_{j}^{\mathrm{IIun}} d_{\xi}^{j} d_{\nu}^{j} d_{\xi}^{k} d_{\nu}^{k}/\Delta E_{kj} \tag{16}$$

Therefore

$$X1 \simeq (\gamma\beta)^2 \rho_{\mathrm{s}}^{1} \pi_{\xi\nu}/(2\Delta) \tag{17}$$

The contribution of the second term in eq 13 ($X2$) is also simplified by assuming that ΔE_{qj} (and therefore ΔE_{qk}) can be expressed as an average energy $-\epsilon$ (<0) which is independent of j and q.

$$\begin{aligned} X2 &= \sum_{q}^{\mathrm{Iocc}} \left\{ \left(\sum_{j}^{\mathrm{IIun}} \frac{V_{qj}\langle\phi|\Delta_\nu|}{\Delta E_{qj}} \right) \left(\sum_{k}^{\mathrm{IIun}} \frac{V_{qk}\phi_k\rangle}{\Delta E_{qk}} \right) \right\}_{\alpha-\beta} \simeq \\ &\quad \frac{(\gamma\beta)^2}{\epsilon^2} \left\{ \sum_{q}^{\mathrm{Iocc}} (c_{\mathrm{s}}^{q})^2{}_{\alpha-\beta} \right\} \left(\sum_{j}^{\mathrm{IIun}} d_{\xi}^{j} d_{\nu}^{j} \right) \left(\sum_{k}^{\mathrm{IIun}} d_{\xi}^{k} d_{\nu}^{k} \right) \end{aligned} \tag{18}$$

Again eq 15 can be used. One also finds that

$$\sum_{j}^{\mathrm{IIun}} d_{\xi}^{j} d_{\nu}^{j} = \delta_{\xi'\nu} - \sum_{j}^{\mathrm{IIocc}} d_{\xi}^{j} d_{\nu}^{j} = \delta_{\xi\nu} - p_{\xi\nu}/2 \tag{19}$$

where $p_{\xi\nu}$ is the bond order between ξ and ν. Therefore

$$X2 \simeq (\gamma\beta)^2 (\delta_{\xi\nu} - p_{\xi\nu}/2)^2 \rho_{\mathrm{s}}^{1}/\epsilon^2 \tag{20}$$

Similar approximations can be used for the summation $\Sigma_q^{\mathrm{Iun}}\Sigma_j^{\mathrm{IIocc}}$ of $B + C$, which give results very similar to eq 17 and 20.

The sum of these terms along with eq 12, 14, and 20 leads to

$$\rho_\nu \simeq (\gamma\beta)^2 (D_{\xi\nu})^2 \rho_{\mathrm{s}}^{\nu} + (\gamma\beta)^2 [\pi_{\xi\nu}/\Delta + P_{\xi\nu}/\epsilon^2] \rho_{\mathrm{s}}^{1} \tag{21}$$

where

$$\begin{gathered} D_{\xi\nu} = \sum_{j}^{\mathrm{II}} d_{\xi}^{j} d_{\nu}^{j}/\Delta E_{nj}^{\beta} \\ P_{\xi\nu} = (\delta_{\xi\nu} - p_{\xi\nu}/2)^2 + (p_{\xi\nu}/2)^2 \end{gathered} \tag{22}$$

Since we cannot evaluate Δ or ϵ^2 accurately, we replace them with empirical parameters a^{-1} (>0) and b^{-1}. This leads to

$$\rho_\nu \simeq (D_{\xi\nu})^2 (\gamma\beta)^2 \rho_{\mathrm{s}}^{0} + [a\pi_{\xi\nu} + bP_{\xi\nu}] (\gamma\beta)^2 \rho_{\mathrm{s}}^{1} \tag{23}$$

An attempt to fit eq 23 to accurate McLachlan spin densities showed that this equation is only qualitative and that the b term is relatively unimportant. By dropping the b term one obtains

$$\rho_\nu \simeq (D_{\xi\nu})^2 (\gamma\beta)^2 \rho_{\mathrm{s}}^{0} + a\pi_{\xi\nu} (\gamma\beta)^2 \rho_{\mathrm{s}}^{1} \tag{24}$$

This equation indicates that the spin density at the various atoms in system II is a product of the spin density at the bridging atom (ρ_{s}^{0} and ρ_{s}^{1}), the square of the resonance integral for the bridge ($\gamma\beta$), and a quantity which describes the propagation of spin density from the bridging atom ξ to atom ν in the aromatic ring [$(D_{\xi\nu})^2$ and $\pi_{\xi\nu}$].

Discussion

Equation 24 was derived in order to obtain some qualitative insight into the mode of spin propagation

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[8] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser. A*, **192**, 16 (1947).

[9] C. A. Coulson and H. C. Longuet-Higgins, *ibid.*, **193**, 447 (1948).

from the nitronyl nitroxide ring to the aromatic ring. This equation predicts that the spin density, at a given atom in the aromatic ring, should be proportional to the spin density at the bridging carbon atom in the nitronyl nitroxide ring. It is also proportional to the square of the resonance integral $(\gamma\beta)^2$ which should show the normal $\cos^2 \theta$ dependence for rotation about the bridging bond's axis. The other terms in eq 24 involve bond orders and polarizabilities. One can estimate the relative contribution of these terms by considering various types of classifications which might arise.

(1) If the spin density at bridging atom s of system I is positive and atom ν of system II belongs to a different class than the bridging atom ξ of system II, then $(D_{\xi\nu})^2$ will be greater than zero and the contribution of the first term to ρ_ν will be positive. If ν and ξ belong to the same class, then $(D_{\xi\nu})$ will be either zero or small and positive, and the contribution of the first term will be unimportant and the second term will dominate ρ_ν. When ξ and ν are in the same class $\pi_{\xi\nu}$ is negative in AH.[8] The McLachlan spin density correction $\rho_s{}^1$ is normally positive when the Hückel density $\rho_s{}^0$ is positive, so ρ_ν will be small and negative.

(2) If the Hückel spin density at bridging atom s is zero, then the first term in eq 23 is zero. The McLachlan correction term $(\rho_s{}^1)$ is normally negative in this case. The polarizability is negative and small for an atom in the same class (except for $\xi = \nu$ where $\pi_{\xi\nu}$ is large). When the atoms are in different classes, the polarizability is large and positive.[8] The spin density for a given atom ν will therefore be large and negative when ν is in a different class from ξ and small and positive when ν is in the same class as ξ. Our qualitative predictions for ρ_ν are summarized as follows

spin density at bridging atom of I	different class for ξ and ν (ortho and para position)	same class for ξ and ν (meta position)
$\rho_s > 0$	large and positive	small and negative
$\rho_s < 0$	large and negative	small and positive

We used eq 24 to examine our model nitroxides (Chart II). Since $\rho_s{}^0 = 0$, only the second term contributed with $\rho_s{}^1 < 0$. In this case, the spin densities in the aromatic rings should be proportional to the polarizability. Column 10 of Table II lists the Hückel polarizabilities. These values are found to parallel the results from the variational calculation (column 6) and the perturbation calculation (column 9). The failure to predict the correct sign for the meta position of the *o*- and *p*-pyridyl radicals is not a failure of eq 24 but is inherent in the McLachlan calculation.

The perturbation procedure used in this section does not apply directly to an INDO calculation where electronic interactions have to be explicitly considered. Considering the approximate nature of eq 24, however, we thought it worthwhile to calculate the "INDO π electron polarizability" $(\pi_{\xi\nu})$ by eq 16. The INDO polarizabilities (column 5 of Table II) are found to qualitatively reproduce the signs and relative magnitudes of the experimental spin densities.

The perturbation treatment which has been outlined is useful in that it yields some insight into the mode of spin propagation in these radicals. Although eq 24 is not quantitative, we think that it will allow one to predict the signs and relative magnitudes of spin densities in radicals of this type.

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Lone Pair Orbitals and Their Interactions Studied by Photoelectron Spectroscopy. I. Carboxylic Acids and Their Derivatives

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Abstract: The helium I photoelectron spectra of carboxylic acid derivatives are reported. The carbonyl oxygen lone pair orbital (n_O) and the approximately nonbonding π_2 orbital are the two highest energy filled molecular orbitals and have very similar ionization potentials. Assignments are proposed based on considerations of vibrational fine structure and inductive effects. The spectra of ethylene carbonate and ethylene trithiocarbonate are also included and discussed.

The valence shell structure of atomic and molecular vapors can be so readily obtained by the use of helium I photoelectron energy analysis (molecular photoelectron spectroscopy) that it has come to provide an important test of the adequacy of quantum calculations. Together with postulates about the degree of adherence to Koopmans' theorem, all the bands in such a photoelectron spectrum can be related in principle to the eigenvalues obtained by such calculations. In the absence of accurate quantum calculations it has often proved expedient, however, to concentrate on some feature or features which relate to particularly interesting portions of the valence shell structure. This more empirical approach has proved to be espe-