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PROGRESS REPORT

STABILITIES OF NITROGEN CONTAINING HETEROCYCLIC RADICALS AND GEOMETRICAL INFLUENCES ON NON-RADIATIVE PROCESSES IN ORGANIC MOLECULES

by

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INTRODUCTION

The following report details the accomplishments of the grant during the period of June 30, 1969 through July 1, 1970. The objectives of the original proposal dealt with attempts to generate measureable quantities of radicals obtained by hydrogen abstraction from imidazole and related heterocyclics. Theoretical calculations were to be directed towards determining the electronic structures of such radicals. In addition some effort was to be directed towards determining the role of geometrical distortion on the energies of the ground and excited states of large organic molecules. The accomplishments of this year's research effort lie almost entirely in the area of theoretical treatment of heterocyclic radicals. To date, no radical of imidazole, or related heterocyclics have been detected.

Besides the principal investigator (E. M. Evleth), two additional investigators have been working on this problem. In September of 1969, Dr. S. Chang came to Santa Cruz as a postdoctoral researcher to work on the experimental problem of radical generation. In addition, Mr. T. S. Lee completed his Master of Science thesis in the area of spin density calculations. His thesis, "Spin Density Calculations for Heterocyclic Radicals Using Annihilation Operator to the Unrestricted Hartree-Fock Wave Function", was completed in June of 1970. In cooperation with Dr. Paul Horowitz, additional calculations have been conducted on heterocyclic radicals using the INDO all-valence electron approximation.

During the year one paper, "Photophysical and Photochemical Properties of Sterically Hindered Aryldiazonium Salts", was published (with R. J. Cox and P. Bushnell), Tetrahedron Letters, 207, (1970). This paper resulted from work accomplished during the previous year of the grant. Another paper, "Quantum Mechanically Based Rules for Thermal and Photochemical Reaction", is in press.

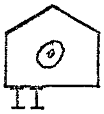
The following report is broken into three main sections. First, a general discussion of the purpose of the work undertaken. Secondly, a detailed account of the theoretical calculations will be given. Thirdly, an accounting of the electron spin resonance measurements will be given.

I A STATEMENT OF PURPOSE

The main object of the research attempted is to determine if the radicals of imidazole, indole, pyrrole, benzimidazole, and other related heterocyclics exist and to determine their electronic structures. All the radicals of interest are neutral, resulting from the removal of a hydrogen from the N-H bond in these molecules. During the past 20 years a large number of radical species have come under experimental investigation using ESR techniques. A vast number of radical cations and radical anions have been generated. Because of coulombic repulsion charged radicals are intrinsically more easily generated i.e., they dimerize or disproportionate less easily than do neutral radicals. Neutral radicals are usually measured at low temperatures either in solution or in the frozen matrix.

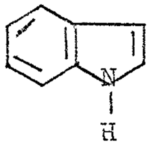
Of primary interest here is the radical imidazoyl (II) which results from the breaking of the N-H bond in imidazole (I). The radical (II) is proposed as an intermediate in oxidative phosphorylation.[1,2] Oxidative phoshorylation is the key process in generating adenosine triphosphate, the main energy source in biological systems. In addition, imidazole is present at the active sight of a number of enzyme systems. The possible radiation or chemical damage of this material may occur through


I
imidazole

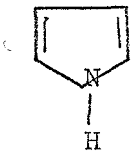

II
imidazoyl

radical intermediates. Thus the study of this material is justified. Other possible heterocyclic radicals exist. Indole (III) and pyrrole (IV) units are present in biological systems as well as purines (V). Removal of hydrogen from the N-H unit will generate neutral radicals.

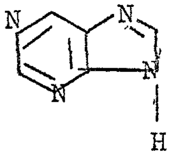
Radicals of the type mentioned here are members of a family of radicals generated from corresponding hydrocarbons cyclopentadiene (VI) and indene (VII).



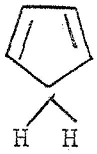
III
Indole



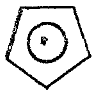
IV
Pyrrole



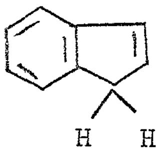
V
Purine



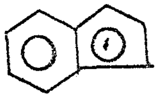
VI
cyclopentadiene



VIR
cyclopentadienyl
radicals



VII
Indene



VIIR
indenyl radical

With the exception of cyclopentadienyl radical (VIR) none of the above mentioned radicals have been characterized by ESR measurements. Thus the area is a rich one for investigation.

II THEORETICAL INVESTIGATION OF THE ELECTRONIC STRUCTURES OF HETEROCYCLIC RADICALS

A) Theoretical nature of the Problem of Spin Density Calculations

The first theoretical approaches to the calculations of the spin densities of neutral radical, radical anion, and radical cation hydrocarbon species used the π-molecular orbitals obtained from the simple Huckel method.[3,4] In the most critical case, the allyl radical, this simple theoretical method predicts the following spin densities at the various carbon atoms[5]

$$\overset{\frac{1}{2}}{CH_2} - \overset{0}{CH} - \overset{\frac{1}{2}}{CH_2}$$

that is, the odd electron spends half of its time at each of the terminal carbon positions. This simple picture results from the nodal property of the second molecular orbital in this molecule. Actual experimental data shows that the approximate spin density is as follows:[6]

$$\overset{0.58}{CH_2} - \overset{-0.16}{CH} - \overset{0.58}{CH_2}$$

The conclusion is that the simple molecular orbital approach is inadequate. The reason for the inadequacy of this model has been explained in standard texts.[5,7] One of the first attempted solutions of this problem was to use the unrestricted Hartree-Fock method.[8] This method leads to other problems in that the wave function obtained for the electrons is in general not an eigenfunction of S^2, the total spin operator.[9,10] To overcome this difficulty, two alternate methods can be used. One is the so-called projection operator methods[10,11] and the other is the application of the annihilation operator.[13-16] The first method gives a wave function which is an eigenfunction of S^2 while the latter is only an approximation which eliminates the most important unwanted component of the multiple spin states. It is the object of this work to describe the theory and procedures of the latter method when applied to the calculations of several heterocyclic hydrocarbon radicals.

The S^2 Problem

In atoms the spin-orbital interactions are assumed weak so that the Russell-Saunder's coupling is a justified approximation.[9] The component of the total spin momentum along the z-axis is a sum of contributions by the individual electrons. In a many-electron system,

$$S_z = \Sigma_j S_{zj} \tag{1}$$

where S_{zj} is the operator corresponding to the z-component of spin momentum of the j^{th} electron. The spin function of electron j must be either α_j or β_j since the electrons are assumed magnetically independent of one another. The two eigenfunctions, α_j and β_j, satisfy the following equations separately with eigenvalues $\frac{1}{2}$ and $-\frac{1}{2}$, respectively.

$$S_{zj}\ \alpha_j = \tfrac{1}{2}\hbar\alpha_j \tag{2a}$$

$$S_{zj}\ \beta_j = -\tfrac{1}{2}\hbar\beta_j \tag{2b}$$

When S_z operates on the total wave function, ψ the following equation results,

$$S_z\psi = \Sigma_j S_{zj}\psi = \Sigma_j \sigma_j \psi = S_z\psi \tag{3}$$

where

$$S_z = \tfrac{1}{2}\ (p-q)\hbar \tag{4}$$

and

$$\sigma_j = \tfrac{1}{2}\hbar \text{ or } -\tfrac{1}{2}\hbar \tag{5}$$

with p and q being the numbers of electrons of α spin and of β spin, respectively. Equation (3) shows that ψ is an eigenfunction of the operator, S_z, if ψ is a product of orbitals of all the electrons. It is also true when ψ is a Slater determinant, since in this case, every term of the determinant is a product of orbitals of all the electrons. However, whether the Slater determinant is an eigenfunction of the operator S^2 or not has to be tested here. The operator, S^2 can be expressed in terms of its components, that is,

$$S^2 = S_x^2 + S_y^2 + S_z^2 \tag{6}$$

where

$$S_x = \Sigma_j S_{xj}; \quad S_y = \Sigma_j S_{yj}; \quad S_z = \Sigma_j S_{zj} \tag{7}$$

The commutation rules require that

$$S_{xj} S_{yj} - S_{yj} S_{xj} = i\hbar S_{zj}$$

$$S_{xj} S_{yk} - S_{yk} S_{xj} = 0 \tag{8}$$

The spin functions α_j and β_j are eigenfunctions of S_j^2 with eigenvalue $\frac{1}{2}(\frac{1}{2} + 1)\hbar$.[9] Hence,

$$S_j^2\alpha_j = \left(S_{xj}^2 + S_{yj}^2 + S_{zj}^2\right) \alpha_j = \frac{3}{4} \hbar^2\alpha_j \tag{9}$$

$$S_j^2\beta_j = \left(S_{xj}^2 + S_{yj}^2 + S_{zj}^2\right) \beta_j = \frac{3}{4} \hbar^2\beta_j \tag{10}$$

Using Equations (2), the following equations are obtained.

$$\left(S_{xj}^2 + S_{yj}^2\right) \alpha_j = \tfrac{1}{2}\hbar^2\alpha_j \tag{11a}$$

$$\left(S_{xj}^2 + S_{yj}^2\right) \beta_j = \tfrac{1}{2}\hbar^2\beta_j \tag{11b}$$

Following Dewar,[7] the two operators, σ_j^+ and σ_j^- are defined by

$$\sigma_j^+ = S_{xj} + i S_{yj} \tag{12a}$$

$$\sigma_j^- = S_{xj} - i S_{yj} \tag{12b}$$

Using these two operators, the operator, S^2 can be expressed as

$$S^2 = \tfrac{1}{2}\Sigma_j \Sigma_k\left(\sigma_j^{+}\sigma_k^{-} + \sigma_j^{-}\sigma_k^{+}\right) + S_z^{2} \qquad (13)$$

by going through some lengthy algebra. When S^2 operates on ψ, a Slater determinant, it is found,[9] with the help of the expression given in (13),

$$S^2\psi = \tfrac{1}{2}\hbar^2\psi + \tfrac{1}{4}(p - q)\hbar^2\psi + \hbar^2\Sigma_j\Sigma_{k\neq j}\psi_{jk} \qquad (14)$$

where ψ_{jk} is a function obtained from ψ by exchanging the j^{th} and k^{th} spin-orbitals. Because of the ψ_{jk}'s occurred in (13), ψ is in general not an eigenfunction of S^2.

The Annihilation Method

For systems having the open-shell configuration, the restricted Hartree-Fock wave function constructed by a single Slater determinant is inadequate. One of the many attempts to improve the treatment of electronic structures is the method of different orbitals for different spin.[13] Pioneer workers like Pople and Nesbet (1954), Lowdin[17,18] (1954, 1955), Pratt[18] (1956) and Hurst, Gray, Brigman and Matsen[20] (1958) all have contributed to the development of this method now known as unrestricted Hartree-Fock wave function. However, a wave function so constructed is in general not an eigenfunction of the operator, S^2. It contains components of several spins,[15]

$$\psi_{uhf} = \Sigma_{m=o}^{q}\ C_{s'+m}\ \psi_{s'+m} \qquad (15)$$

where the subscript uhf denotes that the wave function is the unrestricted Hartree-Fock wave function. The lowest spin component has spin $s = s' = \frac{1}{2}(p - q)$. All the higher spin components are actually unwanted. Amos and Snyder approximated the true wave function by ψ_{uhf} by proper treatment such as the elimination of the second spin component, i.e., the component having a spin just greater than the lowest. Their argument was that the second spin component is practically the most important contaminating component while all the other higher spin components are negligible due to higher energies.

The wave function, ψ_{uhf}, can be obtained by the usual variational method, minimizing the energy in a self-consistent field. Then, an annihilation operator $A_{s'+1}$ is defined by[15]

$$A_{s'+1} = S^2 - (s'+1)\ (s'+2) \tag{16}$$

When $A_{s'+1}$ operates on the unrestricted Hartree-Fock wave function, ψ_{uhf}, it is obtained, using Equation (14), that

$$A_{s'+1}\ \psi_{uhf} = \Sigma_{m=o}{}^{q}\ C_{s'+m}(m-1)(2S' + m + 2)\ \psi_{s'+m} \tag{17}$$

It is obvious that the new wave function, $A_{s'+1}\ \psi_{uhf}$, also contains several spin components except the one with spin $s'+1$. The S^2 problem remains unsolved if the contribution from the components of higher spins is important. In most cases, due to the energy separation, the only important contaminating component in ψ_{uhf} is the one with spin $s'+1$. It is this fact that makes the annihilation method applicable.

In this paper, the annihilation method is extended to perform the spin calculations of certain neutral heterocyclic radicals, namely, the imidazoyl, benzimidazoyl, pyrryl and purinyl radicals. The wave functions of these systems were computed using the SCF method of the Brickstock and Pople's approximation[21] for unsaturated hydrocarbon ions and radicals. The main program was obtained from "Quantum Chemistry Program Exchange."[22] This program is numbered 76 with the title "Pople Pi-Electron Program." A subprogram was added to calculate the spin and charge densities after annihilation. The list of this subprogram is given in Appendix C. The main feature of the Brickstock and Pople's approximation is that the pi-electrons are separated from the σ-core.[21] This separation seems to be acceptable for the alternant hydrocarbon systems.

B) Method of Calculation

Wave Functions, Charge and Bond Order Matrices

Electrons of α - spin and of β - spin are arranged to occupy two entirely distinct sets of molecular orbitals. The unrestricted Hartree-Fock wave function can be written as[14]

$$\psi_{uhf} = \left[(p+q)!\right]^{-\frac{1}{2}}\det\left\{\psi_1(1)\alpha(1)\ldots\psi_p(p)\alpha(p)\varphi_1(p+1)\beta(p+1)\ldots\varphi_q(p+q)\beta(p+q)\right\} \tag{18}$$

The individual orbitals in (18), the ψ_i's and φ_i's are linear combinations of a basis set, $\{\omega_r\}$. This basis set, $\{\omega_r\}$ is assumed to be orthogonal but in practice is a set of truncated atomic pi-orbitals at different nuclei centers. Therefore,

$$\psi_i = \Sigma_r a_{ri}\ \omega_r; \tag{19a}$$

$$\varphi_i = \Sigma_r b_{ri}\ \omega_r. \tag{19b}$$

To obtain the best choice of the coefficients a_{ri} and b_{ri}, the set of self-consistent equations developed by Roothaan[22] is satisfied separately by each set of orbitals, ψ_i and φ_i. As has been mentioned, the Brickstock and Pople's approximation for hydrocarbon radicals and ions is adopted.[21] The one-center integrals and the resonance integrals are parameters as in the usual semiempirical calculations.[23]

In order to simplify the practice of the annihilation method, it is convenient to introduce the charge and bond order matrices, P and Q, for electrons of spin α and spin β, respectively.

$$P_{rs} = \Sigma_{i=1}^{p} a_{ri}^{*} a_{si} \tag{20a}$$

$$Q_{rs} = \Sigma_{i=1}^{q} b_{ri}^{*} b_{si} \tag{20b}$$

The charge and spin density functions before annihilation for the determinant, ψ_{uhf} are defined respectively as[14]

$$q_{sd}(r) = \Sigma_{uv}(P+Q)_{uv}\omega_u^{*}(r)\omega_v(r) \tag{21a}$$

$$\rho_{sd}(r) = \Sigma_{uv}(P-Q)_{uv}\omega_u^{*}(r)\omega_v(r) \tag{21b}$$

First-Order Density Matrix

After the operation of the annihilator, the wave function becomes $A_{s'+1}\psi_{uhf}$. It is desirable to obtain the first-order density matrix for computing the spin and charge densities. By first-order density matrix, it is meant that when the matrix is multiplied by a volume element, dv_1, it equals the number of particles multiplying the probability of finding a particle within the volume dv_1 around the point γ_1 having the spin s_1 when all the other particles have arbitrary positions and spins.[24,25] Mathematically, this density matrix can be expressed as

$$\gamma(1',1)_{aa} = M^{-2}\int A_{s'+1}\psi_{uhf}^{*}(1'23\cdots N)$$

$$\times\ A_{s'+1}\psi_{uhf}(123\cdots N)\,dv_2\cdots dv_N \tag{22}$$

The subscript aa denotes the phrase, after annihilation. M is the normalization constant, given by the following expression

$$M^2 = \int A_{s'+1}\psi_{uhf}^{*}A_{s'+1}\psi_{uhf}\,dv_1\cdots dv_N \tag{23}$$

From equations (14) and (16), the annihilation operator can be found to be

$$A_{s'+1} = S^2 - (s'+1)(s'+2)$$

$$= A + \Sigma_i^{\alpha}\Sigma_j^{\beta}P_{ij}^{s} \tag{24}$$

with

$$A = q - 2(s'+1) \tag{25}$$

The operator P_{ij}^{s} interchanges the spin of the i^{th} α - spin orbital and the j^{th} β - spin orbital.

Amos and Snyder[15,16] proved that a unitary transformation of the orbitals $\{\psi_i\}$ and $\{\varphi_i\}$ in Equation (18) leaves ψ_{uhf} unchanged since it is a determinant. It is convenient to transform these orbitals into the so-called corresponding orbitals which have the property

$$\int \chi_i\eta_j d_\tau = T_i\delta_{ij} \tag{26}$$

where χ_i and η_j are respectively the corresponding orbitals for α - spin and for β - spin. They also pointed out that the matrices P and Q are invariant under such transformation. The statement[13,15] given in their papers that T_i^2 are eigenvalues of the two matrices, PQP and QPQ seems to be a misprint since in general

$$T_r PQP \neq T_r QPQ$$

A proof that T_i^2 are eigenvalues of PQ and QP is given in Appendix A.

To calculate $\gamma(1',1)_{aa}$, the density matrix, it is necessary to evaluate terms of the form

$$\left[ij|k\ell\right] = \int \left\{P_{i\alpha j\beta}{}^{s}\psi_{uhf}(1',\cdots,N)\right\}^{*} \times \left\{P_{k\alpha\ell\beta}{}^{s}\psi_{uhf}(1,\cdots,N)\right\} dv_2\cdots dv_N \tag{27}$$

where ψ_{uhf} has been transformed into corresponding orbitals. The resulting equations are listed as follows:[15]

$$\left[00|00\right] = \Sigma_\ell \eta_\ell^*(1')\eta_\ell(1) \tag{28a}$$

$$\left[00|ii\right] = -\ \eta_i^*(1)\chi_i(1)T_i - \Sigma_{\ell\neq i}\eta_\ell^*(1')\eta_\ell(1)T_i^2 \tag{28b}$$

$$\left[ii|00\right] = -\ \chi_i^*(1')\eta_i(1)T_i - \Sigma_{\ell\neq i}\eta_i^*(1')\eta_\ell(1)T_i^2 \tag{28c}$$

$$\left[ii|ii\right] = +\ \chi_i^*(1')\chi_i(1) + \Sigma_{\ell\neq i}\eta_\ell^*(1')\eta_\ell(1) \tag{28d}$$

$$\left[ii|kk\right] = + \chi_i^*(1')\eta_i(1)T_iT_k^2 + \eta_k^*(1')\chi_k(1)T_kT_i^2$$

$$+ T_i^2T_k^2\Sigma_{\ell\neq i,k}^q\eta_\ell^*(1')\eta_\ell(1), \quad \text{for } i \neq k \qquad (28e)$$

$$\left[ij|ij\right] = + \chi_i^*(1')\chi_i(1)(1-T_j^2)$$

$$+ \Sigma_{\ell\neq j}^q\eta_\ell^*(1')\eta_\ell(1)(1-T_j^2), \quad \text{for } i\neq j,\ i>q \qquad (28f)$$

$$\left[ij|ij\right] = + \chi_i^*(1')\chi_i(1)(1-T_j^2) + \eta_i^*(1')\eta_i(1)(1-T_j^2)$$

$$- \eta_i^*(1')\chi_i(1)T_i(1-T_j^2) - \chi_i^*(1')\eta_i(1)(1-T_j^2)$$

$$+ \Sigma_{\ell\neq i,j}^q\eta_\ell^*(1')\eta_\ell(1)(1-T_j^2)(1-T_j^2)$$

$$\text{for } i\neq j, \quad i\leq q \qquad (28g)$$

Only terms multiplying $\beta^*(1')\beta(1)$ are included so that the results give the density of the β - spin electrons. Similar results for α - spin electrons can be obtained merely by replacing η_r by χ_r and χ_r by η_r when they appear in (28). Some misprint found in Amos and Snyder's[15] original paper has been corrected. The derivations of some of the formulas are given in Appendix B.

Equations (28) allow the density matrix $\gamma(1',1)_{aa}$ to be written as[15]

$$M^2\gamma(1',1)_{aa} = A^2[00|00] + A\Sigma_i^{\alpha}\Sigma_j^{\beta}\{[00|ji] + [ij|00]\}$$

$$+ \Sigma_{ik}^{\alpha}\Sigma_{j\ell}^{\beta}[ij|k\ell] \qquad (29)$$

$$= A^2[00|00] + A\Sigma_{i=1}^{q}\{[00|ii] + [ii|00]\}$$

$$+ \Sigma'^{q}_{ik}[ii|kk] + \Sigma_i^{q}[ii|ii] + \Sigma'^{q}_{ij}[ij|ij]$$

$$+ \Sigma_{i=q+1}^{p}\ \Sigma_j^{q}\ [ij|ij] \qquad (30)$$

J and K Matrices

Since the corresponding orbitals are written in terms of a basis set, each of the terms in Equations (28) can be written as[15]

$$\Sigma_{uv}[ij|k\ell]_{uv}\omega_u{}^*(1')\beta^*(1')\beta(1) \qquad (31)$$

where the $[ij|k\ell]$ depend only on the coefficients $\{a_{ri}\}$ and $\{b_{ri}\}$. Using Equations (30) and (31), the first-order density matrix can be expressed in terms of two matrices,[13] J and K,

$$\gamma(1',1)_{aa} = \Sigma_{rs}J_{rs}\omega_r{}^*(1')\omega_s(1)\alpha^*(1')\alpha(1)$$

$$+ \Sigma_{rs}K_{rs}\omega_r{}^*(1')\omega_s(1)\beta^*(1')\beta(1) \qquad (32)$$

The relations between J, K and P, Q are found to be[15]

$$M^2 J = \left\{A^2-2A\mathrm{tr}PQ+pq-q-N\mathrm{Tr}PQ+3\mathrm{Tr}PQ+2\mathrm{Tr}^2PQ-2\mathrm{Tr}PQPQ\right\}P$$

$$+\left\{p-\mathrm{Tr}PQ\right\}Q+QPQ+\left\{N-4\mathrm{Tr}PQ-3+2A\right\}PQP$$

$$+\left[PQ+QP\right]\left\{2\mathrm{Tr}PQ-p+1-A\right\}-2\left[PQPQ+QPQP\right]$$

$$+4PQPQP \qquad (33)$$

By interchanging P's and Q's and p's and q's, the similar formula for M^2K is obtained. The normalization constant M^2 expressed in terms of P and Q is now

$$M^2 = A^2-2A\mathrm{Tr}PQ+pq-N\mathrm{Tr}PQ+2\mathrm{Tr}PQ+2\mathrm{Tr}^2PQ-2\mathrm{Tr}PQPQ \qquad (34)$$

The spin density on atom i is then given by[15]

$$P_{aa}{}^{i} = J_{ii} - K_{ii} \qquad (35)$$

and the charge density is

$$q_{aa}{}^{i} = J_{ii} + K_{ii} \qquad (36)$$

The Expectation of S^2

The quantity $\langle S^2\rangle_{aa}$ is to measure to what extent the wave function contains other spin components. It is therefore desirable to compute this quantity in order to test the adequacy of the approximated wave function. The formulas are given below:[15]

$$\langle S^2\rangle_{aa} = \frac{\langle S^6\rangle_{sd}-2(s'+1)(s'+2)\langle S^4\rangle_{sd}+(s'+1)^2(s'+2)^2\langle S^2\rangle_{sd}}{\langle S^4\rangle_{sd}-2(s'+2)\langle S^2\rangle_{sd}+(s'+1)^2(s'+2)^2} \qquad (37)$$

where

$$\langle S^2 \rangle_{sd} = B - \mathrm{TrPQ} \tag{38}$$

$$\begin{aligned}\langle S^4 \rangle_{sd} = {} & B^2 + pq + 2(\mathrm{Tr}^2\mathrm{PQ} - \mathrm{TrPQPQ}) \\ & - (2B + N - 2)\ \mathrm{TrPQ}\end{aligned} \tag{39}$$

$$\begin{aligned}\langle S^6 \rangle_{sd} = {} & B^3 + Bpq + pq(2B+N-2) - \left\{3B^2 + 3B(N-2) + (N-2)^2 + pq \right. \\ & \left. + 4(p-1)(q-1)\right\}\mathrm{TrPQ} + 2\left\{3B + 3N - 10\right\}\left[\mathrm{Tr}^2\mathrm{PQ} - \mathrm{TrPQPQ}\right] \\ & - 6\left\{\mathrm{Tr}^3\mathrm{PQ} - 3\mathrm{TrPQTrPQPQ} + 2\mathrm{TrPQPQPQ}\right\}.\end{aligned} \tag{40}$$

with

$$B = s'(s'+1) + q \tag{41}$$

In Amos and Snyder's paper,[15] the letter A was used in those equations instead of using the letter B. This may cause confusion since A has already been defined in Equation (25) and is not the same as B defined in Equation (41). The validity of Equation (41) can be easily seen from Equation (14).

Discussion of the Method

Although this method has been adopted here for calculating the spin densities, the validity of the annihilation after energy-minimization is still questionable. Hiroshi Nakatsuji, Hiroshi Kato and Teijiro Yonezawa[26] have recently analyzed and interpreted in configurational-interaction language by means of the natural orbitals of the ψ_{uhf}, includes only one type of the singly excited configurations and thus the correlation effect included are very limited ones as compared with the usual configuration interaction treatment. Also, the weight of the lowest contaminating spin function, included in the unrestricted Hartree-Fock wave function decreases with increasing spin multiplicity. As far as the decreasing weight of the lowest contaminating spin function is concerned, the unrestricted Hartree-Fock wave function after annihilation[9] is still suitable for the purpose here since all radicals treated in this paper have a spin ½.

The final formulas used in the program are the series of equations from (33) to (41). The derivations of all these formulas are based on two main assumptions, namely, the orthonormality of the basis set and the transformation possibility of the molecular orbitals into corresponding orbitals. However, in practice, the basis set is taken from the set of pi-atomic orbitals at various centers which are not orthogonal. Also the unrestricted Hartree-Fock orbitals are actually used in calculations instead of using the transformed corresponding orbitals. Since in the calculation only P and Q are involved and they are invariant under transformation as stated above, the use of unrestricted Hartree-Fock orbitals is justified. On the other hand, the overlapping between any two members in the basis set is in general negligible and hence the set can be practically treated as an orthogonal set.

C) π-Electron Calculations

First of all, an independent program was written for calculating the spin and charge densities after annihilation using Amos and Snyder's formula described above.[15] Coefficients of molecular orbitals were given to the program as input. The results for allyl and pentadienyl radicals proved to be identical as given in Amos and Snyder's paper.

Having been proved correct, the independent program was then made a subroutine of the main program, Pople pi-electron program, which allows one to obtain the spin and charge densities of planar radicals using geometrical coordinates as input. This program generates a set of simple Huckel molecular orbitals as trial wave functions and then gives the self-consistent field molecular orbitals through iteration.

Allyl Radical

The allyl radical was used again as a test of the combined program. The ionization potential and the one-center integral for carbon atom were chosen to be 10.98 ev and 11.08 ev., respectively.[27,28] The resonance energy which is a parameter known as the β-integral was varied ranging from -2.0 ev to -3.0 ev. Bond lengths were set identical, being 1.4Å each. The results are shown in Table I.

In general, the variation of the β - integral does not affect the charge and spin densities significantly. The expectation of S^2 after annihilation keeps unchanged, giving a value of 0.75 each time. This can be rationalized for the following reason.

$$\psi_{\mathrm{uhf}} = \Sigma_{m=o}{}^{q} C_{s'+m} \; \psi_{s'+m} \qquad (14)$$

For allyl radical, $q = 1$ and Equation (14) becomes

$$\psi_{\mathrm{uhf}}^{\mathrm{Allyl}} = C_{\frac{1}{2}} \; \psi_{\frac{1}{2}} + C_{\frac{3}{2}} \; \psi_{\frac{3}{2}}. \qquad (42)$$

The application of annihilation eliminates the second term leaving

$$A_{s'+1} \; \psi_{\mathrm{uhf}}^{\mathrm{Allyl}} = C_{\frac{1}{2}} \; \psi_{\frac{1}{2}}. \qquad (43)$$

Equation (43) shows that the wave function now is a pure spin multiplet and the expectation of S^2 is of course $\frac{1}{2}(\frac{1}{2} + 1)$, or 0.75.

Pentadienyl Radical

In order to see the effect of the β - integral variation to the expectation of S^2 for cases where the wave function after annihilation contains higher spin-components, the calculation for pentadienyl radical was carried out and the results are shown in Table II. In this case, the expectation of S^2 shows a very sensitive dependence on the β - value chosen. It is possibly due to the mixing of higher spin-components. For this system, $q = 2$ and

$$\psi_{\mathrm{uhf}}^{\mathrm{pent}} = C_{\frac{1}{2}} \; \psi_{\frac{1}{2}} + C_{\frac{3}{2}} \; \psi_{\frac{3}{2}} + C_{\frac{5}{2}} \; \psi_{\frac{5}{2}}. \qquad (43)$$

After annihilation, the wave function becomes

$$A_{\frac{1}{2}+1}\,\psi^{\text{pent}}_{\text{uhf}} = C_{\frac{1}{2}}\,\psi_{\frac{1}{2}} + C_{\frac{5}{2}}\,\psi_{\frac{5}{2}}, \tag{44}$$

and the expectation S^2 is an average of two spin-components.

From Table II, it is clear that by varying the β integral, the relative weight of each spin-component, i.e., the ratio, $C_{\frac{5}{2}}/C_{\frac{1}{2}}$, in the pentadienyl case changes and the expectation of S^2 varies. In general the same effect is expected in every case where the radical has a q greater than unity.

Furthermore, it is found that a larger absolute β - value always gives a smaller value of $\langle S^2 \rangle_{aa}$. The interpretation for this observation may be that the stronger is the interaction among atoms, the better is the stabilization of the system as a whole. Since the first spin-component corresponds to a state of lower energy, the larger absolute value of β - integral tends to increase the weight of the lower spin state. Nevertheless the sensitivity of $\langle S^2 \rangle_{aa}$ to β - variation is indicative that single annihilation may be unsatisfactory.

Table I

Spin Densities of Allyl Radical

	Atom 1	Atom 2	$\langle S^2 \rangle_{aa}$
β = -2.4 ev	0.57111	-0.14221	0.75
-2.6	0.56416	-0.12832	0.75
-2.8	0.55804	-0.11606	0.75
-3.0	0.55304	-0.10606	0.75
Amos & Snyder[15]	0.547	-0.093	0.75
Experimental[6]	0.58	-0.16	--

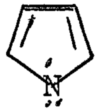
Table II

Spin Densities of Pentadienyl Radical

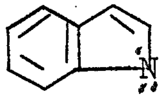
	Atom 1	Atom 2	Atom 3	$\langle S^2 \rangle_{aa}$
β = -2.0 ev	0.47131	-0.16851	0.39440	1.08253
-2.4	0.44836	-0.14321	0.38971	0.88023
-2.6	0.43563	-0.13012	0.38900	0.83026
-2.8	0.41956	-0.11558	0.39205	0.79564
-3.0	0.41091	-0.10587	0.38994	0.78027
Amos & Snyder[15]	0.383	-0.094	0.422	0.73938
Experimental[6]	0.349	-0.103	0.506	--

Heterocyclic Radicals

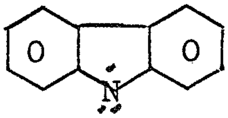
The pi-electron and spin density calculations for the heterocyclic radicals imidazoyl (II), pyrryl (IVR), indolyl (IIIR), carbazyl (VIIIR), benzimidazoyl (IXR), and purinyl (VR) are shown, respectively, in Tables III through VIII. The pi-electron calculations were conducted using the Open-Shell Program No. 76 from the Quantum Chemistry Program Exchange, Indiana University. The program computes the two centered repulsion integrals using the Mataga approximation.[27] The nitrogen and carbon ionization potentials were assigned values of, respectively, 14.63 and 11.08 ev. The one centered integrals for the same atoms were set at, respectively, 12.27 and 10.98 ev. The C=C and C=N resonance integrals are listed in the Tables. Some variation of these parameters were tested and the results are also listed in the Tables. None of these materials have been detected by ESR measurements. The ESR spectrum of both tetraphenyl pyrryl[28] and triphenylimidazoyl[29] radicals have been reported but they are too complex for detailed analysis and only remotely



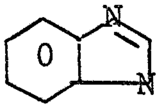
IVR



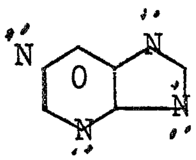
IIIR



VIIIR



IXR



VR

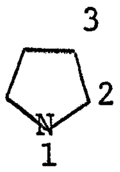
related to the problem presented here. However, the calculations themselves have some interesting features and these will now be discussed in order.

a) Pyrryl Radical (IVR, Table III). The pi-electron calculation indicates that this radical should have nearly zero spin density (the spin density being the difference between the electron density for alpha and beta pi-electrons at the atom being discussed). This nearly zero spin density results not from electron negativity factors but from the C_{2v} symmetry of the pyrryl radical. In the closed shell approximation the highest molecular orbital would be antisymmetric with respect to a symmetry operation which reflects the molecule through the plane of symmetry passing through the nitrogen atom but perpendicular to the plane of the molecule. Such a molecular orbital would have zero spin density at the nitrogen atom. In the open shell approximation the alpha and beta electrons are relegated to different molecular orbitals and negative spin densities are computed. The case of pyrryl is somewhat similar to the previously discussed of allyl radical (in which the closed shell calculation predicts zero spin density at the central carbon atom). However, as seen from inspecting Table III, the spin densities do not dramatically change with annihilation. The expectation value of $\langle S^2 \rangle$ is nearly 0.75 indicating the calculation represents a nearly pure doublet.

b) Imidazoyl Radical (II, Table IV). The point group of imidazoyl radical is C_{2v}, the same as pyrryl, and the expectation was that the spin density on the symmetrically placed carbon

TABLE III

π-Spin and Electron Densities of Pyrryl Radical

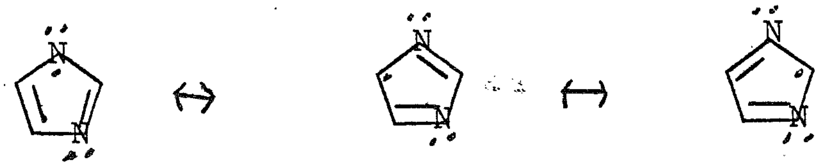


$\beta c = n = \beta c = c = -2.4$ ev

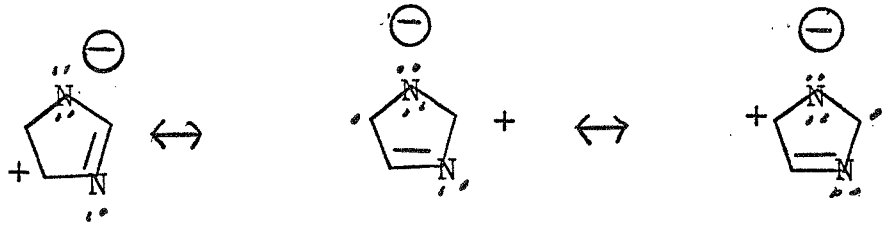
	π-Spin		π-Electron Density (After)
Atom	Before Annihilation	After Annihilation	
1	-0.048	-0.081	1.366
2	0.418	0.445	0.807
3	0.106	0.095	1.010

$\langle S^2 \rangle = 0.75001$

atom would be nearly zero. As seen by inspecting Table IV this is not true, the spin densities on the nitrogen atoms were nearly zero! Clearly no symmetry argument can be imposed to explain such a result. A rationalization of this result can be obtained by inspecting the pi-electron charge densities. The nitrogen atoms accumulate an electron density in excess of unity (becoming negatively charged) while the carbon atoms lose electron density. These electron densities allow us to make some guess at the relative importance of different resonance structures. For instance, if the molecule were cyclopentadienyl radical equal spin density would be expected at each atom. However, the electronegativity of the nitrogen atoms draws electrons into the nitrogen atoms presumably decreasing the relative importance of radical structures having spin densities at the nitrogen atom. This is shown below. Apparently, in the pi-electron calculation of



Nonionic Radical Resonance Structures



Radical-ionic Resonance Structures

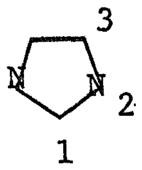
imidazoyl radical the radical-ionic resonance structures are more important than the nonionic structures. The high spin density on the symmetrically disposed central carbon atom indicates that the point group of the molecular wavefunction for imidazoyl radical is probably not the same as with pyrryl radical.

c) Indolyl Radical (IIIR, Table V). The pi-electron calculation on indolyl radical does show a positive spin density on the nitrogen atom which is quite sensitive, computationally, to the choice of the resonance integral (in contrast with pyrryl and imidazoyl). An inordinately high degree of spin is localized on the carbon atom at the 3-position (about ½ the total spin). If this is true for the real indolyl radical (as yet undetected) it would indicate that this species would be highly reactive. Examination of the spin and electron densities indicate that the position of the spin densities in indolyl radical is not easily rationalized in the same way as with imizoyl. On the other hand the concentration of the spin densities in the five member ring rather than the six member ring indicates a reluctance to the breaking of the natural resonance (or aromaticity) of the benzene ring.

d) Carbazyl Radical (VIIIR, Table V). Examination of the two different sets of calculations on carbazyl radical indicates some difficulty in obtaining a good value for the expectation value of $\langle S^2 \rangle$. The spin densities on the carbon atoms are different for both sets of calculations although most of the spin

TABLE IV

π-Spin and Electron Densities of Imidazoyl



$\beta c = n = \beta c = c = -2.4$ ev

Atom	Before	π-Spin After Annihilation	π-Electron Density (After)	(Before)
1	0.355	0.355(0.360)*	0.741(0.732) *	0.746
2	-0.046	-0.044(-0.035)	1.336(1.341)	1.330
3	0.368	0.367(0.356)	0.793(0.793)	0.797

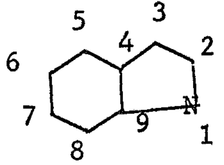
$\langle S^2 \rangle = 0.756$

$\langle S^2 \rangle^* = 0.755$

*$\beta c = n = -2.5$ ev., $\beta c = c = -2.40$

Table V

π-Spin and Electron Densities of Indolyl Radical



Allβ's = -2.4 ev

Atom	π-Spin Density After Annihilation		π-Electron Density After Annihilation	
1	0.276	(0.14)*	1.247	(1.30) *
2	-0.040	(0.06)	0.890	(0.87)
3	0.502	(0.49)	0.921	(0.91)
4	-0.069	(-0.04)	1.057	(1.07)
5	0.190	(0.16)	0.970	(0.94)
6	-0.062	(0.02)	1.012	(1.02)
7	0.140	(0.10)	0.979	(0.96)
8	-0.018	(0.04)	0.970	(0.97)
9	0.081	(0.05)	0.955	(0.95)

$\langle S^2 \rangle = 0.786$

*$\beta c = n = -2.57$, $\beta c = c - 2.40$

$\langle S^2 \rangle^* = 0.750$

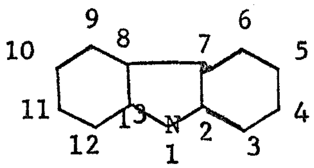
(about ½) is localized on the nitrogen atom. The point group for pyrryl and carbazyl radical are different yet where the former material is predicted to have a nearly zero spin density at the nitrogen atom the latter material has a high spin density. As with indolyl radical apparently the spins are not highly delocalized because of the reluctance in breaking the benzene ring resonance characteristics. A similar thing is observed in the case of the relative acidities of the hydrocarbons fluorene, indene and cyclopentadiene.[30]

e) Benzimidazoyl Radical (IXR, Table VII). This radical represents a case where a change in the resonance parameter of the carbon-nitrogen bond generates two different sets of spin densities. (This is the only case treated in which this was found.) When all resonance parameters were equal the calculations indicated a nearly zero spin density at the nitrogen atoms, similar to the previously discussed case for imidazoyl. A slight increase in the carbon-nitrogen resonance parameter caused a complete reversal of spin densities to the extent that the spin was localized 70% on the two nitrogen atoms. Such a result demonstrates the arbitrary nature of the calculation. We can not predict beforehand the spin density properties of this radical in a manner which is not arbitrary within the context of pi-electron calculations.

f) Purinyl Radical (VR, Table VIII). Resonance parameter changes did not greatly alter the spin density characteristics of the purinyl radical. The nitrogen spin densities for

Table VI

π-Spin and Electron Densities for Carbazyl Radical



β's = - 2.4 ev

Atom	π-Spin Densities		π-Electron Densities	
1	0.487	(.457)*	1.167	(1.19) *
2	-0.075	(-0.020)	0.977	(0.97)
3	0.189	(0.102)	0.972	(0.96)
4	-0.079	(-0.018)	1.005	(1.02)
5	0.155	(0.108)	0.984	(0.98)
6	-0.056	(0.013)	0.986	(1.00)
7	0.122	(0.096)	0.992	(0.99)

$\langle S^2 \rangle = 0.906$

*$\beta c = n = -\ 2.57$ ev, $\beta c = c = -\ 2.40$ ev.

$\langle S^2 \rangle^* = 0.750$

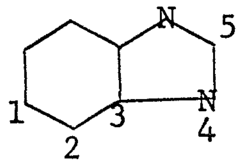
atoms 1, 3, and 8 are negative while for the 6th nitrogen is high. The spin density seems fairly evenly spread throughout the system. Interestingly, the high spin density on 6-nitrogen is accompanied by a lower electron density indicating that high electron density and spin density do not occur together. This supports the argument given in the imidazoyl radical with the difference being that it is difficult to rationalize why one nitrogen should be so much different than the others.

D) All Valence Electron Calculations

The previous pi-electron calculations suffer from a major drawback. This theoretical method completely neglects all the other bonding electrons in the system. In addition, in the case of benzimidazoyl radical, small and rather arbitrary changes in the resonance parameters generated a great change in the calculated electron and spin densities. The most reliable theoretical calculation would be one which incorporated all the electrons in the molecule using the *ab initio* open shell Hartree-Fock molecular orbital method. Although such a calculation is possible, using a minimum basis set, the cost is prohibitive, probably in the range of \$5,000 for imidazoyl for a particular geometry. The corresponding pi-electron calculation is about \$10. A compromise is reached using all valence electron semi-empirical calculations for which the cost runs about \$100.

TABLE VII

π-Spin and Electron Densities for the Benzimidazoyl Radical



$\beta c = c = \beta c = n = -2.40$

Atom	Spin Density After Annihilation		Electron Density Before Annihilation		After Annihilation
1	0.168	(0.049)*	0.937	0.937	(0.980)*
2	-0.048	(0.204)	1.009	1.009	(0.908)
3	0.261	(-0.044)	0.820	0.819	(0.993)
4	-0.023	(0.347)	1.374	1.378	(1.194)
5	0.284	(-0.110)	0.717	0.714	(0.851)

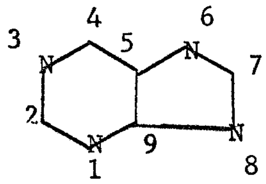
$\langle S^2 \rangle = 0.766$

$\langle S^2 \rangle^* = 0.775$

$^*\beta c = n = -2.57$ ev, $\beta c = c = -2.40$ ev

TABLE VIII

π-Spin and Electron Densities for the Purinyl Radical



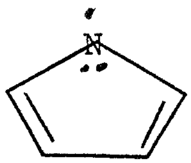
Atom	Spin Density After Annihilation		Electron Density After Annihilation	
1	-0.076	(-0.065) *	1.270	(1.27)*
2	0.197	(0.198)	0.735	(0.73)
3	-0.082	(-0.069)	1.285	(1.28)
4	0.224	(0.224)	0.780	(0.77)
5	0.009	(0.046)	0.945	(0.93)
6	0.389	(0.314)	1.181	(1.21)
7	0.135	(0.152)	0.706	(0.71)
8	-0.012	(-0.018)	1.344	(1.35)
9	0.213	(0.217)	0.753	(0.75)

$\langle S^2 \rangle = 0.796$

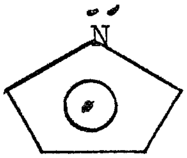
$\langle S^2 \rangle^* = 0.774$

$^*\beta c = n = -2.57, \ \beta c = c = -2.40$

Of particular interest in the case of the heterocyclic radicals treated here is the possible near degeneracy of the sigma and pi-radicals. For instance, in the case of pyrryl, two ground state configurations are possible. The first is where the "extra" odd electron is in an orbital whose wavefunction is symmetric to reflection in the plane of the molecule. A localized picture of such a radical is shown below as IVR-Sigma. It is also possible that the "extra" electron is delocalized in a pi-electron orbital whose wavefunctions is antisymmetric to reflection through the plane of the molecule. A corresponding picture of such a radical is shown below as the IVR-Pi.



IVR-Sigma
(Localized Picture)



IVR-Pi

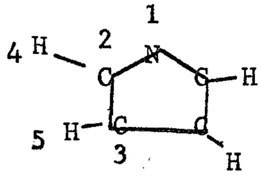
Now the previous pi-electron calculations assumed that the pyrryl radical had a structure akin to IVR-Pi. Application of intuition might argue that the most stable configuration of the lowest electronic state of IVR is IVR-Pi. Such an argument would be based on the higher possible delocatization of IVR-Pi over the corresponding sigma structure IVR-Sigma. Theoretically this problem was treated using the all valence electron calculation of Pople,[31] the INDO method (intermediate neglect of differential overlap). This method has been described in detail.[31] The program used for these calculations was obtained from the Quantum Chemistry Program Exchange (Program 141). No alterations of the program was undertaken; it was used as obtained from the Exchange after several initial calculations of known systems.

i) Pyrryl Radical (IVR, Table IX). Because of the planar symmetry of the pyrryl radical the electron and spin densities are reported in Table IX for the pi and sigma electrons. Since the molecule is symmetrical, symmetrically identical atoms will have the same spin and electron densities. Examination of Table IX shows that the nitrogen atom has a slight electron density in excess of its valence number of 5.000 showing a slight negative charge on the nitrogen. The carbon atom at position 2 has a net positive charge and the carbon atom at position 3 is nearly neutral. Both hydrogen atoms are slightly negatively charged. The calculation using the following basis set of atomic orbitals: for the hydrogen atom, only the 1S orbital; for carbon and nitrogen atoms, the 2s, and 2p (in the x, y, and z directions). The 1s orbitals for carbon and nitrogen are not included in the calculations, the justification being that the electrons in these orbitals are bound strongly to a particular atom and are not involved significantly in molecular bonding.

The spin densities shown in Table IX are divided into three major categories. The spin of the electron may either be partially located in the s or p orbitals. The p orbitals

Table IX

π and σ Electron and Spin Densities for the Pyrryl Radical



Atom	Electron Densities			Spin Densities		Hyperfine Coupling Constants
	σ	π	Total	σ	π	
1	4.017	1.282	5.299	-0.0088s -0.0420p	-0.229	-3.4
2	2.968	0.834	3.802	0.0262s 0.0317p	0.491	21.4
3	2.940	1.025	4.015	0.0017s 0.0066p	-0.244	1.4
4	1.015	--	1.015	-0.0221		-11.9
5	1.020	--	1.020	-0.0054		- 2.9

μ_{calcd} = 2.35 Debyes

s = s - orbital, p = p - orbital

however are symmetrically assigned as being either in the plane of the molecule (or in the sigma network) or perpendicular to the plane of the molecule (or in the pi-network). As seen from examining the Table IX, practically the entire spin is localized in the pi-network showing that the radical is a pi-radical. However, hyperfine coupling structure of the ESR spectrum only results from the interaction of the nuclear spin with the electron wavefunction at the nucleus.[32] Thus only the s-electron density at the atom of interest will generate hyperfine splitting of the ESR spectrum. The hyperfine coupling constants are proportional to the electron densities in the s-orbital. Theoretically, 1st order theory shows that a pi-radical (or spin density in the pi-orbital) will have no hyperfine ESR spectrum.[32] 2nd order theory explains the interaction in terms of polarization of the spins in the sigma network by the spins in the pi-network. This is seen computationally by the weak spin densities in the sigma network in pyrryl radical (Table IX). However, the s-orbital electron densities are what determine the hyperfine coupling constants. In pyrryl radical having only C^{12} the ESR spectrum would be expected to be split by densities at the nitrogen and hydrogen atoms. The calculations predict that the hydrogen atoms adjacent to the nitrogen atom would have a much higher coupling constant than the other hydrogen pair. In spite of the high negative spin on the nitrogen atom (mostly p) the nitrogen atom should generate a small coupling constant. Interestingly, the same general picture of the hyperfine spectrum of pyrryl radical is obtained from the pi-electron calculation previously discussed (Table III). It should be remarked that the all valence electron calculations presented in Tables IX, X, and XI are open shell (obviously) but unprojected or annihilated as was the case for the pi-electron calculations. Thus the high negative spin densities in the pi-orbitals of pyrryl radical (Table IX) are a bit suspicious. Finally it is emphasized that although the calculation predicts a pi structure for the pyrryl radical the sigma radical may not be too far away in energy. Since the INDO method is semiempirical slight adjustment of parameters might cause an inversion in the prediction of what is the ground state of the pyrryl radical.

ii) Imidazoyl Radical (II, Table X). Examination of Table X shows that the radical is predicted to be sigma. The spin is mostly concentrated at the p in plane orbitals on the nitrogen atoms (thus not adding anything to the coupling constant) with very little on the nitrogen s-orbitals. The radical is thus predicted to have a fairly narrow spectrum for a sigma radical, the splitting resulting from the hydrogen atoms are small and the nitrogen atoms not much larger. Although one current ESR spectrum on what is claimed[34] to be the imidazoyl radical indicates a sigma radical there is no correlation between the coupling constants in Table IX (the experimental results[34] show strong coupling between a proton having 32 gauss and two nitrogens having 10.5 gauss). Again it is stressed that the spin densities result from unannihilated wavefunctions. The fairly large Carbon-3 coupling constant indicates that there may be more polarization at the adjacent hydrogen atom than indicated in this particular calculation.

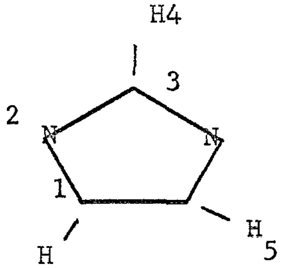
iii) Benzimidazoyl Radical (IXR, Table IX). This radical is predicted to have a pi-electronic structure. The nitrogen atoms are predicted to split the spectrum with a coupling constant of about 4 gauss each. Only weak coupling is predicted from hydrogen atoms 6 and 7 but a fairly large influence from hydrogen atom 8. These results in no way correspond with either pi-electron calculation shown in Table VII.

Discussion of the All Electron Calculations

The all electron calculations are of more fundamental interest than the pi-electron calculations. Yet, the semi-empirical nature of both types of calculations leave doubts as to their validity, especially in the absence of experimental results. The first, and probably most serious, problem results from the prediction that the pyrryl and benzimidazoyl radicals have pi-structures whereas the imidazoyl radical is sigma. This result seems to indicate that the corresponding sigma radical for pyrryl and benzimidazoyl, being an excited state in these calculations, might be within several tenths of an electron volt, energywise, of the pi-radical and thus slight changes in the parameters (either electronegativity or the resonance proportionality constant) might result in a different prediction placing the sigma radical as being the lowest energy

Table X

π and σ Electron and Spin Densities for the Imidazoyl Radical

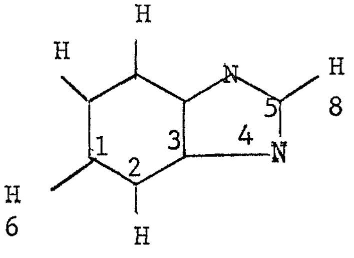


Atom	Electron Densities			Spin Densities		Hyperfine Coupling Constants
	σ	π	Total	σ	π	
1	2.864	1.094	3.957	0.0114s 0.0017p	-0.005	9.4
2	3.720	1.399	5.119	0.0107s 0.4805p	0.033	4.1
3	2.819	1.014	3.833	-0.0455s 0.0275p	-0.056	-37.3
4	0.996	--	0.996	0.0006		0.3
5	1.011	--	1.011	-0.0023		-1.2
	μ = 0.01 Debyes					

s = s - orbital, p = p - orbital

Table XI

π and σ Electron and Spin Densities for the Benzimidazoyl Radical



Atom	Electron Densities			Spin Densities		Hyperfine Coupling Constant
	σ	π	Total	σ	π	
1	2.975	1.001	3.976	0.0006s -0.0008p	0.032	0.5
2	2.991	0.994	3.985	0.0027s 0.0029p	0.063	2.2
3	2.902	1.008	3.910	-0.0049s 0.0165p	-0.018	-4.0
4	4.181	0.097	5.168	0.0252s 0.0283p	0.621	9.6
5	2.821	1.020	3.841	-0.0293s 0.0499p	-0.397	-24.1
6	1.019	--	1.019	-0.0017s		-0.9
7	1.019	--	1.019	-0.0029s		-1.6
8	1.005	--	1.005	0.0142s		-7.7

μ = 1.33 Debyes

state. The converse might be true of imidazoyl. Without supporting calculations as to where the excited states of the radicals are or the parameter sensitivity of the energies of these states the results and predictions of the calculations presented here must not be accepted uncritically. As previously mentioned the spin densities are also in doubt since annihilation was not imposed on the first stage open shell wavefunctions. Still, these calculations are a first shot at these particular molecular systems and have given rise to suggestion as to where we should go next. Similar calculations on aryl radicals[35] are in agreement with the experimental ESR spectra.

II. EXPERIMENTAL STUDIES IN ELECTRON SPIN RESONANCE

The prime object of experimental studies were to generate the neutral radicals of heterocyclics pyrrole, indole, imidazole, carbazole, benzimidazole, purine, and related materials. With the exception of the unanalyzed spectrum of the radicals of triphenylimidazole[29] neither the anion, cation or neutral radicals of these types of materials have ever been reported in the literature. Considering the number of possible radicals this area seems ripe for both theoretical and experimental exploitation. However, at the beginning of the experimental program neither the postdoctoral researcher, Dr. S. Chang, nor the principal investigator had any experimental experience in the determination and interpretation of ESR spectra. After about 9 months of study, none of the desired heterocyclic radicals had been detected in spite of a vigorous study of several different methods of radical generation. To date it can be stated that the problem is outlined and the next direction of attack clearly seen.

The Experimental Equipment

The E-3 Varian ESR spectrometer was used. Other accessories consisted of: i) Varian V-4556 electrolytic cell; ii) Varian V-4549 rapid mixing cell; iv) Varian E-4557 low temperature accessory, and aqueous and nonaqueous measurement tubes.

Experimental Techniques

Electrolytic reductions were carried out in the above mentioned cell using redistilled acetonitrile as a solvent, tetrabutyl or tetrapropylammanium perchlorate (Eastman Kodak) as a supporting electrolyte and the dissolved material of interest. The electrode in this case was a platinum wire net. Direct current voltage was applied from a Heath variable current supply. Both the voltage and current was monitored. The procedure consisted of varying the voltage drop across the solution in progressively increasing levels, monitoring at each voltage to see if any ESR spectrum were generated. Operation of the electrolytic cell was done according to the instructions given in the Varian manual. <u>Electrolytic</u> <u>Oxidations</u> were effected in nearly the same manner with the exception that the oxidations took place at the liquid mercury-acetonirile interface.

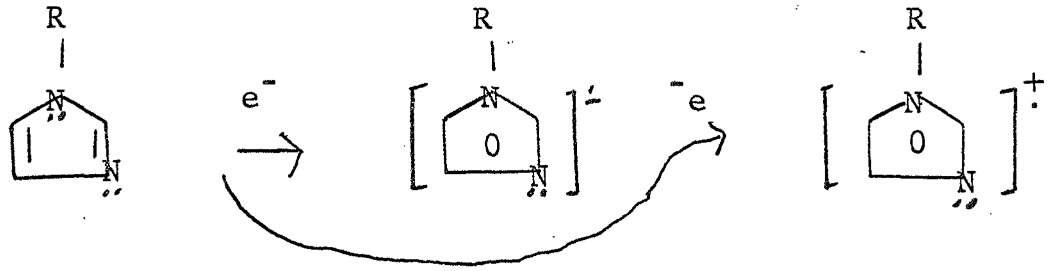
The <u>Electron</u> <u>Transfer</u> <u>Method</u>[36,37] was accomplished using the standard literature method. Donor (principally propiophenone) and acceptor compounds were dissolved in dimethylsulfoxide. A degassed solution of this material was mixed, under vacuum with 0.05 molar potassium t-butoxide. The principal mechanism of the procedure is the generation of the ketone anion followed by electron transfer to the acceptor. The ESR spectrum of the acceptor anion is then determined. The fate of the oxidized ketone anion[36,37] is complex and won't be dealt with here. The method is clean-cut and good acceptor molecules (like nitrobenzene), yield much better spectra than obtained electrolytically. The method is limited in that the acceptor must be capable of oxidizing the ketone anion. Although some very interesting spectra were obtained they were not directly pertinent to the problem under study here.

Chemical oxidation of various materials can be affected by a number of various means. Simple anion radical of benzoquinione was obtained by merely allowing atmospheric oxygen to attack basic solutions of hydroquinone. (It is, in fact, difficult to prepare a basic solution of hydroquinone without obtaining an ESR signal.) Sulfuric acid oxidation is the standard method for preparing solutions of hydrocarbon cation radicals. These were used for calibration.

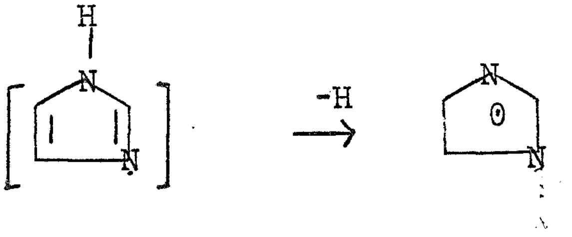
B) ESR Studies in Heterocyclic Radicals

i) General Principals. Although heterocyclic cation and anion radicals have been generated from a number of heteroaromatics (defined as aromatic hydrocarbons where one or more C-H moieties are replaced by N)[38] as well as a few heterocyclic cations have been reduced to neutral radicals[39] only a few are known in compounds having pyrrole type nitrogens.[39] A number of radicals are possible in the case of the basic imidazole structure itself.

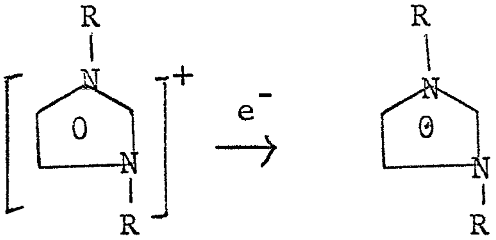
a) Direct reduction or oxidation of Imidazole or substituted
or
Imidazoles to yield anion cations radicals



b) N-H abstraction in Imidazole



c) Reduction of an Imidazolium Cation



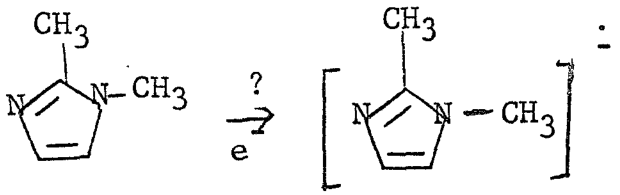
Radical cation or anion generation by process a) can occur with one or more nitrogens but one of the nitrogens must be of the pyrrole type. Process b) requires a N-H bond and Process c) requires two or more nitrogens in the molecule only one of which is of the pyrrole type. The process of principal interest is b) but it is certainly possible that any of the processes could occur in living systems. In neither process a) or c) are the reduction potential definitively reported in the literature for small molecules. Evidence from polarographic reduction potentials might indicate that process c) is most easily arrived at in the case of acid solutions of adenine.[40] In addition, the rate of the reaction of imidazole with the hydrated electron is nearly diffusion controlled in acid media and drops significantly at high pH. Again, however, no supporting ESR information has been reported on possible intermediates.

Following are some specific cases for attempted radical generation in heterocyclic systems.

ii) Heterocyclics in Which Some ESR Signal was Detected

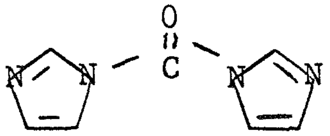
In a few cases ESR signals were detected on a few heterocyclic systems. These were as follows.

1,2-dimethylimdiazole (X), when subjected to electrolytic reduction in acetonitrile, yielded a 68 line spectrum 27 gauss wide. The spectrum did not exhibit symmetrical structure and could not be analyzed.

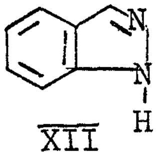


X

Both 1,1'-carbonyldimidazole (XI) and indazole (XII) were treated according to the electron transfer method described above. Both yield single line spectra each 5 gauss wide.



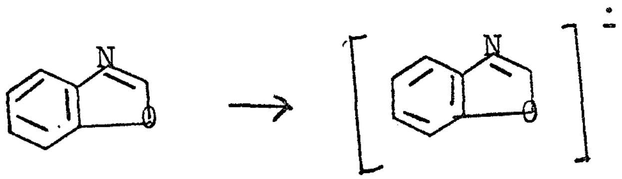
XI



XII

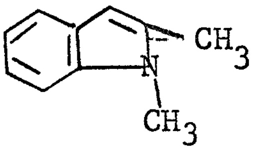
Carbazole (VIII) on electrolytic oxidation in acetonitrile also yielded a one line spectrum, 10 gauss wide. Electrolytic reduction of the same material was without success.

Benzoxazole (XIII) yielded a resolvable spectrum when subjected to electrolytic reduction, 10 gauss wide, 9 lines, interpretable using hydrogen coupling constants of 3.1 and 1.24 gauss for two pairs of hydrogens. However, the possible anion radical of benzoxazole would probably have a reasonable degree of triplet splitting from the nitrogen. Therefore there is considerable doubt that the spectrum seen was that of the anion of this material.



XIII

1,2-dimethyl indole (XIV) was subjected to electrolytic oxidation in acetontrile and a single broad line was observed.



XIV

iii) Heterocyclic Materials in Which No ESR Signal was Detected

Electrolytic reduction and oxidation were attempted on the following heterocyclic without success.

Dibenzofuran
1,2,3-trimethyl imidazolium cation
N-phenylpyrrole
2,6-dimethylpyrone
1-ethyl 2-methyl benzimidazole
4,5-diphenylimidazole
1-methylimidazole
3-acetylindole
2,4,5-tripehnyl-imidazole

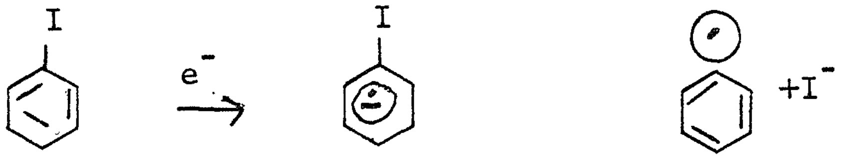
iv) Chemical Oxidation of Heterocyclic Materials

The anions of imidazole, and benzimidazole are formed in strongly basic solutions (pH 14).[41] Chemical oxidation of benzimidazole and imidazole in 1M sodium carbonate solution was attempted by rapid mixing with 0.1 M potassium ferricyanide. This was not successful. Chemical oxidation of these materials was not possible using the ferricyanide-ferrocyanide potential of -0.36

volts. Certainly strongly basic solutions of imidazole and benzimidazole did not undergo obvious decomposition.

v) Non-Heterocyclic Radicals

The electron transfer method failed to yield heterocyclic radicals. The method, however, yields anion radical spectra of good acceptor molecules (like nitrobenzene).[36] Although not closely related to the problem of determining heterocyclic radicals the theoretical problem of where certain aromatic radicals obtain their stability is of fundamental interest. Recent work shows[42] that the anion radicals of halogenated benzenes spontaneously split out halide ion to yield aromatic radicals even at 4°K. An example is iodobenzene.



π-radical σ-radical

The anion radical has undoubtably a pi-structure whereas the resulting neutral aromatic radical has a sigma structure. Theoretically, orbital symmetry rules state that a pi-radical anion can not adiabatically yield a sigma radical and a filled shell halide ion. Some crossing of states must occur. When the halogenated radical anion is substituted with a nitro-group, the anion is perfectly stable and no decomposition to the halide anion and neutral radical is observed.

This problem of the switch-over from pi to sigma structure in the anion radicals of halogenated benzenes in going to halide and phenyl radicals is theoretically related to the previously discussed sigma versus pi structure in the heterocyclic radicals. We were interested in whether all nitrobenzene radical anions were stable when substituted with halide ions. Below is given a survey of the resonance spectra obtained from a number of halogenated nitrobenzene radical anions. ESR experimental spectra are shown in Figures

Table XI
Hydrogen and Nitrogen Hyperfine Coupling Constants for a Series of Substituted Nitrobenzenes

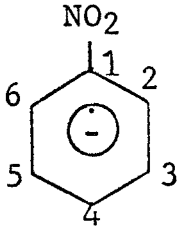
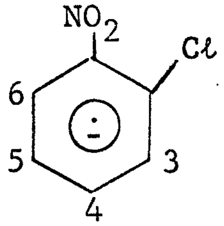
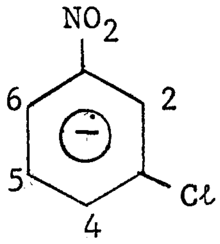
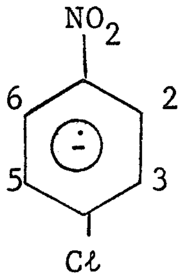
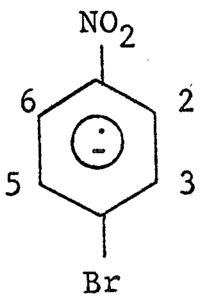
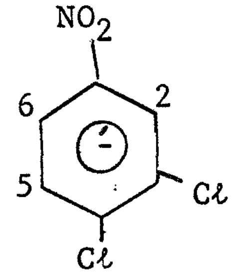
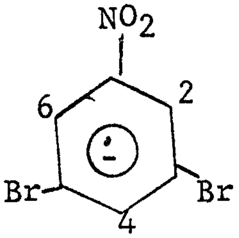
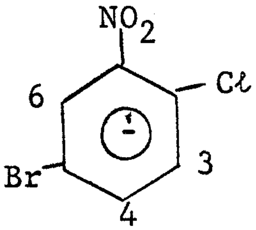
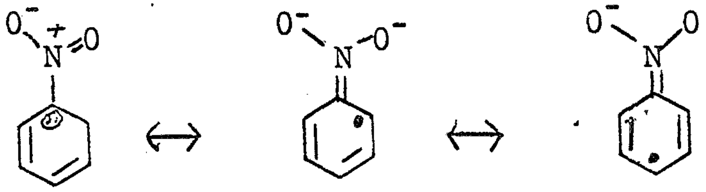
Substance		Coupling^{+} Constant	Previous Values*		Ref.
	a_n	9.80	10.33,	10.62	43
	$a_{2,6}$	3.25	3.45	3.30	
	$a_{3,5}$	1.00	1.16	1.03	
	a_4	3.80	3.86	3.82	
	a_n	9.85	9.95		44
	a_6	3.15	3.30		
	$a_{3,5}$	1.15	1.13		
	a_4	3.90	3.92		
	a_n	9.10	9.60		44
	$a_{2,6}$	3.00	3.70		
	a_5	1.00	0.93		
	a_4	4.00	4.07		
	a_n	9.75	9.70		44
	$a_{2,6}$	3.27	3.27		
	$a_{3,5}$	1.10	1.10		
	a_n	9.42			
	$a_{2,6}$	3.20			
	$a_{3,5}$	1.10			

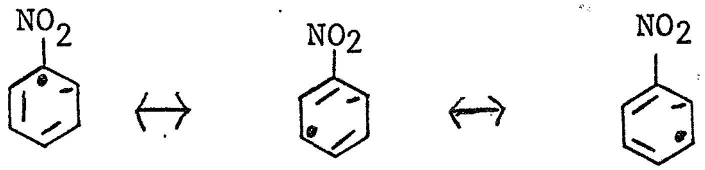
Table XI (Continued)

Substance		Coupling Constant$^+$	Previous Values*	Ref.
	a_n	9.25		
	$a_{2,6}$	3.30		
	a_5	1.10		
	a_n	8.25		
	$a_{2,6}$	3.27		
	a_4	4.25		
	a_n	8.75		
	a_6	3.30		
	a_3	1.10		
	a_4	4.30		

All the chloro- and bromo-substituted nitrobenzenes anion radicals studied were stable species. Examination of the hyperfine coupling constants in Table XII show that the spin densities don't change dramatically throughout the series. This, in turn, indicates that the electrons on the bromine and chlorine moieties do not strongly interact with the ring system. Rationalization of the hyperfine coupling constants within context of the pi-electron valence bond structures is not difficult. For instance, the proton coupling results from ionic-radical structures in the ring system in which the electronegativity of the nitro group forces the dominance of ortho-para structures.

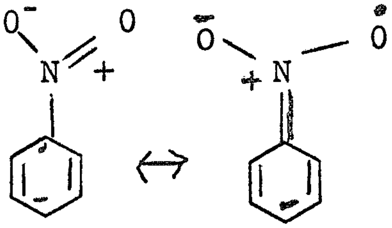


Dominate Ortho-Para Structures

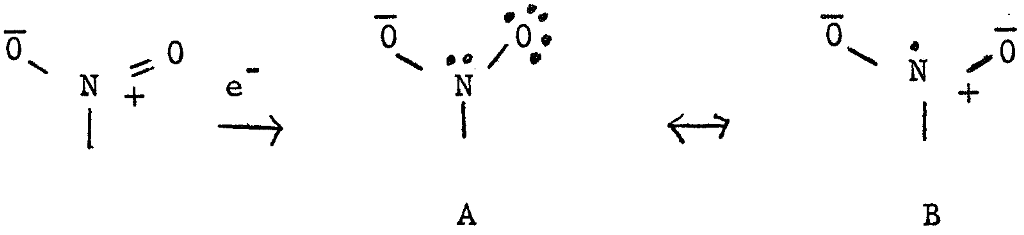


Weak Meta Structures

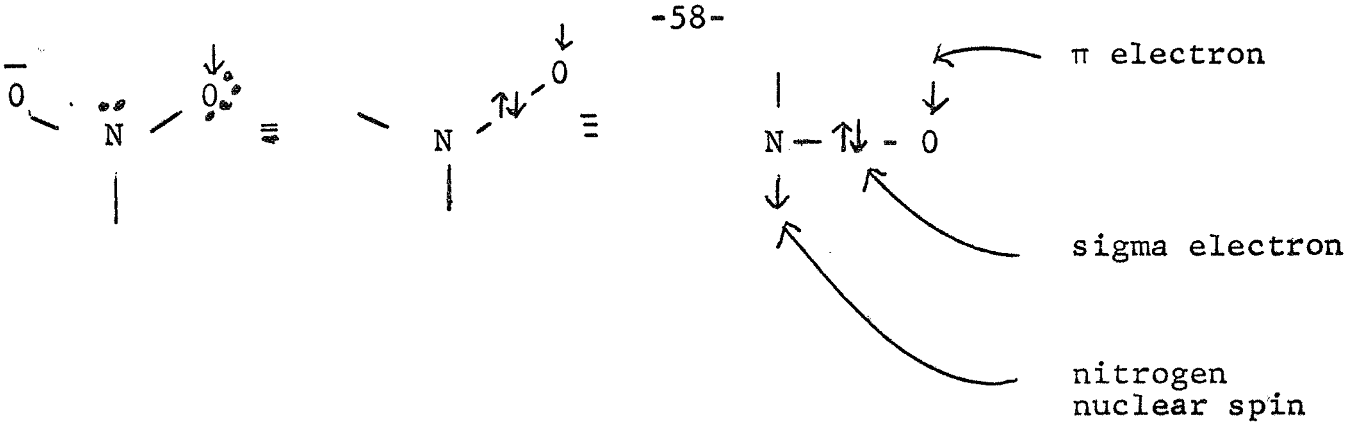
The spin density at the hydrogen nucleus is then rationalized by invoking the usual Fermi-contact terms. However the spin-density at the nitrogen atom is less easily rationalized. Retaining the negative charge in the benzene ring and allowing the radical to interact with the nitro group puts spin density at the oxygen atom.



Thus the nitrogen spin density can only arise (by rationalizing it within the pi-electron approximation) by radical-anion structures within the nitro group itself. However valence structure B appears unfavorable with respect to structure A.

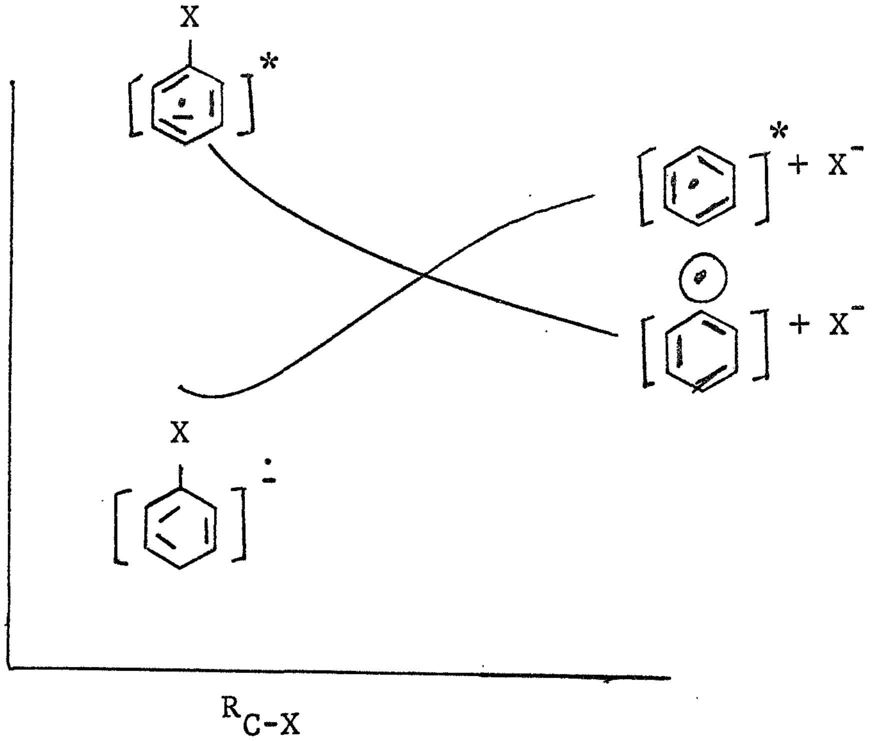


Since it is known that the hyperfine coupling constant results from spin density in the nitrogen 2s orbital the above pi electron arguments are suspect. In analogy with the induced 1s spin on the hydrogen resulting from spin induction from the carbon 2p orbital it makes more sense to argue that above structure A does induce spin at the nitrogen 2s by the interaction of the oxygen spin with the N-O sigma bond. This is shown below by spin and nucleus spin depolarization diagram. Thus, in this picture



resonance structure A assumes the major importance in determining the spin density.

Why are halogenated nitrobenzene anions and radicals stable whereas halogenated benzene anion radicals are not? First, it is obvious that nitro-substituent stabilizes the radical-anion species more than a halogen or other possible electron donating substituents. However, it is doubtful if the final neutral sigma aryl radical is much effected by the nature of the substituent. However, adiabatically the sigma radical is not connected to a pi-electronic state of the anion radical but to an excited pi-sigma* or sigma-pi* state. This is high energy state in the radical anion and probably deeply repulsive. On the other hand, the pi-radical anion is adiabatically connected to an excited state of the aryl radical. It is doubtful that the halide anion is departing in any state other than its ground state. Thus, diagramatically the potential energy surface for the breaking of the carbon-halogen bond looks like the following:



The curve shown above is for halo-benzene anion radical. The anion radical is known to give aryl radical even at very low temperature. Thus, the radical anion is predicted to decompose with some activation energy but the overall reaction is known to be downhill. However, on substitution the potential energy surface of the radical anion is disproportionately lower because of the much higher degrees of resonance interaction of the nitro group. Such an argument would predict that radical anions of halogenated aniline or methoxy benzene would also easily yield radicals.

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33. See also Ref. 31, pages 128-149.

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APPENDIX A

Proof of $\Sigma_i^q Ti^2 = TrPQ$

By definition,

$$\chi_i = \Sigma_r a_{ri} \omega_r \tag{A-1}$$

$$\eta_i = \Sigma_s b_{sj} \omega_s \tag{A-2}$$

$$T_i \delta_{ij} = \int \chi_i \eta_j d\tau. \tag{A-3}$$

Equation (A-3) states that

$$T_i = \int \chi_i \eta_j d\tau, \quad i = j \tag{A-4}$$

and

$$0 = \int \chi_i \eta_j d\tau, \quad i \neq j \tag{A-5}$$

Using (A-1) and (A-2),

$$\begin{aligned} T_i &= \int \left(\Sigma_r a_{ri} \omega_r\right)\left(\Sigma_s b_{si} \omega_s\right) d\tau \\ &= \Sigma_r \Sigma_s a_{ri} b_{si} \delta_{rs} \\ &= \Sigma_r a_{ri} b_{ri}. \end{aligned} \tag{A-6}$$

$$\begin{aligned} Ti^2 &= \left(\Sigma_r a_{ri} b_{ri}\right)\left(\Sigma_s a_{si} b_{si}\right) \\ &= \Sigma_{rs} a_{ri} a_{si} b_{ri} b_{si}. \end{aligned} \tag{A-7}$$

On the other hand,

$$\begin{aligned}
\mathrm{Tr}PQ &= \Sigma_r (PQ)_{rr} \\
&= \Sigma_{rs} P_{rs} Q_{sr} \\
&= \Sigma_{rs}\left(\Sigma_j {}^p a_{rj} a_{sj}\right)\left(\Sigma_i {}^q b_{si} b_{ri}\right) \\
&= \Sigma_{rs}\Sigma_i{}^q\Sigma_j{}^p a_{rj} a_{sj} b_{si} b_{ri} \\
&= \Sigma_{rs}\Sigma_i{}^q a_{ri} a_{si} b_{si} b_{ri} \\
&\quad + \Sigma_{rs}\Sigma_i{}^q\Sigma_{j\neq i}{}^p a_{rj} a_{sj} b_{si} b_{ri} \\
&= \Sigma_{rs}\Sigma_i{}^q a_{ri} a_{si} b_{si} b_{ri} \\
&\quad + \left(\Sigma_{rs}\Sigma_i{}^q\Sigma_{j\neq i}{}^p a_{rj} a_{sj} b_{si} b_{ri}\right)\delta_{ij} \\
&= \Sigma_{rs}\Sigma_i{}^q a_{ri} a_{si} b_{si} b_{ri}. \qquad \text{(A-8)}
\end{aligned}$$

The last line follows from (A-5), since

$$\begin{aligned}
0 &= \int \chi_i \eta_j d\tau, \qquad i \neq j \\
&= \int\left(\Sigma_r a_{ri}\omega_r\right)\left(\Sigma_s b_{sj}\omega_s\right)d\tau, \qquad i \neq j \\
&= \Sigma_{rs} a_{ri} b_{sj}\cdot\delta_{rs}, \qquad i \neq j \\
&= \Sigma_r a_{ri} b_{rj}, \qquad i \neq j. \qquad \text{(A-9)}
\end{aligned}$$

Hence

$$\begin{aligned}
\left(\Sigma_r a_{ri} b_{rj}\right)\left(\Sigma_s a_{si} b_{sj}\right) &= \Sigma_r\Sigma_s a_{ri} a_{si} b_{rj} b_{sj} \\
&= 0, \qquad i \neq j \qquad \text{(A-10)}
\end{aligned}$$

Summing (A-7) over all i, the following result is obtained.

$$\Sigma_i^q T_i^2 = \Sigma_i^q \Sigma_{rs} a_{ri} a_{si} b_{ri} b_{si}$$

$$= \mathrm{TrPQ}. \qquad \text{(because of A-8)}$$

Summing (A-7) over all i, the following result is obtained.

$$\Sigma_i^q T_i^2 = \Sigma_i^q \Sigma_{rs} a_{ri} a_{si} b_{ri} b_{si}$$

$$= \mathrm{TrPQ}. \qquad \text{(because of A-8)}$$

APPENDIX B

Derivation of Equation (28)

B - 1. $$\left[ii|00\right] = -\chi_i^*(1')\eta_i(1)T_i - \Sigma_{\ell\neq i}\eta_\ell^*(1')\eta_\ell(1)T_i^2 \qquad (28c)$$

By definition,

$$\left[ii|00\right] \equiv \int\left\{P_{idi\beta}{}^{s}\psi_{uhf}(1'\cdots N)\right\}^*\left\{P_{odo\beta}{}^{s}\psi_{uhf}(1\cdots N)\right\}$$
$$\times\ d\chi_2\cdots d\chi_N \qquad (A-9)$$

The operation of $P_{odo\beta}{}^{s}$ is easy leaving ψ_{uhf} unchanged. Therefore

$$\left[ii|00\right] = \int\left\{P_{idi\beta}{}^{s}\psi_{uhf}(1'\cdots N)\right\}^*\psi_{uhf}(1\cdots N)$$
$$\times\ d\chi_2\cdots d\chi_N. \qquad (A-10)$$

Observing that each molecular orbital in ψ_{uhf} is either χ_i or η_i depending on whether the spin of the electron is of α - or of β - spin, respectively, the whole set of molecular orbitals can be conveniently denoted by ξ.

Then,

$$\psi_{uhf}(1\cdots N) = |\xi(1)\xi(2)\cdots\xi(N)| \qquad (A-11)$$

Consider the case that the 1′ - electron has the orbital η_i and that the k - electron has the orbital χ_i. It is convenient to denote this particular component of ψ_{uhf} by $\psi_{uhf}{}^{I}$.

$$\psi_{uhf}{}^{I}(1'\cdots N) = |\eta_i(1')\xi(2)\cdots\chi_i(k)\cdots\xi(N)| \qquad (A-12)$$

$$P_{idi\beta}{}^{S}\psi_{uhf}{}^{I}(1'\cdots N) = -|\chi_i(1')\xi(2)\cdots\eta_i(k)\cdots\xi(N)|. \qquad (A-13)$$

Therefore,

$$\left[ii|00\right]^{I} = \int\left\{P_{idi\beta}{}^{S}\psi_{uhf}{}^{I}(1'\cdots N)\right\}\psi_{uhf}{}^{I}(1\cdots N)d\chi_2\cdots d\chi_N \qquad (A-14)$$

$$= -\chi_i{}^*(1')\eta_i(1)\int\chi_i{}^*(k)\eta_i(k)d\chi_k$$

$$\times\int|\xi(2)\cdots\xi(k+1)\xi(k-1)\cdots\xi(N)|^*$$

$$|\xi(2)\cdots\xi(k+1)\xi(k+1)\cdots\xi(N)|$$

$$\times d\chi_2\cdots d\chi_{k-1}d\chi_{k+1}\cdots d\chi_N \qquad (A-15)$$

$$= -\chi_i{}^*(1')\eta_i(1)\int\chi_i{}^*(k)\eta_i(k)d\chi_k$$

$$= -\chi_i{}^*(1')\eta_i(1)T_i. \qquad (A-16)$$

Next, for components of ψ_{uhf} other than $\psi_{uhf}{}^{I}$, the 1′ -electron has the orbital η_ι with $\iota \neq i$. There should be some electron, say, the m-electron, having an orbital η_i and some other electron, say, the k-electron having an orbital χ_i. It is again convenient to denote one of this kind components of ψ_{uhf} by $\psi_{uhf}{}^{II}$.

$$\psi_{uhf}{}^{II}(1'\cdots N) = |\eta_\ell(1')\xi(2)\cdots\eta_i(m)\cdots\chi_i(k)\cdots\xi(N)| \qquad (A-17)$$

$$P_{idi\beta}{}^{S}\psi_{uhf}{}^{II}(1'\cdots N) = -|\eta_\ell(1')\xi(2)\cdots\chi_i(m)\cdots\eta_i(k)\cdots\xi(N)| \qquad (A-18)$$

$$\left[ii|00\right]^{II} = \int\left\{P_{idi\beta}{}^{S}\psi_{uhf}{}^{II}(1'\cdots N)\right\}^{*}\psi_{uhf}{}^{II}(1\cdots N)\,d\chi_2\cdots d\chi_N$$

(A-19)

$$= -\eta_{\ell}{}^{*}(1')\eta_{\ell}(1)\int\eta_i\chi_i d\chi_m\int\chi_i\eta_i d\chi_k$$

$$\times\,|\xi(2)\cdots\xi(N)|^{*}|\xi(2)\cdots\xi(N)|$$

$$d\chi_2\cdots d\chi_{m+1}\cdots d\chi_{k-1}d\chi_{k+1}\cdots d\chi_N$$

(A-20)

$$= -\eta_{\ell}{}^{*}(1')\eta_{\ell}(1)T_i{}^{2}$$

Now,

$$\psi_{uhf}(1'\cdots N) = \psi_{uhf}{}^{I} + \Sigma_{\ell}{}^{q}\psi_{uhf}{}^{II}, \qquad \ell \neq i.$$

$$\left[ii|00\right] = \left[ii|00\right]^{I} + \Sigma_{\ell}\left[ii|00\right]^{II}, \qquad \ell \neq i$$

$$= -\chi_i{}^{*}(1')\eta_i(1)T_i - \Sigma_{\ell}\eta_{\ell}{}^{*}(1')\eta_{\ell}(1)T_i{}^{2} \qquad \ell \neq i$$

Q.E.D.

B - 2. $\left[ii|ii\right] = +\,\chi_i{}^{*}(1')\chi_i(1) + \Sigma_{\ell\neq i}\eta_{\ell}{}^{*}(1')\eta_{\ell}(1)$ (28d)

From (A - 13),

$$P_{idi\beta}{}^{S}\psi_{uhf}{}^{I}(1'\cdots N) = -|\chi_i(1')\xi(2)\cdots\eta_i(k)\cdots\xi(N)|$$

$$P_{idi\beta}{}^{S}\psi_{uhf}{}^{I}(1\cdots N) = -|\chi_i(1)\xi(2)\cdots\eta_i(k)\cdots\xi(N)|$$

$$\left[ii|ii\right]^{I} = \int\left\{P_{idi\beta}\psi_{uhf}{}^{I}(1'\cdots N)\right\}^{*}\left\{P_{idi\beta}\psi_{uhf}{}^{I}(1\cdots N)\right\}$$

$$\times\, d\chi_2\cdots d\chi_N$$

(A-22)

$$= -\chi_i{*}(1')\chi_i(1)\int|\xi(2)\cdots\eta_i(k)\cdots\xi(N)|{*}$$

$$|\xi(2)\cdots\eta_i(k)\cdots\xi(N)|\ d\chi_2\cdots d\chi_N$$

$$= +\ \chi_i{*}(1')\chi_i(1). \qquad \text{(A-23)}$$

From (A - 18),

$$P_{idi\beta}{}^{S}\psi_{uhf}{}^{II} = -|\eta_\ell(1')\xi(2)\cdots\chi_i(m)\cdots\eta_i(k)\cdots\xi(N)|$$

or

$$= -|\eta_\ell(1)\xi(2)\cdots\chi_i(m)\cdots\eta_i(k)\cdots\xi(N)|.$$

Therefore,

$$\left[ii|ii\right]^{II} = \int\left\{P_{idi\beta}{}^{S}\psi_{uhf}{}^{II}(1'\cdots N)\right\}^{*}\left\{P_{idi\beta}{}^{S}\psi_{uhf}{}^{II}(1\cdots N)\right\}$$

$$\times d\chi_2\cdots d\chi_N$$

$$= +\ \eta_\ell{*}(1')\eta_\ell(1)\int|\xi(2)\cdots\chi_i(m)\cdots\eta_i(k)\cdots\xi(N)|{*}$$

$$\times\ |\xi(2)\cdots\chi_i(m)\cdots\eta_i(k)\cdots\xi(N)|d\chi_2\cdots d\chi_N$$

$$= +\ \eta_\ell{*}(1')\eta_\ell(1). \qquad \text{(A-24)}$$

Now,

$$\left[ii|ii\right] = \left[ii|ii\right]^{I} + \Sigma_\ell\left[ii|ii\right]^{II} \qquad i \neq \ell$$

$$= \chi_i{*}(1')\chi_i(1) + \Sigma_{\ell\neq i}\eta_\ell{*}(1')\eta_\ell(1). \qquad \text{(A-25)}$$

Q.E.D.

APPENDIX C

List of the Spin Calculation Programs

```
      SUBROUTINE SPINA%A,B,IP,IQ,M<
      DIMENSION P%24,24%,Q%24,24<,PQ%24,24<,QP%24,24<
      DIMENSION QAA(24),RHO(24),PPPP(24,24),A(24,24),B(24,24)
      DIMENSION PQP(24,24),QPQ(24,24),PQPQ(24,24),QPQP(24,24)
      DIMENSION PQPQP(24,24),QPQPQ(24,24),PMSJ(24,24),PMSQ(24,24)
      DO 1 I=1,M
      DO 2 J=1,M
      P(I,J)=0.
      Q(I,J)=0.
      DO3 K=1,IP
      P(I,J)=P(I,J)+A(I,K)*A(J,K)
3     CONTINUE
      DO4 K=1,IQ
      Q(I,J)=Q(I,J)+B(I,K)*B(J,K)
4     CONTINUE
2     CONTINUE
1     CONTINUE
      WRITE(6,44) ((P(I,J),J=1,M),I=1,M),((Q(I,J),J=1,M),I=1,M)
44    FORMAT(' '2F10.5)
```

```
      DO 20 I=1,M
      DO 20 J=1,M
      QP(I,J)=0.0
      PQ(I,J)=0.0
      DO 20 K=1,M
      PQ(I,J)=PQ(I,J)+P(I,K)*Q(K,J)
      QP(I,J)=QP(I,J)+Q(I,K)*P(K,J)
   20 CONTINUE
      DO 200 I=1,M
      DO 200 J=1,M
      POP(I,J)=0.0
      QPQ(I,J)=0.0
      DO 200 K=1,M
      PQP(I,J)=PQP(I,J)+P(I,K)*QP(K,J)
      QPQ(I,J)=QPQ(I,J)+Q(I,K)*PQ(K,J)
  200 CONTINUE
      DO 2000 I=1,M
      DO 2000 J=1,M
      PQPQ(I,J)=0.0
      QPQP(I,J)=0.0
      PQPQP(I,J)=0.0
      QPQPQ(I,J)=0.0
      PPPP(I,J)=0.0
```

```
      DO 2000 K=1,M
      PQPQ(I,J)=PQPQ(I,J)+PQ(I,K)*PQ(K,J)
      QPQP(I,J)=QPQP(I,J)+QP(I,K)*QP(K,J)
      PQPQP(I,J)=PQPQP(I,J)+PQ(I,K)*PQP(K,J)
      QPQPQ(I,J)=QPQPQ(I,J)+QP(I,K)*QPQ(K,J)
      PPPP(I,J)=PPPP(I,J)+PQP(I,K)*QPQ(K,J)
 2000 CONTINUE
      AA=IQ-2*(FLOAT(IP-IQ)/2.+1.)
      TPQ=0.
      TPQPQ=0.
      TPPPP=0.0
      DO5 I=1,M
      TPQ=TPQ+PQ(I,I)
      TPQPQ=TPQPQ+PQPQ(I,I)
      TPPPP=TPPPP+PPPP(I,I)
5     CONTINUE
      PJ=AA*AA+IP*IQ-IQ
      PK=AA*AA+IP*IQ-IP
      PJ=PJ-2*AA*TPQ-(IP+IQ)*TPQ+3*TPQ+2*TPQ*TPQ-2*TPQPQ
      PJA=IP-TPQ
      PJB=(IP+IQ-4*TPQ-3+2*AA)
      PJC=2*TPQ-IP+1-AA
      PK=PK-2*AA*TPQ-(IP+IQ)*TPQ+3*TPQ+2*TPQ*TPQ-2*TPQPQ
```

```
      PQA=IQ-TPQ
      PQC=2*TPQ-IQ+1-AA
      PMS=AA*AA-2*AA*TPQ+IP*IQ-(IP+IQ)*TPQ+2*TPQ+2*TPQ*TPQ-2*TPQPQ
      DO 6 I=1,M
      DO 7 J=1,M
      PMSJ(I,J)=PJ*P(I,J)+PJA*Q(I,J)+QPQ(I,J)+PJB*PQP(I,J)
      PMSJ(I,J)=PMSJ(I,J)+(PQ(I,J)+QP(I,J))*PJC-(PQPQ(I,J)+QPQP(I,J))*2
      PMSJ(I,J)=PMSJ(I,J)+4*PQPQP(I,J)
      PMSQ(I,J)=PK*Q(I,J)+PQA*P(I,J)+PQP(I,J)+PJB*QPQ(I,J)
      PMSQ(I,J)=PMSQ(I,J)+(QP(I,J)+PQ(I,J))*PQC-(QPQP(I,J)+PQPQ(I,J))*2
      PMSQ(I,J)=PMSQ(I,J)+4*QPQPQ(I,J)
      PMSJ(I,J)=PMSJ(I,J)/PMS
      PMSQ(I,J)=PMSQ(I,J)/PMS
7     CONTINUE
6     CONTINUE
      DO 8 I=1,M
      QAA(I)=PMSJ(I,I)+PMSQ(I,I)
      RHO(I)=PMSJ(I,I)-PMSQ(I,I)
8     CONTINUE
      WRITE(6,500)
500   FORMAT(38H SPIN DENSITIES AFTER ANNIHILATION          )
      WRITE(6,501) (I,RHO(I)),I=1,ISIZE)
501   FORMAT(10(I3,F10.5))
```

```
      S=(FLOAT(IP-IQ)/2.)
      AA=S*(S+1)+IQ+AA-AA
      SSQ=AA-TPQ
      SF=AA*AA+IP*IQ+2*(TPQ*TPQ-TPQPQ)-(2*AA+IP+IQ-2)*TPQ
      N=IP+IQ
      SP=(3*AA*AA+3*AA*(N-2)+(N-2)**2+IP*IQ+4*(IP-1)*(IQ-1))*TPQ
      SPP=6*(TPQ**3-3*TPQ*TPQPQ+2*TPPPP)
      SPPP=2*(3*AA+3*N-10.)*(TPQ*TPQ-TPQPQ)
      SSIX=AA**3+AA*IP*IQ+IP*IQ*(2*AA+IP+IQ-2.)-SP+SPPP-SPP
      SN=SSIX-2*(S+1.)*(S+2.)*SF+(S+1.)*(S+1.)*(S+2.)*(S+2.)*SSQ
      SD=SF-2*(S+1.)*(S+2.)*SSQ+(S+1.)*(S+1.)*(S+2.)*(S+2.)
      SSAA=SN/SD
      WRITE(6,502) SSAA
502   FORMAT(30H EXPECTATION VALUE OF S**2=   ,F10.5)
      CALL EXIT
      END
```

FIGURE CAPTIONS

Figure 1	ESR Spectrum of Nitrobenzene Anion Radical
Figure 2	ESR Spectrum of 2-chloronitrobenzene Anion Radical
Figure 3	ESR Spectrum of 3-chloronitrobenzene Anion Radical
Figure 4	ESR Spectrum of 4-chloronitrobenzene Anion Radical
Figure 5	ESR Spectrum of 4-bromonitrobenzene Anion Radical
Figure 6	ESR Spectrum of 3,4-dichloronitrobenzene Anion Radical
Figure 7	ESR Spectrum of 3,5-dibromonitrobenzene Anion Radical
Figure 8	ESR Spectrum of 2-chloro-5-bromonitrobenzene Anion Radical