of their reliance on the body-centered cubic structure. One must therefore accept only with reservation the specific bonding patterns generated by these theories.

The major deficiencies of the molecular dynamics simulation method for water are that (a) classical statistical mechanics is utilized and that (b) the intermolecular potential has been taken to be pairwise additive. These features doubtless affect the precision of the simulation to a substantial extent, but it is difficult to argue that the qualitative conclusions which we have reached about hydrogen-bond patterns would be significantly altered upon rectifying these deficiencies.

Obviously solutes will perturb the pattern of hydrogen bonds in water in a manner dependent on solute size, charge, shape, and chemical character. These structural shifts should be visible in the distribution of non-short-circuited polygons. It will eventually be important to see if common influences on this distribution can be verified for solutes all classed as "structure makers," or as "structure breakers."[4]

# $\pi$ *vs.* $\sigma$ Structures in Imidazyl and Related Heteroradicals

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*Received May 7, 1973*

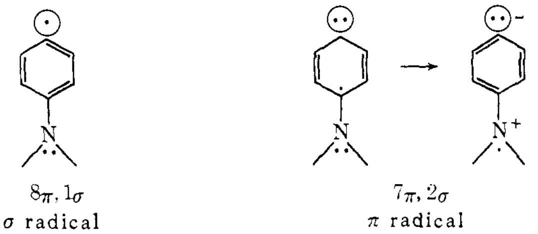
**Abstract:** INDO calculations on imidazyl and a number of heteroradicals indicate that there is some ambiguity as to their predicted ground state symmetries. Experimentally, only a few examples of the esr spectra of these types of radicals are known. Sufficient data exists, however, to allow one to predict that the results obtained from INDO predictions are not necessarily computational artifacts. $\pi$-electron SCF single annihilation calculations of the electronic structures of pyrryl, imidazyl, and other related structures were also carried out. Here, too, there is some doubt as to the reliability of the results. In some cases small parameter changes yield significantly different computed spin and electron densities. Simple resonance structure arguments are imposed to rationalize the spin density variations in the $\pi$-electron calculations. Finally, a state symmetry analysis is proposed which predicts that the potential energy surfaces of ground and excited states of some even and odd electron structures cross at some coordinates involving the stretch of C–H or N–H bonds.

This paper addresses itself to three main topics. First we will explore the intuitive ambiguities of attempting to assign the ground state symmetries of a number of heteroradicals. We will also explore the difficulty of obtaining "good" $\pi$-electron spin density calculations. Finally we will also explore the state symmetry consequences of these assignments with respect to the photogeneration of such radicals from parent filled shell molecules.

Conceptual ambiguities exist with respect to intuitively assigning the symmetry of the ground state of planar radicals. Kasai and coworkers[1] set out to explore this issue with respect to the ground state symmetries of the phenyl and higher polycyclic aromatic radicals. Kasai showed[1] that in the systems studied aryl radicals invariably had $\sigma$ structures. The simplest resonance structure representation of the $\sigma$-phenyl radical is as shown below. The $\pi$ radical is an excited state of the phenyl radical. At this time we will avoid the problem of assigning the proper group theoretical representations for various resonance structures. This would require writing a number of additional structures of proper phasing. In our diagrams we use the Salem–Dauben–Turro convention[2] of circling the $\sigma$ electrons and giving the summation of the total number of $\pi$ and $\sigma$ electrons involved in the critical portion of the bonding picture.

single structure representations of the ground and excited state of the phenyl radical

Kasai's experimental results were also supported by INDO calculations. Kasai specifically explored the possibility that in electron-rich systems the $\pi$ orbitals might yield up an electron to a half-filled $\sigma$ orbital to generate a $\pi$ radical. In the case of a substituted phenyl radical the electron-donating substituent might stabilize the normally energetically unfavorable zwitterionic resonance structure to yield such a $\pi$ radical, as shown below. INDO calculations,[3] however, in-



structure representations of the σ and π *p*-aminophenyl radicals

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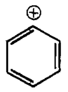
(1) P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Amer. Chem. Soc.*, **91**, 4364 (1969); P. H. Kasai, *Accounts Chem. Res.*, **4**, 329 (1971).

(2) L. Salem, W. G. Dauben, and N. J. Turro, *J. Chim. Phys.*, **70**, 649 (1973).

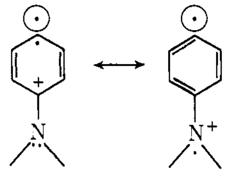
(3) E. M. Evleth and P. M. Horowitz, *J. Amer. Chem. Soc.*, **93**, 5636 (1971). The symmetry of the *p*-aminophenyl cation is predicted to be $^3B_1$ not $^3A_1$ as stated in Table II of this reference.

dicated that the ground state of the π-aminophenyl radical is σ. We know of no case in which the ground state of aryl radicals is predicted to be π.

Although not a radical, the case of the phenyl cation, an even electron molecule, is somewhat more complex. Experimental information is unclear[4] as to the existence of the phenyl or substituted phenyl cations in solution. The INDO calculations[3] predict that although phenyl cation has a σ structure, the *p*-aminophenyl cation has a triplet ground state, π-cationic structure. Here, the hypothesis that the electron rich nature of the substituent could yield an inversion of ground–excited state symmetries has computational support.



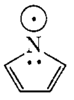
6π, 0σ



7π, 1σ

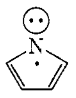
Due to the lack of experimental information this ambiguity as to the real symmetries of the ground state of aryl cations remains. We are attempting to resolve this ambiguity by studying the photoprocesses in arenediazonium salts.

The ambiguity we wish to explore here has to do with the ground state symmetries of radicals generated from the removal of an H atom from $R_2N$–H yielding $R_2N$ radicals. Because of the nitrogen lone pairs an ambiguity exists as to whether such radicals are π or σ. The pyrryl radical (I) is a case in point. The σ and π structures of the pyrryl radical might be represented as follows. We use the convention of having the π electron labeled within the ring.



6π, 1σ
σ

I



5π, 2σ
π

A reasonable guess as to the probable ground state symmetry of the pyrryl radical is obtained from examining the electronic structure of the parent amino radical $NH_2$, or simple alkyl derivatives. In the case of $NH_2$ both experimental[5] and theoretical[6] information shows that the ground state has a $^2B_1$ symmetry, while the lowest excited state $^2A_1$ is only about 1–3 eV higher in energy.[7]

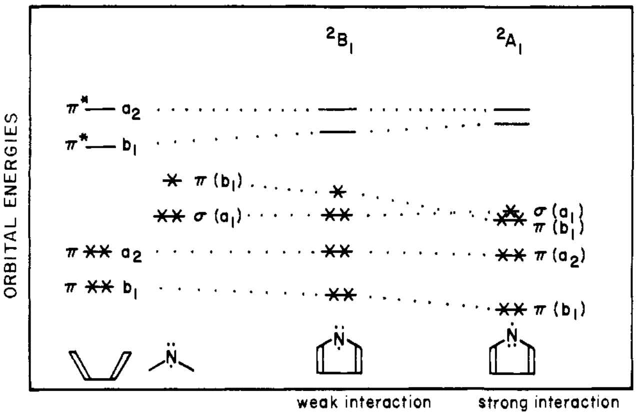
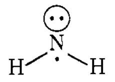
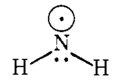


Figure 1. Orbital correlation diagram of butadiene and amino to pyrryl.

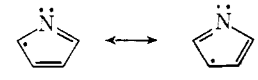


1π, 2σ
$^2B_1$



2π, 1σ
$^2A_1$

Dialkylamino radicals[8] are also theoretically and experimentally π radicals ($^2B_1$). Simple first order perturbation theory leaves an ambiguity as to the prediction of the symmetry of the ground state of the pyrryl radical. The least complicated scheme (Figure 1) of the interaction of the π orbitals of *cis*-butadiene with the π-amino radical predicts on weak interaction a $^2B_1$ structure for pyrryl and on strong interaction a $^2A_1$ structure. Such a simple picture, however, discounts the possibility that the $a_1$ σ orbital on the amino group is stabilized on coalescence into butadiene. In fact, both INDO and π-electron calculations predict a ground state symmetry of $^2A_2$ for pyrryl (*vide infra*). Resonancewise, such a symmetry can only arise from the interaction of structures whose π spins are not localized on the nitrogen atom, as shown above, but on the carbon atoms, as shown below.



It would appear that simple perturbation arguments are useless in rationalizing the likely ground state symmetries of amino type radicals which have adjacent π systems. In a similar way the question as to why $NH_2$ and $NF_2$ have $^2B_1$ ground states and $NO_2$ has a $^2A_1$ ground state has not been rationalized. It would appear that predictions as to the symmetries of these classes of molecules can be made only with some computational effort. Hopefully, after a sufficient number of calculations some rationale can be constructed which will aid intuition.

We are particularly interested in the electronic structures of pyrryl, imidazyl, and benzimidazyl. Here, we report that INDO calculations predict a σ structure for imidazyl, while the other two are π. Additional calculations were conducted on related heteroradicals to see if the π *vs.* σ dilemma could be resolved. Finally,

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(4) See (a) R. A. Ambramovitch and J. G. Saha, *Can. J. Chem.*, **43**, 3269 (1965); (b) R. A. Ambramovitch and F. F. Gahllah, *J. Chem. Soc. B*, 497 (1968); (c) N. Kamigata, M. Kobayashi, and H. Minata, *Bull. Chem. Soc. Jap.*, **45**, 2047 (1972). These authors show that highly electrophilic species exist in the Gomberg–Bachmann reaction. Recent unpublished kinetic work of H. Zollinger and coworkers casts doubt on whether such electrophilic species are actually aryl cations.

(5) (a) For a review of the spectra of $NH_2$, see G. Herzberg, "Molecular Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, p 493; (b) G. Herzberg, *Advan. Photochem.*, **5**, 3 (1968); (c) R. Smith and W. A. Seddon, *Can. J. Chem.*, **48**, 1938 (1970), and the references cited therein.

(6) (a) J. E. Del Bene, *J. Chem. Phys.*, **54**, 3487 (1971); (b) J. A. Pople and G. A. Segal, *ibid.*, **43**, 5136 (1965); (c) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, pp 90–92; (d) K. F. Purcell and W. G. Danen, *J. Amer. Chem. Soc.*, **94**, 7613 (1972).

(7) Broad band absorption, see ref 3. $^2A_1$ and $^2B_1$ are degenerate in the linear molecule.

(8) (a) D. W. Pratt, J. J. Dillon, R. V. Lloyd, and D. E. Wood, *J. Phys. Chem.*, **75**, 3486 (1971), and references cited therein; (b) W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, **92**, 5235 (1970); (c) W. C. Danen and R. C. Rikard, *ibid.*, **94**, 3254 (1972).

we have conducted a number of π-electron calculations on pyrryl, imidazyl, benzimidazyl, carbazyl, and purinyl radicals.

## Method of Calculations

The INDO calculations were conducted using program no. 91 from Quantum Chemistry Program Exchange.[9] The standard parameterizations were used.[6] This program does not compute pure doublet states, however, and thus the results reported here are for calculations containing contaminating higher multiplets. The geometries chosen were those from standard tables[6] (for N–H and C–H) with the exception that all C–N, C–C, and C–O bonds were set at 1.40 Å.

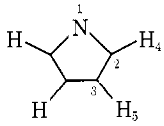
The π-electron calculations were conducted using a standard open shell UHF π-electron technique[10] contained in a modified version of program 76 of QCPE. In this case, however, the contaminating quartet multiplet was removed by single annihilation using a subprogram written with the aid of previous work.[11] The carbon and nitrogen parameters for the valence state ionization potential and one-centered electron repulsion integral were 11.08 and 10.98 eV (carbon) and 14.63 and 12.27 eV (nitrogen), respectively. A test calculation on the allyl radical gave a value of $\langle S^2 \rangle$, after annihilation, of 0.7500, indicating full quartet removal. The calculated terminal and central carbon atom spin densities, after annihilation, were 0.57 and −0.14, using a C–C resonance integral of −2.40 eV. These are in excellent agreement with the experimental values of 0.58 and −0.16, respectively.[12]

## Results and Discussion

### I. INDO Calculations. (A) Pyrryl, Imidazyl, and Benzimidazyl.

The calculations listed in Tables I–III for these radicals show that both pyrryl and benzimidazyl are predicted to be π radicals while imidazyl is predicted to be a σ radical. Experimentally none of these parent radicals are known. The tetraphenylpyrryl and triphenylimidazyl are well characterized[13,14] as being π radicals. However, from resonance considerations alone, it would be anticipated that the polyphenyl-substituted pyrryl and imidazyl would be π radicals even if the parent radicals were σ. The INDO calculations of pyrryl approximate the π-electron calculation in that a very low spin density is predicted for the nitrogen atom and that the symmetry is most

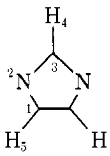
**Table I.** Calculated Electronic Structure for the Pyrryl Radical[a]



| Atom | Orbital[b] | Electron densities | | Spin densities | Hyperfine coupling constant |
|---|---|---|---|---|---|
| | | | Total | | |
| 1 | s | 1.543 | | −0.009 | −3 |
| | $p_x + p_y$ | 2.473 | 5.299 | −0.042 | |
| | $p_\pi$ | 1.282 | | −0.229 | |
| 2 | s | 1.077 | | 0.026 | 21 |
| | $p_x + p_y$ | 1.891 | 3.802 | 0.032 | |
| | $p_\pi$ | 0.834 | | 0.491 | |
| 3 | s | 1.051 | | 0.002 | 1 |
| | $p_x + p_y$ | 1.939 | 4.015 | −0.007 | |
| | $p_\pi$ | 1.205 | | 0.124 | |
| 4 | s | | 1.015 | −0.022 | −12 |
| 5 | s | | 1.020 | −0.005 | −3 |

[a] Symmetry = $^2A_2(\pi)$. [b] $p_x + p_y$ = sum of in-plane orbitals.

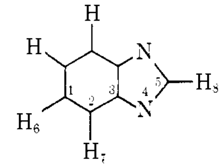
**Table II.** Calculated Electronic Structure for the Imidazyl Radical[a]



| Atom | Orbital | Electron densities | | Spin densities | Hyperfine coupling constant |
|---|---|---|---|---|---|
| | | | Total | | |
| 1 | s | 1.045 | | 0.011 | 9 |
| | $p_x + p_y$ | 1.818 | 3.957 | −0.002 | |
| | $p_\pi$ | 1.094 | | −0.005 | |
| 2 | s | 1.538 | | 0.011 | 4 |
| | $p_x + p_y$ | 2.182 | 5.119 | 0.491 | |
| | $p_\pi$ | 1.399 | | 0.033 | |
| 3 | s | 1.115 | | −0.046 | −37 |
| | $p_x + p_y$ | 1.704 | 3.833 | 0.028 | |
| | $p_\pi$ | 1.014 | | −0.056 | |
| 4 | s | | 0.996 | 0.001 | 0.3 |
| 5 | s | | 1.011 | −0.002 | −1 |

[a] Symmetry = $^2B_2(\sigma)$.

**Table III.** Calculated Electronic Structure of the Benzimidazyl Radical[a]



| Atom | Orbital | Electron densities | | Spin densities | Hyperfine coupling constants |
|---|---|---|---|---|---|
| | | | Total | | |
| 1 | s | 1.037 | | 0.001 | 0.5 |
| | $p_x + p_y$ | 1.939 | 3.976 | −0.001 | 2 |
| | $p_\pi$ | 1.001 | | 0.032 | |
| 2 | s | 1.045 | | 0.003 | 2 |
| | $p_x + p_y$ | 1.947 | 3.985 | 0.003 | |
| | $p_\pi$ | 0.994 | | 0.063 | |
| 3 | s | 1.022 | | −0.005 | −4 |
| | $p_x + p_y$ | 1.880 | 3.910 | −0.017 | |
| | $p_\pi$ | 1.008 | | −0.018 | |
| 4 | s | 1.550 | | 0.025 | 10 |
| | $p_x + p_y$ | 2.631 | 5.168 | 0.028 | |
| | $p_\pi$ | 0.987 | | 0.621 | |
| 5 | s | 1.079 | | −0.029 | −24 |
| | $p_x + p_y$ | 1.742 | 3.841 | −0.050 | |
| | $p_\pi$ | 1.020 | | −0.397 | |
| 6 | s | | 1.019 | −0.002 | −1 |
| 7 | s | | 1.019 | −0.003 | −2 |
| 8 | s | | 1.005 | 0.014 | 8 |

[a] Symmetry = $^2A_2(\pi)$.

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(9) Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana 47401.

(10) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954); A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).

(11) (a) T. Amos and L. C. Snyder, *J. Chem. Phys.*, **41**, 1773 (1964); (b) T. Amos and G. Hall, *Proc. Roy. Soc., Ser. A*, **263**, 483 (1961); (c) T. S. Lee, Master Thesis, University of California, Santa Cruz, 1970.

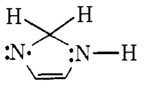
(12) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); (b) C. Heller and Cole, *J. Chem. Phys.*, **37**, 243 (1962).

(13) R. D. Allendoefer and A. S. Pollock, *Mol. Phys.*, **22**, 661 (1971), and references cited therein.

(14) H. Ueda, *J. Phys. Chem.*, **68**, 1304 (1964).

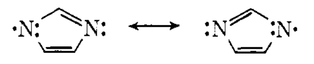
likely $^2A_2$ (experimentally) for the tetraphenyl derivative.[13] Both INDO and $\pi$-electron calculations (Tables I and IX, respectively) predict a much higher spin density at the $\alpha$ than at the $\beta$ hydrogen. Likewise, the triphenylimidazyl shows a low spin density on the nitrogen atoms,[13,14] although the symmetry predicted from $\pi$ calculation (Table IX) indicates a $^2B_1$ symmetry, different from pyrryl. (A rationalization of this will be given later as well as a comparison of the calculations on benzimidazyl presented in Tables III and XII.)

The main anomaly occurs with the predicted $\sigma$ structure of the imidazyl radical. A number of experiments have been directed toward generating the imidazyl and benzimidazyl radicals.[13–17] Imidazyl radical is a proposed intermediate in oxidative phosphorylation, a key biological process.[16] The radical identified from the irradiation of imidazole crystals[15–17] has been established as being structure II. The earlier work of Lamotte and Servoz-Gavin[15a] indicated two different species, one formed at 77°K, as yet unidentified, and a higher temperature species, structure II.



II

A single esr spectrum indicated a species with two equivalent nitrogens with a coupling constant of 10.5 G and one hydrogen atom (32 G). The proposed structure[15a] is close to that of the $\sigma$ imidazyl radical (III).



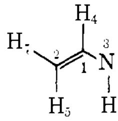
III

The main problem with such a structural assignment from this sparse data is the low coupling constant on the nitrogen. Most authors[18] associate a low nitrogen coupling constant (under 25 G) with a $\pi$ structure, the classical argument being that any $\sigma$ radical would have a high s orbital component and therefore a high coupling constant. The INDO calculation in Table II is somewhat unique in that although most of the spin is localized on the two nitrogen atoms the p orbital, not the s orbital, component is high. Regardless of the possible relationship of this calculation to reality it is now established that using low coupling constant magnitudes as a criteria of $\pi$ *vs.* $\sigma$ structure has no theoretical validity. Another curious result of the calculation on imidazyl is the generally low value of both the hydrogen and nitrogen coupling constants. In any case the high H coupling constant observed experimentally is not duplicated computationally and no conclusion can be drawn. The esr spectrum (a single line) for solution generated imidazyl[16c] indicates rapid spin exchange and is useless for any analysis.

**(B) Structurally Related Radicals.** As previously mentioned, amino and dialkylamino radicals are predicted and found [6,8] to have $\pi$ structures ($^2B_1$). At present, there is no substantiated case of a $\sigma$ radical of the R′RN type. This includes amido[18,19] and hydrazido[20] type radicals as well as *N*-alkoxy[21] radicals. Of major interest are the amido radicals. A great deal of controversy exists over their structure as determined from esr spectra.[18,19] INDO calculations were only reported in detail on a few of the amino type radicals.[8,18] Possibly[22] the acetamido is predicted to be a $\pi$ radical. The main theoretical problem we face here deals with the possible validity of INDO calculations in predicting the relative stabilities of two close lying electronic states. Additional test calculations were conducted in order to explore this situation.

The main question is why is there a $\pi$ to $\sigma$ inversion in going from pyrryl to imidazyl? Does it happen in other heteroradicals? Are the calculations reliable? A plausible hypothesis for the $\pi$ to $\sigma$ radical conversion is that the multiple incorporation of heteroatoms having "nonbonding" electrons into a basic hydrocarbon radical might sufficiently electron enrich the $\sigma$ framework so as to generate an inversion of the "ground" and "excited" states. Conceptually, pyrryl and imidazyl are, respectively, aza- and 1,3-diazacyclopentadienyl radicals. The incorporation of one or more nitrogen atoms into cyclopentadienyl could, conceptually, convert a $\pi$ to a $\sigma$ radical. Computationally this only occurs with imidazyl. To see if a similar thing occurs when heteroatoms are substituted into a parent allyl radical INDO calculations were carried out on aminoethylene (Table IV), 2-azaaminoethylene (Table V), formamido (Table

**Table IV.** Calculated Electronic Structure for the Aminoethylene Radical ($\pi$)



| Atom | Orbital | Electron densities | | Spin densities | Hyperfine coupling constant |
|---|---|---|---|---|---|
| | | | Total | | |
| 1 | s | 1.045 | | −0.022 | −18 |
| | $p_x + p_y$ | 1.850 | 3.865 | −0.044 | |
| | $p_\pi$ | 0.971 | | −0.290 | |
| 2 | s | 1.102 | | 0.027 | 22 |
| | $p_x + p_y$ | 1.936 | 4.028 | 0.038 | |
| | $p_\pi$ | 0.991 | | 0.494 | |
| 3 | s | 1.564 | | 0.034 | 13 |
| | $p_x + p_y$ | 2.604 | 5.207 | 0.029 | |
| | $p_\pi$ | 1.039 | | 0.796 | |
| 4 | s | | 1.014 | 0.010 | 6 |
| 5 | s | | 0.904 | −0.029 | −16 |
| 6 | s | | 0.988 | −0.022 | −12 |
| 7 | s | | 0.996 | −0.022 | −12 |

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(15) (a) B. Lamotte and P. Servoz-Gavin, *Proc. Tihany Symp. Radiat. Chem., 2nd, 1966*, 233 (1967); (b) P. Gloux and B. Lamotte, *Mol. Phys.*, 24, 23 (1972); (c) *ibid.*, 25, 161 (1973).

(16) (a) J. H. Wang, *Science*, **167**, 25, (1970); (b) *Accounts Chem. Res.*, **3**, 90 (1970); (c) S. Tu and J. H. Wang, *Biochemistry*, **9**, 4505 (1970).

(17) A. R. McGhie, H. Blum, and M. M. Labes, *J. Chem. Phys.*, 52, 6141 (1970); H. Blum, A. R. McGhie, A. Kawada, and M. M. Labes, *ibid.*, **55**, 3614 (1971).

(18) W. G. Danen and R. W. Gellert, *J. Amer. Chem. Soc.*, **94**, 6853 (1972), and references cited therein.

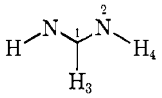
(19) (a) D. C. Straw and G. C. Moulton, *J. Chem. Phys.*, **57**, 2215 (1972); however, see (b) W. C. Lin, N. Cyr, and K. Toriyama, *ibid.*, **56**, 6272 (1972).

(20) (a) L. Muzkat, *Chem. Phys. Lett.*, **18**, 414 (1973); (b) W. C. Lin and J. M. Nickel, *J. Chem. Phys.*, 57, 3581, (1972); **58**, 2664 (1973).

(21) W. C. Danen and C. T. West, *J. Amer. Chem. Soc.*, **93**, 5582 (1971).

(22) P. Tordo, E. Flesia, and J. M. Surzur, *Tetrahedron Lett.*, 183 (1972). These authors imply that the INDO calculation of the acetamido radical predicts a $\pi$ radical.

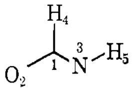
**Table V.** Calculated Electronic Structure for the Azaaminoethylene Radical[a] (Cisoid)



| Atom | Orbital | Electron densities | | Spin densities | Hyperfine coupling constants |
|---|---|---|---|---|---|
| | | | Total | | |
| 1 | s | 1.061 | | −0.032 | −26 |
| | $p_x + p_y$ | 1.757 | 3.755 | −0.053 | |
| | $p_\pi$ | 0.937 | | −0.420 | |
| 2 | s | 1.564 | | 0.030 | 11 |
| | $p_x + p_y$ | 2.604 | 5.200 | 0.034 | |
| | $p_\pi$ | 1.031 | | 0.710 | |
| 3 | s | | 1.056 | 0.014 | 7 |
| 4 | s | | 0.895 | −0.028 | −15 |

[a] Symmetry = $^2A_2$ ($\pi$). Transoid configuration essentially the same with regard to hyperfine coupling constants.

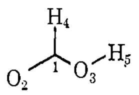
**Table VI.** Calculated Electronic Structure for the Formamido Radical[a] (Cisiod)[b]



| Atom | Orbital | Electron densities | | Spin densities | Hyperfine coupling constant |
|---|---|---|---|---|---|
| | | | Total | | |
| 1 | s | 1.050 | | −0.027 | −23 |
| | $p_x + p_y$ | 1.745 | 3.628 | −0.088 | |
| | $p_\pi$ | 0.823 | | 0.007 | |
| 2 | s | 1.765 | | 0.019 | 17 |
| | $p_x + p_y$ | 2.546 | 6.104 | 0.863 | |
| | $p_\pi$ | 1.794 | | 0.020 | |
| 3 | s | 1.573 | | −0.006 | −2 |
| | $p_x + p_y$ | 2.403 | 5.360 | 0.101 | |
| | $p_\pi$ | 1.383 | | −0.027 | |
| 4 | s | | 1.003 | 0.143 | 76 |
| 5 | s | | 0.906 | −0.004 | −2 |

[a] Symmetry = $\sigma$. [b] Hyperfine coupling constants for isomer with $H_4 + H_5$ in a trans configuration are: atom 1, −24; 2, 16; 3, −7; 4, 49; 5, −7.

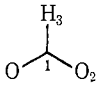
**Table VII.** Electronic Structure of the Formic Acid Cation Radical[a]



| Atom | Orbital | Electron densities | | Spin densities | Hyperfine coupling constant |
|---|---|---|---|---|---|
| | | | Total | | |
| 1 | s | 1.054 | | −0.029 | −24 |
| | $p_x + p_y$ | 1.731 | 3.398 | −0.094 | |
| | $p_\pi$ | 0.610 | | −0.031 | |
| 2 | s | 1.761 | | 0.021 | 18 |
| | $p_x + p_y$ | 2.511 | 5.880 | 0.881 | |
| | $p_\pi$ | 1.608 | | 0.042 | |
| 3 | s | 1.638 | | 0.001 | 1 |
| | $p_x + p_y$ | 2.737 | 6.157 | 0.118 | |
| | $p_\pi$ | 1.782 | | −0.011 | |
| 4 | s | | 0.877 | 0.107 | 58 |
| 5 | s | | 0.688 | −0.004 | −2 |

[a] Symmetry = $\sigma$.

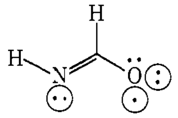
**Table VIII.** Calculated Electronic Structure for the Carboxyl Radical[a]



| Atom | Orbital | Electron densities | | Spin densities | Hyperfine coupling constant |
|---|---|---|---|---|---|
| | | | Total | | |
| 1 | s | 1.052 | | −0.039 | −32 |
| | $p_x + p_y$ | 1.725 | 3.484 | −0.092 | |
| | $p_\pi$ | 0.707 | | −0.024 | |
| 2 | s | 1.802 | | −0.001 | −1 |
| | $p_x + p_y$ | 2.834 | 6.283 | 0.447 | |
| | $p_\pi$ | 1.647 | | 0.012 | |
| 3 | s | | 0.905 | 0.238 | 129 |

[a] Symmetry = $^2A_1$ ($\sigma$).

VI), the formic acid cation (Table VII), and the carboxyl radical (Table VIII). The latter three materials were predicted to be $\sigma$ radicals. Both aminoethylene and 2-azaaminoethylene radicals are perturbationally related to the $^2A_2$ structure of the allyl radical.[23] In contrast with acetamido,[22] formamido is predicted to have a $\sigma$ structure. As with imidazyl, formamido is predicted to have a curious electronic structure. Most of the spin density is localized on the oxygen atom and the structure representation is closer to that shown below. In addition the nitrogen coupling constant is



small. Experimental results on the methylated amido radicals indicate a $\pi$ structure,[18,19] and thus the experimental results are not necessarily in conflict with the INDO calculations. It is known, from photoelectron spectroscopy,[24,25] that the formic acid cation is most probably a $\sigma$ ($n$-electron excitation) radical. Here too, the $\pi$ *vs.* $\sigma$ structures are quite sensitive to methylation.[25]

Carboxyl is predicted to be a $\sigma$ radical, and there is some experimental evidence for this[26] in the case of malonic acid. However, with phenylcarboxyl radical a $\pi$ structure is predicted and found.[27] Thus, in all cases apparently minor structural variations can cause a $\pi$ to $\sigma$ inversion.

**(C) Conclusions of the INDO Calculations.** Enough information exists to support the statement that the prediction that imidazyl is a $\sigma$ radical is not necessarily a computational artifact. At a minimum the calcula-

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(23) This is treated in standard quantum chemistry texts; see also ref 12.

(24) C. R. Brundle, D. W. Turner, M. B. Robin, and H. Basch, *Chem. Phys. Lett.*, **3**, 292 (1962).

(25) D. A. Sweigart and D. W. Turner, *J. Amer. Chem. Soc.*, **94**, 5599 (1972).

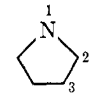
(26) B. Eda and M. Iswaki, *J. Chem. Phys.*, **55**, 3442 (971).

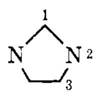
(27) J. Bargon, IBM Research, San Jose, comments made during a seminar held at the University of California, Santa Cruz, February 1973.

tions indicate that there is no strong intuitive basis on which to predict what kind of structures should be $\pi$ or $\sigma$ radicals. However, there is also some support for the idea that loading a particular parent radical with heteroatoms having "nonbonding" electrons should tend to favor $\sigma$ structures.

**II. $\pi$-Electron Calculations.** The results of the open shell single annihilation SCF $\pi$-electron calculations of the spin and electron densities of pyrryl, imidazyl, indolyl, carbazyl, benzimidazyl, and purinyl radicals are shown in Tables IX–XIII. Unlike allyl radical,[28] it was found that annihilation had little effect on calculated spin and electron densities. Therefore, all the spin and electron densities, as well as the expectation value of $\langle S^2\rangle$, are reported after annihilation of the contaminating quartet. As usual, there is some ambiguity as to what values to use for the C–C and C–N resonance integrals. Two separate calculations were attempted in all cases. One set of parameters used resonance integrals for C–C and C–N of $-2.40$ eV each. Another set used a value of $-2.40$ for C–C and $-2.57$ for C–N. In most cases this small parameter change had little effect on the calculated spin and electron densities and, therefore, all the results are not presented. An example of a lack of effect of changing resonance parameters is shown in purinyl (Table XIII). With carbazyl, however, a major effect was noted with regard to $\langle S^2\rangle$ and a minor effect in the spin and electron densities. In one case, benzimidazyl (Table XII), the symmetry of the ground state was altered by this small change in the resonance integral. Indolyl (Table X) showed some variation in spin densities.

**Table IX.** $\pi$ Spin and Electron Densities of Pyrryl and Imidazyl Radicals[a]

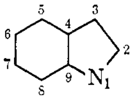




| Atom | Spin density | $\pi$ electron density |
|---|---|---|
| | Pyrryl | |
| 1 | $-0.08$ | 1.37 |
| 2 | 0.45 | 0.81 |
| 3 | 0.10 | 1.01 |
| | $\langle S^2\rangle = 0.750$; Sym = $^2A_2$ | |
| | Imidazyl | |
| 1 | 0.36 | 0.74 |
| 2 | $-0.04$ | 1.34 |
| 3 | 0.37 | 0.79 |
| | $\langle S^2\rangle = 0.756$; Sym = $^2B_1$ | |

[a] All $\beta$'s = $-2.4$ eV, all values after annihilation.

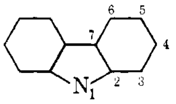
**Table X.** $\pi$ Spin and Electron Densities in the Indolyl Radical[a]



| | Spin density | | Electron densities | |
|---|---|---|---|---|
| Atom | All $\beta$'s = $-2.4$ | $\beta_{C=C} = 2.40$ $\beta_{CN} = -2.57$ | All $\beta$'s = $-2.4$ | $\beta_{CC} = -2.40$ $\beta_{CN} = -2.57$ |
| 1 | 0.28 | 0.14 | 1.25 | 1.30 |
| 2 | $-0.04$ | 0.06 | 0.89 | 0.87 |
| 3 | 0.50 | 0.49 | 0.92 | 0.91 |
| 4 | $-0.07$ | $-0.04$ | 1.06 | 1.07 |
| 5 | 0.19 | 0.16 | 0.97 | 0.94 |
| 6 | $-0.06$ | 0.02 | 1.01 | 1.02 |
| 7 | 0.14 | 0.10 | 0.98 | 0.96 |
| 8 | $-0.02$ | 0.04 | 0.97 | 0.97 |
| 9 | 0.08 | 0.05 | 0.96 | 0.95 |
| | | | $\langle S^2\rangle = 0.786$ | 0.750 |

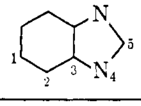
[a] All values after annihilation.

**Table XI.** $\pi$ Electron Spin and Electron Densities for the Carbazyl Radical



| | Spin densities | | Electron densities | |
|---|---|---|---|---|
| Atom | All $\beta$'s = $-2.40$ | $\beta_{CC} = -2.40$ $\beta_{CN} = -2.57$ | All $\beta$'s = $-2.40$ | $\beta_{CC} = -2.40$ $\beta_{CN} = -2.57$ |
| 1 | 0.49 | 0.46 | 1.17 | 1.19 |
| 2 | $-0.08$ | $-0.02$ | 0.98 | 0.97 |
| 3 | 0.19 | 0.10 | 0.97 | 0.96 |
| 4 | $-0.08$ | $-0.02$ | 1.01 | 1.02 |
| 5 | 0.16 | 0.11 | 0.98 | 0.98 |
| 6 | $-0.06$ | 0.01 | 0.99 | 1.00 |
| 7 | 0.12 | 0.09 | 0.99 | 0.99 |
| | Sym = $^2B_1$ | | $\langle S^2\rangle = 0.906$ | 0.750 |

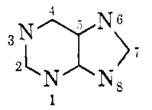
**Table XII.** $\pi$ Spin and Electron Densities for the Benzimidazyl Radical[a]



| | Spin densities | | Electron densities | |
|---|---|---|---|---|
| Atom | All $\beta$'s = $-2.4$ | $\beta_{CC} = -2.40$ $\beta_{CN} = -2.57$ | All $\beta$'s = $-2.40$ | $\beta_{CC} = -2.40$ $\beta_{CN} = -2.57$ |
| 1 | 0.17 | 0.05 | 0.94 | 0.98 |
| 2 | $-0.05$ | 0.20 | 1.01 | 0.91 |
| 3 | 0.26 | $-0.04$ | 0.82 | 0.99 |
| 4 | $-0.02$ | 0.35 | 1.38 | 1.19 |
| 5 | 0.28 | $-0.11$ | 0.71 | 0.85 |
| | Sym = $^2B_1$ | | $^2A_2$ $\langle S^2\rangle = 0.766$ | 0.755 |

[a] All values after annihilation.

**Table XIII.** $\pi$ Spin and Electron Densities for the Purinyl Radical[a]



| | Spin densities | | Electron densities | |
|---|---|---|---|---|
| Atom | All $\beta$'s = $-2.40$ | $\beta_{CC} = -2.40$ $\beta_{CN} = -2.57$ | All $\beta$'s = $-2.40$ | $\beta_{CC} = -2.40$ $\beta_{CN} = -2.57$ |
| 1 | $-0.08$ | $-0.07$ | 1.27 | 1.27 |
| 2 | 0.20 | 0.20 | 0.74 | 0.73 |
| 3 | $-0.08$ | $-0.07$ | 1.29 | 1.28 |
| 4 | 0.22 | 0.22 | 0.78 | 0.77 |
| 5 | 0.01 | 0.05 | 0.95 | 0.93 |
| 6 | 0.39 | 0.31 | 1.18 | 1.21 |
| 7 | 0.14 | 0.15 | 0.71 | 0.71 |
| 8 | $-0.01$ | $-0.02$ | 1.34 | 1.35 |
| 9 | 0.21 | 0.22 | 0.75 | 0.75 |
| | | | $\langle S^2\rangle = 0.796$ | 0.774 |

[a] All values after annihilation.

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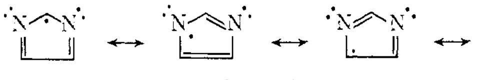
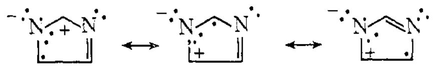
(28) For a detailed discussion, see L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, pp 72, 73, 269.

Two major conclusions can be drawn from the computational features of the calculations presented in Tables IX–XIII. First, unlike allyl, annihilation is not particularly important in effecting the spin and electron densities. The effect shows up with regard to the expectation value of $\langle S^2 \rangle$, but even in this case single annihilation is not always sufficient in producing a value near the 0.75 required for a pure doublet. Second, the fact that a minor variation in the resonance integral can lead to great changes in spin and electron densities, as well as produce a change in the symmetry of the ground state, is a serious development. Such a symmetry change is unlikely for a small system in which there are a limited number of orbitals. In large systems the number of molecular orbitals increases and their close energetic proximity may make the system of interest susceptible to perturbational sensitivity resulting from minor parameter changes. If so, the results obtained do not reflect topological effects but merely are artifacts of the parameters used.

Without going through a full perturbational treatment of the electronegativity effects of the inclusion of nitrogen atoms into the basic parent hydrocarbon radicals, cyclopentadienyl, indenyl, and fluorenyl, the results obtained in Tables IX–XIII show some interesting effects. The suppression of the spin density on the N atom in pyrryl is due to the $^2A_2$ symmetry of the radical. This can be reexplained in orbital terminology as resulting from a node through the N atom in the one electron filled orbital if one uses a closed shell approximation. Under such conditions, the spin density at the N atom would be zero. The situation as to why there is a negative spin density in the open shell calculation is identical with the classic case of the allyl radical,[28] which also has an $^2A_2$ symmetry. No such argument can be used with imidazyl and the near zero spin density on the nitrogen atoms must result from electronegativity effects. The simplest hypothesis for imidazyl, or any other radical in which symmetry does not dominate the N spin densities, is that high spin densities and the accumulation of a negative charge on the N atom tend to be mutually incompatible. The reason for this is best seen from resonance structure arguments. Like cyclopentadienyl uncharged resonance structures (of proper phasing and belonging to the $^2B_1$ representation in the case of imidazyl) merely scatter the spin density equally about the five-membered ring. However, ionic resonance structures in which N atoms possess a negative charge suppress the spin densities at the N atom.



noncharged



ionic

If this hypothesis is true one would expect to find a correlation between N spin densities and electron densities in the calculations presented in Tables IX–XIII. In fact, with the exception of the 1 and 3 positions on purinyl radical (Table XIII), there is a fair linear correlation. High N spin densities are associated with electron densities in the 1.15–1.20 region. Negative spin densities are associated with electron densities in the order of 1.35. Even in purinyl radical the low spin densities of the nitrogen atoms in the six-member ring are associated with a high electron density. Simply stated, it would seem that nitrogen would prefer to attract two electrons instead of one. This fits our intuition as to the relative electronegativities of carbon and nitrogen.

A comparison of the INDO (Table III) and the $\pi$-electron calculations (Table XII) for the $^2A_2$ state of benzimidazyl radical shows a strong difference in the predicted hyperfine coupling constants. As implied from the $\pi$-electron spin densities the $\pi$-electron calculation shows a fairly high coupling constant for atom 2 in the six-member ring. The INDO calculations predict very little spin density in the six-member ring, with the five-member ring being allyl like. In particular the lack of annihilation in the case of the INDO calculations shows up in the large negative spin density at carbon 5. This is also shown in the INDO calculations in pyrryl (Table I) and 2-azaaminoethylene radicals (Table V). In $\pi$-electron calculations on pyrryl we found $\pi$ spin densities of $-0.048$, 0.418, and 0.106 before annihilation and $-0.081$, 0.445, and 0.095 after (Table IX), for the nitrogen atom 1 and carbon atoms 2 and 3, respectively. Any presumption that if annihilation is not important in determining spin densities in open shell $\pi$-electron calculations they will also be unimportant in the INDO calculations is obviously not supported by these results.

Experimentally, there is a lack of information in which to test these calculations. In the parent hydrocarbon radicals, the esr spectrum of cyclopentadienyl has been reported.[29] In the aza derivatives, only carbazyl has been characterized.[30] Here, our calculations indicate a nitrogen spin density (0.46) somewhat in excess of the 0.24 estimated from the coupling constant of 6.9 G. We are in qualitative agreement with the observed spectrum, however, and the symmetry of the carbazyl radical must be $^2B_1$. The only other material reported is indolyl radical.[29] The radical is a possible intermediate in the photodecomposition of indole derivatives, including tryptophan. The proposed mechanism[31] involves the photoejection of an electron to give an indole cation followed by ionization to the conjugate base, the indolyl radical. The observed spectrum consists of a single line, however.[29] The argument of Pailthorpe and Nicholls[32] that the spin density is localized totally on carbon atom 3 is computationally not supported (Table X) nor is it logical from a purely resonance viewpoint. The calculation does indicate an unusually high C spin density of 0.50 at the 3 position but the spin densities at the other locations should create significant splitting in the spectrum of indolyl.

**III. State Symmetry Consequences of the $\pi$ *vs.* $\sigma$ Structure of Radicals.** The symmetries of the ground

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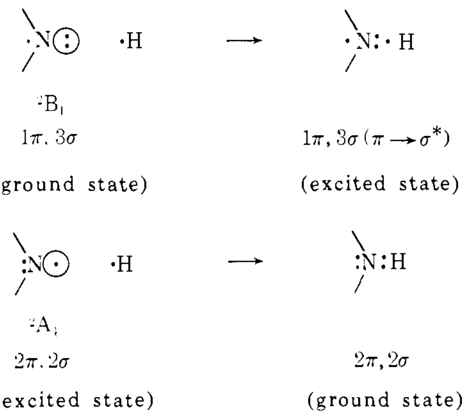
(29) (a) D. Krusic and J. Kochi, *J. Amer. Chem. Soc.*, **90**, 7155, 7157 (1968); (b) P. J. Zandstra, *J. Chem. Phys.*, **40**, 612 (1964).

(30) (a) F. A. Neugebauer, H. Fischer, S. Bamberger, and H. Smith, *Chem. Ber.*, 105, 2694 (1972); (b) R. D. Allendoefer, *Chem. Phys. Lett.*, **17**, 172 (1972).

(31) (a) J. Feitelson, *ibid.*, **13**, 87 (1971); (b) R. Santus and L. I. Grossweiner, *ibid.*, **15**, 101 (1972); (c) V. Subramanyan and G. Tollin, *ibid.*, **15**, 449 (1972); (d) L. I. Grossweiner and Y. Usui, *ibid.*, **11**, 53 (1972).

(32) M. T. Pailthorpe and C. H. Nicholls, *Photochem. Photobiol.*, **14**, 135 (1971).

and excited states of radical species are of importance in determining some of the qualitative features of the potential energies surfaces of even electron molecules which give radical products. This is best seen in how ammonia might yield the amino radical and the hydrogen atom. It has already been shown that the ground state of $NH_2$ is $^2B_1$ and the first excited state is $^2A_1$. Conceptually we can join planar $NH_2$ with H in a coplanar fashion to give planar ammonia. The structure representations are given below.



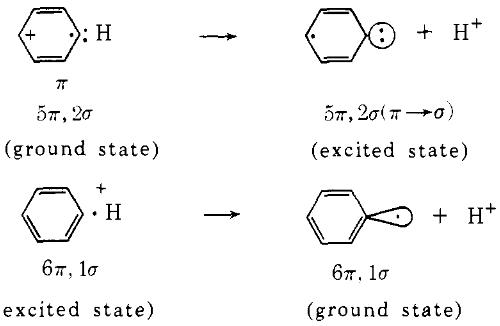
We have purposely written a 3-electron σ bond for the N–H bond in the $^2B_1$ $NH_2$–H reaction. In orbital terminology a 3-electron σ valence bond is a $(\sigma)^2\sigma^*$ configuration. The concept of a 3-electron bond is useful in attempting to keep the state symmetries in order when writing valence bond structures.

The above argument shows that the ground state of the amino radical is correlated with an excited state of ammonia, and the excited state of the amino radical is correlated with the ground state of ammonia. This has already been shown diagrammatically by Herzberg and Douglas.[33] Thus, it is predicted that the potential energy surface of the ground state planar ammonia must cross with a singlet excited state of planar ammonia at a N–H bond length less than the dissociation limit. Because of configuration interaction and the breakdown of symmetry this crossing does not necessarily occur when other geometrical variations are added to the N–H stretch. Conceptually, however, crossing does occur at least at one set of geometrical coordinates.

With the possible exception of imidazyl and formamido, the experimental results show that all other R′RN type radicals are amino like and yield π rather than σ radicals in the ground state. With pyrrole, for example, the stretching of the N–H bond in a coplanar fashion should yield a σ pyrryl radical, which is predicted to be an excited state of pyrryl. As with amino, then, the ground state of pyrrole is correlated with an excited state of pyrryl ($^2A_1$) and some π–σ* excited state of pyrrole is correlated to the ground state of pyrryl ($^2A_2$). It seems likely that in most molecules of the type calculated here, there is a crossing between the ground and excited states at some N–H stretching coordinate.

The behavior of planar heteromolecules having N–H bonds is to be contrasted with the arene–aryl radical correlation curves. The ground state of planar benzene should smoothly give the ground state of the phenyl radical $(\sigma)^1$ and an H atom without ground–excited state crossing. A similar analysis will also show that ground–excited state surface crossing is possible in other cases. For instance, the phenoxy radical is known to have a π-structure.[34] If one constricts the departure of the H atom from phenol in a coplanar fashion this can only generate a σ phenoxy radical. Thus, at some geometrical coordinate along the O–H stretch the ground and some excited state of phenol come into contact. We have proposed a similar ground–excited state crossing in the thermal and photodecomposition of arenediazonium cations to give aryl cations.[35]

Similar ground and excited state curve crossings are proposed for radical cations or anions in their ionization processes. The benzene cation $(\pi)^{36}$ cannot correlate with the ground state of the phenyl radical (its conjugate acid) which is $\sigma^1$ if the proton departs in a coplanar fashion. Likewise, the ground state of the chlorobenzene anion (presumably a π-radical anion) cannot correlate the ground state of the chloride ion and the phenyl radical. Both in the benzene cation and chlorobenzene anion, surface crossing must occur along the breaking of the C–H or C–Cl bond.



The theoretical consequences of these curve crossings are that when attempts are made to calculate the potential surfaces for reactions in which the final states indicate curve crossing the situation will become increasingly complicated as certain bonds are stretched. The experimental consequences of these curve crossings are that ground–excited state to ground state relaxation might occur at or near the crossing coordinates. Salem, Dauben, and Turro have already[2] proposed that surface crossing of this type occurs in the singlet Norrish type II photoreaction. In this case the n–π* singlet evolves along the O–H coordinate to directly give the singlet biradical intermediate in its ground state. Thus, there is no general theoretical difficulty in conceiving how ground and excited state surfaces may directly interconnect or come into contact. Whether a number of photochemical mechanisms occur by such adiabatic routes is an interesting question as yet insufficiently explored.

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(33) Reference 5a, p 465.

(34) For example, see P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen and Co. Ltd., London, 1967, pp 286–288.

(35) R. J. Cox, P. Bushnell, and E. M. Evleth, *Tetrahedron Lett.*, 207 (1970).

(36) M. K. Carter and G. Vincow, *J. Chem. Phys.*, **47**, 292 (1967); (b) T. Osa, A. Yildiz, and T. Kuwana, *J. Amer. Chem. Soc.*, **91**, 3994 (1969).