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NASA CR 108261

QUARTERLY STATUS REPORT

Grant NGL 05-061-004

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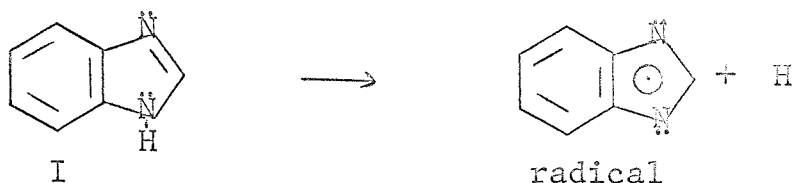
Grant Title: Radical Stabilities in Nitrogen Containing Heterocyclic Systems

Progress to Date:

Experimental Studies in Heterocyclic Radicals

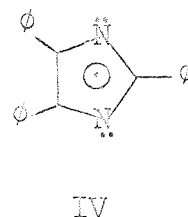
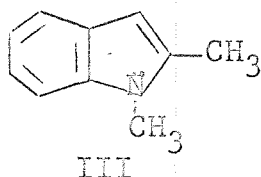
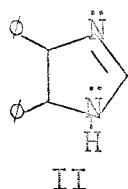
Dr. S. Chang arrived in September of 1969 to do postdoctoral research on nitrogen containing heterocyclic radicals. His principal effort during the support period is directed towards generating the neutral radicals of the molecules imidazole, benzimidazole, pyrrole, indole, and purine. Since Dr. Chang was unfamiliar with the experimental techniques of generating and measuring the electron spin resonance of radicals, the first few months of his activities at Santa Cruz were directed towards generating known radicals. So his initial work yielded the electron spin resonance of perylene cation radical (generated in sulfuric acid), the anthracene cation radical (sulfuric acid), tetracene cation radical (sulfuric acid), the semiquinone radical anion (air oxidation), the diethylaminophenoxy radical (photolysis), dimethoxybenzene cation radical (sulfuric acid), phenazine radical anion (electrolytic reduction), nitrobenzene radical anion (electrolytic reduction).

The above preliminary investigations used the basic experimental methods of radical generation: i) simple chemical oxidation or reduction; ii) photolytic generation; and iii) electrolytic generation. From this point, Dr. Chang went on in attempts to generate the neutral radical from benzimidazole (I)



The following methods were used in attempting to generate this radical. All have been, to date, unsuccessful. i) Chemical oxidation of a basic solution of benzimidazole (partially benzimidazole anion) with potassium ferricyanide either in solution or by the flow method; ii) Electrolytic reduction and oxidation in acetonitrile (with supporting electrolyte); and iii) Photolysis (direct). Similar attempts with imidazole also proved unsuccessful. Obviously, the generation of these radicals is difficult.

Electrolytic oxidation and reduction of both 4,5-diphenylimidazole (II) and 1,2-dimethylindole (III) have also been attempted without success. Since the neutral radical of triphenyl imidazole (IV) has been observed to be generated either chemically or by simple photolysis the most recent attempts have been to photolytically generate this radical.



This has as yet proved unsuccessful. Present efforts are directed towards low temperature photolysis of materials in the presence of t-butylperoxide.

The lack of success in generating these as yet unknown radicals of I, II, and III has opened up suggestions within the group that perhaps we should expand our search to include related radicals in the same compounds. For instance, in the case of benzimidazole (I) in addition to the radical written above, simple derivatives of I should provide other electronically related radicals.



Simple Derivatives of Benzimidazole

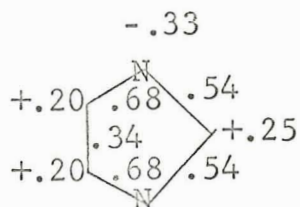
Synthetic efforts have begun on the preparation of both N-methylbenzimidazole and 1,3-dimethylbenzimidazolium perchlorate. Oxidation and reduction of the former and reduction of the latter should be easily effected.

Theoretical Studies in Heterocyclic Radicals

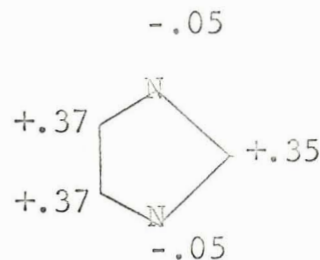
Mr. T. S. Lee has been working on spindensity calculations on the above radicals.

During the late summer of 1969, it was concluded that the simple open shell approach had some critical drawbacks. Theoretically, a proper wave function must not only be an eigenfunction of the molecular Hamiltonian (describing the kinetic and electrostatic interactions of the electrons and nuclei) but also of the spin operators S_z and S^2 . The open shell solution of the self-consistent

field equations do not, in the first approximation, yield the latter and it is necessary to project out the "unwanted" portions of the spin. Mr. Lee has been able to do this in large part using the theoretical method of Amos and Snyder (J. Chem. Phys., 41, 1773 (1964)). Mr. Lee has prepared the program combination which will now i) calculate the open shell wavefunctions; ii) project out the more nearly correct wavefunction, and iii) yield spin densities. Calculations have been performed in allyl radical, the radicals from imidazole, benzimidazole, and purine. As an example, the calculations on imidazole are instructive. Below are shown the charge densities (both alpha and beta electrons) and spin densities in imidazole radical. Positive spin densities imply alpha spin and negative beta spin.



Charge density
Bond and Orders



Spin density

The above calculations indicate that unlike the isoelectronic cyclopentadienyl radical the spin densities in imidazolyl radical are not equal at all locations, in fact the nitrogen goes negative! Simple rationalization of this result is obtained by examining some of the resonance structures containing charge transfer.



Calculation of the same quantities in the benzimidazolyl radical indicate much the same thing. Calculations will continue on other related structures. It is hoped that experimental measurements will support the theoretical findings.

Work over the next quarter will continue along the same lines as discussed above.

E. M. Evleth
December 31, 1969