

PRNC-128 PUERTO RICO NUCLEAR CENTER MATRIX ISOLATION STUDIES OF THE GAMMA RADIOLYSIS OF HETEROCYCLIC MOLECULES Progress Report 4 April 1969 OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT NO. AT (40-1)-1833 FOR U.S. ATOMIC ENERGY COMMISSION. ---Page Break--- PRNC-128 CHEMISTRY (T1D-4500) PUERTO RICO NUCLEAR CENTER MATRIX ISOLATION STUDIES OF THE GAMMA RADIOLYSIS OF HETEROCYCLIC MOLECULES Progress Report 4 A. Grimison and G. A. Simpson April 1969 OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT NO. AT (40-1)-1833 FOR U.S. ATOMIC ENERGY COMMISSION ---Page Break--- TABLE OF CONTENTS Personnel Participating - Section A - Experimental Results - Section B - Theoretical Work Appendix 1 Appendix 2. ---Page Break--- PERSONNEL PARTICIPATING Dr. A. Grimison, Chief Scientist, Principal Investigator Dr. G. A. Simpson, Associate Scientist M. Trujillo Sánchez, Graduate Student Assistant F. Bernasconi, Graduate Student Assistant O. Pérez, Research Assistant (Part time) ---Page Break--- The results achieved in this project from May 1966 to April 1969 were previously presented in Technical Progress Reports No. 1 (FRNC No. 8), No. 2 (ERNC No. 99) and No. 3 (PRC No. 126). The present Technical Progress Report reviews the results obtained in the period from April 1968 to April 1969, the time of preparing this Report. As has been done previously, the report is divided into two sections, Experimental and Theoretical. Section A. Experimental Results I. General Procedures Purification of solvents, such as 2-methyltetrahydrofuran (MTHF) or 3-methylpentane (3MP), has been described previously. All compounds used were of highest commercial purity. Absorption spectra were obtained as before. Visual observations of either high or low temperature irradiated compounds were made in a darkened room after suitably dark adapting the observer's eye. Quantitative measurements of relative thermoluminescent intensities were obtained with a commercial instrument, the Con Red Thermoluminescent detector, under nitrogen.

purging to minimize combustion, No evidence of combustion was found, 'The device is calibrated in terms of rad-equivalents of LiF thermoluminescence, Thus, absolute comparisons are possible. ESR measurements were performed both with the Varian 4500 at IVIC, Venezuela, and with the Varian E-3 of the Chemistry Department, U.P.R. Estimates of "spin" concentration were made in terms of the rated instrument sensitivity  $10^{\circ}$  spins/eauss. ---Page Break--- -2- A description of the experimental conditions for observing luminescence effects is found in Figures 3, 4 and 5 along with a detailed list of components in Table 2. A discussion of their applications can be found in the Section "Phototonization of Heterocyclics at  $77^{\circ}\text{K}$ ' II, Absorption Spectra of Radiolytic Intermediates at  $77^{\circ}\text{K}$  'A copy of a paper submitted to the Journal of Physical Chemistry is found in Appendix 1, This paper, entitled "Electron Attachment by Pyridine and the Diazines in Gamma-Radiolysis at  $77^{\circ}\text{K}$ ", represents a finalization of studies revealed in previous Technical Progress Reports. Electron attachment in these compounds has been observed following gamma radiolysis in MIF glassy solutions. This observation has been confirmed by studies of bleaching effects, solvent concentration effects and through competition effects with added electron scavengers. The experimental spectra of anions are in excellent agreement with spectra obtained by classical chemical procedures, IIT. Thermoluminescence Following Gamma-Radiolysis at  $77^{\circ}\text{K}$  Thermoluminescence of irradiated biologically significant compounds on warming from  $77^{\circ}\text{K}$  has been reported previously.<sup>27</sup> Etman and Wallace have made extensive quantitative studies on a large number of compounds. Among them are adenine, having a thermoluminescence maximum at 460 nm, cytosine, DNA, guanine (maxima at 510 nm), thymine and uracil. Approximate estimates of the G values for thermoluminescence can be made from their data and are of the order  $10^{\circ}$  photons per 100 eV absorbed for adenine, the most efficient and for uracil,  $10^{\circ}$ .

photons/100 eV. This technique ---Page Break--- -3- is very sensitive, with a minimum thermoluminescence yield on the order of  $10^3$  photons/100 eV detected. Fleming and Kerr have observed thermoluminescence from adenine and cytosine with maxima near 480 nm, which was identical to the crystal phosphorescence under UV excitation. Charlesby and Singh have likewise reported identified UV-induced blue phosphorescence and thermoluminescent bands of irradiated purine and pyrimidine bases. Thus, our visual observations of blue thermoluminescence from those compounds reported in Table 1 are in agreement both in relative magnitude and in wavelength region with the previous studies. Studies of the phosphorescence of these compounds in aqueous solutions would place the emission bands of those compounds in the violet rather than the blue regions of the spectra. For example, Longworth has reported emissions occurring between 365 and 425 nm, and guanine at 400 nm in neutral water. Nevertheless, the fact remains that UV excitation of the crystals produces blue emissions. Thus it may be concluded that the entities in neutral water are strongly aquated. Shifts of 50 nm may well be ascribed to strongly perturbed N- $\pi$  transitions, and can be observed in aqueous solutions. IV. Thermoluminescence and ESR Signals after Room Temperature Gamma-Radiolysis Production of long-lived free radicals in the crystalline purine of pyrimidine bases by ionizing radiation has been observed previously. The works of Andros and Calvin, or Cook and Eliot provide good references. Similarly, for those compounds irradiated at 77°K, literature ---Page Break--- -4- exists for comparative studies of both ESR and thermoluminescence of irradiated bases, viz. Sonner and Pinl. However, comparative ESR and thermoluminescence studies for those compounds irradiated at room temperature have not been made. Presumably, the existence of a high temperature thermoluminescence has not been observed. In figures 1 and 2 we report the ESR spectra of irradiated

cytosine and uracil. 'The G values for production of those radicals are estimated to be of the order  $10^7$  and  $10^{-3}$  epins/100 eV respectively. 'The radicals associated with these unsymmetrical and unresolved spectra have g values of 2.02 and widths at half maximum intensity of less than 20 gauss. The absence of detail is characteristic of powdered samples. The g values, width and absence of large splittings suggest the presence of neutral radicals having unpaired electrons localized on a carbon atom joined to at least one hydrogen atom. 'The similarity in the spectra of the cytosine and uracil radicals allows the suggestion that a hydrogen may have added to the carbon atoms at the 4 or 5 position in the ring. This interpretation is at least consistent with the single crystal study of Cook and Elliot," where the presence of a radical of cytosine with an extra H atom in the 5 position in addition to a radical with an H atom vacancy from the nitrogen in the 3 position is reported. In addition, the ESR spectra are sensitive to moderate heating following gamma irradiation. Heating samples of irradiated cytosine or uracil to 50°C causes a reduction in the intensity of the ESR spectra. High temperature thermoluminescence from purine or pyrimidine bases has been observed in these laboratories. The following compounds and their ---Page Break--- The relative intensities of thermoluminescence were obtained with a commercial 'thermoluminescence detector after irradiating to a dose of  $3.5 \times 10^9$  rads: cytosine 1, Thymine 1.3, Adenine 1, Purine 0.6, Uracil 9.1, Guanine on the order of  $10^{-1}$ . All of the thermoluminescent intensities were linear in dose up to the value noted. Further, the visual observation of the temperature dependence of the luminescence places the maximum glow intensities in the range 64°C to 155°C (which were limits of temperatures at which feeble glows could be observed). Work is anticipated to determine the quantitative aspects of the temperature dependence of both the free radical concentration and the thermoluminescence.

process. A tentative hypothesis, which we wish to test, is that the destruction of the free radical centers gives rise to thermoluminescence; that it may be chemiluminescence. This process is

distinct from that responsible for the luminescence reported in part III, which we suspect to be due primarily to recombination of an electron-cation pair that has stability at 77°K. The assistance in experimental work of Dr. H. Bemski, IMC, Venezuela, is gratefully acknowledged. Photoionization of Heterocyclics at 77°K. A survey of the pertinent literature indicates the existence ---Page Break --- -6- of some four mechanisms whereby a neutral atom or molecule may be liberated from a valence electron. These are: 1. Direct photoionization 2. Charge transfer to the solvent (CTTS) 3. Biphotonic photoionization 4. Lim proposal The first mechanism is, perhaps, the most well-known of the four and is the process responsible for the production of the ionosphere. On absorption of a photon having energies greater than or equal to the ionization potential of the compound, a cation and a separated electron are produced. Presumably, this process can also occur in condensed phases, but the photon energy required may be lowered due to the solvation energies of the resultant ions. Since there is a one-to-one correspondence between photons absorbed and ions produced, the rate law for the overall process is linear with respect to the intensity of the exciting light. The second mechanism is suitable for the effect of light absorption by ions in highly polar solvents such as water. It differs from the first in that it applies to a specific solution electronic transition - charge transfer absorption bands - and is highly influenced by temperature, solvent dielectric, and the presence of added salts. It is also a one-photon process and can be characterized by the equation:  $(ion) + hv \rightarrow (ion)^* \rightarrow (ion^{+}) + e_{solvated}$  ---Page Break --- -T- This mechanism is known to occur for the halide ions, ferric salts, and some neutral species.

process may well be the most important for biological entities. It can provide a low energy route towards photobiological damage, energy storage, or conversion in biological systems. 'The mechanism has been demonstrated to occur in aromatic amines by Albrecht, and in aromatics by Porter. 'The mechanism requires that a long lived triplet state, initially produced by light absorption by a neutral, absorb a second photon to produce the electron-cation pair. Generally the photon energy required is less than half that of the gaseous ionization potential. Since two photons are required the rate is a function of the square of the light intensity. The final mechanism, a one photon ionization of the negative acridine dye ions has been proposed by Lim. The mechanism has many features in common with the CTTS mechanism and requires further experimental work to substantiate its uniqueness. Thus, the problem in demonstrating the occurrence of photoionization among heterocycles becomes one of determining the appropriate mechanism of the process. In Progress Report No. 116 we have demonstrated that some compounds on exposure to ultraviolet light at 77°K produced colored intermediates. We suggested that photoionization occurs in those cases. However, the procedures used were unsatisfactory in producing measurable amounts of absorbances. 'Thus, it was decided to use an altogether different approach, luminescence detection, which would be inherently more sensitive than an optical absorption technique. Therefore, we will present our investigations of the luminescence behavior of indole, indazole, purine and tetra- phenylpyrrole (triphenylamine and aniline were used as referents). The tests we employ are designed to demonstrate the occurrence of recombination luminescence, whether it is produced in the forms of prolonged isothermal luminescence, infrared stimulated luminescence, or thermoluminescence. The time dependence of isothermal prolonged luminescence was described by Debye and Edwards as having an

intensity-time relation of the form  $I = ky$ , where  $k$  is a constant and proportional to the total integrated prolonged luminescence;  $t$  is time after cessation of exciting light, and  $M$ , a number having an unknown dependence on concentration, being very close to unity for very low concentrations of the test compound and decreasing with increasing concentration. This time dependence results from the diffusion-controlled migration following thermal excitation of trapped

electrons in the fields of cationic centers in rigid media at reduced temperatures. Skelly and Hamilton have shown that absorption of infrared light into the trapped electron absorption band causes migration of trapped electrons resulting in stimulated luminescence on recombination with a neighboring trapped cation. Finally, Daniels has shown that thermal stimulation by increasing temperatures causes recombination luminescence in the form of thermoluminescence. Typically, the luminescence observed under all of these conditions is the phosphorescence of the neutral compound. The experimental arrangement consisted of an intense UV light source, with appropriate filters for isolating the excitation wavelength, a light-tight housing for the optical detector and cell, and a high-intensity grating monochromator, along with photomultipliers, power supply, electrometer, and recorders. The actual arrangements are found in Figures 3, 4, and 5, with a legend of the components in Table 2. In Figure 3, the arrangement used in obtaining normal phosphorescence, fluorescence, or prolonged luminescence spectra is described. Figure 4 shows the arrangement used in obtaining emissions under infrared stimulation. Finally, in Figure 5 is shown the arrangement used to measure total luminescence during isothermal, infrared, or warm-up stimulation of the photolyzed glassy solutions. A demonstration of the resolution achieved by this apparatus can be found in Figure 6, where the emission spectra of benzene produced by 250 nm excitation in 5MP at 77°K is

demonstrated. Comparison with data given in Pringshen shows the position of the maxima to be correct to within  $\pm 0.8$  nm with a resolution of 10 nm. Higher resolution is possible. The reference curve shown below the benzene emission was obtained with pure JMP and demonstrates the absence of contaminating impurities, scattered light, or dewar emission. The lifetime of benzene phosphorescence was also determined as a test by shutting off the light source rapidly or flashing the General Radio Co. stroboscope and monitoring the decay on a recorder or oscilloscope. This result can be found in Figure 7. The lifetime obtained,  $4.7 \pm 0.3$  sec, is in good agreement with some recent work of Kalantar. As a further test of technique, the lifetime of the stroboscope flash was determined. The result of this test is found in Figure 8. ---Page Break--- -10- The half-intensity durations, and the decay times are measured as: low intensity, 2.74 sec duration and 1.84 sec decay; medium intensity, 3.0 sec duration and 2.24 sec decay; and high intensity, 5.3 sec duration and 3.14 sec decay. The relative intensities of the three levels shown in Figure 8 are proportional to the actual lamp intensities. The manufacturer quotes the duration as approximately 2 seconds shorter than those obtained here. This indicates that some undesired capacitances are present in our detection circuit. The presence of departures from linearity in the decay plot is consistent with this. Thus, emission lifetimes can be measured to some 10's of  $\mu$  sec with good accuracy. The results of the luminescence measurements on indole, indazole, purine, tetraphenylpyrrole, aniline, or triphenylamine in MTEF at 77° can be characterized by Figures such as No. 9 through 13. In general, if any of those compounds are exposed to the full output of a high-pressure mercury arc for times as low as 1 second, the decay of luminescences shows a time dependence similar to that found for indole in Figure 9. The overall time dependence can be expressed by the equation  $I =$

$A \exp(-t/\tau) + B t^m$ , 'The departure of the curve in Figure 9 at early times is a result of plotting the  $\exp(-t/\tau)$  function on a log-10 scale. Equations for the six compounds have been found for 5 second exposures and are expressed as: ---Page Break--- Compound Function Aniline  $T = 3.0\% \cdot 10^7 \exp(-t/4.8 + 0.3 \text{ sec}) + 3.8 \times 10^7 M \phi - 1.02 \text{ amp}$ , Indole  $I = 1.9 \times 10^{-2} \exp(-t/6.4 + 0.2 \text{ sec}) + 1.7 \times 10^7$  5 470-95 Indazole  $I = 6.0 \times 10^0 \exp(-t/3.5 + 0.1) + 3.6 \times 10^{-6} \text{ tugh}$  'Triphenylamine  $I = 1.6 \times 10^{-4} \exp(-t/1.8 + 0.3 \text{ sec}) + 5.0 \times 10^0$  4-0.85 Purine  $I = 5.0 \times 10^0 \exp(-t/1.6 + 0.1 \text{ sec}) + 2.8 \times 10^0$  77 48% Tetra-phenylpyrrole  $I = 6.3 \times 10^7 \exp(-t/1.6 + 0.2 \text{ sec}) + 2.5 \times 10^{-6}$  70.92 'The concentrations of all compounds are of the order  $10^{-4}$  in mrxF. The rapidly decaying portion of the

mathematical function is the normal first order decay function, and the values of "Y" obtained here agree well with the literature values where available. The prolonged luminescence is described well by the Debye-Edwards function. There is no departure from this function for a time range from 90 seconds to at most 3 hours later when the photo multiplier dark current is reached. There is a good correlation between the magnitude of the phosphorescence decay constants and the magnitude of the Debye-Edwards proportionality constant. That is, the greater the lifetime, the greater the prolonged luminescence. This suggests the involvement of the triplet state in the photoionization of these compounds. ---Page Break---

2- In figure 10 is found the emission spectra obtained during a period from 90 seconds to six minutes after the cessation of the exciting light for indole, indazole and aniline (with a 40 nm band pass). The spectrum obtained for indole agrees with that obtained by Freed and Siantre, and that of aniline with the spectrum of Lewis and Kasha. Thus, as pointed out earlier, the phosphorescent state of the neutral is produced by recombination. The effect of infrared stimulation on the prolonged luminescence of a 2 x 10<sup>-4</sup> M solution of aniline is found in Figure.

LL, The effect of infrared stimulation is to change the value of the Debye-Edwards exponent from 0.8 to 1.6. This observation is consistent with effects noted by Skelly and Hant<sup>124</sup>. We also observe an increase in the Debye-Edwards exponent during iF stimulation of indole and indazole solutions. The dependence of the total recombination luminescence on the intensity of exciting light is shown in Figures 12 and 15 for aniline and indole as the ratio of the square of the total exciting light intensity  $I_{ex}$  divided by the integrated luminescence  $E$ . If a biphotonic photoionization involving the triplet state occurs, then the process can be described by the following mechanism.

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B- Aniline, at 1)  $A \xrightarrow{h\nu} A^*$  2a  $A^* + \text{nila} \rightarrow A^+ + e^-$  (trapped 3) at  $+e^-$  par 4)  $(e^-)_{trapped} + \text{heat (or } h\nu_{ar}) \rightarrow e^-$ . A represents a neutral compound,  $A^*$  its excited triplet state, and  $A^+$  its cation.  $\phi$  represents the quantum yield of intersystem crossing and the product of  $\phi$  and  $I_g$ , the light absorbed by the neutral, is the rate of populating the triplet state.  $I'_t$  is the intensity absorbed by the triplet state. The trapped electron is indicated by  $(e^-)_{tr}$  and  $e^-$  is a free electron. These equations can be solved by the steady state approximation if we assume that the overall rate of repopulating the triplet state, by steps 3 and 4, is very much slower than the rates of formation. This is a justifiable approximation, since we observe that a one second exposure to the exciting light produces cation and electron pairs that require two to three hours to recombine. The particular solution we present here requires weak absorption - which we can control by concentrations, and ideally narrow wavelength band absorptions. Narrow band absorptions were not possible, so that extinction coefficients referred to are the average over the absorption bands. The solution is

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$J = I_0 \frac{\epsilon' \phi}{\epsilon + \epsilon'}$ . Z refers to the total number of ionization events produced during the excitation period  $\Delta T$ ,  $I_0$  is the incident exciting light.

intensity;  $\epsilon$ , and  $\epsilon'$  refer to the extinction coefficients of the neutral and triplet states respectively,  $d$  the optical path length; i.e. 1 cm, and 'T' is the natural lifetime of the triplet or  $(\tau + 5)$ . Thus, the relationship requires that  $J$  have a linear dependence on the exciting light intensity. We take the value of the quantity  $J$  to be proportional to either the total amount of prolonged luminescence, the total amount of infrared stimulated luminescence, or the total amount of thermoluminescence. This quantity, measured in coulombs of photomultiplier current, is plotted in Figures 12 and 13, according to the above expression, and the data is obtained from the three forms of recombination luminescence. The ratio  $J/Z$  is linear with  $I_g$ , but is plotted on a semi-log scale for convenience. The data referred to as electrical integration was an attempt to accumulate the photomultiplier current on a capacitor, in contrast to a manual method of integrating the photomultiplier current vs. time from strip chart recordings by a graphical method. The TZ acquired in this fashion is very

much lower than from the other methods. This is not to be taken as evidence that considerably less recombination occurs during warming but rather that the capacitor used in the measurement ---Page Break--- -35- lost a considerable fraction of its accumulated charge through leakage during the course of the experiment. Comparative data for the Z obtained during warming showed that the electrical method gave data lower by two orders of magnitude than the manual integration method. In Figure 12, the isothermal and infrared stimulation data were performed with a concentration of  $2 \times 10^4$  aniline, while the thermoluminescent data for aniline were obtained with a concentration of the order  $10^7$ . The data presented in Figure 15 were obtained with an indole concentration of  $5 \times 10^7$  M. The existence of the Debye-E $\rightarrow$ wards intensity dependence, the effects of infrared stimulation, and the thermoluminescence indicate the occurrence of photoionization.

among these compounds. The existence of a squared intensity dependence in agreement with a biphotonic mechanism involving the triplet state indicates the path by which photoionization has occurred in the cases of indole, indazole, and aniline. The occurrence of biphotonic photoionization in aniline has been observed previously.<sup>2</sup> as Section B: Theoretical work 'The theoretical work has continued along the basic lines indicated previously. One objective of this part of the program is the calculation of excitation energies of radical anions and cations of heterocyclic molecules, to aid the assignment of experimental spectra. The other objectives include the general features of the electronic structure of such species, and work has also been begun on electron-molecule interactions. ---Page Break--- see T. Electronic spectra of Heterocyclic Radical Cations and Antong The results which have been obtained for the doublet-doublet transitions of the radical anions of pyridine, pyrimidine, pyrazine, and pyridazine are fully described in the appended article, which has been submitted for publication. These calculations use the Pariser-Parr-Pople self-consistent field method, with and without Configuration Interaction. The results can be summarized by saying that an excellent agreement was obtained with experimental and theoretical results of other groups of workers, as well as with the experimental work reported earlier. The use of limited Configuration Interaction does not improve the agreement with experiment, in harmony with recent theories. In addition to the above calculations, the radical cations of the following molecules were examined: pyrrole, furan, thiophene, pyridine, pyrimidine, pyrazine, and pyridazine. A very much poorer agreement with experiment is obtained for the radical cations. 'The Pariser-Parr-Pople method uses the pi-electron approximation, so that these results question its validity for such radical cations. For the anions, the unpaired electron is certainly in an antibonding p-orbital, and the

Approximation appears to give good results. However, for the radical cations of heterocyclic molecules, it is by no means certain whether an electron has been removed from a sigma (non-bonding) or from a pi-orbital. Pyrrole is the only cation which has been examined that has no non-bonding electrons available, but ---Page Break--- -- the results for the pyrrole cation are equally bad. This indicates that, as well as taking account of the sigma-electrons, it may be necessary to specifically include the sigma-pi interaction terms. These give rise to a reorganization in the sigma-framework on ionization of a pi-electron, which will significantly affect the stability of the radical cation. This point is currently being investigated. No method exists at present, apart from all ab initio calculations, which includes this type of interaction. II. Valence-Bond Calculations on Heterocyclic Systems These calculations use cyclopentadiene as a preliminary model, and aim at the electronic structure of simple heterocyclic molecules and radicals, using a non-empirical valence bond method, as described in previous Reports. During this year, work has been principally on the modification of a program originally written by Dr. Palmieri (University of Bologna). This uses as input the atomic integrals whose calculation was described in Technical Progress Report No. 3 (PRNC-116). All possible determinantal basis functions of a given multiplicity are generated, and

the integrals among them evaluated using Löwdin's density matrix formation for non-orthogonal Slater determinants. III. Hetaryne Intermediates In collaboration with Dr. W. Adam (U of Puerto Rico) and Dr. R. Hoffmann (Cornell U.), a study has been completed of the 'hetaryne intermediates' formed by removal of hydrogen atom(s) from heterocyclic molecules. This work has been accepted for publication, and a copy is appended to this Report. The electronic structure of these ---Page Break--- -18 = intermediates was examined by the Extended Hückel Theory, which includes sigma-

and pi-valence electrons. The trends in stability correlate very well with experimental data and were analyzed in terms of orbital splitting patterns. IV. Electron-Molecule Interactions Work is beginning on the calculation of exact molecular potentials between an electron and a many-electron molecule, in the form of a multipole expansion. This potential is to be used in investigations of electron-molecule attachment processes. ---Page Break--- 3. a 20. ne --- 'BIBLIOGRAPHY a) A. Grimieon, Technical Progress Report No. 1, PRIC No. 88. b) As Grimieon, Technical Progress Report No. 2, FRNC No. 99. c) A. Grimison and G. A. Simpson, Technical Progress Report No. 43, PRNC No. 116. Re Ly Letman and B. Wallace, p. 43, "Electronic Aspects of Biochemistry," Academic Press, N.Y., (1964). R. J. Fleming and R. M. Kerr, Nature 206, 119 (1965). B. B. Singh and A. Chatlesby, Photochem. and Photobiology, 5, 63 (1966). J. W. Longworth, R. O. Ran and R. G. Schulman, J. Phys. Chem. 45, 2930 (1956). G. M. Andros and M. Calvin, Biophysical Jour. 2, 227 Suppl. (1963). J. B. Cook, J. Pe Elliott and S. J. Wyard, Mol. Phys. 23, 49 (1967). I. Sooner and A. Pihl, Acta Chem. Scand. 20, 266 (1966). G. Stein, p. 250, "The Solvated Electron", Advances in Chemistry No. 50, Washington, D.C. (1965). K. D. Cadogan and A. C. Albrecht, J. Phys. Chem. 72, 929 (1968). W. A. Gibbon, G. Porter, and M. I. Savadatti, Nature 205, 1355 (1965). 12. Es Cs Lim, C. P. Lazzarro and G. W. Swenson, J. Chem. Phys. 43, 970 (1965). P. Debye and J. O. Bavards, J. Chem. Phys. 20, 236 (1952). D. W. Skelly and W. H. Hamill, J. Chem. Phys. 43, 3497 (1965). F. Daniels, D. F. Saunders, "Thermoluminescence of Crystals, Final Report", University of Wisconsin (1951). B. Pringshein, "Fluorescence and Phosphorescence", Interscience, Wiley, (1961). I. B. Martin and A. H. Kalantar, J. Phys. Chem. 72, 2055 (1968). I. S. Freed and W. Selmre, Science 128, 1341 (1958). ---Page Break--- of a 19. G. M. H. Lewis and M. Kasha, J. Am. Chem. Soc. 66, 2100 (1964). 20. Js tt.

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Table 1: COMPOUNDS IRRADIATED ATTPX GIVING ERMOWINESCNE count se inenity serine strong haine Stora free wae canis Wk ential Sirens Eentrasie wor Stoo 'Sore Srenoutc Stone pone Storm oan eat Ein ne Foren ne Guanine ae tenaoprorn We Cisne weak tna west Imale Wet tna ae Snehyeyine West Lightning Wot Fore Strong Prratle war rea fee rie 5 Sou ode wea" Stern 4 Tease ye wa Thorne = Tovey aie % 2A 54rphen inant PD wat Tiymin Wat tren bt xanthine Ky ovate na, ta eat

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## SR OF GAMMA = IRRADIATED CYTOSINE

Figure 1 — aerimtive ctr

## ESR OF GAMMA IRRADIATED URACIL

Figure 2

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### TABLE 2: INSTRUMENT DESCRIPTION FOR FIGURES 3, 4 AND 5

- A. General Electric AH6 high pressure mercury arc
- B. Arc power supply
- C. Ni-Co solution filter
- D. Baird Atomic interference filter 254 nm
- E. Slit
- F. Photographic shutter
- G. Dewar box
- H. Quartz dewar
- I. Quartz solution cell
- J. Stroboslave 1539A flash lamp
- K. Flash power supply and trigger unit
- L. Bausch & Lomb 603AB high intensity grating monochromator
- M. Wavelength drive unit
- N. Emi 9526B photomultiplier
- O. Fluke 4128 high voltage power supply
- P. Keithley 610B electrometer
- Q. Leeds & Northrup 10 mV recorder
- R. Tektronix 561A oscilloscope
- S. RG-1000 Jena filter
- T. Boxtor Corp. 5900 variable intensity tungsten lamp

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he 9 sansa 4 ean3za "on 'azn 30) 70H SoMDSINT Sv anon yrs RDS

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6 eanSya

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eandya, ue) ALISNAINE SALLY ot anita Vulo3dS ONDSINIWM G3ONOTOUd oe oo ws ---Page Break--- ---Page Break--- ---Page Break--- -2- APPENDIX 1. Submitted to the Journal of Physical



Chemistry, January, 1969 BY PYRIDINE AND THE DIAZINES IN  $\gamma$ -RADIOLYSIS: 'THEORETICAL CONSIDERATIONS' A. Grinison, G.A. Sixpson, M. Trujillo Sánchez, and J. Jhavers Puerto Rico Nuclear Center, \*\* and Departments of Chemistry and Physics, University of Puerto Rico, San Juan, PR., 00935 Abstract:- Absorption spectra characterizing the radical anions of pyridine, pyrimidine, pyrazine and pyridazine have been produced by  $\gamma$ -radiolysis of the parent compounds in a dimethyl-tetrahydrofuran matrix at 77°K. These spectra are in good agreement with those obtained by chemical reduction or electrolysis, but some additional transitions at longer wavelengths have been observed. Pariser-Popper-Pople calculations of 'the theoretical doublet-doublet transitions of the radical anions yield good correlations with the experimental transitions. 'The best correlation is obtained by not including configuration interaction, at least for a very limited number of configurations. Irradiation of pyridine in 3-methylpentane leads to a thermoluminescence assigned to the phosphorescence of pyridine. 'Presented in part at the Second Inter-American Radiochimia Conference, Mexico City, Mexico, April 1958. \*\*Puerto Rico Nuclear Center is operated by the University of Puerto Rico for the U.S. Atomic Energy Commission under Contract AT(H0-1)-1833. ---Page Break--- -30- Our primary interest in the production and characterization of sonic intermediates formed by the  $\gamma$ -radiolysis of heterocyclic structures. This identification can provide important information on the effects of radiation on biological systems. The technique being used is that of isolation in a solid matrix at liquid nitrogen temperature.) From the es 2) A.M. Bass and H. P. Broide, "Formation and Trapping of Free Radicals", Academic Press, New York (1960). Chemical viewpoint, perhaps the most intriguing aspect of

such work is the extreme simplicity of the final processes forming these intermediates. Thus the work of Hamill and co-workers has indicated how radical anions can be formed by attachment of low energy electrons to solute molecules. Radical cations can apparently be produced by a simple positive charge exchange between the matrix and the solute molecule. In a previous study, Grinison and As Sinfoon have described one radiolytic technique suitable for the production and stabilization of radical cations. By this means, absorption maxima measured at 77°K were assigned to the radical cations of pyridine, pyrrole, and thiophene. In general, the production of radical anion intermediates is experimentally much less difficult. Hush and Hopton have reported the absorption spectra of the radical anions of pyridine, pyrazine, pyrimidine, and pyridazine, produced by reduction with sodium metal in tetrahydrofuran at room temperature. Kinnel and Strouse reported the optical spectra of some radical anions, produced by electrolysis in liquid ammonia solutions. The observation of a maximum at 330 nm from alkali metal solutions in anhydrous pyridine at room temperature is in good agreement with the earlier reports for the pyridine anion. The present paper describes our results on the effects of irradiation on the optical spectra of pyridine and the diazines in organic.

glasses at 77°K. The major process observed under these conditions is shown to be the attachment of an electron to the neutral azine molecule to form the radical anion. The experimentally observed optical transitions from the different experimental techniques are shown to be in excellent accord. Finally, the semi-empirical theoretical excitation energies for the radical anions, calculated by us, by Hush and Hopton, and by Kimsel and Strauss, are compared with the experimental values. ---Page Break--- -32- Experimental Techniques Pyridine, Eastman Spectrograde, was distilled from barium oxide before use in absorption spectra determination. For emission studies, pyridine solutions were prepared either from the distilled pyridine or from a middle fraction of the main peak of samples injected on a 6 ft. GIC column at 80°C. Good separation of pyridine and its luminescent impurity, pyrazine, was achieved under these conditions, see (9) C.J. Bradey, J. Chem. Phys. 24, 572

(1955). Pyrazine, pyridazine, and pyrimidine were best commercial grade, and were used without further purification. 2-Methyltetrahydrofuran (MTHF) was purified by passage over alumina and stored under vacuum in a storage vessel containing Na-K alloy. 3-Methylpentane (MP), Phillips Research Grade, was passed over a silica gel column, then stored under vacuum over Na-K alloy. Solutions of required concentrations were prepared from these purified solvents on the vacuum line by standard techniques.  $\gamma$ -Irradiations were performed in the FRIC 2700 curie  $^{60}\text{Co}$  source, using the Fricke technique for dosimetry. Absorption spectra were obtained with the apparatus and techniques described previously. Optical bleaching was effected with a 250 watt quartz-iodine lamp and appropriate transmission filters. Emission spectra under thermal stimulation were obtained either with an Aminco-Bowman spectrofluorimeter operated with a 100 nm band pass and a 1728 photomultiplier, or a motor driven Bausch and Lomb "High Intensity" monochromator (No. 33-06-25) at 50.

mm band pass and an EMT 95263 photomultiplier. The sample cell and optical device were maintained ---Page Break--- -33- to warm up in the spectrofluorimeter by removing the liquid nitrogen. Emission spectra were then obtained by repeated scanning of the spectra at a rate of one scan (200-700) per minute. The heating rate under these conditions is linear during the first five minutes, at approximately  $20^\circ\text{K}/\text{minute}$ . THEORETICAL CALCULATIONS 'Theoretical excitation energies and oscillator strengths corresponding to doublet-doublet electronic transitions in the azine anion have been carried out using the semi-empirical Pariser-Parr-Pople (PPP) self-consistent field technique.' Recent non-empirical calculations 20) R. G. Parr, "The Quantum Theory of Molecular Electronic Structure", W. Benjamin, N.Y. 1953. on the excited states of the ethylene molecule, including OT interactions 2a) 8. H. Dunning and V. McKey, J. Chem. Phys. 47, 1755 (1967). have given a sorely-needed justification for the reduction of the pi-electron integrals in the PPP method below the theoretical values. This can be considered as taking account of the effect of screening of the pi-electron repulsions by the pi-electron distribution. In heterocyclic molecules, there is no reason to expect the similarity between radical anion and radical cation spectra suggested for the alternate hydrocarbon systems. In particular, in calculating the electronic properties of the azine radical cations, some thought must be given as to whether the missing electron has been removed from a lone pair orbital or from a pi-orbital. However, for the radical anions, the additional electron enters a pi-antibonding orbital, so that the use of a pi-electron calculation in predicting electronic excitations is justified. Input wavefunctions for the PPP calculation were obtained from Huckel calculations on the appropriate neutral heterocyclic molecule, using

conventional parameter values. As a variant on this approach in some preliminary calculations, wavefunctions from a 10-iteration W- technique calculation on the actual radical anions were used as input (15) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", John Wiley and Sons, Inc., NY, 1961, pp. 115, to the PEP program. However, the comparative "weakness" of the W- technique in making electron density corrections to the Coulomb integrals was shown up immediately. Thus, after one iteration of the PPP calculation, identical results were obtained from Huckel and @-input wavefunctions. The parameter values which were used are listed in Table 1, in the PPP calculations. A limited configuration interaction (CI) was considered for the ground state and 5 excited doublet states. The diagonal and off-diagonal elements of the relatively limited configuration interaction were not surprising (2) N. L. Allinger and W. Stuart, J. Chem. Phys., 47, W611 (1957). that CI actually caused a slight deterioration of the agreement between theory and experiment. The CI values are therefore not reported in this paper. RESULTS AND DISCUSSION The spectrum shown in Figure 1 illustrates the absorption bands produced on radiolysis of MTHF

solutions of pyridine. The 1200 nm band corresponds to the position of the trapped electron band in pure MTHF. The band at 340 nm is characteristic of pyridine in MTHF. Liberation of electrons by photolysis into the trapped electron band is expected to increase authentic radical anion absorption bands, as the liberated electrons are captured by unreacted neutral solute molecules. Bleaching the trapped electron band in irradiated pyridine-MTHF solutions causes an increase in the band near 340 nm, as shown in Figure 1. Addition of  $2 \times 10^{-3}$  trifluoroethanol, an electron scavenger, to the pyridine-MTHF solution prior to irradiation results in the non-appearance of the 340 nm band. Figure 2 shows the dependence of the absorption at 340 nm and at 1200 nm on the initial pyridine.

concentration, The net absorption at 1200 nm falls off very sharply with decreasing pyridine concentration, reaching a limiting (but non-zero) value at about  $1 \times 10^{-7}$  M pyridine. This suggests that the efficiency of pyridine for capturing electrons against solvent traps is fairly high. Simultaneously, the 340 nm absorption decreases but reaches a limiting value at a greater pyridine concentration. This is due to a decrease in the underlying trapped electron and associated methyltetrahydrofuran radical absorptions in the 340 nm region, counteracted by a build-up in the pyridine 540 nm absorption. At concentrations greater than  $4 \times 10^{-2}$ , a component of the absorption can also be observed with a maximum at 500 nm. Only in the concentration region  $8 \times 10^{-7}$  to  $4 \times 10^{-2}$  does bleaching the trapped electron band result in an increase in the 340 nm band. The fact that the 340 nm band can be increased on bleaching the trapped electron band and is decreased on addition of an electron scavenger demonstrates the presence of an anionic intermediate of pyridine. This is believed to be the pyridine radical anion, formed by the attachment of an electron to pyridine. The assignment of the 340 nm band to the pyridine radical anion is supported by a number of independent observations, discussed below. However, the fact that an increase in the 310 nm absorption following trapped electron bleaching does not occur at high pyridine concentrations requires some discussion. One explanation is to assume a weak optical transition of the pyridine anion at wavelengths greater than 1000 nm, which can give rise to a photo-ejection process. Thus, the bleaching process at pyridine concentrations greater than  $4 \times 10^{-7}$  would cause two escaping processes: capture of electrons released from matrix traps and photo-ejection from pyridine anions. Where there is a low trapped electron yield, the photo-ejection process.

dominates the capture of trapped electrons released by photostimulation, and a decrease in the 340 nm absorption results. Supporting evidence for the existence of a long wavelength transition of the pyridine anion may be taken from the appearance of the limiting concentration yields of the trapped electron band in Figure 2. The non-zero value of the absorption suggests that the extinction coefficient of the pyridine anion at 1200 nm may be as high as 204 of the value at 340 nm. To confirm the assignment made in MTHF, and to investigate possible emission from irradiated samples, a series of studies were made in a 3-methylpentane (MP) matrix at 77°K. The advantages in using this matrix are that the trapped electron band occurs at a longer wavelength (2,700 nm), and that recombination luminescence has been observed. D. W. Skelly and W. H. Hamill, *J. Chem. Phys.*, 43, 3497 (1965), and W. Hy Hani, private communication. A. Dérouléde and F. Kieffer, *Nature* 215, 1475 (1967). See G. Peerey et al., *Acad. Sci. Paris*, 264, 1013 (1957). Figure 3 shows the absorption spectrum at 77°K following radiolysis of pyridine in MP glass. In addition to the trapped electron band, absorption maxima are observed near 1200 nm and at 360 nm, with an inflection near 500 nm. All of these bands disappear on warming the sample. If the sample is allowed to decay isothermally in the dark for 8 hours, the trapped electron band is reduced to less than 10% of the original value. Simultaneously, the bands at 1200 and 360 nm become more pronounced, as shown in Figure 3. The absorption at 1200 nm after decay, which is clearly in

excess of 10% of the original absorptions, confirms the existence of a long wavelength transition of the pyridine intermediate, suggested earlier. The failure of the 350 nm band to increase after the escape of trapped electrons suggests the presence of an additional intermediate which acts as an electron.

Scavenger in the MP matrix, some preliminary luminescence observations of the pyridine MP system may be reported here since they are pertinent to the discussion of pyridine intermediates and are novel in their significance. On warming solutions of irradiated pyridine-MP glasses, luminescences were observed. In addition to the solvent emission band at 425 nm, a structureless emission band at  $355 \pm 10$  nm was observed, lasting up to 10 minutes after removal of the liquid nitrogen. This emission band was absent in pure MP glasses. Use of GIC purified pyridine gave the same result. The warm-up luminescence obtained from an irradiated MP glass containing pyrazine, the luminescent impurity in pyridine, had a maximum at  $380 \pm 5$  nm. Phosphorescence of pyrazine occurs near 380 nm. Therefore, the emission observed with pyridine-MP glasses is associated only with pyridine and not a contamination. The wavelength corresponding to the maximum of pyridine phosphorescence can be estimated from the oxygen perturbed singlet-triplet absorption spectra to be greater than or equal to 337 nm. Thus, the emission may be due to pyridine phosphorescence following recombination reactions. The direct phosphorescence of pyridine via intersystem crossing from an excited singlet state has apparently not been reported yet. The above interpretation requires the presence of the pyridine cation radical, which we have reported previously to have a maximum at solely 380 nm. The observed band at 360 nm may thus contain unresolved components of both the anion radical (340 nm) and cation radical (380 nm) absorptions. The formation of both anionic and cationic intermediates in MP has been suggested by other workers. The decrease in the 360 band on decay of the trapped electron band would then be attributable to the disappearance of the cation.

component, The long lifetime of the observed emission band suggests that, in addition to electron-cation recombination, Phosphorescence can be produced by anion-cation recombination processes at higher temperatures. Table 2 gives a summary of the transitions attributed to the pyridine radical anion in this work, and the experimental assignments of Hush and Hopton and Kimmel and Strauss. The agreement on the position of the near UV band is excellent, considering the very different experimental techniques. Thus Hush and Hopton's (HH) results refer to solution in tetrahydrofuran at room temperature, and Kimmel and Strauss' results refer to Miguta emonta solutions. These other workers observe additional shorter wavelength transitions which cannot be verified under our experimental procedure. The theoretically predicted doublet transitions of the pyridine radical anion are collected on the right of Table 2. Our results, which do not include Cl, give high oscillator strengths as expected, but are otherwise in better accord with the experimental results. The band at 3.7 eV is calculated at 4.29 eV, whereas KS results give 3.07 eV, and HH have no corresponding band. The band observed by HH at 5.08 eV and by KS at 4.75 eV is calculated by Hit at 5.25 eV (allowed band), by YS at 5.26 eV, and by us at 5.40 eV. The suspected band at 2.5 eV (500 nm) corresponds to a predicted pyridine anion absorption at 2.66 eV or at 2.25 eV (this work). Finally, our calculations alone suggest a forbidden long wavelength transition. By using the extinction coefficient of HH for the 3.37 eV band, we estimate a G value of 2.7 for the production of the pyridine anion at high pyridine concentrations. PYRAZINE: Figure 4 shows the absorption spectrum at 77° after  $\gamma$ -radiolysis of Pyrazine in a MTP glass, and the result of bleaching the trapped electron band. An absorption maximum is produced near 345 nm, and in a suitable concentration region, an increase in this absorption is produced by bleaching.

the treppea electron band. The concentration dependence of these bands has not been studied extensively, but it has been observed that the position of the Amex increases with increasing initial concentration of pyrazine at constant dose. Specifically, an Amex of 320 nm is found at a concentration of  $1 \times 10^7$ , which increases monotonically with concentration to a max of 345 nm at a concentration of  $\sim 10^8$ . We attribute this effect to an artifact of the technique of determining spectra. Difference spectra are obtained by subtracting the initial glass spectrum from that after irradiation. This assumes no decrease in the near UV bands of the parent heterocyclic during radiolysis. Pyrazine has been found to have an Amex of 315 nm in MTP, in comparison with the value of 328 nm in cyclohexane. This marked blue shift characterizes the  $n^*$  nature of the transition. M. Kasha, "A Symposium on Light and Life", Johns Hopkins Univ. Press, Baltimore, 1961, p. 31. Thus, depletion of pyrazine at low initial concentrations can cause a shift in the apparent position of the nearby absorption of the pyrazine intermediate. This was demonstrated further by repeated irradiation of the same solution to successively higher doses. On obtaining difference spectra in the usual manner, a shift in the  $\lambda_{max}$  to shorter wavelengths with increasing dose was observed. The position of the near UV band of the radiation-induced intermediate of pyrazine is thus assigned to be equal to or greater than that observed at the highest concentration studied. As a result of the above observations, an absorption maximum at 345 nm is assigned to the anionic intermediate of pyrazine. This is believed to be the pyrazine radical anion, formed by electron attachment to pyrazine. The general features of the concentration dependence of the spectra show qualitative similarities to that observed for pyridine. At high concentration ( $7 \times 10^7$ ), a maximum is resolved at 400 nm. Also at these concentrations the 340 band

Decreases on bleaching the trapped electron band. This suggests the existence of an unobserved long wavelength transition of the pyrazine anion. Table 3 compares the above assignment for the pyrazine radical anion with the results of 12° and x5. Again, there is substantial accord among the three groups of investigators for the near UV band, remembering that our experimental value represents an upper limit to the transition energy. Again, the theoretical excitation energies provide a reasonable account of the observed transitions. All three calculations give excellent accord with the high energy transition near 5 eV. For the band near 3.5 eV, KS (3.15) are in good agreement, whereas our value of 1.70 eV is very high, and that of Hi is very low (2.90 eV). This latter value may be related to the suggested 2.45 eV (500 nm) band, for which we calculate 2.28 eV. A forbidden long wavelength transition is predicted near 0.5 eV. By using the extinction coefficient of Hi for the near UV band, we estimate a G value of 1.7 for the production of the pyrazine anion at high pyrazine concentrations. PRDGDE Figure 5 illustrates the absorption bands produced by radiolysis of pyrimidine in MTHF at 77°K, and the result of bleaching the trapped electron band. An absorption maximum is produced near 320 nm, which is increased by bleaching the trapped electron band for a suitable initial pyrimidine concentration. As for pyrazine, a shift was observed in the position of the maximum with increasing initial pyrimidine concentration at constant dose. This effect is again attributed to depletion of the underlying neutral pyrimidine absorption. The band is assigned a maximum of 320 nm, in MTHF at 77°K. For concentrations above  $2 \times 10^7$  M, a further absorption band can be resolved near 400 nm. Table 4 compares our results for the pyrimidine radical anion with those of Hf and 13. Again, our experimental transition energy for the near UV band is very slightly higher than the values of these other workers, for the reason explained.

Earlier, our theoretical calculation gives a predicted band at 4.04 eV, in better accord with the experimental value of about 3.8 eV than the result of Hi (2.8 eV) or of KS (3.01 eV). For the band near 5 eV, the values of HH (5.09 or 5.47 eV), those of KS (5.36), and our value of 4.73 or 4.94 eV are all in reasonable accord with experiment. In addition, the existence of a transition near 3 eV

(400 nm) reported by us is supported by calculated transitions at 2.86 eV (Hi), 3.02 eV (KS, but may refer to the 3.8 eV band), and at 2.53 eV (this work). A virtually forbidden long wavelength transition is again predicted. Using the extinction coefficient of Hi for the near UV band, we estimate a G value for the production of the pyrimidine anion of 2.1 at high pyrimidine concentrations.

---Page Break--- Figure 6 shows Pyridazine in absorption bands produced by radiolysis at 77°K and the result of bleaching the trapped electron band. An absorption band is produced with dex at 35; intensity is increased on bleaching the trapped electron band, radical anion. Figure 6 also shows at 900 nm, and between 800 and 700 nm. The data in Table 5 indicate the excellent agreement of the UV band of the pyridazine radical anion among the different groups. Our theoretical excitation energy of 4.54 eV does not agree very well with the experimental value of 3.5 - 3.6 eV. The value of XS (3.20 eV) is satisfactory, but Hi have no closely corresponding value. The band found by Hi at 5.13 eV is satisfactorily accounted for in all three calculations. In addition, the possible existence of bands at 2-3 eV (410-700 nm) and at 1.75 eV is partly supported by a calculated band at 2.73 eV (ii) and at 2.15 eV (this work). Using the extinction coefficient of Ei for the near UV band, we estimate a G value of 0.8 for the production of the pyridazine radical anion. The results of these investigations, taken jointly with the measurement of authentic radical anion spectra by two other groups of workers, demonstrate the formation of the azine radical.

enters {2 radiolysis at 77°K by the electron attachment process Azine + e<sup>-</sup> → (Azine)<sup>•-</sup>. spectra of the four azine radicals The experimental absorption ---Page Break --- = us. are therefore fairly well established, the reasonable record between the experimental transitions and the theoretical transitions, in the f-electron approximation, confirms that the additional electron enters a 7\* antibonding level. In the present calculations, no direct account was taken of the T-reorganization expected as a result of this additional electron. We feel that specific inclusion of this effect would provide a more adequate account of the electronic structure of the radical anions, and are currently investigating this possibility. The present thermoluminescence results suggest a pyridine phosphorescence near 305 nm. If this assignment proves correct, then a fruitful area of spectroscopic investigation will become possible. Since many compounds have little or no phosphorescence, such as pyridine due to its negligible intersystem crossing efficiency, the production of triplets (2h) J. Lemaire, J. Phys. Chem. 71, 612 (1957). --- via ion recombination may well provide the only method of characterizing the phosphorescence. Extensive work is in progress not only to substantiate the pyridine emission, but also the thermoluminescence from other non-phosphorescent compounds. ACKNOWLEDGMENTS this work was supported by a research grant from the Division of Biology and Medicine of the U.S. Atomic Energy Commission. We also wish to acknowledge the kindness of Professor Hush and Professor Strais in communicating unpublished results, to thank Professor Hontil for helpful discussions. ---Page Break --- 'TABLE 2 PARAMETER VALUES IN PARISER-PARR-POPLE CALCULATIONS Molecule Pyridine, Pyridine Radical Anion Furezine, Pyrazine Radical Anion Pyridine, Pyridine Radical Anion Pyridazine, Pyridazine Radical Anion Coulomb and Resonance Ky = -5.865 Hoge Hog = -2.535 ig, Hog = -2.374 iy, = -2.303 Hy = -2.62 Tigg = -2.29 Hygy \* -52.502 Hoar Haz» Hess 2

gg" "6 Hoy = 2.62 Yop \* 2.29 Hygit ~50.736 Byp © -2.862 Hy > Hyg = 2.610 Hy, = -2.550 Roy = -2.62 gg = -2.29 Figg = 048.755 Hopp Hg = -2.595 Byyy gg \* -42.to3 Bygy © -2.25 Roy, © -2462 Bigg = -2.29 Repulsion Integrals (ev) a) = 32.310 fe), (jee) TIO ae y eg) \* = 5.608 22/38), 03 CH), (04/5), 'ul), 1» (ev de efi (33/55), (22/55), (33/66) = 4.950 (Qiai/iai) = 12.340 fes/e2) = 11,230 za), (11/66), (5/88), On), On/5) (al, 22/55) = 540: (22/66), (33/55) = 5. 3° ray/iat) = 22,340 lectoc) = 11.330 "Gal, (22/68), (22/53), = 75776 5 2 4.989 3/55), (33) af 4 eres, "diy = 54560 22/55) 1/55), (65/68) = 1.555, ae Bi =e en 55, By, fe 1 fe (44765) = 950 ---Page Break--- =u. TAB 2 TRANSITION

ENERGIES (eV) FOR THE PYRIDINE ANION Experimental values Calculated values a7 This work 6 Rett This work 026.000, 25 266 Loon 2wioy 370m) 3.46LoM) 3. 30700) 4294195 46.0 ania 5.05 coon 50.17 5.08 20) 5 B80 5.25.00 (scillator strength values in parenthesis. TABLES TRANSITION ENERGIES (eV) FOR THE PYRAZINE ANION Exgerimenta Cateuites values fag RET 6 RT 290.068 3aoca 3580m 3 315 055 anisa 56.29 496029 5.211) 52m 3s4L2e Oscillator strength values in parenthesis. TABLE 4 TRANSITION ENERGIES (eV) FOR THE PYRIMIDINE ANION imental values atelated valves TT sere Re6 RT This work 29.003) a 2.85 com 253085 315LOM = -ATL06) 89 ROL) — 4084710 asrase 51429 5.0L 5.3601) ATL 5.47 C060 a mciR Oscillator strength values in parenthesis, ---Page Break--- = 48 = TABLE 5 TRANSITION ENERGIES (eV) FOR THE PYRIDAZINE ANION Experimental values Calculated values Ref. 6 Ri This work Ref. 6 Ref. 7 This work LIS 0.27 (000, 23 2.73 .05)) 213.6169) 3.521.052) 3.64 (065) 35 3.20 032) 4,54 (185) 4.59 (030) 4B 1.235) 5.13 (182) 5.24062) 5, 63 (125) 5.27 (210) Oscillator strength values in parenthesis. oo. scorpion spectrin of an rvttte aeation of Pyridine, id 830° fa ne. attr tne ot 6 eof, LA er 5 eines Bet b= 690 mm (Coming no, 652.64 fiser) os 4 L Toso T2060 1300 am Figure 1 ---Page Break--- ah e Region where uv 0-0] band increases on ir bleaching Les Figure 2

Concentration dependence of absorption bands produced on radiolysis of Pyridine in TIP « ° dose = 2.9 x 20 ov/t © optical density at 30 ma, os 4 optical density at 1200 a, 00, Figure 3 of rine ho x 20% steer toe of 228 0? t/t, ---Page Break--- on, 20] serpice spectrin of orale patient 'of Pyrazine, 2.0 x 10°%H sn Mere. ts ater tne ce 12 rf er 15 mins each 972000 m, 12] (estets no-texo fuer) 2 4 L L 1 1 L L 700 300 305 7500 20d 400 am Figure 4 00, 1 'Absorption spectra of an teretinted solution of Pyrtnttine, 5.2 5 74 So He, etter aone of 3.8 3 ef stter 2 ute Beach, 29 1000 mm, (eanote roaioo einter) 300 Figure 5 ---Page Break--- - ol senate of ridacne, 045 WA etter one of 1.2 0 20 ef ster 3 minste watateres exposure x to Quarts Katine emp. L 380" 560.400 605 Figure 6 ---Page Break--- ---Page Break--- -53- APPENDIX 2 Accepted for publication by the Journal of the 'American Chemical Society HETARYNE INTERMEDIATES Woldemor Mum, Alec Gritison, ond Roald Hoffmann' (Department of Chemistry 2 cond Puerto Rico Nuclear Center, University of Puerto Rico, Rio Picdias, P.Rey 00931, and Department of Chemistry, Cornell University, Ithaca, N. Y., 14250). ABSTRACT: 'The electronic structures of all of the possible 1, 2, 1,3, and I, = aromatic intermediates derived from pyridine and the diazines (boteryns cs) have been calculated using the extended Huckel theory (HT) opytidines, it is found that of the six possible isomers, the 34 are stable, and the 2, 6-didehydropyridine the least Iso predicted for 4,5-didehydropyrazine «nd nal rnd in the hotnyne For the didchdropyti stable. Great relative stability 4, 6-didehydropyrimidine, The complex co stabilities can be rationalized of the enol interactions among neighboring redox-type orbitals, A dominant effect is shown to be a nitrogen lone pair of nearby radical lobes. The calculated stability sequences and total electron distribution provide an excellent correlation of the available experimental data and orientation effects in the hetaryne intermediates, ---Page Break--- = 5h The

Chemistry of dehydroaromatic intermediates derived from heterocyclic molecules has been actively investigated during the last decade. Numerous papers have been published on this subject, together with extensive reviews by den Hertog and van der Plas®, by Kauffmann, and by Hoffmann®. Principal attention has been focused on the 1,2-dehydroaromatics derived from nitrogen heterocycles such as pyridine, quinoline, isoquinoline, and the various diazines. These intermediates, such as pyridine intermediates, are usually formed by the dehydrohalogenation of the corresponding halogenated heterocycle on treatment with a strong base. The two adjacent radical lobes in the 1,2 intermediates are thought to overlap appreciably, forming a partial triple

bond in the heterocyclic ring. These species have been designated as existing, in principle, of forming 1,3- and 1,4-dehydroheterynes. The possibility of aromaticity, in which the radical lobes are respectively in meta- and para-positions, has been considered. However, no such intermediates appear to have been reported to date. The only member of the 1,3-series that has received some attention is 2,6-dehydropyridine. Here it has been postulated that conjugation through the dehydropyridine nitrogen lone pair, which is flanked by the two radical lobes, should provide the necessary stabilization for the formation of such an intermediate. In comparison to the dehydrobenzenes, the heterynes are considerably more complex. While benzene can only form one 1,2-dehydro intermediate, pyridine can form either 2,3-dehydropyridine or 3,4-dehydropyridine. Of these two possible heterynes, 3,4-dehydropyridine is formed preferentially in the dehydrohalogenation of 3-halopyridine. It has only been possible to prepare 2,3-dehydropyridine by blocking the 4-position by substitution. While the symmetric dehydrobenzene intermediate gives a single product on reaction with a nucleophile, the unsymmetric 3,4-dehydropyridine can form two products, by substitution at either the 3-position or the 4-position. The preferential attack at the

A-position in 3, 4-dehydropyridine provides some evidence for an important orientation effect. Very little theoretical work seems to be available on these interesting heteryne intermediates. For this reason, we decided to examine a number of dehydroheteroaromatic molecules, using all-valence electron calculations of the extended Hückel type. THEORETICAL ANALYSIS Extended Hückel calculations on the six possible didehydropyridines result in the following stability order: O O 500.23 eV -499.74 eV -499.69 eV A B C 499.41 eV 499.51 eV 496.53 eV E F ---Page Break--- - 56 = ; In contrast to a previous simple Hückel calculation, which indicated the 2, 3-dehydropyridine (B) as the most stable, the 3, 4-dehydropyridine (A) clearly emerges as the most stable isomer. The 2, 5-dehydropyridine isomer in fact is so destabilized that it appears in our calculations with a high energy than some methylenes and paracyclophanes. This agreement with one of the few experimental facts known about the heterynes is gratifying. However, the above ordering of stabilities is initially puzzling. An explanation of this stability sequence must begin with a review of what is known of the electronic structure of the dehydrobenzenes themselves. When two hydrogen atoms are removed from the aromatic ring, two orbitals may be pictured as remaining. These orbitals each formally contain one electron, and they are termed the radical lobes  $n$  and  $m$ . The radical lobes can be combined to form wavefunctions  $n$  and  $n - p$ , which are respectively symmetric (6) and antisymmetric (A) with respect to the two-fold rotation which interchanges  $n$  and  $m$ . In the absence of any interaction,  $n + m$  and  $n - m$  are degenerate. Direct overlap between  $n$  and  $m$  (through-space) and indirect interaction with other  $p$  and  $p$  orbitals (through-bond) removes the degeneracy of the symmetric and antisymmetric molecular orbitals. The magnitude of the energy splitting between the symmetric and antisymmetric is a direct measure of the quantum-mechanical interaction. It is of controlling influence as to whether the ground state of

The dehydrobenzyne should be a singlet or triplet state. The magnitude and direction of the calculated splittings were surprising; we found S below A by 1.52 and 0.92 eV, thus for ortho- and meta-benzyne respectively, while for para-benzyne A was below S by 1.44 eV. These results together with other unexpected splitting patterns led us to an interpretation of each splitting as a superposition of a direct through-space coupling and an indirect through-bond coupling. The through-space coupling always puts the positive overlap combination at a lower energy. This may be S or A depending on whether the radical lobes are in a cis- or a trans-arrangement. The through-bond coupling leads to a lower A level when the radical lobes are separated by an odd number of  $\sigma$  bonds, and to a lower S level when they are separated by an even number of  $\sigma$  bonds. We will construct two models for the analysis of the energy level patterns of the dehydroazines and



dehydrodiazines. In the first model, the energy levels of tridehydro- and tetradehydrobenzenes are considered; the introduction of nitrogen atoms is treated as a small perturbation. The second model takes the stability ordering of the monodehydropyridine intermediates and treats the subsequent dehydrogenation as a small perturbation. There are three tridehydrobenzenes, each having three nearly non-bonding molecular orbitals. The tridehydrobenzenes can be labelled 123, 124, and 135 in an obvious notation, and the non-bonding orbitals designated as X1, Xp, and Xq in order of increasing energy, as below.

135 10.59 eV A -s9 + 5 112.535 @

The wave functions X can be classified as S or A under the two-fold rotation interchanging orbitals 1 and 3 in 128 and 135. For 124, there are two-fold symmetries, so that the orbitals are simply C'-orbitals. We would anticipate that the molecular orbitals formed from the radical lobes in 123 should fall into a typical allylic pattern.

s 2 and this they do. For instance, 1 is about 94% localized on atoms 1, 2, and 3. Yore has the following coefficients (xls normal to the molecular plane and "y-axis along Co Ce) @ to the molecular plane 4 @P,) 0.4205 €.) 0.000 1 @p,) 0.2000 ep) 0.5499 ej @) 0.1262 en) 0.0474 © al.) ~ 0.4205 €3(@py) 0.2000 2302) 0.1262 The molecular orbitals %, Xp and Xg of 123 can therefore be sketched as follows ---Page Break--- lo 'The splitting patterns found for the benzyne indicated that for an ortho interaction of two radical lobes the \$ combination was stabilized with respect to the A combination, for @ mats-interaction the S combination was also favored, whereas for © para interaction the A combination was favored. From the above diagram we see that %X has two favorable (6) ortho-interactions ( ny: ng and ng: ng ) and one favorable (S) meta-interaction (ny :ng)» —"%g has one unfavorable (A) meta-interaction, while Xg has two unfavorable (A) ortho-interactions, and one favorable (5) meta-interaction. By using the symbols (+) and (-) for favorable and unfavorable interactions, we can summarize the energetics of the above interactions as X% - + ° % ° 9° o % + + ° For the molecule 124 the orbitals %, , Xp and Xq are less straightforward to construct. A logical approach is to generate the orbitals by allowing the combinations nj £ ng to interact with ng. The primary interaction is ---Page Break--- -0- taken at a through-bond coupling of nj and ng which places © combination n= m4 (A) below ny + m4. This corresponds to the stabilization of the A combination by the para-interaction in the benzyne, and the fact that the meta interaction between np and ng should be much weaker. The equivalent interaction rule, derived from perturbation theory, is invoked - namely if two orbitals interact, the lower mixes in the upper in a bonding way, but the upper mixes in the lower in an antibonding manner. This is shown below, 6 O- OF 6 ---Page Break--- -61- The actual molecular orbitals have the predicted composition Xs = © (nyo my) + mg Xp = (en tmz)

#04) + (gre boy ~ mg) = emg + m4 xyz elm tm) = my The interactions may now be enumerated as was done above for the 123 system, therefore at the para position %, ° + ° % + - + The orbitals for 135 follow directly from symmetry. Three equivalent symmetrically disposed orbitals must interact to yield a totally symmetric combination, and a degenerate orbital pair? The degenerate orbitals may be chosen arbitrarily, and the particular combination illustrated below is picked to reflect symmetry on rotation around the C2 = C4 axis, CF 0 x, degenerate X. 3 'The energetics of the interactions in this case are ortho e's) pom ---Page Break--- -62- Referring back to the extent of the stabilization produced by the ortho-, meta, and para-interactions in the benzyne" In terms of the energy splitting produced, gives E (ortho) = 1.52 eV, E (meta) = 0.92 eV, and E (para) = 1.44 eV. The use of these values, and the previous interaction schemes, predicts the following energy

ordering for the nine orbitals of 123, 124, and 135: 23) <% 135) Hj 124 X12) < KH I12B) XL (199  
 <% 123}< 30124 The actual calculated energy values have been given earlier. They are in exact  
 agreement with the above sequence, supporting the analysis of the interactions. In the  
 tridehydrobenzene radicals, the radical lobes are each formally occupied by one electron. Of  
 greater significance to the present analysis are the tridehydrobenzene cations, with two electrons in  
 the non-bonding levels, and, more importantly, the anions, with four electrons. The total computed  
 energies for the tridehydrobenzene cations are 123 ~462.81 eV 24 461.48 eV a5 7462.06 eV The  
 stability ordering of these total energies is clearly in qualitative agreement with the ordering of the  
 one-electron 24 energies. The total energies of the tridehydrobenzene anions can be obtained from  
 the cation energy values by adding twice the one-electron energy of the appropriate Xp orbital. Xp  
 of 124 is of much lower energy than the other Xp orbitals, so that the final anion energies ---Page  
 Break--- - 63 -

ore 05 follows 123 483.99 eV 24 404.50 eV 135 483.26 eV. 'The importance of the  
 tridehydrobenzene anions is that we now suppose that the stability order is approximately  
 preserved if the isoelectronic substitution is made of N for a C, to form the didehydropyridines. One  
 of the radical lobes is now formally occupied by a nitrogen lone pair. The stability ordering E (124) <  
 E (23) < E (135) for the tridehydrobenzene anions thus implies the following grouping of the  
 didehydropyridines, under the above assumption ABO < OF < CE. A further ordering in each group  
 can be made by simply assuming that the nitrogen preferentially enters the position of highest  
 electron density in the tridehydrobenzene anion. For 123 and 124 these charge densities are such  
 that this would predict the ordering A < CCBCD < FK < E, quite close to the actual alphabetical  
 ordering obtained by the direct calculation. We now turn to the second model for the stability  
 sequence of the dehydropyridines. Table I below compares the energies of the nj + no(S) and nj  
 ~ng (A) molecular orbitals calculated for the benzyne, monodehydropyridines, and diazines. In the  
 benzyne, the radical lobes are each formally occupied by one electron; three electrons are shared  
 between the radical electrons. In the monodehydropyridines, the "radical lobes" are fully occupied  
 with four electrons, and in the diazines. For example, the ortho series is ---Page Break --- - 65 -  
 Table I: Energies (in eV) of Non-Bonding Orbitals in meta, and para Benzyne,  
 Monodehydropyridines, and Diazines. Benzyne 'Monodehydropyridine Diazine ortho- 10.19 A 1.00  
 "A" 712.40 A s 213.39 \_s Lael 0.99 meta- A "An" 12.58 A s "s" 213.39 FI 0.81 para- -10.37 \$ -10.83  
 "s" 712.58 HIL.el\_ A 713.24 "A" -13.85\_ A JOEL 14 2.Ai 1.67 It should be noted that whereas  
 symmetry requires the relation  $c_j = t \phi$  in the molecular orbital  $o_j n_j \epsilon p n_g$  in the benzyne and  
 diazines, there is no such restraint for the pyridinyl radicals. If  $n_y$  is on N and  $n_g$  is on C, then  
 invariably tion on N), and.

the lower energy orbital has  $Hejl > leg!$  (considerable localizability) the higher energy orbital has  $ley!$   
 $Z le gl$ . However, the molecular orbitals are such that they can be identified as approximately "S"  
 ( $e_1$  same sign as  $e_2$ ) and "A" ( $e_1$  opposite sign to  $e_2$ ). In all cases the ortho- and para- interactions.  
 The specific trends are not completely understood by us, though it is clear that the relative  
 efficiency of through-space versus through-bond interaction must be involved. Particularly  
 interesting is the greater magnitude of the "homonuclear" benzyne and splitting in the  
 "heteronuclear" pyridinyl case over diazine splittings. This can be attributed to the separation of the  
 C and N orbital energies before the interaction is "turned on." In confirmation of this, we obtain  
 large splittings in the following molecules, which are isoelectronic with the benzyne and diazine  
 systems. The results in the upper molecular orbital (A in this case) being destabilized less than the  
 upper molecular orbitals for ortho- (A) and para- (B) oriented lobes. The consequence is that when  
 two electrons occupy the non-bonding diazine dication molecular orbitals, as in benzyne,

monodehydropyridinyl cation, and the ortho-isomer (benzyne) or the para-isomer (pyridinyl, diazine) is the most stable. However, the meta-isomer becomes progressively stabilized relative to the other isomers by the addition of one, and two further electrons. The actual energies are summarized in Table 2. Table 2: Total Energies (in eV) of Benzyne, Monodehydropyridines, and Diazines as a Function of the Number of Non-Bonding Electrons. 2-electron case benzyne pyridinyl diazine (492.58) 507.76 520.75 491.99 507.68 521.45 492.37 508.17 3-electron case benzyne diazine (502.58) 518.75 533.15 502.58 518.84 534.03 502.74 517.00 4-electron case diazine benzyne (512.96) (513.17) 513.11 Our primary conclusions are based on the results for the

neutral pyridinyl ( $\beta$ -electron) and neutral diazine (4-electron) systems. The pyridinyl results imply orientation, that a lone pair para to a radical lobe is more stable than the meta, which is more stable than the ortho orientation. The diazine results further suggest a strong destabilization of two adjacent nitrogens (lone pair repulsion?) and a stabilization of a meta interaction of two lone pair orbitals. We can now examine the didehydropyridine results in the light of the above considerations on lone pair-radical lobe interactions. The number and type of N-radical interactions in the various didehydropyridines are listed below. N-radical Interactions Structure ortho meta pes, A ° 1 1 B I ° I c 1 1 ° D 1 I o E ° 2 o C 2 ° ° Taking the above stabilizing effect para > meta > ortho, gives the energy sequence ACBLE<C,DCF. Only the order of E and C, D is inconsistent. This can be explained by the presence of a stabilizing ortho radical-radical lobe interaction of the benzyne type present in C and D, but absent in E. ---Page Break--- -6- We now turn to the different possible dehydrodiazines which exhibit the following stability sequence CRE & - 507.55 oV — 506.83 - 506.74 - 506.63 G ' 508.10 - 507.87 - 507.39 - 507.05 K L M N ND ND N> ~ 507.57 - 506.68 - 506.43 ° P Q see 3a, WE ---Page Break--- Once again the analysis is two-fold. We begin by considering the three a OBO 1234 1235 1245. The molecular orbitals of 1234 and 1245 are essentially determined by symmetry. tetrahydrobenzenes We write them as Po, Pg and by an arbitrary order, since their final energy ordering is not obvious in every case. For 1234, the symbols \$ and A refer to the symmetry operation interchanging nj and ny, and ng and ng. For 1245 the symbols SS, AA, AS, and SA refer first to the symmetry operation interchanging nj and ng, and ng and ng, then to the symmetry operation interchanging ny and ny, and ng and ng. Note the obvious and not accidental resemblance of the orbitals of 1234 and 1245 to the T-orbitals of a butadiene. ---Page Break--- \$s) \$14)

bts) ea Of CG  $\phi$ Y og 6 0 @ \$, (ss) \$,(As) \$,(SA) 4, (AA) The composition of the 1235 molecular is totally predicted. They emerge from the calculation resembling a sort of cyclobutadiene & & \$(s) 41s) #,(a) \$s) ---Page Break--- -12- We now estimate the favorable and unfavorable interactions for each of these molecular orbitals as was done for the tridehydrobenzenes. eri) mete Pore, " ooo + + ©) \$3 -G- ) = - 1234 WW G +444 = + ©) Ae + - 6) too + = 1235 " gs 9 od 0 ) fo 0 0 + 6) + +t - (AA) boo - - rus 6A) fe - + + as) Bo +4 = 3 (5) +4 +4 \_ ---Page Break--- -B- Recalling that an ortho= or para-interaction is more stabilizing than @ my interaction, we would predict for 1234 the energy ordering ra P roy ordering BL < hy < Gy <b yr wri Zo P, < Py < Gy, endtorias J, < g, ~ d3 < P4- These conclusions are confirmed by the calculated energy level orderings (in eV), 1234 1235 1245 -9.78 (S) 9.58 (5) -9.29 (AA) 10.04 (A) 10.59 (A) -U1.49 65) 11,83 (A) -I.78 (5) -11.55. (SA) 212.72. () 12.76 (8) "11.97 (AS) The calculated total energies for the six electron systems which correspond to the tetrahydrobenzene dianions are (1234) dianion ~475.39 eV (1235) dianion 476,00 eV (1245) dianion ~476.54 eV The stabilization of 1245 is essentially due to the relatively low energy of its highest occupied molecular orbital. In fact, the total energy order 1245 < 1285 < 1234 is paralleled by the highest occupied level energies -11 49 < -10.59 < -10,04, respectively. ---Page Break--- - th To obtain the didehydrediazines, we proceed to replace two carbon atoms by nitrogen

atoms in the tetrahydrobenzene dianions. For each type of diazing the stability sequence presented earlier is completely predicted by the above considerations, that is (245) < (2H SB c < oun < os kK < UM < N 0 <P < @ Placing all eleven isomers on a single energy scale is difficult, since relative 'weights would have to be assigned to the effects of radical lobe interactions and lone pair lobe interactions. The second analysis, starting from the stabilities of the pyridinyl

Radicals are quite successful in rationalizing the observed trends for the dehydropyridazines and pyrimidines (G to N), as illustrated below. However, it fails to distinguish among the dehydropyrazines where each isomer has two ortho and two meta interactions.

Nitrogen Radical Interactions Structure ortho meta ora, 6 ° 2 2 H ' 2 1 1 1 2 1 J 2 2 0 K 2 0 2 L ! 2 0 M 2 2 ° N 3 o '

---Page Break---

-B- We have gone into great detail in the above qualitative analysis to illustrate how the complex computational trends we have observed are understandable in terms of qualitative molecular orbital arguments. In addition to the molecules already mentioned, our actual calculations covered a number of other dehydro heterocyclics. The results are summarized in Tables 3-5 below, where the heterocycles are grouped as 1-2, 1-3, or 1-4 diradicals.

Table 3: 1,2 Dehydroaromatics Splitting Total Electron Densities Molecule E\_total (V) 2E (eV) fox. Ja. °, we 492.58 1.52 4.20 4.20 wee 499.77 0.86 3.77 4.25 KOR ~500.60 1.63 4.35 3.97 @E 505.95 til 3.94 4.10 1 4.29 3.94 7 LOL -506.60 54 OS -506.74 0.89 3.98 3.91 ~507.55 1.57 4AM 4M hE toe -507.87 1.04 3.55 4M ~505.43 0.04 3.81 3.81

---Page Break---

- 6 - Table 4: 1, 3-Dehydroaromatics Splitting Overlap Population Total Electron Densities Molecule Tool) eee) Thy fe a IGF 491.99 0.92 0.041 4.21 4.21 NSP -500.13 1.33, 0.034 3.97 4.07 IGP 498.88 0.04 ~ 0.008 3.85 3.85 "or 499.72 0.69 0.047 418 AAS SP -505.93 LI 0.047 4.01 3.89 "éP -505.29 0,59 0.001 3.87 3.87 TeP -505.89 0.94 0.046 4.18 4.18 SGP 7506.83 1.15 0.039 3.90 4.02 S6Pr -507.05 0.70 ~ 0.037 3.96 3.41 WSR -2.10 70 0.037 3.81 3.81 "EP 7506.68 0.28 -0.173 4.06 4.06

---Page Break---

-71- Table 5: 1, 4-Didehydroaromatics Overlap Population Total Electron Densities Molecule F\_total (eV) aé lev) Re 7 te oe 492.37 1.44 -0.119 4.90 4.99 g 500.05 1.43 -0.108 3.89 4.39 JD 500.99 1.28 -0.110 3.97 4.24 m 506.63 1.22 0.098 3.87 3.87 iy -507.39 1.37 -0.05 3.62 4.26 igy 507.57 1.52 -0.097 3.99 3.99

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-B- of the nitrogen lone pairs has

on effect on the energy Clearly the pos splitting AE between \$ and A molecular orbitals. Of great interest is the fact that there is a consistent correlation between stability and the magnitude of this

one-electron energy splitting. Compare, for example, the dehydropyridines in Tables 3-5. The largest splittings are associated with molecules for which we predict great relative stability. These are 3, 4-dehydropyridine, 4, 5-dehydropyrazine, and 4,6-dehydropyrimidine, which probably have singlet ground states. INTERPRETATION OF EXPERIMENTAL DATA, We first turn to the experimental evidence available on the stability of the 1,2-hetarynes. Treatment of a S-halopyridine with a strong base (usually an alkylated amide ion) leads to the 3- and 4-amino-substituted pyridines, as shown in the equation below:  $xWR, .ors A RNT/ RZNH \rightarrow oO + oy$  No 2-aminopyridine is observed in these reactions, unless the A-position is blocked by an allyl group. 3,4-didehydropyridine must be the preferred intermediate in this reaction, rather than the 2, 3-isomer. Naturally, the 2, 3-isomer would be expected to be more stable, since two electrons from the radical lobes, together with the nitrogen lone pair can be delocalized over three atoms. This suggestion has been forwarded, resting on the basis of a Huckel molecular orbital calculation. As pointed out in the theoretical analysis, our extended Hückel calculations, which are in agreement with the experimental data, argue against the utility of simple delocalization over the three adjacent atoms. On the contrary, whenever the nitrogen lone pair is adjacent to the radical lobes, we have seen that the intermediate experiences a pronounced destabilization. If the accepted mechanism of dehydrohalogenation of S-halopyridines is considered, two reasons emerge for the formation of 3- and 4-aminopyridines, rather than 2-aminopyridine. The mechanism is very complex. First of all, the formation of the 1,2-hetaryne necessitates the removal of a.

Proton by the amide ion to form a carbanion. Two carbanions are possible, the 2-pyridinyl anion and the 4-pyridinyl anion. We have calculated the relative stability of these carbanions in the case where X is hydrogen. The results are shown in Table 6 and indicate that the 4-carbanion is 0.08 eV (1.9 kcal) more stable than the 2-carbanion. Fortunately, recent experimental data confirms this stability.

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Table 6: Heteroaromatic Carbanions E Potential total (CV)

x 2 529.75

2 oS 3 530.00

4 529.83

rn 2 -536.04

2 oS b 3 -536.18

A 4 -535.06

x oy 3 -536.78

8.7 4 -536.85

8.70 a 2 7597.00

9.01 5, tor. 4 -537.67

8.94 5 598.07

8.54 S 2 -537.45

8.81 since base-catalyzed deuterium exchange studies on pyridine and 3-chloropyridine indicate that exchange predominates at the 4-position over the 2-position in both

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The carbonions subsequently eliminate halide ion to form the 1, 2-hetaryne. The combination of the preferred formation of the 4-carbanion, which is the precursor of the 3, 4-didehydropyridine,

together with the greater stability (0.83 eV or 19 kcal/mole, Table 5) of this hetaryne over the 2, 3-didehydropyridine, accounts for the facts. It is worth reiterating that the predominant factor against the 2, 3-hetaryne is the nitrogen lone pair destabilization of the radical levels. In this context, on removal of the nitrogen lone pair by protonation, alkylation, or N-oxide formation, deuterium exchange takes place preferentially at the 2-position, through the respective 2-pyridinyl carbanions. Again these experimental results harmonize with EHT calculations, since the results of Table 6 indicate comparable stability for the 2- and 4-carbanions once the nitrogen lone pair has been protonated. Although little information is available on the 1,2-didehydro intermediates derived from the diazines, some excellent experimental work has recently been reported on base-catalyzed deuterium exchange in these molecules. The half-lives (in minutes)

obtained for the exchange, using 0.23M sodium methoxide in Oxideuteromethanol at 165°C or a Al Saad ie ey a g © Inspection of Table 6 shows again that within each diazine the relative order of exchange half-lives is correctly predicted by the carbanion stabilities. The ---Page Break--- = 82+ Comparison of the total energies of carbanions from different diazines cannot be made, since the total energies are dominated by the relative disposition of the nitrogens. To obtain a crude estimate of such a stability sequence the anion energies are subtracted from the parent energies in Table 6. This gives the energy ordering I < G < Ge < Joe < oy Although the general trend is reproduced, our calculations reverse the sequence for the 4-pyridazinyl anion and 5-pyrimidinyl anion (but the experimental value for the former is only approximate), and for the 4-pyrimidinyl anion and 2-pyrazinyl anion (where the experimental half-lives are very close). Considering the neglect of solvent exchange mechanisms, perfect vent effects, and the possibility of competition. Some experimental data is available on the orientation effects in the addition of nucleophiles to the 1,2-didehydro intermediates. Whereas only one final product is possible from 1,2-didehydrobenzene, 3,4-didehydropyridine could undergo nucleophilic attack at the 3- or 4-positions to give different products. The addition of ammonia or piperidine to 3,4-didehydropyridine indicates a preference for nucleophilic addition at the 4-position. Previously we have shown that EHT electron densities and total energies of the reaction intermediates successfully correlate orientation effects in nucleophilic substitution! The total electron densities of Table 3 suggest that for 3,4-didehydropyridine preferential nucleophilic attack ---Page Break--- -83- should occur at the 4-position, as a consequence of its lower total electron density (8.97 against 4.35 electrons). In addition, the total energies of the anions confirm this preference. Localizing a

hydride ion, chosen as a model for the amine nucleophile, at the 3- or 4-radical lobes of 3, 4-didehydropyridine produces respectively the 4- or 3-pyridinyl anion. Since the 3-pyridinyl anion is 0.17 eV more stable than the 4-isomer (Table 2) nucleophilic attack should be preferred at the 4-position. As we have indicated, when both representations exert lead to the same conclusion, we can be confident that they provide a reasonable account of the observed effects. In this case, the preferred nucleophilic attack occurs at the 4-position. Although no experimental data has been published, our calculations indicate that the 3,4-didehydro intermediate derived from the pyridinium ion should undergo preferential nucleophilic addition at the 4-position also. In 3,4-didehydroquinoline the preferred addition takes place again at the 4-position, which is also reproduced by our calculations. Of some interest is the exclusive formation of A-substituted products in the reaction of 5-bromopyridine with piperidine. This suggests that the 4,5-didehydropyrimidine intermediate undergoes preferential nucleophilic attack at the 4-position, rather than the 5-position. Again, total electron densities and the total energies of the pyrimidinyl anions are both in agreement with this orientational effect. On the basis of this experimental result, it can be seriously questioned whether the 2,3-didehydropyridine is not formed during the

dehydrohalogenation of the 5-bromopyridines. As a result of this reaction, the 2-substituted product is formed exclusively, and it was therefore argued that 2,3-didehydropyridine would have led to the formation of some 5-substituted product. In fact, it was concluded that if the 2,3-hetaryne intervenes, the 3-isomer should be the predominant product, as a consequence of the electron withdrawal by nitrogen. Objections have been raised to this interpretation, since a strong orientation effect, similar to that found in 4,5-didehydropyrimidine, may be operative. Our calculations provide

evidence in favor of this objection. Both total electron densities and total energies of the pyridine ions predict preferential nucleophilic attack at the 2-position, rather than the 3-position. On the basis of our calculations, deprotonation of pyridine at the 3-position is energetically favored over the 2- and 4-positions. This renders it rather likely that the 2,3-didehydropyridine may indeed be the intermediate in this reaction, and a more detailed experimental study of this point seems advisable. In the dehydrohalogenation of 4-halopyridazine, two 1,2-didehydro intermediates could be formed, the 3,4- and 4,5-didehydropyridazines. Our calculations indicate that the 4,5-isomer should be more stable, again due to the dominant effect of the lone pair destabilization. Because of the symmetry of the 4,5-isomer, no orientation effects are possible. In the unsymmetric 3,4-isomer, nucleophilic attack could lead to either a 3- or a 4-substituted product. However, the differences in the total electron densities and in the anion energies are exceedingly small, and predict opposite orientations. This suggests that very little, if any, orientation effect is expected for the intermediates from 4-halopyridazine. Unfortunately, no experimental data is available. The lack of experimental data on the 1,3- and 1,4-didehydroaromatics prevent us from confirming some of the interesting conclusions reached in these calculations. However, there has been some speculation on the 2,6-didehydropyridine as a reaction intermediate. Again, we predict this 1,3-dehydro system to be stabilized by conjugation with the nitrogen lone pair. In our EHT calculations, and the attendant theoretical analysis, the 2,6-isomer clearly emerges as the least stable of the six possible heterocycles formed from pyridine (AF). Once again, we attribute this finding to destabilization by the nitrogen lone pair, since even the 3,5-isomer in which the lone pair is furthest from the radical lobes is energetically favored by

0.84 eV over the 2,6-isomer. This provides an explanation of the failure of all reported attempts to generate this species. The effect of the nitrogen lone pair is also revealed in an interesting way in the 1,3-overlap populations. Except in those instances where the lone pair flanks the radical lobes, the 1,3-overlap populations are all small but positive, close to that of 1,3-benzyne. In

2,6-didehydropyridine, 2,4-didehydropyridine, and 2,6-didehydropyrazine, where the nitrogen flanks the radical lobes, the overlap populations are still small, but more significantly of negative sign. It is interesting to find that protonation of the nitrogen lone pair in 2,6-didehydropyridine again results in a slightly positive 1,3-overlap population, therefore restoring the direct, through-space interaction found in 1,3-didehydrobenzene. Recently we have noted a preliminary account of semiempirical SCE calculations on the heteroarynes by Yonezawa, Konishi, and Kato, which we would like to bring to the reader's attention. These calculations are able to decide if the ground state of the molecule is in fact a singlet, something which our calculations are not able to do. ---Page Break---

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