[CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, LIVERMORE, CALIFORNIA]

Electron Spin Resonance Studies of the Diazine Negative Ions[1]

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Pyrazine and pyridazine negative ions have been prepared and their hyperfine structure observed. The theory of McLachlan, *et al.*,[7] has been adapted to relate the coupling constants and spin densities of the nitrogen atoms. Molecular orbital theory has been used to calculate the spin densities, and reasonable agreement is found with the experimental results. The concept of spin density on the nitrogen nucleus is discussed. The reaction between pyrimidine and an alkali metal has also been carried out, but the product appears to be the result of a coupling reaction.

Introduction

In recent years the study of isotropic hyperfine interactions in polyatomic free radicals has led to a wealth of information about electron distribution in these radicals. The proposal by McConnell that proton hyperfine interactions could be used to determine spin densities on adjacent carbon atoms has indeed turned out to be correct.[2,3] Theoretical estimates of carbon spin densities are usually correlated with the observed proton hyperfine splitting by means of the relation $a_H = Q\rho_C$.[4] The spin density ρ_C can be either negative or positive. For aromatic negative ions the value of Q has been determined from the total splitting of benzene negative ion, -22.5 gauss. The negative sign of Q indicates that the unpaired spin density at the proton in question tends to be antiparallel to the average spin density of the π-electron.

Recent investigations[5-8] of hyperfine interactions of nuclei which lie in the plane of the aromatic ring, *e.g.* C^{13}, show that the hyperfine interaction depends not only on the spin density of the nucleus in question, but also on the spin density of other carbons which are attached to it. A study of heterocyclic free radicals will lead to information about this in-plane hyperfine interaction without recourse to difficult isotopic synthesis. In this article we will investigate the hyperfine interactions in the three diazine isomers: pyrazine, pyridazine and pyrimidine negative ions. Spin densities will be estimated in the framework of the Hückel theory and compared with experiment. The concept of spin density on the nitrogen atoms will also be discussed. Estimates of coupling constants of a few other heterocyclic negative ions will be made and compared with experimental results.

Results

Pyrazine.—Pyrazine (*p*-diazine) negative ion was prepared at $-70°$, in the usual manner, by reduction with potassium metal in 1,2-dimethoxyethane, and its spin resonance spectrum recorded. The observed spectrum is consistent with the symmetry of the molecule and consists of 23 of the possible 25 lines. The total splitting, measured from first inflexion to the last inflexion, is 39.3 gauss. An assignment of 7.1 gauss for the nitrogen coupling constant and 2.76 gauss for the proton coupling constant reproduces the spectrum in good detail.

Pyridazine.—Pyridazine (*o*-diazine) negative ion was prepared in the same manner as pyrazine negative ion. The spectrum consists of seven very well resolved lines with the intensity ratios very nearly 1:4:8:10:8:4:1. The total splitting is 38 ± 1 gauss. An assignment of a coupling constant of 6.3 gauss to the two nitrogens and a coupling constant of 6.3 gauss to two protons reproduces the observed spectrum. There was no splitting observed from two of the protons in the molecule.

Pyrimidine.—Pyrimidine (*m*-diazine) reacted with potassium metal in the same manner as did the other two diazines. The reaction, however, was quite slow in comparison and resembled somewhat the reaction of pyridine with an alkali metal.[9] The observed spectrum consists of at least 100 lines spread over 25.6 gauss. If pyrimidine negative ion had been formed, the spectrum would have exhibited the same total spread as the other two diazines, namely, 39 gauss, and the number of lines would not have exceeded 60. The total splitting, however, is consistent with that of bipyridyl negative ion,[9] which was formed when pyridine was treated with potassium metal. We therefore suggest that pyrimidine has undergone a coupling reaction similar to that of pyridine, and the negative ion of the product was formed. No assignment of coupling constants or identification of the reaction product has been made.

Analysis of Results.—McLachlan, *et al.*,[7] have extended the theory of isotropic hyperfine interactions to include spin polarization of C–C bonds, while Karplus and Fraenkel[8] have shown that spin polarization of the 1s electrons can also be important. Das and Mukherjee[10] have pointed out that the hyperfine interaction in the nitrogen atom can be accounted for by the difference in the spin polarization of the 1s and 2s electrons.

We will attempt to correlate spin densities and coupling constants of heterocyclic negative ions within the framework of the Hückel theory without a specific assignment of values to each type of interaction which contributes to the hyperfine splitting. The observed nitrogen coupling constant a_N is therefore given by equation 1

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

[3] H. M. McConnell, *ibid.*, **24**, 632 (1956).

[4] H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

[5] F. C. Adam and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 2057 (1958).

[6] T. R. Tuttle, Jr., *J. Chem. Phys.*, **32**, 1579 (1960).

[7] A. D. McLachlan, H. H. Dearman and R. Lefebvre, *ibid.*, **33**, 65 (1960).

[8] M. Karplus and G. Fraenkel, *ibid.*, **35**, 1312 (1961).

[9] R. L. Ward, *J. Am. Chem. Soc.*, **83**, 3623 (1961).

[10] T. P. Das and A. Mukherjee, *J. Chem. Phys.*, **33**, 1808 (1960)

$$a_N = Q_1\rho_N + Q_2\sum_i \rho_i \qquad (1)$$

where ρ_N is the nitrogen spin density, ρ_i the spin densities of the nuclei attached to the nitrogen and Q_1 and Q_2 are constants chosen to fit the data. We will use McConnell's relation, $a_H = Q\rho_C$, with $Q = -22.5$ gauss to estimate carbon spin densities from known proton hyperfine coupling constants.

It will be necessary to estimate Q_1 and Q_2 from coupling constants and spin densities of similar compounds as data are lacking on the magnitude and signs of the different contributions to the Q's. These different contributions are discussed more thoroughly in the section on nitrogen spin density. We will use the results from pyrazine and 4,4-bipyridyl negative ions. The proton coupling constant of 2.76 gauss for pyrazine negative ion yields a carbon spin density of $\rho_C = 0.12$. The nitrogen spin density may be obtained from conservation of spin and the reasonable assumption that the spin density is everywhere positive. This value is $\rho_N = 0.26$. The spin densities and coupling constants of interest for 4,4′-bipyridyl[9] negative ion are $a_N = 3.6$ gauss, $\rho_N = 0.159$, $a_0 = 0.45$ gauss, $\rho_O = 0.02$, where a_O is the ortho proton coupling constant and ρ_O the ortho carbon spin density. It should be noted that in the case of 4,4′-bipyridyl negative ion the nitrogen spin density was estimated by molecular orbital calculations with $\alpha_N = \alpha_C$ as this value for the nitrogen coulomb integral gave the experimentally observed proton coupling constants. A value of $\alpha_N = \alpha_C + 0.5\ \beta$ for this integral, however, changes the nitrogen spin density only slightly, *i.e.*, $\rho_N = 0.147$. Substitution of these values of spin densities and coupling constants for 4,4′-bipyridyl and pyrazine negative ions into equation 1 yields two equations in Q_1 and Q_2 from which we obtain the values $Q_1 = 20.9$ gauss and $Q_2 = 7.0$ gauss.

Equation 1 can now be used to estimate coupling constants in nitrogen heterocyclics once spin densities are known. de Boer and Weissman[11] have been able to estimate spin densities in aromatic hydrocarbon negative ions, with reasonable success, by use of the Hückel theory. Hückel type calculations may be extended to heterocyclic negative ions by the use of the following approximations: (1) the nitrogen coulomb integral is given by $\alpha_N = \alpha_C + \beta h$ and $h = 0.5$, (2) all exchange integrals of nearest neighbors are assumed equal, *i.e.*, $\beta = \beta_N$ and all other exchange integrals are set equal to zero. The spin densities are then the squares of the coefficients of the wave function for the lowest non-bonding orbital. Coupling constants then may be estimated by use of equation 1 and McConnell's relation. The Hückel theory applied to pyrazine negative ion yields the values $\rho_C = 0.10$ and $\rho_N = 0.29$. These values compare quite well with the experimental values; $\rho_C = 0.12$ and $\rho_N = 0.26$. Self consistent fields calculations[12] yield essentially identical results for the spin densities. Hückel theory, therefore, appears to be a reasonable approximation for heterocyclic negative ions.

We have used equation 1 with $Q_1 = 20.9$ and $Q_2 = 7.0$ and the Hückel theory to estimate coupling constants for a few heterocyclic negative ions. We obtain these results

	Calcd.	Obsd.
Quinoxaline	$a_N = 5.4$	$a_N = 5.7$
	$a_{H_2} = 2.4$	$a_H = 2.3$
	$a_{H_7} = 1.2$	$a_H = 1.5$
Phenazine	$a_N = 4.8$	$a_N = 5.0$
	$a_1 = 1.6$	$a = 2.0$
	$a_2 = 1.1$	$a = 1.6$

We also have compared the calculated and observed spectra of 1,10-phenanthroline and quinoline negative ions and found reasonable agreement. The complexity of the spectra however limits the validity of observed coupling constants without isotopic substitution. Equation 1 and molecular orbital calculations appear to yield reasonable results for nitrogen splittings in heterocyclic negative ions.

Spin densities for pyrimidine (*o*-diazine) may be obtained from the observed proton coupling constants and conversion of spin. These values are $\rho_N = 0.22$, $\rho_C = 0.28$ and $\rho_C' \cong 0$. It is possible to decide, from molecular orbital theory, which protons give rise to the observed hyperfine interaction. The calculated spin densities are $\rho_N = 0.27$ and $\rho_C = 0.23$, and for the carbons attached to the nitrogens $\rho_C' = 0.004$. This indicates that the ortho proton is the one which does not exhibit a hyperfine interaction. The value of β_{NN} used in this calculation was 1.25. This value gives the best agreement with experimental results. The nitrogen spin density, however, was rather insensitive to β_{NN} and therefore not too much significance should be given to this value.

It will be necessary to determine new values for Q_1 and Q_2 for a molecule like pyrimidine as these values should be different from those for pyrazine. These values could be obtained from a comparison of the spectra of pyrimidine and s-tetrazine negative ions. Unfortunately, the spectrum of s-tetrazine negative ion has not yet been reported.

Nitrogen Spin Density.—In the theory of isotropic hyperfine interactions of aromatic free radicals presented by McConnell and Chesnut,[3] the proton hyperfine interaction arises from a $\sigma-\pi$ configuration interaction. McLachlan, *et al.*,[7] have extended this work to include hyperfine interactions from nuclei which are in the plane of the ring such as C^{13} and N^{14}. In their theory, the Q's which appear in equation 1 depend on the ratio $J(\sigma\pi)/\Delta E$, where $J(\sigma\pi)$ is the exchange integral for the carbon sp^2 orbital with the π-orbital and ΔE is the singlet–triplet separation of a C–C bond. In the case of nitrogen containing heterocyclic free radicals, it is necessary to consider what contribution the non-bonding pair of electrons will make to the hyperfine interaction. At first, it might seem that the interaction could depend on a term of the form $J(n\pi)/\Delta E_{n\rightarrow\pi^*}$, where $J(n\pi)$ is the exchange integral between the non-bonding pair of electrons and the π-orbital, and $\Delta E_{n\rightarrow\pi^*}$ is the energy separation between the energy level of the non-bonding pair and the first π^*-antibonding state. This type of promotion, however,

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[11] E. de Boer and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 4549 (1958).

[12] N. Mataga and K. Nishimoto, *Z. Phys. Chem.*, **13**, 140 (1957).

leads to a vanishing of the exchange integral. Another possible promotion is from the non-bonding level to a σ^*-antibonding state. This promotion should lead to a non-vanishing of the exchange integral. A comparison of the nitrogen splitting in NH_2 with that of NH_3^+, recently observed by Cole,[13] however, indicates that this contribution is small. Karplus and Fraenkel have pointed out that the spin polarization of the 1s electrons will also contribute to Q_1 of equation 1. No value for this contribution is available at the present time for nitrogen atoms in heterocyclic molecules.

Conclusion.—The use of equation 1 in relating spin densities and coupling constants of nitrogen atoms in heterocyclic negative ions appears to be substantiated. The Hückel theory is a reasonable approximation for these ions.

Acknowledgment.—I wish to thank Professor A. Streitwieser for helpful discussions.

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[13] T. Cole, *J. Chem. Phys.*, **35**, 1169 (1961).

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The Microwave Spectrum and Structure of NSF_3[1a]

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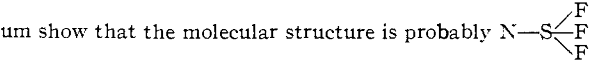
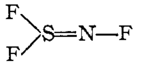
The action of AgF_2 on S_4N_4 in CCl_4 produces a gaseous compound, NSF_3, the structure of which has been in some doubt. A pure sample was prepared. Fragments in the mass spectrum show that the molecular structure is probably  as most recently claimed by Glemser. The microwave spectrum was studied in the region 8000 to 60,000 mc. with a conventional Stark modulated spectrograph. The spectrum has the simplicity and first order Stark effects characteristic of a symmetric top. From lines assigned to the normal and also to the ^{34}S and ^{15}N species occurring in natural abundance, the following set of structural parameters was obtained: $d(S–N) = 1.416$ Å., $d(S–F) = 1.552$ Å. and $<FSF = 94° 2'$. The above structure is thus confirmed and made quantitative. In addition, the dipole moment was measured and found to be 1.91 ± 0.03 Debye. The quadrupole coupling constant of the ^{14}N nucleus is $+1.19 \pm 0.05$ mc.

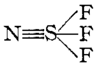
Introduction

The compound NSF_3 was first reported by Glemser and Schroeder[2] who initially proposed the structure



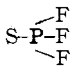
(A)

on the basis of hydrolysis experiments. After the present work was initiated, Richert and Glemser[2b] interpreted infrared and fluorine nuclear magnetic resonance data in favor of the structure

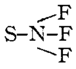


(B)

The compound PSF_3 is also known and has the structure[3]



so that the possibility



(C)

existed. The microwave spectrum of NSF_3 was investigated in order to determine the structure unambiguously and quantitatively. As shown below, the form (B) was confirmed.

Experimental

The Preparation of NSF_3.—NSF_3 is formed by the action of AgF_2 on S_4N_4 in an inert solvent. The preparation of S_4N_4 has been described by Arnold, Hugill and Hutson[4] and by Brauer.[5,6] A freshly prepared sample of S_4N_4 was dissolved in carbon tetrachloride which had been dried over phosphorus pentoxide. This solution was poured into a two-necked copper reaction flask which was fitted with a copper reflux condenser. The reflux condenser was followed by two U-traps which were both cooled by liquid nitrogen. The whole system was kept under an atmosphere of dry nitrogen.

The solution in the copper flask was then heated and, as it began to reflux, enough AgF_2 was added so that the reaction mixture contained twelve moles of AgF_2 for each mole of S_4N_4. The mixture then was refluxed for approximately 3 hr. The first trap contained the reaction products which consisted of SO_2, SOF_2, CCl_3F and SiF_4 in addition to the main product NSF_3. The use of a copper flask, as suggested by Dr. Glemser, rather than Pyrex substantially reduced the formation of these side products.

The reaction products were distilled *in vacuo* through three cold traps. The first was cooled by a toluene slush (−96°), the second by a methylcyclohexane slush (−126°) and the third by liquid nitrogen (−196°). The fraction trapped at −126° was collected for further purification. This sample still contained small amounts of SO_2, SOF_2 and CCl_3F. Further purification was achieved by the use of gas chromatography. The separation of NSF_3 from the impure reaction product was carried out in a conventional gas chromatographic apparatus using fifty grams of tricresyl phosphate per hundred grams of Chromosorb (manufactured by the Johns–Manville Co.) for a stationary phase and helium for the moving phase. The separation was quite clean and the resulting sample was at least 99% pure NSF_3. The purity of the sample was estimated from the mass spectrum.

The Mass Spectrum of NSF_3.—The mass spectrum of NSF_3 was useful not only in giving an estimate of the purity of the sample but also in revealing evidence for the possible structure of NSF_3. The mass spectrum contained peaks at the mass numbers of the following fragments: NSF_3, SF_3, NSF_2, SF_2, NSF, NS, S, F and N. No mass peaks

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[1] (a) This research was supported by a contract with Harvard University from the Office of Naval Research. (b) National Institutes of Health Fellow, 1959–1962.

[2] (a) O. Glemser and H. Schroeder, *Z. Anorg. u. Allgem. Chem.*, **284**, 97 (1956). (b) H. Richert and O. Glemser, *ibid.*, **307**, 328 (1961).

[3] Q. Williams, J. Sheridan and W. Gordy, *J. Chem. Phys.*, **20**, 164 (1952).

[4] M. H. M. Arnold, J. A. C. Hugill and J. H. Hutson, *J. Chem. Soc.*, 1645 (1936).

[5] G. Brauer, "Handbuch der Praeparativen Anorganischen Chemie," Ferdinand Enke, Stuttgart, 1954, p. 316–318.

[6] G. Brauer, *ibid.*, 1960, p. 368–369.