

Figure 7. The experimental values of k_a as a function of ω for $\lambda_{ex} = 313$ nm. Propane is the diluent. The solid line is a calculated curve with $E_{mp} = 76$ kcal mol $^{-1}$ and $\sigma = 12$ kcal mol $^{-1}$. These data are taken from the M.A. Thesis of A. Squillace, California State University—Fullerton, 1971.

energy being partitioned to the internal degrees of freedom of the hydrocarbon fragment.

Using the known frequency assignment¹⁴ and thermal kinetic parameters²⁸ for 1-pyrazoline one may calculate the internal energy distribution function of the CP* if there were statistical intramolecular energy relaxation^{8,31} when 1-pyrazoline fragments to trimethylene and nitrogen. If λ_{ex} were 333 nm, statistical intramolecular energy relaxation would result in a cyclopropane with a most probable energy of ~ 86 kcal mol $^{-1}$ (assuming that the reaction trimethylene \rightarrow cyclopropane is 54 kcal mol $^{-1}$ exothermic³²). It appears that at longer

(31) F. H. Dorer and S. N. Johnson, *J. Phys. Chem.*, **75**, 3651 (1971).
 (32) H. E. O'Neal and S. W. Benson, *ibid.*, **72**, 1866 (1968).

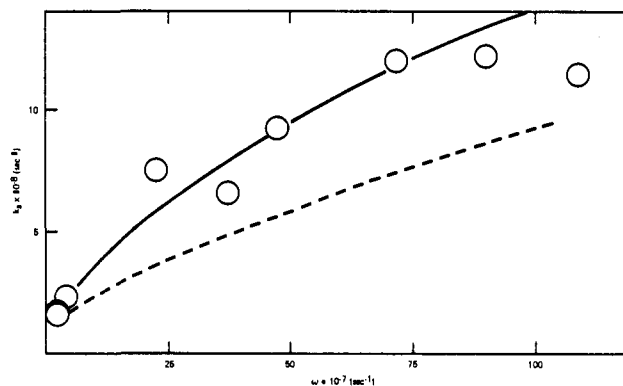


Figure 8. The experimental values of k_a as a function of ω for $\lambda_{ex} = 333$ nm. *n*-Pentane is the diluent. The solid line is a calculated curve with $E_{mp} = 91$ kcal mol $^{-1}$ and $\sigma = 15$ kcal mol $^{-1}$. The broken line is a calculated curve with $E_{mp} = 86$ kcal mol $^{-1}$ and $\sigma = 12$ kcal mol $^{-1}$.

wavelengths of excitation there is approximately statistical intramolecular energy relaxation on fragmentation. However, photolysis in the shorter wavelength region of the first singlet band, where τ_{nr} is decreasing with increased excitation energy, results in a nonrandom distribution of the available energy. In the short wavelength region more of the available energy is partitioned to degrees of freedom other than the internal degrees of freedom of the hydrocarbon fragment.

Acknowledgments. This work has been supported in part by the National Science Foundation Grant No. GP-28266. We wish to express our gratitude to Professor E. K. C. Lee of the University of California—Irvine for allowing us to use the facilities in his laboratory to carry out the fluorescence emission and lifetime studies, and for his interest in this work. We also thank M. Ezell and A. Squillace for their contributions during the initial stages of this study.

Electron Spin Resonance Study of Heterocycles.

II. Pyrrole, Pyrazole, Imidazole, and Indole Anion Radicals¹

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Abstract: Anion radicals of pyrrole, pyrazole, imidazole, and indole were generated in argon matrices, and their esr spectra were examined. For pyrrole, pyrazole, and imidazole, the anion radicals were found to exist in their tautomeric α -pyrrolenine form, e.g., **2** as shown in the text. In the case of indole anion, the N-H proton was found to transfer to the benzene ring giving rise to the anion radical of the form VII (see text).

Early studies of pyrroles noted the similarity between the chemistry of pyrroles and phenols. The noted similarity was initially attributed to their tautomerism: IA \rightleftharpoons IB and IIA \rightleftharpoons IIB. Subsequent studies, however, showed that neither phenol nor pyrrole exists in its keto (IB) or imine (IIB) tau-

(1) For an account on pyridyl radicals, see P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **94**, 720 (1972).

omeric form. The similarity of the chemistry is now understood in terms of the positive charge imparted into the resonating π orbitals by the electro-negative heteroatoms.²

Recently we have examined the electron spin reso-

(2) For a historic account of the comparison of the chemistry of pyrroles and phenols, see R. C. Elderfield, Ed., "Heterocyclic Compounds," Vol. 1, Wiley, New York, N. Y., 1950.

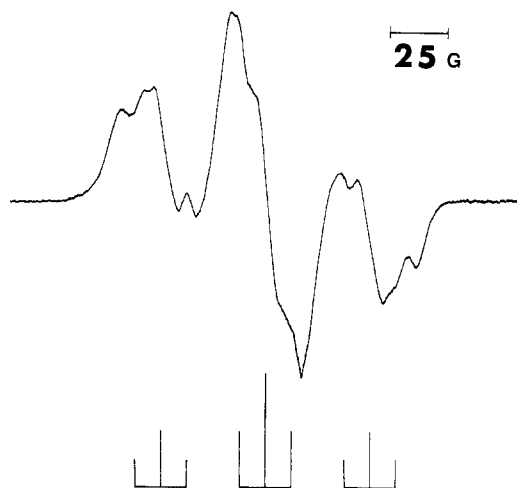
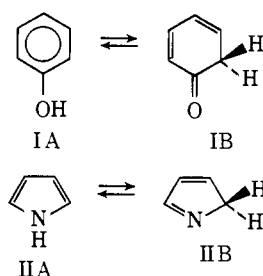
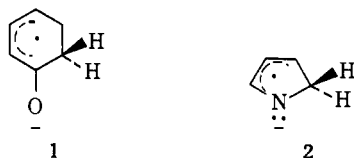


Figure 1. ESR spectrum of anion radicals of pyrrole generated in an argon matrix.



nance (ESR) spectrum of phenol anion radicals generated within an argon matrix and found that they exist in the keto form³ 1. This somewhat surprising result



can be understood as a manifestation of the effect of an extra electron upon the enol-keto tautomerism of the phenol molecule. Phenol itself, due to its low ionization potential (~ 8.5 eV), tends to behave as an electron donor. On the other hand, a carbonyl group linked to a conjugated system (e.g., IB) is known to constitute a good electron-accepting system. Substituted amines also possess low ionization potential (~ 8.5 eV). An imine group linked to a conjugated system such as IIB, however, should also behave as an electron acceptor giving rise to a radical of type 2.

Reported in this paper are the ESR spectra and their analyses of the anion radicals of pyrrole, pyrazole, imidazole, and indole generated within argon matrices at $\sim 4^\circ\text{K}$ by the photoelectron transfer process.⁴ In each case the radical was found to possess the proton transferred structure of the type proposed above.

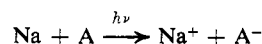
Experimental Section

The detailed description of the apparatus and the method which would permit generation of charged species within a rare gas matrix at $\sim 4^\circ\text{K}$ and the observation of the ESR spectrum of the resulting ion

(3) P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **94**, 6872 (1972).

(4) P. H. Kasai, *Accounts Chem. Res.*, **4**, 329 (1971).

radicals has been reported previously.⁴ In the present series of experiments, the parent molecules (electron acceptors) were trapped together with Na atoms (electron donors) within an argon matrix, the composition being roughly 1000:10:1 for argon atoms, the parent molecules, and Na atoms, respectively. The ESR spectrum of the resulting matrix was then examined prior to, and after the irradiation of the matrix with "yellow" light ($\lambda > 5500 \text{ \AA}$).⁵ Prior to the irradiation, the matrix exhibited only the ESR signals due to Na atoms. The irradiation resulted in the disappearance of the Na signals and the appearance of a signal consisting of several hyperfine components centered about the position corresponding to $g = 2.002$. The photoinduced signals are assigned to the anion radicals produced by the photoelectron transfer process

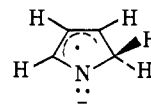


All the ESR spectra were obtained while the matrix was maintained at $\sim 4^\circ\text{K}$. The frequency of the spectrometer locked to the loaded sample cavity was 9,435 GHz.

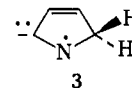
The chemicals, pyrrole, pyrazole, imidazole, and indole were obtained from Aldrich Chemical Co., and purified further by distillation or sublimation prior to matrix deposition. *N*-Deuterio-pyrrole ($\text{C}_4\text{H}_4\text{ND}$), perdeuterio-pyrrole ($\text{C}_4\text{D}_4\text{ND}$), and tetra-deuterio-pyrrole ($\text{C}_4\text{D}_4\text{NH}$) were prepared by the method described by Bak, *et al.*⁶ 2-, 4-, and 6-methylindoles were obtained from Research Organic/Inorganic Chemicals Corp.

Spectra and Assignments

Pyrrole. Figure 1 shows the photoinduced spectrum obtained from an argon matrix containing Na atoms and pyrrole molecules. The triplet-of-triplet feature indicated in the figure is quite discernible. The large isotropic triplet with a spacing of 45 G immediately precludes the possibility that the signal arises from a π -type pyrrole anion radical possessing a planar aromatic structure. We propose that the observed spectrum be assigned to the anion of pyrrole in its imine form IIB. We note that, in this configuration, the extra



negative charge is essentially localized at the nitrogen $2p_\pi$ orbital, whereas the spin density is delocalized over the C-3 to C-5 allylic system. The large triplet with a spacing of 45 G is attributed to the hyperfine interactions with the two protons at the C-2 projected above and below the skeletal plane. The large isotropic coupling constant results from a direct overlap of the $1s$ orbitals of these protons with the $2p_\pi$ orbital of the C-3. The smaller triplet feature with a spacing of 11 G is attributed to protons 3 and 5. Since these protons are π protons (i.e., they are situated within the nodal plane of the $2p_\pi$ orbitals), the spin density ρ at C-3 and C-5 can be estimated using the McConnell's relation⁷ $A_{\text{iso}} = Q\rho$, where $Q = 23$ G. A large spin density of $+0.48$ thus estimated at each of these carbons indicates, in turn, a small spin density at the nitrogen $2p_\pi$ orbital, hence a small contribution of the valence bond structure such as 3. Figure 2



(5) Here the lowest resonance absorption of Na atoms (the D line transitions at 5890 \AA) is being utilized for the electron-transfer process. Irradiation with more energetic light often led to photodegradation of the primary radicals. See ref 1, for example.

(6) B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, **24**, 720 (1956).

(7) H. M. McConnell and D. B. Chestnut, *ibid.*, **28**, 107 (1958).

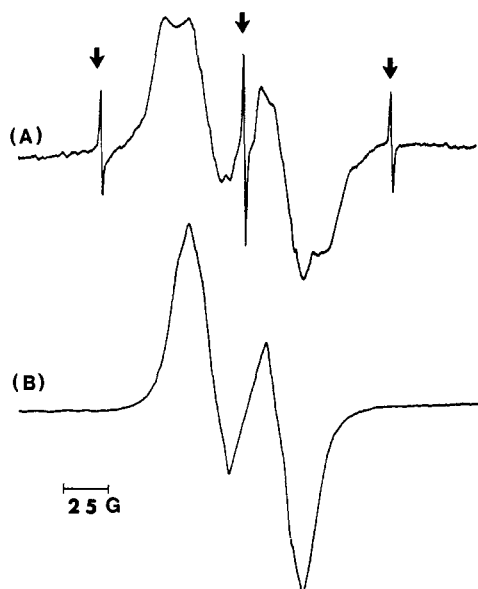
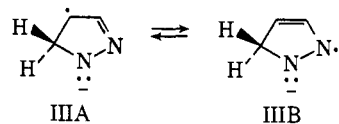


Figure 2. (A) ESR spectrum of monodeuteriopyrrole (C_4H_4ND) anion radicals generated in an argon matrix. The sharp triplet signals indicated by the arrows are due to deuterium atoms. (B) ESR spectrum of tetradeuteriopyrrole (C_4D_4NH) anion radicals generated in an argon matrix.

shows the resultant spectra obtained when the experiment was repeated using monodeuterated pyrrole (C_4H_4ND) and tetradeuterated pyrrole (C_4D_4NH), respectively. The doublet-of-triplet pattern obtained with the former and the doublet pattern obtained with the latter are exactly those expected from the proposed assignment, and provide an unequivocal proof for the migration of the N-H proton. Shown in Figure 3 is the spectrum obtained when the perdeuterio species (CD_4ND) was used. It is compared with the quintet pattern expected from the CD_2 group. In an agreement with the conclusion reached earlier, the spectrum shows very little, if any, effect of the hyperfine interaction with the ^{14}N nucleus.

Pyrazole. Figure 4 shows the esr spectrum of photo-induced anion radicals of pyrazole. The triplet-of-double feature can be easily recognized. Again, the possibility of the radical being a π -type anion radical of pyrazole possessing the original structure is excluded by the triplet feature with a large spacing of ~ 50 G. We assigned the spectrum to the proton-transferred form III. The triplet feature is attributed to the two



protons at C-5, and the doublet with a spacing of ~ 15 G to proton 4. Thus the spin density at C-4 is quite substantial ($\sim +0.7$), and indicated a smallness of the contribution of the valence bond structure IIIB. This is understandable since the π -bond contribution in a C=N double bond is much larger than that in a C=C double bond.

Imidazole. If a similar proton transfer is to occur for imidazole anion radicals, an intriguing question is whether it would occur to the position 2 giving rise to the radical IV or to the position 5 giving rise to the

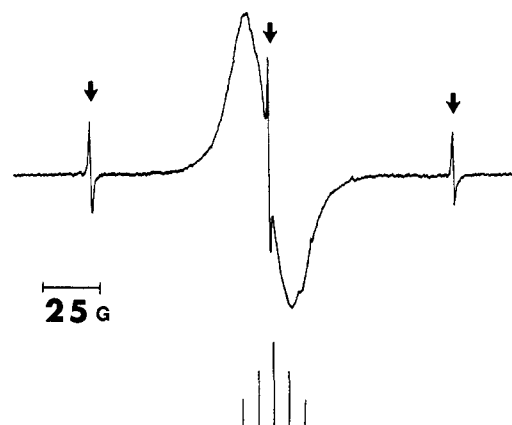


Figure 3. ESR spectrum of perdeuteriopyrrole (C_4D_4ND) anion radicals generated in an argon matrix. The sharp triplet signals indicated by the arrows are due to deuterium atoms.

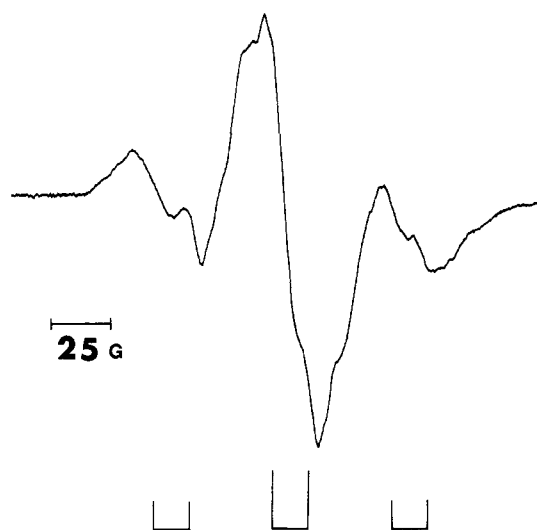
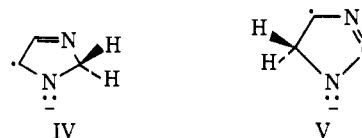


Figure 4. ESR spectrum of pyrazole anion radicals generated in an argon matrix.

radical V. The radical IV is expected to have a smaller



coupling constant to the CH_2 protons than the radical V, the spin density of which is essentially localized at the carbon adjacent to the CH_2 group. The coupling constant of the latter should be comparable to those observed with pyrrole or pyrazole anion radicals. Figure 5 shows the spectrum obtained from the imidazole anion radicals generated in an argon matrix. The large triplet feature with a spacing of 50 G strongly suggests that the radical V has been formed. A doublet splitting of ~ 15 G attributable to the proton 4 is barely recognized in each component of the triplet. The resolution of the doublet, we believe, is obscured by the presence of coupling to the ^{14}N nucleus at the position 3. A further substantiation to our assignment was obtained when the experiment was repeated on 2-methylimidazole. The resultant spectrum was identical with that shown in Figure 5.

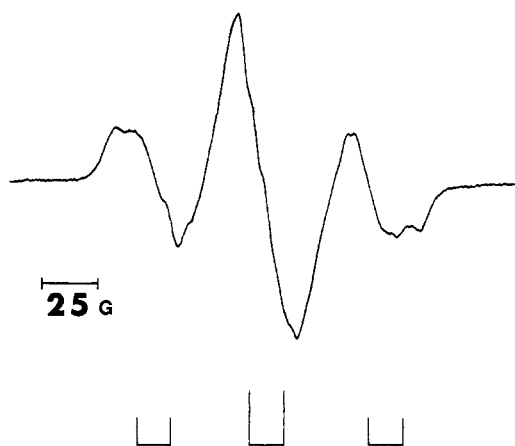


Figure 5. ESR spectrum of imidazole anion radicals generated in an argon matrix.

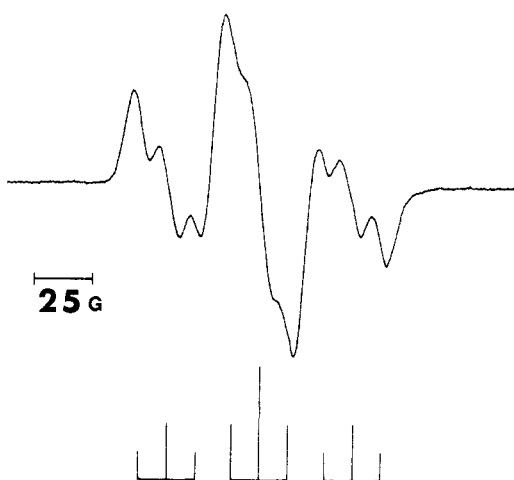
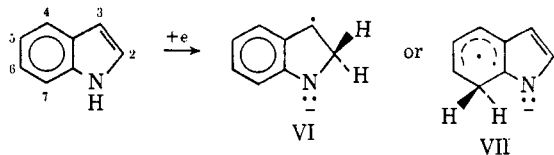


Figure 6. ESR spectrum of indole anion radicals generated in an argon matrix.

Indole. When one considers the acidic nature of the N proton in indole, one can not help noting that the $C_6H_5-N(H)-$ section of indole is isoelectronic to phenol C_6H_5OH . Then a question of extreme interest is whether in its anionic form, an indole molecule would behave like pyrrole giving rise to the radical VI, or like phenol giving rise to the radical VII. The esr spectrum of



indole anion radicals generated in an argon matrix is shown in Figure 6. The well-resolved triplet-of-triplet pattern indicated in the figure strongly suggests that the proton transfer occurs to C-7 resulting in the formation of VII. As in the case of phenol anion,³ the large triplet with a spacing of 40 G is assigned to the two protons at C-7, and the small triplet with a spacing of 12 G is assigned to protons 4 and 6. Further substantiation to this assignment was provided by the esr spectra of 3-methylindole, 4-methylindole, and 6-methylindole anion radicals similarly generated in argon matrices. The spectrum of anion radicals of 3-methylindole was identical with that of indole anion

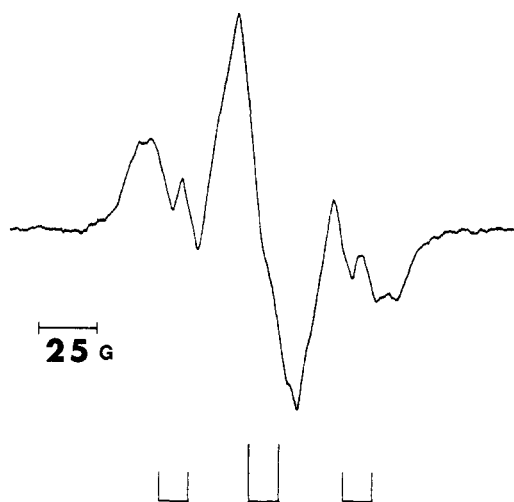


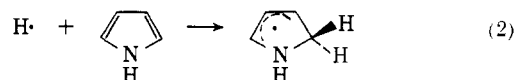
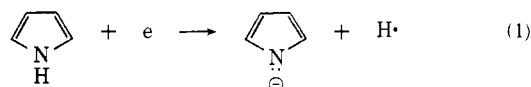
Figure 7. ESR spectrum of 4-methylindole anion radicals generated in an argon matrix.

radicals. The spectra of both 4- and 6-methylindole appeared as triplet of doublets (Figure 7).

It may appear surprising that indole would behave more like phenol rather than pyrrole under strongly reducing conditions. However, evidence to this effect is not without a precedent. O'Brien and Smith⁸ have shown that, in Na-EtOH-NH₃ solution, indoles and carbazoles are reduced preferentially in the benzene ring.

Discussion

The triplet-of-triplet pattern such as that observed with pyrrole (Figure 1) can also be expected from a radical formed by addition of a hydrogen atom to a neutral pyrrole molecule. For example, see eq 1



and 2. The possibility that radicals reported in the present study result from intermolecular transfer of hydrogen atoms has been ruled out for the following reasons: (1) only a mild radiation ($\lambda > 5500 \text{ \AA}$) is used for the generation of the anions; (2) only a trace amount of atomic hydrogen was detected in the matrix;⁹ and (3) only one kind of radical was detected from a molecule such as indole for which hydrogen atom addition could occur at several different places. We believe that the structures proposed for the anions result entirely from the intramolecular transfer of the imino hydrogen.

Experimentally determined isotropic hyperfine coupling constants of the anions are tabulated in Table I and are compared with those calculated by INDO molecular orbital theory.¹⁰ For the calculation, the structures of pyrrole, pyrazole, and imidazole anions

(8) S. O'Brien and D. C. C. Smith, *J. Chem. Soc.*, 4609 (1960).

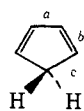
(9) Whenever hydrogen atoms are released within an argon matrix, a strong esr signal due to hydrogen atoms (a doublet with a spacing of $\sim 500 \text{ G}$) is detected. See, for example, ref 1 or P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **94**, 7975 (1972).

(10) J. A. Pople, and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

Table I. Observed and Calculated Isotropic Hyperfine Coupling Constants to Protons (in Gauss)

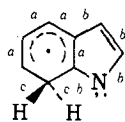
Anion	Proton	Obsd	INDO
2	C-2	45 ± 2	45
	C-3	11 ± 2	8
	C-4		0.5
IIIA	C-5	11 ± 2	5
	C-3		1
	C-4	15 ± 2	9
V	C-5	50 ± 2	52
	C-2		2
	C-4	15 ± 4	11
VII	C-5	50 ± 2	50
	C-2		1
	C-3		1
	C-4	12 ± 2	9
	C-5		5
	C-6	12 ± 2	11
	C-7	40 ± 2	49

were assumed to be the same as that of cyclopentadiene.¹¹



$$\begin{aligned} \text{all C-H} &= 1.09 \text{ \AA} \\ a &= 1.46 \\ b &= 1.35 \\ c &= 1.53 \\ \angle ab &= 110^\circ \quad \angle \text{HCH} = 109^\circ \end{aligned}$$

The structural parameters assumed for indole anion (VII) are

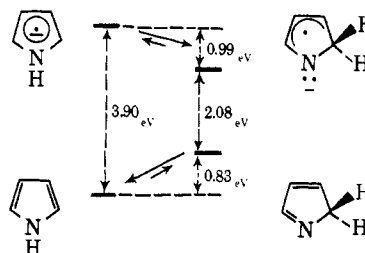


$$\begin{aligned} \text{all C-H} &= 1.09 \text{ \AA} \\ a = b &= 1.40 \\ c &= 1.50 \\ \angle aa &= 120^\circ, \quad \angle ab = 110^\circ \\ \angle \text{HCH} &= 109^\circ \end{aligned}$$

(11) V. Schomaker and L. Pauling, *J. Amer. Chem. Soc.*, **61**, 1796 (1939).

In spite of the assumptions made for the structures of the radicals, the overall agreement between the observed and calculated coupling constant is quite reasonable, and can be accepted as a further substantiation to the proposed assignments.

As stated earlier, the tautomerism between pyrrole (IIA) and α -pyrrolenine (IIB) is almost nonexistent, the pyrrole form IIA totally dominating the equilibrium. The observed reversal of the tautomeric equilibrium in the anionic state must be a consequence of the fact that α -pyrrolenine is a much better electron acceptor than pyrrole. We have examined the energetic relations between pyrrole and α -pyrrolenine both in their neutral state and anionic form using INDO molecular orbital theory. The known structural parameters were used for pyrrole,⁶ and the structure of cyclopentadiene was assumed for α -pyrrolenine. Comparison of the total energies of the respective species gave the result shown in Chart I. Because of the assump-

Chart I

tions made for the structures of pyrrole anion, α -pyrrolenine and its anion, the exact energy differences given above should be accepted with some reservation. Nevertheless, the relative stabilities of the four species predicted by the theory are in complete agreement with the experimental results encountered in this study.

Theoretical Study of the Fluorine-Fluorine Nuclear Spin Coupling Constants. II. Stereochemical Dependences

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Contribution from the Faculty of Engineering, Kyoto University, Kyoto, Japan. Received April 3, 1972

Abstract: Stereochemical dependences of F-F coupling constants are studied theoretically by using the INDO-MO's and the sum-over-states perturbation method. The F-F coupling is sensitive to the geometrical relationship of the two spin-coupled fluorines although far different from that of the H-H coupling. The origin of the angular dependence of geminal F-F coupling on the FCF angle is chiefly due to the FC term and both the SD and OB terms are insensitive to the angular changes. In vicinal F-F coupling, no clear tendency as a function of the dihedral angle is found. The long-range F-F coupling exhibits steric dependence strongly, which originates also from the FC term. The "fragment" coupling shows a dramatic dependence on the internuclear separation of the coupled fluorines. The origin of the fragment coupling is considered in more detail. From the striking angular dependences of the five-bond F-F couplings, nonplanarity of hexafluorobutadiene is supported.

As nuclear magnetic resonance (nmr) spectroscopy takes first place in importance for the organic chemist, the number of experimental values of coupling constants between fluorine nuclei is increasing rapidly. However, unlike H-H coupling constants, there is no

satisfactory theoretical interpretation of these data until recently because of the lack of knowledge of the mechanisms of F-F coupling constants. In this series of papers our aim is to present a systematic theoretical study of the F-F coupling constants. In part I of this