

Carbon-13 Magnetic Resonance. XII. Five-Membered Nitrogen Heterocycles and Their Charged Species¹

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Abstract: Carbon-13 chemical shifts are reported for several five-membered nitrogen heterocycles and for their anionic and cationic forms found, respectively, in basic and acidic solutions. The effect on the chemical shift of removing or adding protons to these nitrogen bases was found to follow an additive relationship with the greatest deviations noted in the diprotonated species. Extended Hückel and self-consistent-field molecular wave functions in both σ and π electrons were used to rationalize the chemical shifts. Protonation effects, +9.04 ppm at α carbons and -1.59 at β carbons, are explained in terms of variations in the orbital charge densities and in the bond orders. The upfield protonation shift at the α carbon is associated with a decrease in the order of the N-C $_{\alpha}$ bonds, whereas the change in charge density with protonation at the α carbon is in the wrong direction to explain the α -protonation shift. Conversely, shifts at β positions appear to be dominated by inductive effects.

The carbon-13 chemical shifts of the six-membered azines were originally reported by Lauterbur,² who used a modification of a chemical shift expression proposed by Karplus and Pople³ to estimate the C-N σ -bond polarization in these simple heterocyclic systems. Pugmire and Grant⁴ then extended the measurement of the chemical shifts of the six-membered nitrogen heterocycles to include their protonated cationic species. Using a form of the paramagnetic shielding expression of Karplus and Das,⁵ which is similar to that proposed by Karplus and Pople,³ the authors⁴ discussed the theoretical basis of these protonation effects. This work stressed the importance of both charge-polarization and bond-order features. Adam, *et al.*,⁶ have proposed that our data on nitrogen heterocycles correlate fairly well with theoretical charge densities provided σ as well as π electrons are considered, and Bloor and Breen⁷ have reached a similar conclusion. These latter workers further suggest that the inclusion of bond-order terms leads to a deterioration in the correlation between experiment and theory.

The carbon-13 chemical shifts of some five-membered heterocycles (pyrrole, thiophene, and furan along with selected derivatives) have been reported previously.⁸ This present study is concerned with some of the five-membered azines (pyrrole, imidazole, pyrazole) and the effect of protonation and deprotonation to give their respective cationic and anionic species. Protonation parameters, observed to be similar with those found in the six-membered azines, are rationalized along the theoretical lines previously outlined⁴ using both the extended Hückel theory (EHT) of Hoffmann⁹ and the complete neglect of differential overlap-self-consistent-field (CNDO-SCF) approach of Pople and co-workers.¹⁰⁻¹² The five-membered azines offer a wider

range of polarization than the six-membered series because some of these species can exist in both the anionic and cationic forms. As these effects give rise to a chemical shift range of better than 41 ppm, this class of compounds affords an excellent opportunity for testing not only the validity of carbon-13 chemical shift theory, but also the effectiveness of various molecular wave functions as a means for estimating chemical shifts.

Experimental Section

A. Equipment. A Varian high-resolution spectrometer equipped with a V-4311 transmitter operating at 15.085 Mcps was used to observe the carbon-13 magnetic resonance spectra. Proton decoupling was accomplished with a Varian V-4320 spin decoupler operating at 60 Mcps in the manner described previously.¹³

B. Spectroscopic Details. With the exception of the pyrrole anion, solid samples were dissolved and run in distilled water while pyrrole was run as a neat liquid. The decoupled carbon-13 resonance peaks were obtained under conditions of adiabatic rapid passage to determine the approximate decoupler frequency, and then a precise determination was made of the decoupling frequency under slow sweep conditions with sample spinning. The chemical shift in parts per million from benzene is determined from Γ_i , the ratio of the decoupler frequency to the transmitter frequency (f_i/ν_i), and the corresponding proton chemical shift in accordance with eq 1.

$$\delta_{C^{13}} = \frac{\Gamma_i - \Gamma_0}{\Gamma_i} + \frac{\Gamma_0}{\Gamma_i} \delta_H \cong \frac{\Gamma_i - \Gamma_0}{\Gamma_i} + \delta_H \quad (1)$$

C. Sample Preparation. All samples were degassed under vacuum by the normal freeze-thaw method in a methanol and Dry Ice bath and then sealed in 12-mm tubes. Samples for proton analysis were prepared in a similar manner in 5-mm tubes. TMS was used in pyrrole and its anion as an internal standard, and the sodium salt of 3-trimethylsilylpropane-1-sulfonic acid was used as an internal standard in the aqueous solutions.

Pyrrole, pyrazole, and imidazole were obtained from standard commercial sources and pyrrole was run as a neat liquid. Pyrazole and imidazole were run as saturated aqueous solutions. Lithium pyrrolate was prepared according to the method of Hobbs, *et al.*,¹⁴ and observed in saturated tetrahydrofuran. Potassium imidazolate, potassium pyrazolate, imidazole hydrochloride, and pyrazole hydrochloride were prepared in the laboratory from simple acid-base reactions and were run as saturated aqueous solutions.

(1) Previous paper in series: W. M. Litchman and D. M. Grant, *J. Am. Chem. Soc.*, **90**, 1400 (1968).

(2) P. C. Lauterbur, *J. Chem. Phys.*, **43**, 360 (1965).

(3) M. Karplus and J. A. Pople, *ibid.*, **38**, 2803 (1963).

(4) R. J. Pugmire and D. M. Grant, *J. Am. Chem. Soc.*, **90**, 697 (1968).

(5) M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961).

(6) W. Adam, A. Grimison, and G. Rodrigues, *Tetrahedron*, **23**, 2513 (1967).

(7) J. E. Bloor and D. L. Breen, *J. Am. Chem. Soc.*, **89**, 6835 (1967).

(8) T. F. Page, Jr., T. D. Alger, and D. M. Grant, *ibid.*, **87**, 5333 (1965).

(9) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(10) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965).

(11) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); **44**, 3289 (1966).

(12) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).






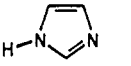




(13) W. R. Woolfenden and D. M. Grant, *ibid.*, **88**, 1496 (1966).

(14) C. F. Hobbs, C. K. McMillin, E. P. Papadopoulos, and C. A. VanderWerf, *ibid.*, **84**, 43 (1962).

Results

A. Proton Chemical Shifts. The proton chemical shifts of all molecules studied in this work are given in Table I. These species consist of the anionic free bases, the parent compounds, and the protonated cations of imidazole and pyrazole. When the free pair of electrons in a nitrogen heterocycle are protonated, the values of the proton chemical shifts move downfield

Table I. C^{13} Chemical Shifts of the Five-Membered Azines and Their Charged Species

Compound	Position	Γ_i	$\delta_H,^a$ ppm	$\Delta\delta_{C^{13}},^a$ ppm
	...	3.976449164	0	0
	1.58 ^b	+25.7 ^c
	2	3.976453448	0.37	1.45
	3	3.976532534	1.15	22.12
	2	3.976486295	0.75	10.09 ^d
	3	3.976526733	0.97	20.48 ^d
	2	3.976385043	-0.42	-16.55
	4,5	3.976456175	0.02	1.78
	2	3.976421305	-0.68	-7.69
	4,5	3.976473941	-0.02	6.21
	2	3.976434099	-2.26	-6.05
	4,5	3.976485938	-0.81	8.44
	3,5	3.976410032	-0.18	-10.02
	4	3.976544538	1.12	25.10
	3,5	3.976426936	-0.48	-6.06
	4	3.976537777	0.85	23.13
	3,5	3.976429522	-1.58	-6.52
	4	3.976527038	-0.01	19.57

^a Values are all taken relative to benzene. ^b T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963). ^c H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, **14**, 468 (1961). ^d Reference 8.

with respect to the nonprotonated species⁴ except for the pyrrolate-pyrrole pair. Adding a proton to the pyrrole anion results in a normal downfield shift at the α proton but an upfield shift for the β proton.

B. Carbon-13 Chemical Shifts. The carbon-13 chemical shifts for the five-membered azines and their charged species are given also in Table I. Spectral assignments for imidazole, pyrazole, and their charged species were made on the basis of peak intensities, while the pyrrole peak assignments were taken from Page, Alger, and Grant.⁸ The spectra of the pyrrole anion was interpreted on the basis of the chemical shifts of

pyrrole and the additivity parameters found when imidazole and pyrazole anions are protonated.

For the purpose of discussing protonation effects, we have considered pyrrole, imidazole, and pyrazole to be species derived from protonation of their corresponding anions. The carbon-13 chemical shifts at α positions C-2,5 in pyrrole and C-2 in imidazole move upfield +8.6 and +8.9 ppm, respectively, when the free-pair electrons on the nitrogen in the anions are protonated. The β positions C-3,4 in pyrrole and C-4 in pyrazole move downfield -1.6 and -2.0 ppm, respectively, when their corresponding anions are protonated. It is interesting to note that these α -protonation parameters are nearly the same as that found in the six-membered azines⁴ (+7.8 ppm), while the β parameters are smaller in magnitude than the downfield shift value (-4.4 ppm) noted previously in pyridine and related compounds. Tautomeric proton exchange in imidazole averages the α - and β -protonation shifts at C-4,5. Using the pyrrole α and β parameters to predict the effect of this tautomerism, one anticipates a +3.5-ppm shift in C-4,5 of imidazole, whereas the experimental value was observed to be +4.4 ppm. Similar arguments applied to pyrazole also predict a protonation shift of +3.5 ppm in the resonance of positions C-3,5. This compares fairly well with the experimental shift of +4.0 ppm.

Introducing the second proton into imidazole results in an upfield shift which is significantly less than that observed for the protonation of the anion. One can only conclude that the successive perturbations associated with the first and second protons are too severe to preserve the additivity features at C-2 because this carbon is sandwiched in between the two nitrogens. Positions C-4,5 simultaneously have α - and β -protonated nitrogens in the cation, and one can expect a chemical shift change due to protonation of about +7.6 ppm at these carbons. This compares reasonably well with the experimental value of +6.7 ppm measured with respect to the anion.

When pyrazole is protonated to give the cation, the C-3,5 and C-4 resonance lines move downfield -0.5 and -3.6 ppm from their respective positions in the neutral species. While the -3.6-ppm β shift has the same sign as the β shift due to the first hydrogen, the magnitude of the shift is almost twice as large. It is assumed that the greater magnitude results from some sort of buttressing effect, as C-4 is simultaneously β to both protonated nitrogen atoms. The relatively small downfield shift at C-3,5 reflects a reduced α -protonation parameter with diprotonation. When two protonated nitrogen atoms are adjacent to one another, some cancellation of the two perturbations apparently is realized. Deviations from simple additivity were previously noted in the case of imidazole cation as well as in diprotonated pyrimidine.⁴

The preceding discussion indicates that relatively simple relationships exist between the chemical shifts and the degree of protonation for the monoprotinated species, and therefore in these species a regression analysis was undertaken in terms of the position of the protonated nitrogen relative to the designated carbon atom to determine the best set of additivity parameters. The parameters resulting from this analysis are given in Figure 1 which also depicts the success of the linear

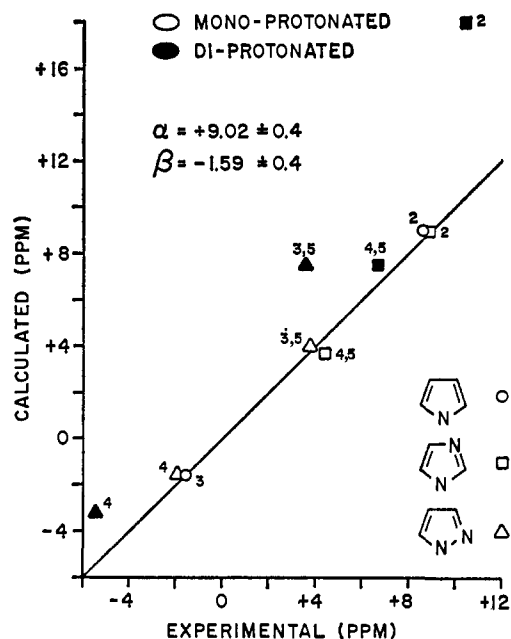


Figure 1. Two protonation parameters, obtained from a regression analysis, are used to correlate carbon-13 chemical shifts of the parent five-membered heterocycles with respect to the unprotonated anions. These protonation parameters are then used to predict the shifts of the doubly protonated cations with respect to their anions.

regression fit of the data. The α - and β -protonation parameters of +9.04 and -1.59 ppm, respectively, found in the five-membered azines are similar in direction and magnitude with the corresponding values (+7.8 and -4.4 ppm) obtained in the six-membered azines.⁴ The reasonably close correlation in values for the two systems suggests that the results are produced by similar chemical shift mechanisms.

The α - and β -protonation parameters obtained on the monoprotinated species were used to approximate the shifts in the diprotinated pyrazole and imidazole cations, and these results (filled symbols) are shown also in Figure 1. While the monoprotination parameters predict the correct trends in the diprotinated species, the increased scatter indicates that additivity does begin to break down in the cations. In all probability, these deviations result from anticipated competitive and buttressing effects which violate the requirements for additive results. Linear additive relationships can only be expected when two perturbations are sufficiently small that the accumulative effect of both perturbing groups is still small. As this apparently is not the case in some of the five-membered diazines, we now turn to approximate quantum mechanical treatments as a means of rationalizing the chemical shift data.

Calculations and Discussions

Readily available¹⁵ computer programs for calculating approximate molecular wave functions for both σ and π electrons now make it possible to explore the electronic features important in the carbon-13 magnetic shielding tensor. In the EHT method,¹⁶ all exchange

(15) The authors wish to express appreciation to R. Hoffmann and G. A. Segal for providing computer programs No. 30 (EHT) and 91 (CNDO-SCF), respectively, through the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind. 47401.

integrals are estimated from orbital ionization potentials¹⁷ given in units of electron volts in eq 2, where

$$\begin{aligned} I_N(2s) &= -27.43 - 13.64\Delta_N \\ I_N(2p) &= -14.02 - 13.64\Delta_N \\ I_C(2s) &= -21.16 - 11.56\Delta_C \\ I_C(2p) &= -11.20 - 11.56\Delta_C \end{aligned} \quad (2)$$

Δ_N and Δ_C represent formal charges on the nitrogen or the carbon atom, respectively. To study sizeable charge-polarization effects, as found in protonation of nitrogen heterocycles, it is necessary in this formalism to vary the Δ 's in some consistent manner. Protonation of a nitrogen free pair in the six-membered azines required a value of Δ_{NH} equal to 0.3 to achieve the best fit of the carbon-13 data. Unless Δ_N values are varied with protonation the π -electron densities do not change in the EHT method because of the separation of σ and π effects by symmetry consideration. In the CNDO-SCF approach, iterative self-consistent field methods are used to obviate this need for selecting Δ parameters. The only serious difficulty encountered in the use of the CNDO-SCF functions to calculate carbon-13 shifts arises from the neglect of overlap in these LCAO functions. This makes bond-order parameters artificially high¹⁸ and accounts in part for the greater scatter in the CNDO-SCF calculations of Bloor and Breen⁷ when bond-order type terms were included in the chemical shift calculations.

In the five-membered nitrogen heterocycles, one finds four types of nitrogens if classical valence-bond structures are drawn for this series. These include unprotonated nitrogen atoms with a neutral and negative formal charge and protonated nitrogens which exhibit a neutral and positive charge. When this problem is further complicated with tautomeric averaging, it becomes evident that it is not possible to vary the Δ_N 's to account for all of the classical types of nitrogen without overparameterizing the problem. For this reason we have calculated shifts by the EHT method for the assumption of $\Delta_N = 0$, and these results are given in Figure 2. The chemical shifts were calculated using eq 12 and 13 of ref 4.

While the gross features in the chemical shifts are characterized by the EHT method, many of the more refined features, due in the main to protonation effects, are not rationalized with this calculation. In Figure 2 note especially the shifts for C-2 in the three imidazole species and for C-4 in the various forms of pyrazole. In each of these examples the predicted trends are opposite in direction from the experimental ones. Careful study of Figure 2 will indicate that there are several other minor discrepancies of this nature which indicate certain inadequacies of the EHT treatment. The success of the over-all correlation, which is some-

(16) See ref 9 for complete details of the EHT method and ref 4 for how the method is applied to the calculation of carbon-13 shifts.

(17) L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, **43**, S160 (1965).

(18) See T. D. Alger, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.*, **88**, 5397 (1966), for a fairly complete discussion of this problem as it relates to carbon-13 chemical shift calculations of bridge-head carbons. The large deviation of predicted values in ref 7 for the bridge-head shifts in quinoline and isoquinoline follows directly from the inordinately large bond orders calculated for bridge-head carbons when overlap is neglected in the normalization of the wave functions. The authors have a manuscript in preparation discussing the problem of predicting bridge-head shifts.

what reasonable when one considers the gross approximations required in any quantum mechanical treatment of this nature, reflects the faithful representation by almost all MO functions of significant polarization features arising from the presence of a nitrogen atom, protonated or otherwise, in an aromatic system. Only when more refined features are considered do problems arise with the EHT formalism. In the case of protonated pyridine and related compounds discussed earlier,⁴ it was found that an increase in the effective electronegativity of protonated nitrogens reduces the N-C α bond orders sufficiently to realize an upfield shift in the α carbons. As the protonation parameters are similar for both five- and six-membered nitrogen heterocycles, we can only assume that similar changes in Δ_N would be required in the five-membered heterocycles if the upfield α -protonation parameter is to be predicted.

Because of the large number of Δ parameters in eq 2, it is obvious that these values could be varied to give an exact fit of the chemical shifts for any member of the series, e.g., pyrrole. However, as we are desirous of delineating the validity of chemical shift expressions in this paper, it was felt that little benefit would be derived from over parameterizing the calculation to achieve a perfect fit. An interesting result was obtained from the EHT approach, however, by varying the Δ 's given in eq 2 until both σ and π electron densities from the EHT treatment were in agreement with the corresponding values obtained by Newton, Boer, and Lipscomb¹⁹ with a more sophisticated SCF-MO wave function. Agreement in orbital charges between the EHT and SCF-MO charge densities were realized for $\Delta_N(2s) = -0.35$, $\Delta_N(2p) = -0.165$, $\Delta_{C\alpha}(2s) = +0.10$, and $\Delta_{C\alpha}(2p) = +0.025$ with the Δ values zero for the β carbon. It should be observed that the change in the Δ values and therefore in the ionization potentials are relatively small especially at the α carbons. The negative sign for a Δ value allows electronic charge to flow out of the designated orbital, whereas a positive Δ has the opposite effect. The chemical shift estimates obtained from this modified EHT wave function are given in Table II

Table II. Theoretical Estimates of the Carbon-13 Chemical Shifts in Pyrrole

Method	Carbon-13 chemical shifts in ppm relative to C ₆ H ₆	
	C α	C β
1. EHT	-5.0	+9.0
2. Modified EHT ^a	+9.1	+19.8
3. CNDO-SCF	+15.7	+15.4
4. Experimental ^b	+10.09	+20.48

^a Ionization potentials given in eq 1 were modified so as to give charge densities which agree with the results of Newton, Boer, and Lipscomb.¹⁹ ^b Reference 8.

along with the several other theoretical estimates for pyrrole. While the excellent agreement of the modified EHT calculation may be somewhat fortuitous, it is felt that the success does suggest the superiority of the

(19) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2367 (1966). The authors fully appreciate that the use of the pyrrole wave function of these workers would have been preferable in the chemical shift calculation. The unavailability of these wave functions in a form convenient for our chemical shift subroutine prevented for the present the pursuit of this approach and required the use of this admittedly *ad hoc* treatment.

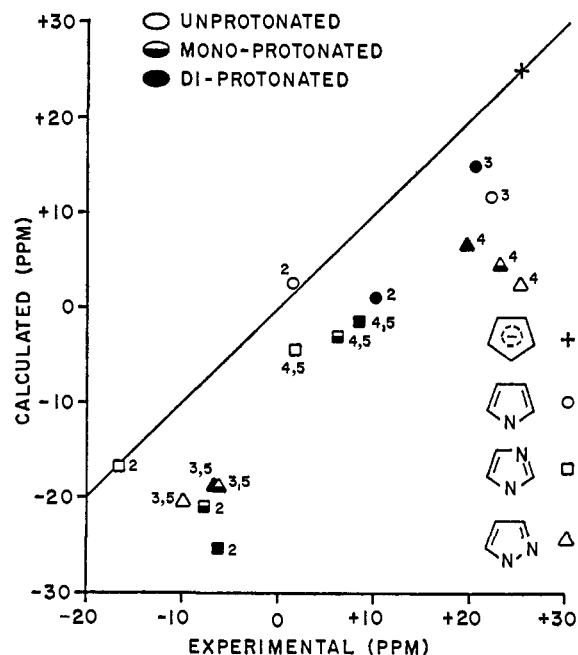


Figure 2. Theoretical chemical shifts predicted by the EHT method are plotted against the experimental shifts for the five-membered nitrogen heterocycles and their cationic and anionic species. It is assumed that protonation of the nitrogen atoms does not affect the Coulomb integral for the nitrogen atom ($\Delta_N = 0$). The average excitation energy is assumed to be 10 eV.

SCF-MO wave function of ref 19 over both the EHT and CNDO-SCF functions.

In spite of the overlap difficulties encountered in the CNDO-SCF treatment of chemical shifts, several factors favor this approach over other formalisms. First, one utilizes the self-consistent-field approach to obviate the need to vary specific exchange integrals in a somewhat arbitrary way. Second, the calculation is relatively economical when compared with other SCF quantum mechanical methods. Finally the output of the CNDO-SCF program has a particularly convenient form for calculating carbon-13 chemical shifts.

Using eq 6 and 7 of ref 4, the theoretical shifts were estimated with the CNDO-SCF method, and the values are plotted *vs.* the experimental quantities in Figure 3. Once again, the over-all chemical shift trend is predicted by this method, and in a few instances (e.g., C-2,5 in pyrrole) the correct positive sign is predicted for the α -protonation parameter. It can be observed from Figure 4 where charge densities and Mulliken overlap populations are given for the various species that the upfield shift at C-2,5 does not come from an increase in charge density (the σ charge decreases by -0.016 and the π density by -0.044) but from a significant decrease (-0.048) in the overlap population of the N-C α π bond.²⁰ Changes in the N-C α σ -bond overlap populations appear to be of less importance than those for π bonds. As can be noted in Figure 4, the overlap population of the N-C α π bond drops in every instance when the anionic species is protonated to give the neutral species, and this decrease in bond order is accompanied by an upfield shift in the α carbon. It is interesting to note that protonation of each anionic species is also

(20) See ref 4 for a complete discussion of both charge-transfer and bond-order effects.

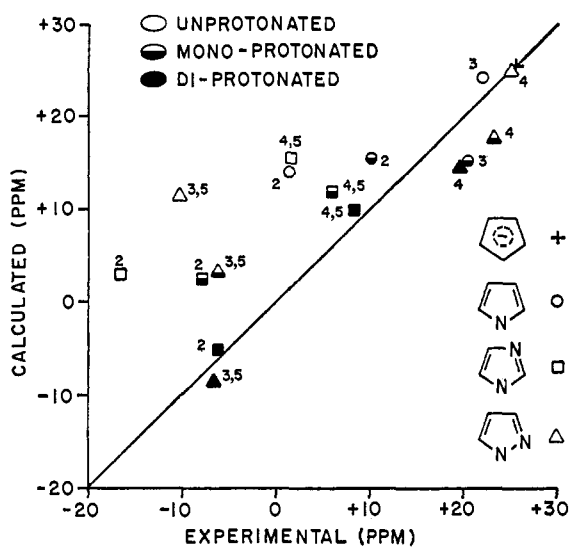


Figure 3. Theoretical chemical shifts predicted by the CNDO-SCF method are plotted against the experimental shifts for the five-membered nitrogen heterocycles and their charged species. The average excitation energy is assumed to be 10 eV.

in imidazole and pyrazole. Note how the overlap populations of the two π bonds at C-2 in imidazole changes from 0.254 to 0.208 and 0.294 (average, 0.250) with the first protonation and then assumes the value of 0.254 with the second protonation. This variation accounts in part for the very low second α -protonation shift at C-2 in imidazole (see Figure 1) as increasing bond orders are associated with downfield shifts. Likewise the π -overlap populations about C-4 in pyrazole anion change dramatically from 0.320 to the two values 0.196 and 0.360 (average, 0.278) with the addition of the first proton, and then in the cation a value of 0.332 is realized for the two π bonds. This value is 0.012 greater than that found in the anion and will result in an enhanced downfield shift. It is a buttressing effect of this type which probably best explains the unusually large second β -protonation shift to lower fields for C-4 in pyrazole (see Figure 1).

While less significant than π -electron effects, changes in the σ -electron system must also be considered. The variations in σ -overlap populations are not as great as those in π -overlap populations, but from

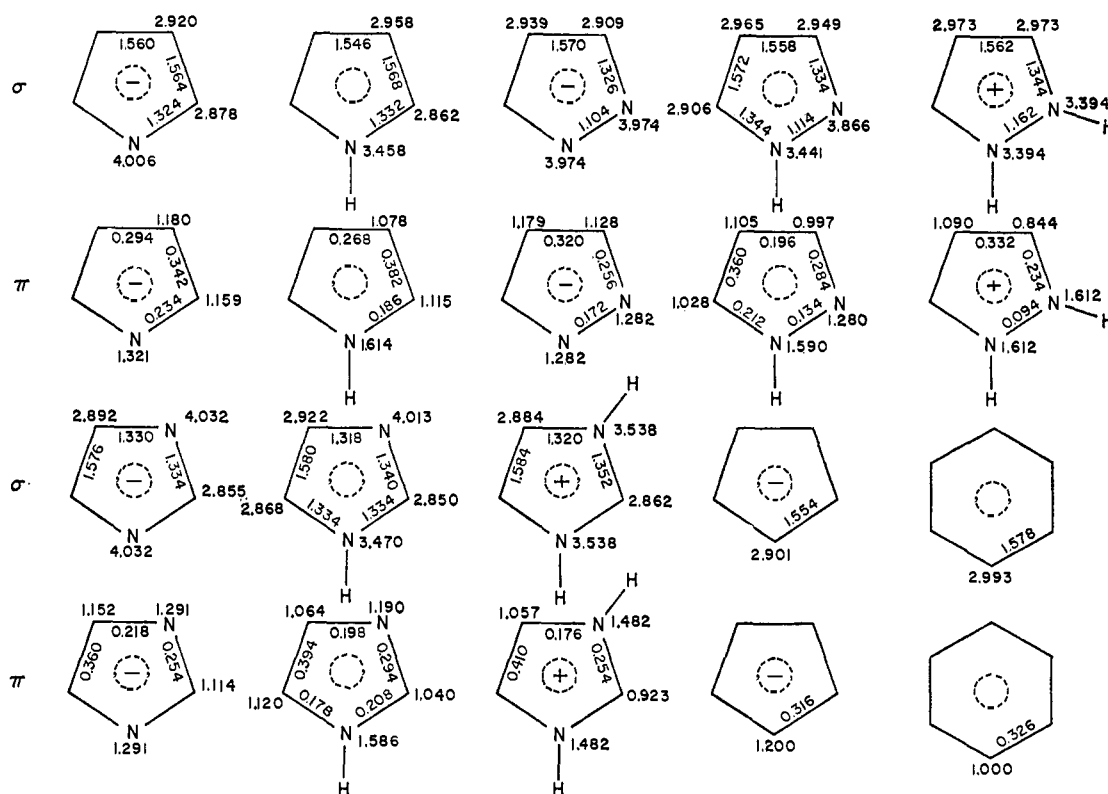




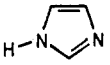






Figure 4. Change densities and Mulliken overlap populations for all five-membered heterocyclic species studied were calculated with the CNDO-SCF method. Overlap populations are given inside the several rings, and charge densities appear external to the rings. σ values are given in the first and third rows while the π system is represented by the second and fourth rows. The overlap populations are defined as $2N \sum_{\mu} \sum_{\nu} c_{i\mu} c_{i\nu} S_{\mu\nu}$, where N is the orbital population (usually 2) and $S_{\mu\nu}$ is the overlap integral between the μ th and ν th atomic orbitals; the index i runs over all occupied molecular orbitals.

accompanied by an increase in the α - β π -bond overlap population and a decrease in the β - β' π -bond overlap population indicating a greater contribution of the traditional bond structure in all of the neutral species than in the anionic or cationic forms. Because of the pronounced effects of protonation on the α - β and β - β' π -bond populations, unusual changes in chemical shifts accompany both the first and second protonation

Figure 4 it can be seen that changes in the σ -charge densities are comparable with those found in the π -electron densities, and therefore make a comparable contribution to the chemical shift calculation. Table III summarizes the relative magnitudes of so-called on- and off-centered terms in the chemical shift expression. The on-centered terms, $\sigma^{(1)}$, are primarily dominated by charge densities while the off-centered terms, $\sigma^{(2)}$,

Table III. Theoretical Estimates of C^{13} Chemical Shifts in the Five-Membered Azines and Their Charged Species

Compound	Position	Theoretical estimates ^a				f	$\sigma^{(total),b}$ ppm	Exptl ^a $\delta_{C^{13}}$, ppm
		$\sigma^{(1)}$, ppm	$\sigma^{(2)}$, ppm	$\sigma^{(total)}$, ppm				
	...	0	0	0	1.000	0	0	
	2	-3.1	-8.6	-11.7	0.985	-17.5	-24.2	
	3	0.2	-1.3	-1.1		-6.3	-3.6	
	2	-6.3	-3.7	-10.0	0.999	-10.3	-15.6	
	3	-4.8	-5.5	-10.3		-10.6	-5.2	
	2	-5.5	-17.2	-22.7	0.970	-34.0	-42.3	
	4, 5	-2.3	-8.3	-10.6		-21.7	-23.9	
	2	-9.4	-13.7	-23.1	0.983	-29.6	-33.4	
	4, 5	-6.1	-7.3	-13.4		-19.4	-19.5	
	2	-16.2	-14.3	-30.5	0.998	-31.2	-31.8	
	4, 5	-9.1	-6.5	-15.6		-16.3	-17.3	
	3, 5	-2.8	-11.1	-13.9	0.970	-25.0	-35.7	
	4	1.3	-1.7	-0.4		-11.0	-0.6	
	3, 5	-9.9	-12.3	-22.2	0.984	-27.4	-31.8	
	4	-2.2	-5.6	-7.8		-13.6	-2.6	
	3, 5	-21.9	-12.2	-34.1	0.998	-34.8	-32.2	
	4	-2.9	-8.0	-10.9		-11.6	-6.1	

^a Taken with respect to cyclopentadienyl anion. ^b Calculated with the assumption $\Delta E = f \times 10$.

reflect bond-order changes. When protonation occurs the on-centered term moves the shift downfield in every instance due to the withdrawal of charge by the additional proton. The upfield protonation shifts at α carbons on the other hand are paralleled in almost every case by a similar shift in the off-centered term.

Combination of the $\sigma^{(1)}$ and $\sigma^{(2)}$ terms at times gives a total shift which fails to account for all experimental trends. However, this failure of the calculation to predict the correct over-all experimental trend for every shift should not obscure the information contained in the theoretical calculations regarding the nature of the screening mechanism derived from an analysis of the factors important in the two separate terms. Furthermore it must be appreciated that severe approximations are invoked in both the formulation of the wave functions and the chemical shift expressions, and one must be content with predicting correct trends and with reasonable semiempirical correlations with structural features. The average energy approximation is one of the more damaging assumptions used in the derivation of the chemical shift expression, and we have investigated the magnitude of this error by varying the ΔE value for the various species.²¹ Using the suggestion of Pople and Santry^{22,23} that ΔE is associated with an

excitation from the bonding to antibonding levels, we have modified ΔE in each compound by an excitation factor " f " given in Table III. To determine f , the separation between the average energy of filled molecular orbitals and unfilled molecular orbitals in the CNDO-SCF program was determined for each species and this value then compared in a direct ratio with the corresponding value calculated for the cyclopentadienyl ion. Each ΔE was then taken (in electron volts) to be $10f$. The results of this modification of the CNDO-SCF chemical shift calculation are given in Table III and portrayed in Figure 5. The scatter in the plot of theory *vs.* experiment is considerably reduced by this approach with the data for the anions (open symbols in Figure 5) showing the greatest improvement. Reduction in the over-all excitation energies for these species having the maximum number of unprotonated nitrogens might have been expected, as $n-\pi^*$ transitions are known to be considerably lower in energy than similar transitions in the protonated molecules. This suggestion that low-lying energy levels will affect the paramagnetic shielding term of incompletely protonated nitrogen heterocycles has been made previously by several investigators.²⁴⁻²⁶

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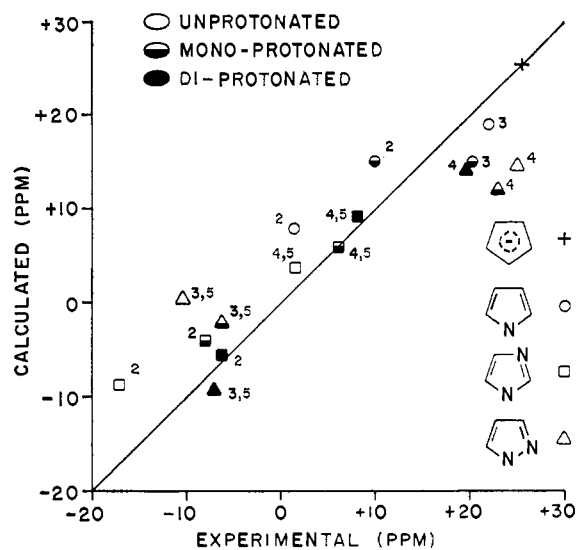


Figure 5. Theoretical chemical shifts predicted by a modified CNDO-SCF treatment are plotted against the experimental values for the five-membered nitrogen heterocycles and their charged species. The treatment is modified by taking $\Delta E = f \times 10$ eV. The f values, given in Table III, reflect the effect of nitrogen lone pairs on the average excitation parameter.

The calculated f values indicate that only relatively small changes are noted between compounds, but, because of the relatively large magnitude of the paramagnetic shielding term, these variations can make significant contributions to the chemical shift. An

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examination of the f values in Table III reveals a consistent set of parameters for the various species. Those compounds with two unprotonated nitrogen lone pair (imidazole and pyrazole anions) have the lowest f values (both 0.970). Imidazole, pyrazole, and pyrrole anion, each with one unprotonated nitrogen atom, have slightly higher f values (0.983, 0.984, and 0.985, respectively) which are intermediate between the 0.970 value and the value of 1.00. The completely protonated species (pyrrole, and imidazole and pyrazole cations) have values 0.999, 0.998, and 0.998, respectively, which for all practical purposes may be considered to be 1.00 indicating the similarity of these compounds with the reference cyclopentadienyl anion. The improved correlation noted in Figure 5 over that of Figure 3 lends merit to the Pople and Santry^{22,23} approach.

Considerable optimism would appear to be justified in the use of carbon-13 chemical shift data as a means of investigating refined features of molecular wave functions. As the carbon-13 chemical shift parameter has been rationalized in terms of changes in the charge density and in the bond orders, it is evident that both of these features may be studied in a theoretical assessment of carbon-13 magnetic resonance data. While there is a temptation to correlate chemical shifts with only charge densities because of recent successes in such studies,^{6,7} protonation data of the type contained herein suggests the need to include bond order effects in future considerations of carbon-13 chemical shifts.

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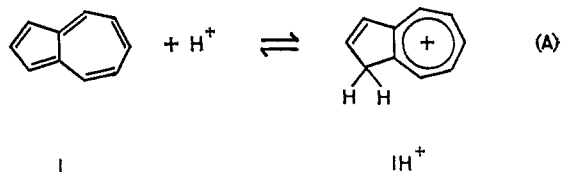
Proton Dissociation of Azulenium Cations in the Excited State

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Abstract: Solutions of many azulenum cations in aqueous sulfuric acid (corresponding to H_0 values below -5 on a Hammett scale) fluoresce strongly. This fluorescence is quenched in less acidic solutions (H_0 between -4 and -1). By means of flash experiments it can be shown that the quenching mechanism involves the proton dissociation of the excited azulenum cation. One of the transients generated is azulene in its ground state, which leads to a distortion of the ground-state equilibrium, azulene \rightleftharpoons azulenum cation. The relaxation time of the distorted equilibrium has been measured as a function of H_0 and compared with the known values obtained by a fast-flow method.

Azulene (I) and its derivatives protonate in strongly acidic media to yield the azulenum cation IH^+ and the corresponding derivatives.² In contrast to the azulenes which fluoresce only weakly at room temperature,^{3a} their conjugate acids exhibit a strong fluores-



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