

equimolar quantity of olefin. The 3-*t*-butylcyclohexyl chlorides had previously been obtained<sup>14</sup> only as an epimeric mixture by reaction of *t*-butyl chloride with cyclohexane in the presence of hydrogen fluoride or a Friedel-Crafts catalyst. This reaction involves rearrangement and does not lead to a pure product. In the present work the *trans*- and *cis*-3-*t*-butylcyclohexyl chlorides were prepared through the chloroformates exactly as their conformational analogs (the *cis*- and *trans*-4 isomers); the *trans* isomer was obtained essentially epimerically pure and the *cis* isomer was purified by preferential destruction of the contaminating *trans* (axial) material through reaction with thiophenolate.<sup>32</sup> Gas chromatography in this case led to partial dehydrohalogenation of the chlorides.<sup>33,34</sup>

The preparation of the 4-*t*-butylcyclohexyl fluorides is described in the accompanying paper<sup>1</sup> and the compounds in the 3 series were prepared analogously.

(32) Cf. E. L. Eliel and R. G. Haber, *J. Amer. Chem. Soc.*, **81**, 1249 (1959), regarding the rates of reaction of the corresponding 4-*t*-butylcyclohexyl bromides with thiophenolate.

(33) It is not entirely clear whether the chlorides in the 3 series are more thermally sensitive or whether the column used in their attempted separation for unknown reasons behaved differently from that used for the 4 isomers.

(34) NOTE ADDED IN PROOF. After submission of this paper, an essentially identical synthesis of the 4-*t*-butylcyclohexyl chlorides was published by A. B. Foster, R. Jefferis, and J. M. Webber, *Carbohydrate Res.*, **4**, 352 (1967).

Since rearrangements may occur in the conversion of alcohols to halides, the structures of the 4-*t*-butylcyclohexyl chlorides here prepared were proved by conversion to the known<sup>12</sup> 4-*t*-butylcyclohexyl phenyl thioethers through treatment with thiophenoxide. Since this reaction involves inversion of configuration, it also serves to confirm the configuration of the starting materials, that of the product being known.<sup>12</sup> The structure and configuration of the 4-*t*-butylcyclohexyl bromides had been previously<sup>32</sup> proved in this fashion. The structure, homogeneity, and configuration of the 3-*t*-butylcyclohexyl chlorides was inferred from their gas-chromatographic behavior and the similarity of their infrared and nmr spectra with those of the conformationally analogous 4 isomers. The structure of the 4-*t*-butylcyclohexyl fluorides was established in the accompanying paper<sup>1</sup> and that of the 3 isomers was inferred by analogy.

**Acknowledgment.** This work was supported by National Science Foundation Grant G-20555 and by a grant of the Air Force Office of Scientific Research, AF-AFOSR-772-65. We are grateful to Professor D. J. Pasto for assistance with the interpretation of the nmr spectra, to the Dow Chemical Co. for generous gifts of 4-*t*-butylcyclohexanol and 4-*t*-butylcyclohexanone, and to Professor R. S. Bottei for assistance with the infrared measurements.

## Carbon-13 Magnetic Resonance. X.<sup>1a</sup> The Six-Membered Nitrogen Heterocycles and Their Cations<sup>1b</sup>

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**Abstract:** Carbon-13 chemical shift data on the azines and their protonated cations are presented. Simple additivity parameters were found to account for the effect of nitrogen protonation on the chemical shifts of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -carbon atoms. These parameters are highly reproducible with monoprotonation but deviate from additivity quite significantly for diprotinated species. A theoretical analysis of the chemical shift expression indicated that carbon-13 shifts are critically dependent on both charge-transfer features and a variation in the bond-order parameter. The upfield protonation parameter for the  $\alpha$ -carbon is explained with a decrease in bonding between N-C $\alpha$ , while the  $\beta$  and  $\gamma$  parameters arise from charge polarization effects. Extended HMO wave functions were used to estimate the carbon-13 shifts. It was found that a protonated nitrogen must be made more electronegative than corresponding basic nitrogens if reasonable agreement between predicted and experimental results are to be obtained in all of the essential features.

Attempts to relate proton and carbon-13 chemical shifts with  $\pi$ -electron densities<sup>2-8</sup> and/or Hammett  $\sigma$  constants<sup>9</sup> in aromatic systems have been reported

(1) (a) Previous paper in this series: D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967). (b) Taken in part from the Ph.D. dissertation of R. J. Pugmire, University of Utah, June, 1966.

(2) (a) A. Viellard and B. Pullman, *Compt. Rend.*, **253**, 2418 (1961); (b) A. Viellard, *J. Chim. Phys.*, **1056** (1962).

(3) B. P. Dailey, A. Gawer, and W. C. Neikam, *Discussions Faraday Soc.*, **34**, 18 (1962).

(4) T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

(5) A. H. Gawer and B. P. Dailey, *J. Chem. Phys.*, **42**, 2658 (1965).

(6) T. K. Wu and B. P. Dailey, *ibid.*, **41**, 2796 (1964).

(7) H. Spiesscke and W. G. Schneider, *Tetrahedron Letters*, **14**, 468 (1961).

by several groups of workers. These approaches have been especially successful in accounting for the chemical shifts at the *para* position of monosubstituted benzenes where steric interactions are unimportant and where anisotropic magnetic field effects due to substituent groups are reduced to a negligible value by the remoteness of the substituent group. Reasonable correlations between  $\pi$ -electron densities and the proton chemical shift parameter have also been proposed<sup>2-5</sup> for nitrogen heterocycles where polarization of the  $\pi$  charge is quite

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

(9) H. Spiesscke and W. G. Schneider, *ibid.*, **35**, 731 (1961).

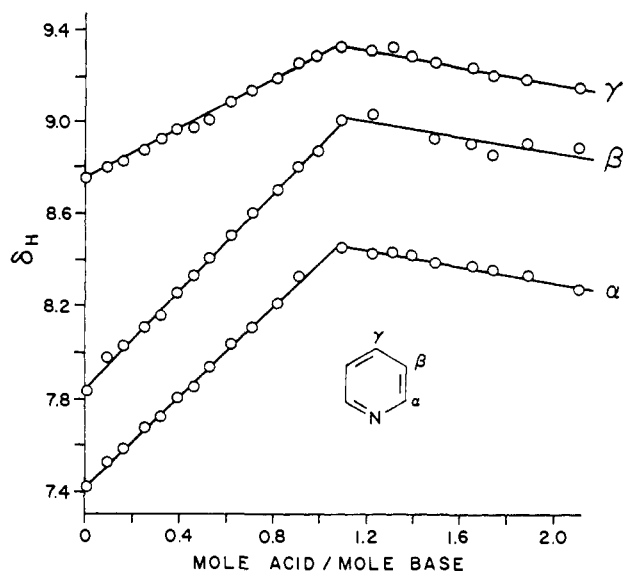


Figure 1. The proton chemical shifts of pyridine are given for various concentrations of aqueous trifluoroacetic acid. The break in the curves is identified with the completion of the protonation reaction. Dilution shifts can be recognized in all three positions by the parallel decrease in the  $\delta$  value to the right of the break.

large. If one considers the magnetic anisotropy of the nitrogen lone pair and if  $\sigma$ -bond polarization is allowed at the  $\alpha$  carbon, then the pmr<sup>4</sup> and carbon-13<sup>8</sup> chemical shifts in nitrogen heterocycles have been found to correlate with the  $\pi$ -charge density.

It should be emphasized, however, that an experimental chemical shift value cannot be easily divided into its several theoretically significant terms, and thus it is not always possible to extract that part of the shift value which is due only to  $\pi$ -electron density. In purine<sup>10</sup> it was shown that the several proton and carbon-13 chemical shifts are not in the same order for the various positions in the molecule, and thus one should not always expect to find a simple relationship between both proton and carbon-13 shift data and  $\pi$ -electron densities. Adam, *et al.*,<sup>11</sup> have just recently proposed that our data presented in tabular form for the first time in this paper correlate with theoretical charge densities providing  $\sigma$  as well as  $\pi$  electrons are considered.

Karplus and Pople<sup>12</sup> have derived an equation for estimating the carbon-13 chemical shifts in aromatic systems in terms of variations both in the  $\pi$ -electron density and mobile bond orders. The effect of  $\sigma$ -bond polarization in the C-H bond was also reflected in their equation. Lauterbur<sup>9</sup> utilized this treatment by estimating the C-N  $\sigma$ -bond polarization in simple heterocyclic systems. Variations in both the  $\sigma$ -electron structure as well as the  $\pi$ -electron system in the alternant aromatics have been studied by Alger, Grant, and Paul<sup>13</sup> and an extension of their formulation is used in this paper. Use of the MO formalism in the discussion of carbon-13 chemical shifts for nonaromatic compounds has been given by Yonezawa, *et al.*,<sup>14</sup> and by Sichel and Whitehead.<sup>15</sup>

(10) R. J. Pugmire, D. M. Grant, R. K. Robins, and G. W. Rhodes, *J. Amer. Chem. Soc.*, **87**, 2225 (1965).

(11) W. Adam, A. Grimison, and G. Rodriguez, *Tetrahedron*, **23**, 2513 (1967).

(12) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

(13) T. D. Alger, D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.*, **88**, 5397 (1966).

Using the proton decoupling technique<sup>16</sup> this study considers the six-member nitrogen heterocycles and all of the protonated cationic species which could be prepared in concentrations sufficiently high for observation of the carbon-13 magnetic resonance signal.

## 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 in previous papers in this series.

**B. Spectroscopic Details.** Solid samples were dissolved in distilled water while liquid samples were run as neat liquids. 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  $\Gamma_i$ , the ratio of the decoupler frequency to transmitter frequency ( $f_i/v_i$ ), and the corresponding proton chemical shift in accordance with eq 1.<sup>17</sup>

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

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

Pyridine, pyridazine, and pyrimidine were obtained from standard commercial sources and examined as neat liquids. Solid pyrazine and pyridine hydrochloride were also obtained from commercial sources, redissolved in distilled water, and run as saturated solutions. The mono- and diprotonated pyrazine sulfate, mono- and diprotonated pyrimidine sulfate, and pyridinium sulfate salts were prepared in this laboratory from simple acid-base reactions and were run as saturated aqueous solutions.

## Results

**A. The Effect of Protonation on Proton Chemical Shifts.** The proton chemical shifts of the molecules studied in this work are given in Table I. These species consist of free bases and their protonated cations. When the free pair of electrons in a nitrogen heterocycle are protonated, the values of the proton chemical shifts increase with respect to the nonprotonated species. The results of adding an acid such as trifluoroacetic acid to aqueous solutions of pyridine are shown in Figure 1. It is assumed that the maximum in the chemical shift curve occurs when protonation is complete, and the subsequent decrease in the  $\delta$  value is probably due to dilution effects. Similar protonation curves were obtained for pyridazine, pyrimidine, and pyrazine. A second plateau in the chemical shift plot occurs in the case of pyrazine, and this is attributed to the formation of the diprotonated species. Pyrimidine also begins to form the diprotonated species in the aqueous solution, but completion of diprotonation is realized only in the absence of water when 100%  $H_2SO_4$  is added directly to pyrimidine. No plateau
























(14) T. Yonezawa, I. Morishima, and H. Kato, *Bull. Chem. Soc. Jap.*, **39**, 1398 (1966).

(15) J. M. Sichel and M. A. Whitehead, *Theoret. Chim. Acta*, **5**, 35 (1966).

(16) E. G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, **86**, 2977 (1964).

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

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

No.	Compd	Position	$\Gamma_1$	$\delta_H$ , ppm	$\delta_{C^{13}}$ , ppm		Theoret estimates <sup>c</sup>		
					Present work	Lit.	$\Delta\sigma^{(total)}$ , ppm	$\Delta\sigma^{(1)}$ , ppm	$\Delta\sigma^{(2)}$ , ppm
1			3.976449164	0	0	0	0	0	0
2		2,6	3.976368419	-1.41	-21.72	-21.9 <sup>a</sup>	-18.94	-22.09	+3.15
3		3,5	3.976467128	+0.07	+4.59	+4.2 <sup>a</sup>	-2.47	+1.13	-3.60
4		4	3.976421055	-0.35	-7.42	-7.7 <sup>a</sup>	-4.26	-12.54	+8.28
5		2,6	3.976403535	-2.49	-13.94		-18.34	-30.77	+12.43
6		3,5	3.976453917	-1.64	-0.45		-3.29	+1.30	-4.59
7		4	3.976378612	-2.10	-19.84		-6.18	-17.74	+11.56
8		2,3,5,6	3.976387759	-1.70	-17.14	-17.4 <sup>a</sup> -16.77 <sup>b</sup>	-18.20	-23.12	+4.92
9		2,3,5,6	3.976399845	-2.11	-14.47	-14.72 <sup>b</sup>	-16.76	-28.42	+11.66
10		2,3,5,6	3.976397856	-2.58	-15.48		-14.41	-34.40	+19.99
11		2	3.976334864	-2.25	-30.99	-30.5 <sup>a</sup> -31.44 <sup>b</sup>	-32.14	-36.38	+4.24
12		4,6	3.976341029	-1.77	-28.96	-28.9 <sup>a</sup> -28.91 <sup>b</sup>	-22.26	-33.08	+10.82
13		5	3.976475933	-0.31	+6.42	+6.1 <sup>a</sup>	-4.95	+2.32	-7.27
14		2	3.976366196	-2.84	-23.71	-23.57 <sup>b</sup>	-27.18	-38.92	+11.74
15		4,6	3.976338857	-2.55	-30.29	-29.21 <sup>b</sup>	-22.63	-39.63	+17.00
16		5	3.976468352	-1.45	+3.38		-6.22	+2.62	-8.84
17		2	3.976372242	-3.14	-22.48		-15.97	-36.70	+20.73
18		4,6	3.976338340	-2.66	-30.53		-21.17	-45.42	+24.25
19		5	3.976457506	-1.77	+0.33		-7.12	+2.88	-10.00
20		3,6	3.976362102	-2.42	-24.31	-23.9 <sup>a</sup> -24.07 <sup>b</sup>	-28.69	-30.80	+2.11
21		4,5	3.976455575	-0.76	+0.85	+1.0 <sup>a</sup> +1.29 <sup>b</sup>	-3.77	-12.99	+9.22
22		3,6	3.976366825	-2.50	-23.21	-22.57 <sup>b</sup>	-28.30	-38.28	+9.98
23		4,5	3.976418830	-1.60	-9.23		-5.88	-16.05	+10.17

<sup>a</sup> Reference 8. <sup>b</sup> A. Mathias and V. M. S. Gil, *Tetrahedron Letters*, 3163 (1965). <sup>c</sup> All values are calculated relative to benzene. Larger positive values indicate upfield shifts.

was found in the vicinity of 50 mol % of pyrimidine in  $H_2SO_4$  because the salt formed at this point precipitates from solution. Addition of more  $H_2SO_4$  redissolves the salt and a plateau corresponding to a doubly protonated product is observed.

Iwaizumi and Azumi,<sup>18</sup> using spectrophotometric data, reported the formation of the diprotonated pyridazinium cation in 36 *N*  $H_2SO_4$ . However, the pmr spectra give no evidence for the existence of this species at the concentration which is required to observe the proton magnetic resonance signal. The acid-base ratios which have plateaus in the pmr data plots were used to prepare solutions of the desired molecule composition for determining the carbon-13 chemical shifts.

**B. Carbon-13 Chemical Shift Data.** The carbon-13 chemical shifts for the azines and their charged species are presented also in Table I. The chemical shifts of the free bases agree with the work of Lauterbur<sup>8</sup> within the experimental error of the two techniques, and our assignments are made on the basis of this former work. Carbons between two nitrogen atoms are shifted to low fields, while carbons which are not adjacent to any nitrogens appear at high fields. Carbon atoms with

(18) M. Iwaizumi and H. Azumi, *J. Chem. Soc. Jap.*, 84, 694 (1963).

only one  $\alpha$ -nitrogen atom are found at intermediate field positions. Protonation of these bases, however, leads to a scrambling of the chemical shifts for certain of the molecular species and these simple rules for assigning carbon resonant positions no longer apply in every instance. In the case of pyridine hydrochloride, C-4 can be assigned to the only peak of unit intensity but the assignment of the two doubly intense peaks arising from C-2 and C-3 cannot be determined from the peak intensities. Using the proton-decoupling technique to remove this ambiguity, each decoupled carbon-13 singlet was identified with the proton multiplet associated with the directly bonded hydrogen atom. As the proton shifts had already been assigned, it was possible to assign C-2 to the downfield carbon-13 peak and C-3 to the upfield peak. The chemical shifts were then calculated with eq 1 from the "decoupling shifts,"  $(\Gamma_i - \Gamma_0)/\Gamma_i$ , and the corresponding proton shifts,  $\delta_H$ . These data indicate that protonation of the nitrogen atom results in changes in the chemical shifts of +7.78, -5.04, and -12.42 ppm for the  $\alpha$ ,  $\beta$ , and  $\gamma$  positions, respectively, when compared to the free base. The changes in chemical shifts in pyrimidine, pyrazine, and pyridazine with protonation can be rationalized with the

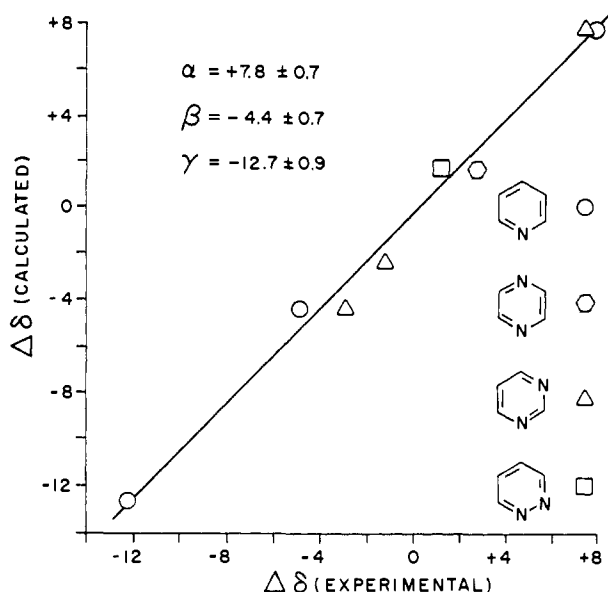


Figure 2. Three protonation parameters, obtained from a regression analysis, are used to correlate the carbon-13 shifts in the protonated species with the shifts in the unprotonated heterocycles. Proton tautomerism in the monoprotonated diazines is taken into consideration by averaging the effect of the proton in both equivalent nitrogen positions.

$\alpha$ -,  $\beta$ -, and  $\gamma$ -protonation parameters found in the simpler pyridine molecule. Both charged species of pyrimidine have two peaks of unit intensity and one of double intensity. Because of uniqueness, the doubly intense peak may be readily assigned to C-4,6, while C-2 and C-5 are assigned by applying the pyridine protonation parameters. Position 5 is in a  $\beta$  position to both N-1 and N-3 and exhibits successive downfield shifts of  $-3.04$  and  $-3.05$  ppm for mono- and diprotonation. This compares reasonably well with the  $-5.04$ -ppm  $\beta$  shift noted in pyridine hydrochloride. Position 2 is in an  $\alpha$  position to both nitrogen atoms and exhibits a  $+7.28$ -ppm upfield shift on monoprotection, a value which compares very well with the  $+7.78$ -ppm-shift noted with protonation in pyridine. A smaller ( $+1.23$  ppm) upfield shift is realized when the second nitrogen atom is protonated indicating that the additivity parameter breaks down at C-2 in pyrimidine with diprotonation. In monoprotonated pyrimidine rapid tautomeric proton exchange between N-1 and N-2 averages the chemical shift expected for each extreme form. The average of an  $\alpha$  plus  $\gamma$  effect at C-4 and C-6 is predicted to be  $-2.3$  ppm, and this value compares favorably with the experimental shift of  $-1.33$  ppm. Addition of the second proton causes an additional downfield shift of  $-1.57$  ppm, which is similar to the value found for the first step in the protonation process.

Positions 2, 3, 5, and 6 in pyrazine and its diprotonated species are chemically equivalent because of symmetry whereas the monoprotonated cation has only one peak because of the rapid averaging of the equivalent tautomeric forms. The chemical shifts of the two charged species demonstrate the expected average of an  $\alpha$ - plus  $\beta$ -protonation parameter similar to the effects noted for pyrimidine. Although the diprotonated species is shifted downfield slightly from the monoprotonated cation, the chemical shifts of both charged molecules are upfield, as expected, from the free base.

The pyridinium cation has two peaks of double intensity and these are also assigned on the basis of additive protonation parameters. The proton tautomerism in the singly protonated cation produces an average upfield shift of  $+1.10$  ppm at C-3 and C-6 to be compared to the expected value of  $+1.37$  ppm. Positions 4 and 5 move downfield  $-10.08$  ppm while the average of  $\beta$ - and  $\gamma$ -protonation parameters predicts a change of  $-8.73$  ppm.

The preceding arguments indicate that a relatively simple relationship exists between the chemical shifts and the degree of protonation. A regression analysis of the experimental data was undertaken in terms of the position of the protonated nitrogen relative to the carbon atom being considered to determine the best additive protonation parameter. Only monoprotonated species were considered in the analysis as large deviations from additivity were observed in the diprotonated cations. In the monoprotonated diazines tautomeric averaging of the proton position was included in the population factors used in the analysis. The regression parameters resulting from the analysis are given in Figure 2 which also depicts the success of the linear regression fit of the data. It is evident that additivity relationships do exist providing allowance is made for proton tautomerism. Application of the parameters given in Figure 2 to predict the shifts in the diprotonated molecules does indicate that a simple additive relationship is lacking in these doubly charged species. To the extent that these substituent parameters reflect charge polarization effects on the chemical shift, one might anticipate deviations from simple additivity as successive protonation leads to competitive effects in the degree of polarization. This is to be expected whenever the successive changes in the molecular charge distribution are not relatively small perturbations. As might be expected, the largest deviation from additivity is found at C-2 in the doubly protonated pyrimidine where competitive effects will be maximized.

### C. Hydration Effects on the Chemical Shifts.

The effect of dilution with water on the carbon-13 chemical shifts in pyridine was also studied. Increasing the concentration of water from 0 to 50 mol % causes the proton chemical shift to move downfield by  $-0.07$ ,  $-0.15$ , and  $-0.09$  ppm for the  $\alpha$ ,  $\beta$ , and  $\gamma$  positions, respectively. The effects of dilution on the carbon-13 chemical shifts are shown in Figure 3. The  $\beta$  and  $\gamma$  peaks move downfield by  $-0.39$  and  $-0.93$  ppm, respectively, whereas the  $\alpha$  peak moves upfield by  $+0.55$  ppm in the 50 mol % solution. The magnitudes of these three shifts are somewhat smaller than those noted for direct protonation, but the ratios between the dilution shifts are about the same as those found for the protonated species. Calculations of the extent of hydrolysis of pyridine indicate that the concentration of the hydrolyzed protonated species is two orders of magnitude too low to account for the observed changes in the chemical shifts. Maciel and Ruben<sup>19</sup> have noted a downfield shift of  $-9.1$  ppm in the carbonyl carbon in a 1:6 acetone-water solution and have attributed this shift to intermolecular hydrogen bond formation. Thus, the existence of hydrogen bonds between water and the nitrogen atom is proposed as an explanation for

(19) G. E. Maciel and G. C. Ruben, *J. Amer. Chem. Soc.*, **85**, 3903 (1963).

the changes in chemical shifts with dilution in water. Since the sign and relative magnitudes between  $\alpha$ ,  $\beta$ , and  $\gamma$  shifts associated with hydration are similar to those of direct protonation it is proposed that the effect of hydrogen bond formation upon the electronic structure of pyridine is similar, although greatly reduced in value, to that observed for complete protonation.

### Theoretical Considerations

**A. Molecular Wave Functions.** In the calculations of Alger, Grant, and Paul<sup>13</sup> on the alternant aromatics, the  $\sigma$ -electron bond orders were taken to be constant consistent with the assumption of a localized  $\sigma$ -electron system. This assumption, which was made for computational simplicity, fails to account for changes in the chemical shift arising from possible variations in the  $\sigma$ -electron spin-pairing scheme. As the work of Karplus and Pople<sup>12</sup> emphasized the importance of bond order changes in the  $\pi$ -electron system, the effect of such two-electron terms arising in the  $\sigma$ -electron system is explored in this paper. The extended HMO approach used by Hoffmann<sup>11,20</sup> provides us with a generalized wave function that characterizes variations in bond orders for both the  $\sigma$  and  $\pi$  electrons and that gives both  $\sigma$  and  $\pi$  charge polarization parameters. The simple assumptions used to estimate the various components of the secular equation allows one to obtain approximate wave functions by this method from a relatively small number of atomic and molecular parameters. The off-diagonal elements of the secular equation are given by

$$\mathcal{H}_{ij} = 0.5K(\mathcal{H}_{ii} + \mathcal{H}_{jj})S_{ij} \quad (2)$$

where  $K = 1.75$ ,  $S_{ij}$  is the overlap integral between the atomic orbitals  $\varphi_i$  and  $\varphi_j$ , and the diagonal terms,  $\mathcal{H}_{ii}$ , are coulombic integrals given in electron volts by Cusachs and Reynolds<sup>21</sup> as follows

$$\begin{aligned} \mathcal{H}(2S)_N &= -27.43 - 13.64\Delta_N \\ \mathcal{H}(2P)_N &= -14.02 - 13.64\Delta_N \\ \mathcal{H}(2S)_C &= -21.16 - 11.56\Delta_C \\ \mathcal{H}(2P)_C &= -11.20 - 11.56\Delta_C \end{aligned} \quad (3)$$

$\Delta_N$  and  $\Delta_C$  represent the formal charge on a nitrogen or a carbon atom, respectively. Using these assumptions the  $i$ th molecular orbital obtained as a LCAO can be written for our purposes as follows

$$\psi_i = \sum_{\mu} c_{i\mu} \varphi_{\mu} = c_{is} s^A + c_{iz} p_z^A + c_{iy} p_y^A + c_{ix} p_x^A + \sum_{I \neq A} (c_{is}^I s^I + c_{iz}^I p_z^I + c_{iy}^I p_y^I + c_{ix}^I p_x^I) \quad (4)$$

The index  $A$  refers to the carbon atom whose chemical shift is being computed, and  $I$  is an index running over all other atoms in the molecule. All eigenvectors,  $c_{i\mu}$  ( $\mu = 2p_x, 2p_y, 2p_z$ ), without a superscript are identified with the orbitals on atom  $A$ .

**B. Chemical Shift Formulation.** The general expression for the paramagnetic term given by eq 21 of Karplus and Das<sup>22</sup> is reproduced as follows as a point

- (20) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).  
 (21) L. C. Cusachs and J. W. Reynolds, *ibid.*, **43**, S160 (1965).  
 (22) M. Karplus and T. P. Das, *ibid.*, **34**, 1683 (1961).

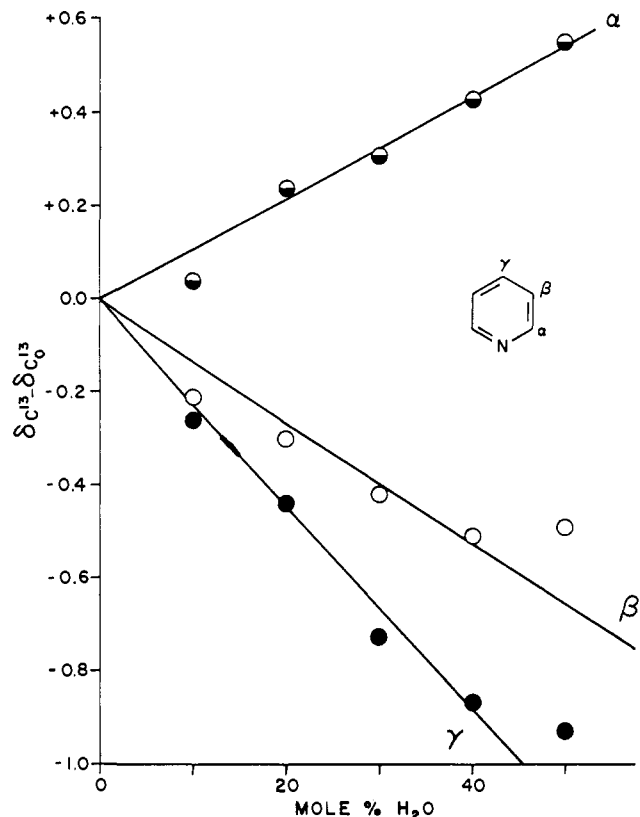


Figure 3. The carbon-13 chemical shifts are affected by diluting pyridine in water. The dilution shifts are similar in direction but differ in magnitude with those found for direct protonation of the nitrogen atom.

of departure

$$\sigma_p = \sigma_p^{(1)} + \sigma_p^{(2)} = \frac{-e^2}{m^2 c^2 \Delta E} \sum_j 2 \left\{ \langle \psi_j(k) \left| \frac{\vec{l}_k \vec{l}_k}{r_k^3} \right| \psi_j(k) \rangle - \sum_{j'} \langle \psi_j(k) \left| \frac{\vec{l}_k}{r_k^3} \right| \psi_{j'}(k) \rangle \langle \psi_{j'}(k') \left| \frac{\vec{l}_{k'}}{r_{k'}^3} \right| \psi_j(k') \rangle \right\} \quad (5)$$

where  $\sigma_p^{(1)}$  includes all terms in eq 5 with atomic orbitals centered solely on the atom of interest and  $\sigma_p^{(2)}$  includes the remaining terms which have orbitals centered both on the specified carbon as well as other atoms in the molecule. If all terms involving the overlap integral,  $S_{\mu\nu}$ , are set equal to zero, substitution of eq 4 into eq 5 yields the following chemical shift expressions

$$\sigma_p^{(1)} = -\frac{2e^2 \hbar^2}{3m^2 c^2 \Delta E} \left\{ \sum_{\mu} P_{\mu A \mu A} \langle R(\xi_{\mu}) | 1/r^3 | R(\xi_{\mu}) \rangle + \frac{1}{4} \sum_{\mu \neq \nu} (P_{\mu A \nu A}^2 - P_{\mu A \mu A} P_{\nu A \nu A}) \langle R(\xi_{\mu}) | 1/r^3 | R(\xi_{\nu}) \rangle \langle R(\xi_{\mu}) | R(\xi_{\nu}) \rangle \right\} \quad (6)$$

$$\sigma_p^{(2)} = -\frac{e^2 \hbar^2}{6m^2 c^2 \Delta E} \sum_{\mu \neq \nu} (P_{\mu A \nu I} P_{\nu A \mu I} - P_{\mu A \mu I} P_{\nu A \nu I}) \langle R(\xi_{\mu}) | 1/r^3 | R(\xi_{\nu}) \rangle \langle R^I(\xi_{\mu}) | R^I(\xi_{\nu}) \rangle \quad (7)$$

where the various  $P$ 's are defined in the usual way

$$P_{\mu A \nu I} = 2 \sum_{i}^{\text{occ}} c_{i\mu} c_{i\nu}^I \quad (8)$$

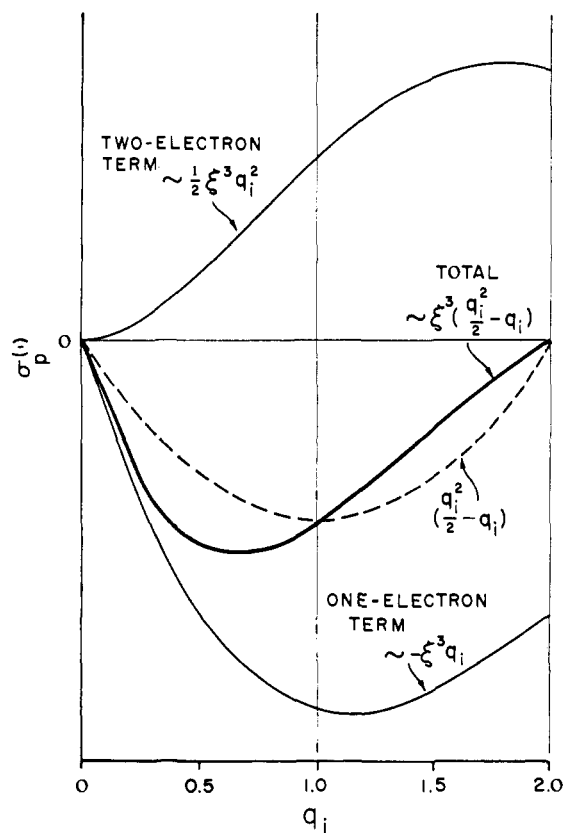


Figure 4. Plots of the one- and two-electron terms of eq 15 along with the total effect is given as a function of orbital charge. The importance of  $\xi$  in eq 15 is graphically portrayed for the total shift curve by comparing this line with the dashed curve where the  $\xi$  dependence is not considered.

and the radial integrals<sup>13</sup> are given as follows

$$\begin{aligned} \langle R(\xi_\mu) | 1/r^3 | R(\xi_\mu) \rangle &= \xi_\mu^3 / 24a_0^3 \\ \langle R(\xi_\mu) | 1/r^3 | R(\xi_\nu) \rangle &= (\xi_\mu \xi_\nu)^{5/2} / 6a_0^3 (\xi_\mu + \xi_\nu)^2 \quad (9) \\ \langle R(\xi_\mu) | R(\xi_\nu) \rangle &= 32(\xi_\mu \xi_\nu)^{5/2} / (\xi_\mu + \xi_\nu)^5 \end{aligned}$$

The effective nuclear charge parameter is defined in the following manner

$$\xi_l = 3.25\beta - 0.35 \sum_{k \neq l} Q_k \quad (10)$$

in keeping with previous practice.<sup>12,13,23,24</sup> This expression based on simple Slater screening concepts provides a direct relationship between the effective nuclear charge,  $\xi_l$ , of orbital  $l$  and the various electron densities,  $Q_k$ , in the remaining  $k$  orbitals centered on the atom of interest. The Coulson  $\beta$  parameter was taken as 1.05 for the  $\pi$  electrons and 1.15 for  $\sigma$ .<sup>13</sup> Thus, the chemical shift expressions 6 and 7 exhibit not only a direct dependence upon the orbital charges represented by terms of the type  $P_{\mu A \mu A}$ , but these equations are affected also by an indirect cubic dependence upon charge through the effective nuclear charge parameter given by eq 10.

Although the Hoffmann extended HMO wave function is of identical form with that used to derive the chemical shift expressions, they differ in the way in which overlap is treated. Overlap is included in the Hoffmann wave function but was neglected in the chemi-

cal shift equations as a means of simplifying the derivation. To compensate in part for this discrepancy between the two equations the following computational substitutions are employed.

$$P_{\mu A \mu A} = Q_{\mu A}$$

$$P_{\mu A \nu A} = \left[ \frac{Q_{\mu A} Q_{\nu A}}{P'_{\mu A \mu A} P'_{\nu A \nu A}} \right]^{1/2} P'_{\mu A \nu A} \quad (11)$$

$$P_{\mu A \mu I} = \left[ \frac{Q_{\mu A} Q_{\mu I}}{P'_{\mu A \mu A} P'_{\mu I \mu I}} \right]^{1/2} P'_{\mu A \mu I}$$

$$P_{\mu A \nu I} P_{\nu A \mu I} = \left[ \frac{Q_{\mu A} Q_{\nu A} Q_{\mu I} Q_{\nu I}}{P'_{\mu A \mu A} P'_{\nu A \nu A} P'_{\mu I \mu I} P'_{\nu I \nu I}} \right]^{1/2} P'_{\mu A \nu I} P'_{\nu A \mu I}$$

The  $Q$ 's are orbital charge densities and the primed  $P$ 's are overlap populations. Both of these values may be obtained directly from the output of the Hoffmann program. Aside from compensating for the neglect of overlap, it is felt that the substitutions given in eq 11 help to focus attention upon some important conceptual features contained in the chemical shift expression. Thus, eq 9 and 11 are substituted into eq 6 and 7 to yield the following expressions

$$\sigma_p^{(1)} = -\frac{965.9}{\Delta E} \left\{ \frac{1}{24} \sum_{\mu} Q_{\mu} \xi_{\mu}^3 - \frac{4}{3} \sum_{\mu \neq \nu} Q_{\mu} Q_{\nu} \left[ 1 - \frac{P'^2_{\mu A \nu A}}{P'_{\mu A \mu A} P'_{\nu A \nu A}} \right] \frac{(\xi_{\mu} \xi_{\nu})^5}{(\xi_{\mu} + \xi_{\nu})^7} \right\} \quad (12)$$

$$\sigma_p^{(2)} = +\frac{965.9}{\Delta E} \left\{ \frac{4}{3} \sum_{\mu \neq \nu} \left[ \frac{Q_{\mu A} Q_{\nu A} Q_{\mu I} Q_{\nu I}}{P'_{\mu A \mu A} P'_{\nu A \nu A} P'_{\mu I \mu I} P'_{\nu I \nu I}} \right]^{1/2} \times (P'_{\mu A \mu I} P'_{\nu A \nu I} - P'_{\mu A \nu I} P'_{\nu A \mu I}) \frac{(\xi_{\mu} \xi_{\nu} \xi_{\mu}^I \xi_{\nu}^I)^{5/2}}{(\xi_{\mu} + \xi_{\nu})^2 (\xi_{\mu}^I + \xi_{\nu}^I)^5} \right\} \quad (13)$$

### C. Factors Important in Carbon-13 Chemical Shifts.

To extract the physical significance from the expression for  $\sigma_p^{(1)}$  it is helpful to assume a completely random spin orientation between any two electrons centered on the same atom. This may be done by setting  $P'_{\mu A \nu A} = 0$  in eq 12. The effect of charge polarization may then be examined by further simplifying eq 12 with the following assumptions

$$\begin{aligned} \xi &= \xi_{\mu} = \xi_{\nu} = \dots \\ q &= Q_{\mu} = Q_{\nu} = \dots \\ \Delta E &= 10 \text{ eV} \end{aligned} \quad (14)$$

thereby giving the ensuing equation for  $\sigma_p^{(1)}$

$$\sigma_p^{(1)} = -12.07 \xi^3 (q - q^2/2) \quad (15)$$

The first term comes from the one-electron integrals while the squared term arises from the two-electron integrals both centered on the atom under consideration. The relative contribution of the one- and two-electron terms as a function of orbital charge can be readily visualized in Figure 4, along with a plot of the sum of the two terms. It is observed that all three of these curves are skewed by the dependence of the  $\xi^3$  term upon charge in accordance with eq 10. The effect of skewing can be visualized by comparing the plot of  $\xi^3((q^2/2) - q)$ , solid line, with that for  $((q^2/2) - q)$ , dashed line. The two curves have been adjusted to give the same shift value at  $q = 1$ . It should be noted for a

(23) D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, **87**, 3994 (1965).

(24) B. V. Cheney and D. M. Grant, *ibid.*, **89**, 5319 (1967).

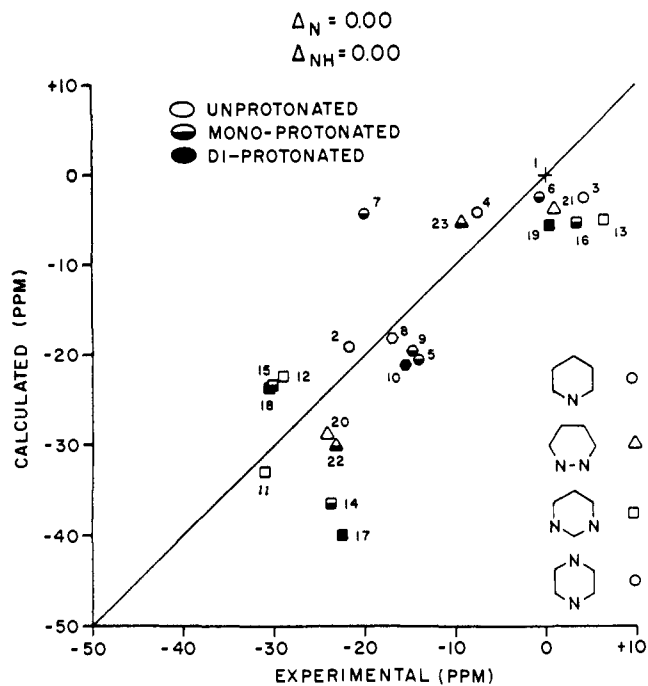


Figure 5. Calculated and experimental carbon-13 chemical shifts are plotted for the six-member nitrogen heterocycles and their protonated species. It is assumed that protonation of the nitrogen atoms does not affect the coulomb integral for the nitrogen atom. The points are designated by their numbers given in Table I.

constant  $\xi$  value that the charge dependence of the chemical shift of a carbon atom is predicted to have a slope of zero in the most significant region where  $q$  equals one electron. It is the dependence of  $\sigma_p^{(1)}$  upon  $\xi^3$  which gives rise to the charge relationships proposed initially by Spiessecke and Schneider<sup>7</sup> and by Lauterbur.<sup>25</sup> Figure 4 clearly indicates, however, that the chemical shift will not continue to move to lower fields without bounds as electronic charge is removed, but will eventually level off and then move again to higher fields if the net charge on an atom becomes too positive. As expected, the one- and two-electron terms are both zero for no orbital electrons, but the downfield, one-electron term overpowers the two-electron term of opposite sign for the whole range between  $q = 0$  and  $q = 2$ . When an orbital contains two electrons,  $q = 2$ , the one- and two-electron terms cancel each other exactly and the paramagnetic contribution vanishes, as expected, in any atom in which the p-electron subshell is completely filled.

The factor of 0.5 in front of the squared term in eq 15 arises from spin-pairing features and specifies the situation in which the spins of the two electrons are completely randomized. Cheney and Grant<sup>24</sup> have discussed in the VB approximation the various aspects of spin pairing of two electrons both centered on the same atom, and conceptually the MO and VB theoretical approaches somewhat compliment one another on this point. Both methods indicate that antiparallel spin pairing (deviations from perfect pairing in VB and  $P'_{\mu A \nu A} > 0$  in the MO) of two electrons centered on the same atom enhances the paramagnetic term by reducing the coefficient on the  $q^2$  term in eq 15. This effect can be seen easily in eq 12 for the situation in which  $P'^2_{\mu A \nu A}$  is no longer zero. On the other hand, a single configura-

(25) P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 1838 (1961).

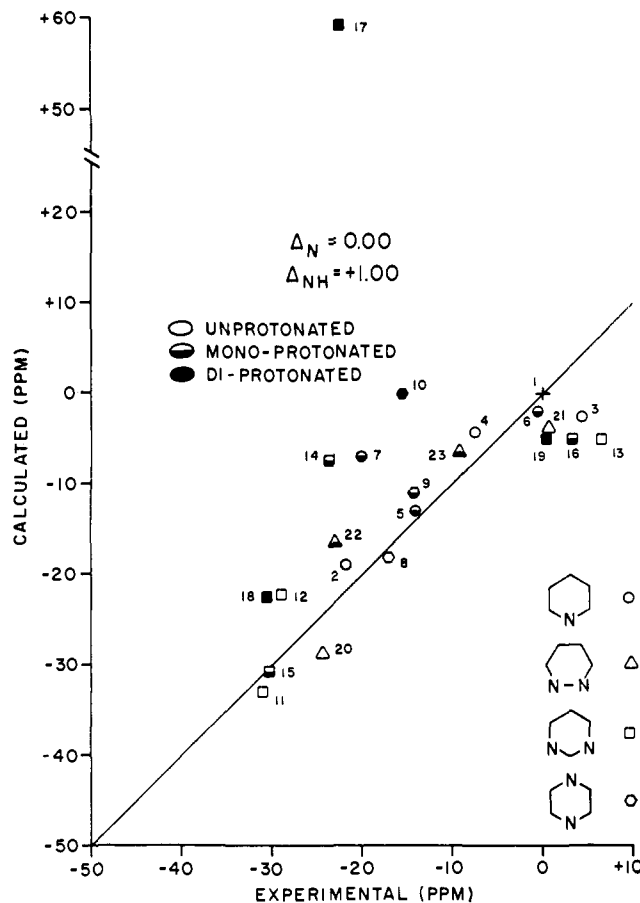


Figure 6. Calculated and experimental carbon-13 chemical shifts are plotted for the six-member nitrogen heterocycles and their protonated species. It is assumed that the protonated nitrogen atom carries a +1 formal charge and the coulomb integral is varied in accordance with eq 3.

tion MO wave function does not allow for the possibility of a parallel spin orientation for two electrons on the same atom, as  $P'^2_{\mu A \nu A}$  will always have a positive sign. In the VB approximation, however, such spin-pairing features are obtained directly from nonclassical canonical structures and an upfield shift in the two-electron part of  $\sigma_p^{(1)}$  arise from such structures. Use of a MO wave function which includes configuration interaction<sup>26</sup> is essential if one is to predict the upfield shift associated with a parallel spin orientation of two electrons. As the Hund exchange integral for two electrons in the same atom normally favors the parallel spin configuration between such electrons, the simple MO theory will always fail to predict the appropriate shift arising from this particular feature in the electronic structure. It should be indicated that our calculations to date give values for  $P'_{\mu A \nu A}$  which are relatively small and thus errors, to the extent that they exist from this source, are not due to the inclusion of a sizeable downfield shift term, but are introduced from neglect of possible upfield shift terms arising from a parallel spin orientation of two electrons both centered on the carbon-13 atom. Valence-bond calculations<sup>24</sup> on the simple alkanes have

(26) See M. Barfield and D. M. Grant, *Advan. Magnetic Resonance*, **1**, 170 (1965), and previous papers cited therein for a discussion of electron spin correlation and the problems encountered in the simple MO formulation. While this reference deals with theoretical considerations of nuclear spin-spin coupling, the conclusions are equally appropriate in a discussion of chemical shifts.

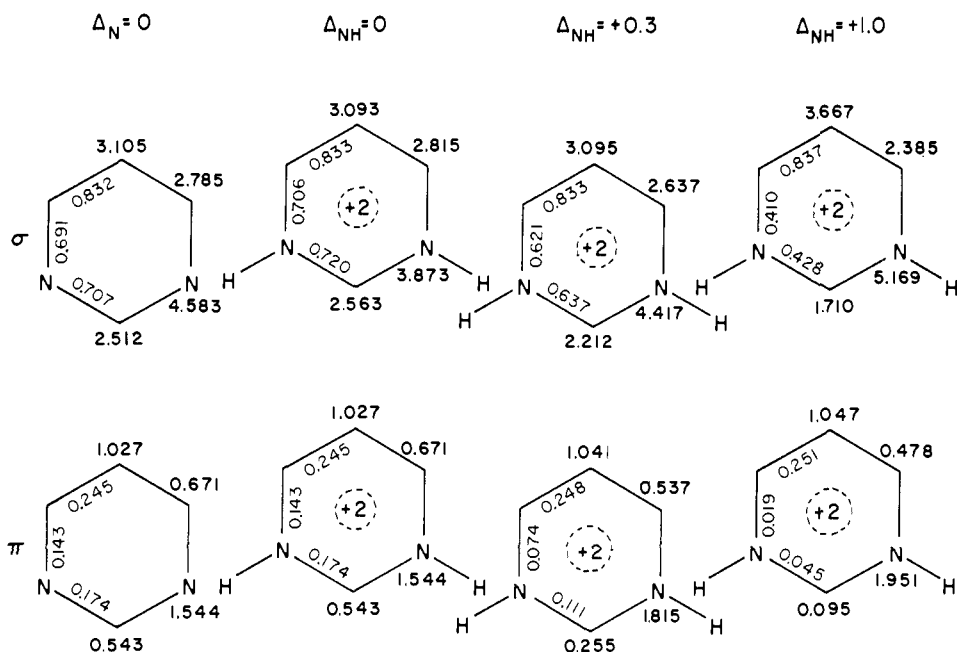


Figure 7. Overlap populations and charge densities in the  $\sigma$ - and  $\pi$ -electron frameworks of pyrimidine and its diprotonated cation are given for various assumed formal charges on the protonated nitrogen atom.

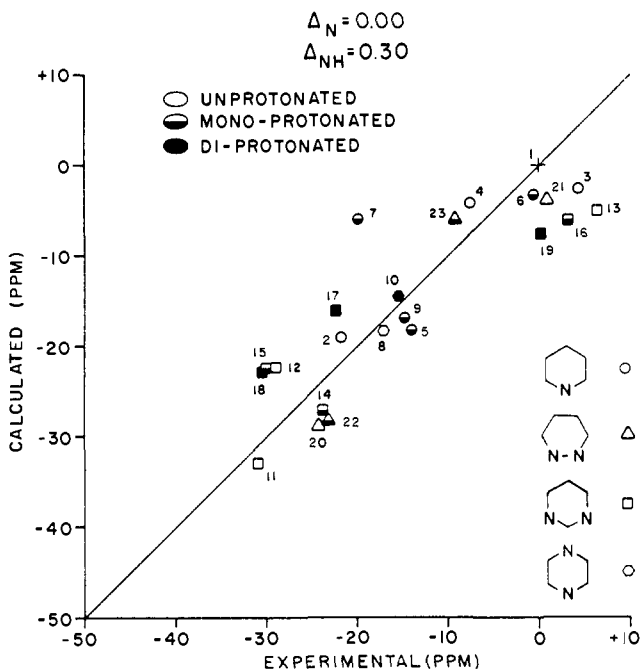


Figure 8. Calculated and experimental carbon-13 chemical shifts are plotted for the six-member nitrogen heterocycles and their protonated species. A formal charge of +0.3 is assumed for all protonated nitrogens as a means of approximating the coulombic integrals with eq 3.

indicated that such terms may be as large as several parts per million but no estimate has been made of the size of such terms for the molecules considered in this work. It should be remembered that all shifts are compared with those in benzene, and some internal canceling of this error will result if benzene and the heterocycles are similar in their spin-pairing features. As all the molecules in this paper are isoelectronic, a situation not realized in the work<sup>24</sup> on the alkanes, it is felt that no great error has been included in the calculation as a result of neglecting the effect of configuration interaction.

Both charge polarization and spin-pairing effects, therefore, have been shown to influence the  $\sigma_p^{(1)}$  term. It is the charge polarization features, however, which dominate expression 12, and in this regard the MO formulation offers a particularly attractive method for studying the accompanying effects upon the carbon-13 chemical shifts. Conversely, the simple VB approach does not characterize the charge-transfer features in a molecule as does the MO approximation, but the VB method is much superior to the simple MO theory for characterizing important spin-pairing features.

Many of the points stressed above in the discussion of  $\sigma_p^{(1)}$  also apply to a discussion of the two-centered term,  $\sigma_p^{(2)}$ . Charge polarization still affects eq 13 through the various  $\xi_i$ 's in accordance with eq 10, but spin-pairing effects are now of greater importance as this term arises completely from two-electron integrals where the spin relationships between the two electrons are of fundamental importance. While spin-pairing effects are introduced into  $\sigma_p^{(1)}$  as deviations from a situation in which the two electrons can be considered to have completely random spins, the significant terms in  $\sigma_p^{(2)}$  usually arise from a variation of the situation in which the two electrons have the preferred antiparallel spin orientation associated with an electron pair bond. Thus, changes in  $\sigma_p^{(2)}$  primarily reflect variations in the bond order between two atoms. This aspect of the carbon-13 chemical shift theory is of significance in valence theory. Associated with an increase in bonding or an increase in antiparallel spin correlation is an enhancement of the paramagnetic term, and the resonance position moves to lower fields. Conversely, any decrease in the bond order between two electrons decreases the paramagnetic shift and the chemical shift moves upfield.

In pyridine the chemical shift of C-2 moves upfield with protonation primarily because of a decrease in the bond order between N-1 and C-2. Protonation results in a polarization effect which, in a simple way, can be thought of as removing electrons from the N<sub>1</sub>-C<sub>2</sub> bond.



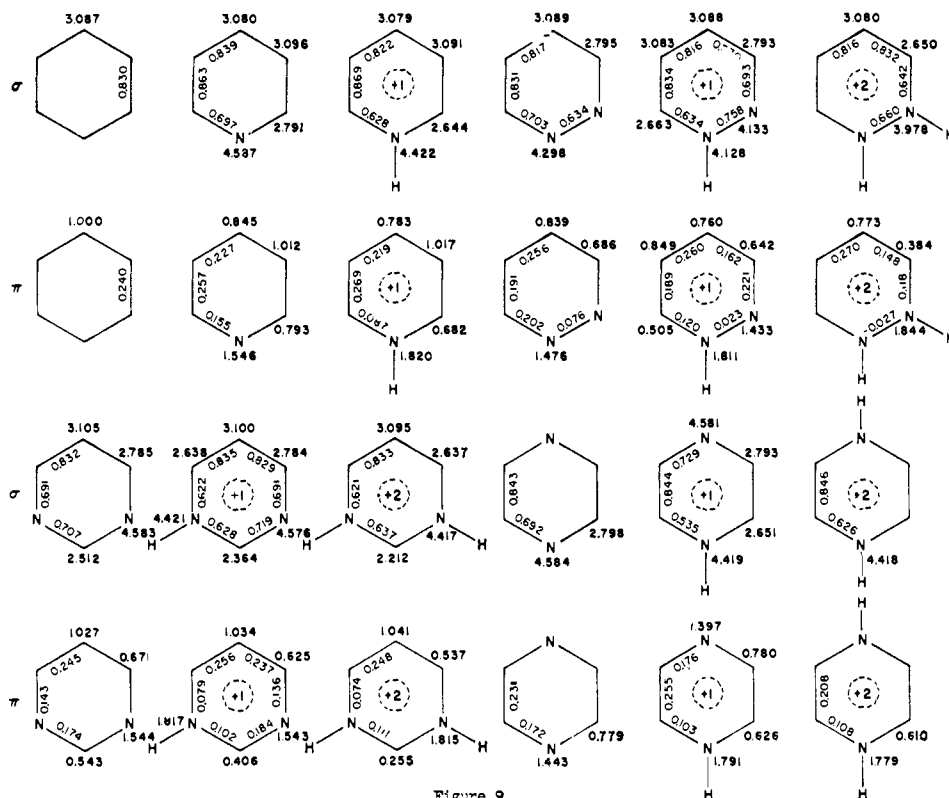


Figure 9

Figure 9. Overlap populations and charge densities are given for formal charges of 0.00 and +0.30 for unprotonated and protonated nitrogens, respectively. Overlap populations are given inside the several rings and charge densities appear external to the rings.  $\sigma$  values are given in the first and third rows while the  $\pi$  system is represented by the second and fourth rows.

This effect decreases the paramagnetism associated with spin pairing in the  $\sigma_p^{(2)}$  term by an amount which more than compensates for the increase in paramagnetism of  $\sigma_p^{(1)}$  as exhibited for a small charge decrease in Figure 4. Thus, the effect of varying the bond order in the two-centered term may actually override polarization effects in some instances, and this is the best explanation for the upfield chemical shift of C-2 when pyridine is converted to the pyridinium cation.

### Calculations

The success of the extended HMO wave function in eq 12 and 13 was investigated for a variety of molecular parameters. The ionization potentials given in eq 3 were varied with the  $\Delta_N$  term as a means of estimating the elements of the secular equation. Figure 5 portrays a plot of calculated *vs.* experimental results when  $\Delta_N$  in eq 3 is set equal to zero for all types of nitrogen atoms, both protonated and unprotonated. The agreement in Figure 5 might be considered to be reasonable when the rather gross approximations used in the calculations are acknowledged. The over-all correlation reflects the major charge-transfer features which are characteristic of practically all existing nitrogen heterocyclic wave functions. In every instance, however, the calculations fail to predict the upfield shift noted in carbons next to a nitrogen atom which has been protonated.

The inability of the  $\Delta_N = 0$  assumption to deal successfully with the positive protonation parameter results from the failure to distinguish between the nitrogen ionization potentials of N and NH. Utilizing the variable electronegativity concept first proposed by Brown and Heffernan<sup>27</sup> for nitrogen heterocycles the

calculations were repeated with  $\Delta_{NH} = 1.0$  for protonated nitrogens and  $\Delta_N = 0$  for the other nitrogen atoms. The  $\Delta_{NH} = 1.0$  presumes a +1 formal charge on the protonated nitrogen. These results, given in Figure 6, exhibit an overall correlation which is similar to that shown in Figure 5, again because the wave functions exhibit the same over-all charge-transfer features. With the  $\Delta_{NH} = 1.0$  approximation the upfield protonation shifts in the  $\alpha$  positions are now predicted correctly by the calculation. Increasing the effective electronegativity of both nitrogens in diprotonated pyrimidine, however, artificially withdraws too much electronic charge from the C-2 carbon atom bonded directly to both nitrogens. This can be observed in Figure 7 which gives the  $\sigma$ - and  $\pi$ -charge densities and bond orders in pyrimidine and its diprotonated cation for various values of  $\Delta_{NH}$ . For  $\Delta_{NH} = +1.0$  the  $\sigma$  charge has dropped to 1.710 electrons at C-2 while the  $\pi$  charge is only 0.095 electron. It is quite obvious that this assumption of a +1 formal charge on the nitrogen is too severe to calculate reasonable charges, bond orders, and the accompanying chemical shifts. In fact the large upfield shift calculated for C-2 in part is a result of reducing the average orbital charge,  $q$ , to the extent that the paramagnetic term has been attenuated as indicated in Figure 4 for small  $q$ . The remaining part of the discrepancy between predicted and experimental shifts for C-2 in the diprotonated pyrimidine arises from the overly large decrease predicted for the bond orders about C-2 with  $\Delta_{NH} = +1.0$ . The upfield  $\alpha$  shifts noted in Figure 6 for all of the remaining compounds

(27) R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).

arise solely from decreases in the N-C $_{\alpha}$  bond orders. Charge polarization shifts are all downfield as the charge densities in these compounds have not been decreased below the minimum point in the curve given in Figure 4.

It is obvious that an additional proton in the protonated species is going to affect the whole molecule and not just the nitrogen atom. For this reason, the effect of various intermediate values of  $\Delta_{\text{NH}}$  upon the chemical shift were investigated. Values of  $\Delta_{\text{NH}}$  between 0 and 1.0 in steps of 0.1 were employed and the best visual fit, given in Figure 8, was realized for  $\Delta_{\text{NH}} = 0.3$  and  $\Delta_{\text{N}} = 0$ . The predicted C-2 shift in diprotonated pyrimidine is significantly improved by the choice of this intermediate value as is also the carbon resonance in diprotonated pyrazine and the C-2 shift in monoprotonated pyrimidine. The calculated charge densities and bond orders in diprotonated pyrimidine are given in Figure 7 for  $\Delta_{\text{NH}} = 0.3$  to allow a convenient comparison with the results of the two previous calculations using  $\Delta_{\text{NH}} = 0$  and  $\Delta_{\text{NH}} = 1.0$ . It is felt that these new charge densities are more reasonable than those observed for the case of  $\Delta_{\text{NH}} = 1.0$ . Furthermore the predicted shift values in Figure 8 for the parent compound and their protonated derivatives continue to reflect the correct  $\alpha$ -protonation parameter, and at the same time, the scatter in the plot is reduced from that found in Figures 5 and 6. In all three calculations the predicted value for C-4 in the pyridinium ion deviates significantly from the agreement line. Here we see a failure of the HMO approach to properly characterize the long-range polarization effects in the *para* position which are suggested experimentally as being important by the relatively large  $\gamma$ -protonation parameter. To properly treat polarization effects at  $\beta$  and  $\gamma$  positions one should vary the effective electronegativities of all atoms in the

ring in some self-consistent manner. Qualitatively one can see how such a treatment would improve Figure 8. If all  $\beta$  positions were made slightly more "electronegative" (larger ionization potential), their charges would increase and the predicted shift values for these atoms would move upfield and onto the line. Likewise C-4 in pyridine hydrochloride and C-4,6 in pyrimidine and its cationic species would have charge removed and shift down onto the line. Such additional quantum mechanical improvements, however, were considered to be beyond the scope of this study as the essential chemical shift features have been discussed and identified with certain important aspects of the electronic structure of these molecules. It is felt, however, that theoretical workers interested primarily in refined molecular wave functions of the SCF variety will want to check their results against carbon-13 chemical shift data.  $\sigma$  and  $\pi$  densities and bond orders are given in Figure 9 for the  $\Delta_{\text{N}} = 0$  and  $\Delta_{\text{NH}} = 0.3$  approximation for all the molecules considered in this study. In every instance one notes a charge depletion at  $\alpha$  carbons with protonation. This result is at variance with the calculations of Adam and Grimson<sup>11</sup> in which an increase in electronic charge at  $\alpha$  carbons was found and then proposed as an explanation for the upfield protonation shifts. The change in bond order terms is suggested as a preferable explanation of the upfield  $\alpha$ -protonation parameter.

**Acknowledgment.** This investigation was supported primarily by the Public Health Service under Grant GM 0-8521 awarded by the National Institutes of Health. The University of Utah Computer Center allowed us complimentary time to complete a large part of our calculations. Our gratitude is extended to Professor R. Hoffmann for making his program available through the Quantum Chemistry Program Exchange.

## New Heteroaromatic Compounds. XXVII.<sup>1</sup> Boron-11 Chemical Shifts of Some Heteroaromatic Boron Compounds<sup>2</sup>

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**Abstract:** <sup>11</sup>B nmr spectra have been measured for 19 of the heteroaromatic boron compounds whose preparation was reported in an earlier paper of this series. The results provide further evidence that these compounds are indeed aromatic, and also throw light on the relationship between chemical structures and <sup>11</sup>B chemical shifts.

Previous papers of this series<sup>1,4</sup> have described the preparation and properties of a number of novel heteroaromatic compounds, isoconjugate with "normal" aromatic systems and derived from them by re-

placing pairs of carbon atoms with boron and nitrogen, or boron and oxygen. The physical and chemical properties of these novel compounds seemed to indicate that they too are aromatic; for example, they show a resistance to oxidation or hydrolysis of a different magnitude from that displayed by organoboron compounds of more conventional types.

It seemed to us that a study of the <sup>11</sup>B chemical shifts in the nmr spectra of these boron-containing heteroaromatics would not only provide additional informa-

(1) Part XXVI: K. M. Davies, M. J. S. Dewar, and P. Rona, *J. Am. Chem. Soc.*, **89**, 6294 (1967).

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(3) Robert A. Welch Postdoctoral Fellow.

(4) See M. J. S. Dewar, *Progr. Boron Chem.*, **1**, 235 (1964), and papers referred to in ref 1.