Table IV. Predicted and Experimental Sulfur-33 Splitting Constants

Compound	a^S,[a] predicted	a^S, actual
Phenoxathiin	11.76	11.91
2,7-Dihydroxythianthrene	8.02	8.10
2,7-Dimethylthianthrene	8.74	8.73

[a] Predicted from eq 3.

Solving this equation for **1–3** gives $Q_S{}^S{}_{(C_2P)} = 33.4 \pm 0.7$ G. This parameter may be tested by calculating a^S for phenoxathiin, and 2,7-dihydroxy- and 2,7-dimethylthianthrene for which the molecular-orbital calculations are also available. Table IV shows the predicted values from eq 3. Excellent agreement is found for all three compounds, lending additional weight to the conclusions reached above. Added significance may be attached to these results when it is remembered that the molecular-orbital calculations were fitted to the proton splitting constants only.

Acknowledgments. The author thanks Professor J. R. Bolton of the University of Minnesota and Professor W. F. Forbes of the University of Waterloo, under whose guidance this work was carried out. The author is also indebted to Professor H. J. Shine of Texas Technological College for helpful discussions. This research was supported under Grant No. GP-5847 from the National Science Foundation and a departmental equipment grant (No. GP-6991) from the National Science Foundation.

Calculation of the Carbon-13 and Proton Chemical Shifts in Pyridine

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Abstract: Nmr parameters are given for pyridine in a variety of solvents. Using several sets of π-electron wave functions together with symmetry MO's for the σ electrons, diamagnetic and paramagnetic contributions to the proton and carbon-13 shifts were evaluated. Paramagnetic shifts were calculated by the methods of McConnell, Karplus, and Pople. The diamagnetic term for protons was equated to $-10z$ where z is the charge on carbon. The calculated proton shifts obtained with an SCF treatment nearly reproduced the experimental shifts. However, for the carbon-13 shifts the calculated values are always lower than the experimental ones. An empirical term which when added to the paramagnetic contribution fits the experimental results is $-160z$, where z is the charge on carbon. The best results for carbon-13 shifts were obtained, also with the SCF wave function. Altogether it is found that the paramagnetic contribution to these shifts together with a direct π-charge term nicely account for the shifts.

The analysis of the nmr spectrum of pyridine and related compounds has been the object of intensive investigation. Studies have been made of pyridine,[1,2] deuteriopyridines,[1,2] polymethylpyridines,[3,4] 3-substituted pyridines,[5–7] γ-substituted pyridines,[6–8] and pyridine derivatives.[9] Recently the original analysis of pyridine by Schneider, Bernstein, and Pople[1–3] has been refined by the use of higher resolution nmr equipment together with iterative computer-based analyses which fit a set of nmr parameters to the experimental data. These analysis are the work of Merry and Goldstein,[10] Castallano, Sun, and Kostelnik,[11] and Fraenkel, Adams, and Dean.[12]

Ordinarily the calculation of chemical shifts from first principles presents insurmountable problems.[13] However, for certain types of compounds, it is possible to simplify the calculations by means of reasonable assumptions such as those described by McConnell[14] and Pople[15,16] and Karplus.[16]

Gil and Murrell have calculated contributions to the proton shifts in pyridine[17] using the anisotropy of nitrogen, the effect of the dipole associated with the lone pair on nitrogen, the perturbation of the ring current by nitrogen, and π-electron densities.

It is the object of this paper to show that shifts can be calculated quite accurately using approximate methods which have been already described in the literature.[14–16] In this work we give nmr parameters for pyridine in different solvents. The various para-

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(1) W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Can. J. Chem.*, **35**, 1487 (1951).

(2) W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Ann. N. Y. Acad. Sci.*, **70**, 806 (1958).

(3) H. J. Bernstein and W. G. Schneider, *J. Chem. Phys.*, **24**, 469 (1956).

(4) E. B. Baker, *ibid.*, **23**, 1981 (1955).

(5) V. J. Kowalewski and D. G. de Kowalewski, *ibid.*, 36, 266 (1962).

(6) S. Castellano and A. A. Bothner-By, *ibid.*, **41**, 3863 (1964).

(7) S. Castallano, H. Günther, and S. Ebersole, *J. Phys. Chem.*, **49**, 4166 (1965).

(8) B. P. Dailey and T. K. Wu, *J. Chem. Phys.*, **41**, 3307 (1964).

(9) W. Brugel, *Z. Electrochem.*, 66, 159 (1962).

(10) J. B. Merry and J. H. Goldstein, *J. Am. Chem. Soc.*, **88**, 5560 (1966).

(11) S. Castellano, C. Sun, and R. Kostelnik, *J. Chem. Phys.*, **46**, 327 (1967).

(12) G. Fraenkel, D. G. Adams, and R. R. Dean, *J. Phys. Chem.*, **72**, 944 (1968).

(13) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **86**, 243 (1952); N. F. Ramsey and E. M. Purcell, *ibid.*, **85**, 143 (1952).

(14) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(15) J. A. Pople, *ibid.*, **37**, 53 (1962).

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

(17) V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, **60**, 248 (1964).

Table I. Nmr Parameters for Pyridine in Various Solvents, 1.0 *M*

Solvent	τ_2[a]	τ_3	τ_4	J_{23}[b]	J_{24}	J_{25}	J_{26}	J_{35}	J_{34}
Neat	1.31	2.82	2.45	4.76	1.80	0.94	0.05	1.50	7.65
Ether	1.45	2.82	2.42	4.82	1.77	0.96	−0.14	1.25	7.64
Cyclohexane	1.48	2.93	2.54	4.99	1.70	1.16	−0.14	1.15	7.67
CCl_4	1.48	2.84	2.45	4.99	1.69	1.06	−0.07	1.33	7.59
$CDCl_3$	1.40	2.75	2.36	4.93	1.80	1.00	−0.03	1.44	7.66
Acetone	1.43	2.69	2.29	4.88	1.76	0.99	−0.02	1.39	7.70
Methanol	1.47	2.60	2.19	5.07	1.72	0.96	0.03	1.47	7.72
2-Propanol	1.48	2.67	2.27	5.03	1.76	0.94	−0.01	1.43	7.70
D_2O	1.50	2.69	2.29	5.02	1.72	0.94	−0.11	1.25	7.67
D_2SO_4–D_2O	1.22	1.91	1.38	5.82	1.69	0.90	0.69	2.16	7.69
Ether + R_2Mg[c]	1.49	2.71	2.39	5.18	1.80	0.90	0.13	1.38	7.47

[a] τ values ±0.005. [b] Hz ± 0.01. [c] Bis(2-methylbutyl)magnesium, 0.5 *M*.

magnetic and diamagnetic contributions to the ^{13}C and ^1H shifts are evaluated using separate wave functions for the π and σ systems.

Experimental Section

All nmr spectra were obtained with Varian A-60 and HA-60 nmr spectrometers. The spectra were calibrated by audio-side-band modulation. All solutions were degassed. The methods used in analyzing the spectra have been published elsewhere.[12]

Results

The nmr parameters for pyridine in various solvents are listed in Table I. These results compare favorably with those of other investigators.[10–12] The various nmr parameters vary comparatively little among the nonpolar solvents. However, proceding from nonpolar media through a succession of ever stronger hydrogen-bonding solvents, τ_2 remains relatively constant while τ_3 and τ_4 both decrease. Among the coupling constants the only discernible trend is the increase in $J_{2,3}$. The limiting case of strong hydrogen bonding is protonation, so D_2SO_4–D_2O properly belongs at the end for the series of ever stronger H-bonding media. Also the nmr parameters for pyridinium ion[10] fall at the end of the trends described above. Thus, compared to values for pyridine, the shifts in pyridinium ion are all lower and in the same order, while $J_{2,3}$ and $J_{2,6}$ are both 0.7 Hz higher than the corresponding values, respectively, for pyridine. The other coupling constants in pyridinium ion are quite similar to those for pyridine.

It is of interest that the results for pyridinium ion are independent of the solvent and substitution on nitrogen. N-Methylpyridinium iodide in DMSO and D_2O and pyridinium perchlorate in acetonitrile gave results little different from those for pyridinum ion in D_2SO_4–D_2O.[18] Thus specific solvation has little influence on the values of the nmr parameters.

Most of the line widths in these spectra are in the region 0.1–0.25 Hz; however, the α-proton line widths are strongly dependent on the nature of the solvent. They are wide in nonpolar media, become narrower with stronger hydrogen-bonding media, and then broaden considerably in pyridinium ion. Evidently the effect of hydrogen bonding at nitrogen is to increase the local electric field gradients and thereby decouple the nitrogen from the α-hydrogens.

Calculations of Chemical Shifts

The methods for calculating shifts in pyridine are now outlined. We consider diamagnetic and paramagnetic contributions to the ^{13}C shifts. The effect of charges in the σ framework will be described. Then these same contributions to the proton shifts will be evaluated.

As shown by Saika and Slichter[19] and Pople,[20] the screening constant for the nucleus of atom A may be expressed as

$$\sigma^{A} = \sigma_d^{AA} + \sigma_p^{AA} + \sum_{B \neq A} \sigma^{AB} + \sigma^{A,\ \mathrm{ring}} \qquad (1)$$

where σ_d^{AA} is the contribution from the diamagnetic Langevin-type circulation on atom A, σ_p^{AA} is due to the paramagnetic currents on this atom, which results from the mixing of electronic ground and excited states by the magnetic field, $\sum_{B \neq A} \sigma^{AB}$ is the contribution from currents on other atoms, and $\sigma^{A,\ \mathrm{ring}}$ is the contribution from ring currents.

In the case of the carbon-13 chemical shift, Karplus and Pople have suggested that the main contribution originates in changes in the second term, the local paramagnetic term, in eq 1.[16] We consider the paramagnetic terms first.

In the presence of a magnetic field, molecular orbitals are approximately written as linear combinations of gauge-invariant atomic orbitals (LCGI–MO) in place of LCAO–MO.[21,22] In the LCGI–MO approximation, a general expression for the local paramagnetic tensor of atom A, a first-row element, has been derived on the basis of a systematic set of approximations. These involve the neglect of multicenter integrals, overlap integrals, and the replacement of electronic excitation energies by a mean value. In conventional nmr experiments, only the mean value of the tensor is of interest and is written as[16,23]

$$\sigma_p^{AA} = -[e^2\hbar^2/2m^2c^2(\Delta E)]\langle r^{-3}\rangle_{2p}\sum_{B} Q_{AB} = -2N^{-1}\chi_p^{A}\langle r^{-3}\rangle_{2p} \qquad (2)$$

with

$$Q_{AB} = {}^4/_3[\delta_{AB}](P_{xAxB} + P_{yAyB} + P_{zAzB}) - {}^2/_3(P_{yAyB}P_{zAzB} + P_{zAzB}P_{xAxB} + P_{xAxB}P_{yAyB}) + {}^2/_3(P_{yAzB}P_{zAyB} + P_{zAxB}P_{xAzB} + P_{xAyB}P_{yAxB}) \qquad (3)$$

Here ΔE is the average electronic excitation energy, $\langle r^{-3}\rangle_{2p}$ is the mean inverse cube of the distance from

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(18) G. Fraenkel, The Ohio State University, unpublished results.

(19) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(20) J. A. Pople, *Discussions Faraday Soc.*, **34**, 7 (1962).

(21) F. London, *J. Phys. Radium*, **8**, 397 (1937).

(22) J. A. Pople, *Proc. Roy. Soc.* (London), **A239**, 541, 550 (1957).

(23) J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 303 (1961).

the nucleus of atom A for the 2p atomic orbitals, Σ_B runs over all atoms in the molecule (including A), $\chi_p{}^A$ is the paramagnetic susceptibility of atom A, and N is the Avogadro number. Lastly δ_{AB} is the Kroneker delta. The $P_{\mu\nu}$'s are elements of the charge density and bond-order matrix of the unperturbed molecule.

$$P_{\mu\nu} = 2\sum_i^{\text{occ}} c_{i\mu'} c_{i\nu} \qquad (4)$$

The summation in (4) extends over all occupied molecular orbitals, i, and $c_{i\mu}$ is the coefficient of the μth atomic orbital of the ith molecular orbital in the LCAO-MO approximation. The subscripts xA, xB, yA, yB, zA, and zB in eq 3 correspond to the various 2p atomic orbitals of atom A and B, all referred to equivalently oriented coordinated systems.

The effect of the electron density on $\sigma_p{}^{AA}$ is also introduced *via* the factor $\langle r^{-3}\rangle_{2p}$ in eq 2. By use of Slater atomic 2p orbitals together with a reasonable extension of Slater's rules to atoms with fractional electron populations, $\langle r^{-3}\rangle_{2p}$ for a Slater 2p orbital of carbon atom is given by[16]

$$\langle r^{-3}\rangle_{2p} = {}^1/_{24}(Z_A/a_0)^3 \qquad (5)$$

with

$$Z_A = 3.25 - 0.35(q_A - 1) \qquad (6)$$

where a_0 is the Bohr radius and q_A is the electron density on atom A.

Thus in the calculation of ^{13}C chemical shifts, coefficients from the wave function for the molecule in question are required to evaluate $\langle r^{-3}\rangle_{2p}$ and Q_{AB}.

We have employed three different π-electron, $2p_z$, wave functions for pyridine in these calculations. These are the SCF treatment by Mataga and Nishimoto,[24] Streitwieser's LCAO-MO ω[25] calculation, and the VESCF MO's of Brown and Heffernan.[26]

The average excitation energy ΔE was assigned to be 10 eV as suggested by Karplus and Pople.[16]

In conjunction with the π system it is necessary to treat the σ framework of pyridine. The simplest approach is to assume that the σ bonds are nonpolar. In that case the required coefficients come from assuming sp^2 hybridization for all C-C and C-N bonds while the C-H bond is C_{sp^2}, H_{1s}.

Evidence that σ charges should be considered in the chemical shift calculations comes from Kier's work on the dipole moment of pyridine.[27] An LCAO-MO ω calculation of the π-electron densities[25] together with a Del Ré[28] treatment for the σ charges accounted most satisfactorily for the dipole moment of pyridine.[27] Del Ré's procedure is an adaptation of the LCAO-MO method, treating σ bonds as localized orbitals to which inductive effects are introduced from neighboring atoms.

Thus, since the σ framework of pyridine is most likely polarized to a small degree, we have constructed, by symmetry, a set of *symmetry of molecular orbitals*[29] from combinations of localized bond orbitals. The latter are written as

$$\psi(\sigma_{AB}) = \frac{1}{\sqrt{2}}[(1 + \lambda)^{1/2}\phi(A) + (1 - \lambda)^{1/2}\phi(B)] \qquad (7)$$

where $\phi(A)$ and $\phi(B)$ are both sp^2 hybrids or an sp^2 hybrid and a 1s orbital, and λ is the fractional polarity of the bond in question. The 12 equivalent σ MO's composed of the various C-C, C-N, and C-H bond orbitals are listed in the Appendix of this paper. The σ bond orders and electron densities are evaluated as in the usual LCAO-MO procedure (eq 4). For molecules with a polar σ framework, these parameters are functions of the λ values for the different bonds. Finally, λ is obtained by equating the expressions for the σ-electron densities from eq 4 to the values calculated independently by the method of Del Ré[22] (see Table II). This procedure gives a self-consistent set of polarity parameters, λ. One example as to how this is done is given in the Appendix.

Table II. σ Charges and Bond Polarity Parameters, λ, in Pyridine from Del Ré Calculations

Atom	z_σ	Bond	λ
N	-0.1424	$N-C_\alpha$	0.0712
C_α	$+0.0266$	$C_\alpha-C_\beta$	0.0082
C_β	-0.0241	$C_\beta-C_\gamma$	0.0008
C_γ	-0.0293	$C_\alpha-H_\alpha$	0.0364
H_α	$+0.0364$	$C_\beta-H_\beta$	0.0315
H_β	$+0.0315$	$C_\gamma-H_\gamma$	0.0310
H_γ	$+0.0310$		

In summary, by the use of eq 2-7, a set of π-electron MO's for the $2p_z$ electrons and σ-electron MO's for the $2p_x$ and $2p_y$ electrons and assigning ΔE to be 10 eV, we have calculated the paramagnetic atom contributions to the ^{13}C chemical shifts in pyridine. The same calculation has been undertaken for the ^{13}C shift of benzene. The different cases treated are listed: case 1, homopolar σ bonds and Mataga SCF π-electron wave function;[24] case 2, polar σ bonds (Del Ré)[28] and Mataga SCF wave function;[24] case 3, homopolar σ bonds and LCAO-MO ω treatment;[25] case 4, polar σ bonds (Del Ré)[28] and LCAO-MO ω treatment;[25] case 5, homopolar σ bonds and VESCF π-electron function;[26] case 6, polar σ bonds[25] and VESCF function. The various paramagnetic shifts with respect to benzene from these calculations are listed in Table III and will be discussed later.

Up to this point no account has been taken of the diamagnetic contribution to the ^{13}C shifts, σ_d. This is given by[16]

$$\sigma_d{}^A = \frac{e^2}{3mc^2}\sum_k \left\langle \frac{1}{r_{kA}} \right\rangle_{2p,2s} \qquad (8)$$

where the summation runs over the electrons, k, on the atom considered, and r has the same definition as before (eq 5 and 6). Diamagnetic ^{13}C shifts for pyridine with respect to benzene are listed in Table IV. It is seen that these values are much smaller than the paramagnetic ones and need not be considered to account for the observed shifts.

We consider next the calculation of proton shifts in pyridine. This is more difficult than for other nuclei. We have calculated two terms in rough approximation. They are the local diamagnetic term σ_d and the contribution from the neighbor anisotropy effect.

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(24) N. Mataga and K. Nishimoto, *Z. Physik. Chem.* (Frankfurt), 13, 140 (1957).

(25) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

(26) R. D. Brown and M. L. Heffernan, *Australian J. Chem.*, 12, 554 (1959).

(27) L. B. Kier, *Tetrahedron Letters*, 3273 (1965).

(28) G. Del Ré, *J. Chem. Soc.*, 4031 (1958).

(29) J. Lennard-Jones, *Proc. Roy. Soc.* (London), **198**, 1, 14 (1949).

Table III. Calculated ^{13}C Shifts[a] in Pyridine

Case	χ_p^A	$\langle r^{-3}\rangle_{2p}$	σ_p^A	σ_{obsd}[b]
		α		
1	8.362	9.921	−6.87	−21.9
2	8.359	10.006	−9.11	
3	8.368	9.829	−4.50	
4	8.366	9.913	−6.77	
5	8.375	9.800	−3.92	
6	8.373	9.884	−6.20	
		β		
1	8.385	9.597	+1.40	+4.2
2	8.385	9.522	+3.49	
3	8.383	9.698	−1.34	
4	8.383	9.623	+0.73	
5	8.380	9.638	+0.42	
6	8.380	9.563	+2.50	
		γ		
1	8.389	9.793	−4.19	−7.70
2	8.391	9.701	−1.68	
3	8.377	9.772	−3.21	
4	8.379	9.680	−0.69	
5	8.383	9.712	−1.73	
6	8.384	9.620	+0.80	

[a] Ppm with respect to benzene. [b] P. C. Lauterbur, *J. Chem. Phys.*, **43**, 360 (1965).

Table IV. Diamagnetic Contributions to the ^{13}C Shifts in Pyridine

		σ_d	
Case	C_α	C_β	C_γ
1	−0.36	+0.07	−0.19
2	−0.47	+0.17	−0.07
3	−0.23	+0.06	−0.16
4	−0.35	+0.04	−0.04
5	−0.20	+0.02	−0.08
6	−0.31	+0.12	+0.04

In the LCGI–MO approximation the local diamagnetic term is expressed as[30]

$$\sigma_d{}^H = \frac{e^2}{3mc^2a_0}\rho_H \tag{9}$$

where ρ_H is the electron density on the hydrogen atom. Unfortunately it is not possible to evaluate ρ_H directly, and we have to choose another way to evaluate $\sigma_d{}^H$. For hydrogens bound to aromatic carbons there is an empirical correlation between the proton chemical shift with respect to benzene, σ_q, and the local charge, z, on the corresponding carbon (eq 9a).[31] Using pro-

$$\delta_q = -kz \tag{9a}$$

ton shifts in various cyclic aromatic species, k is found to be 10.7 ± 0.2 ppm/electron.[31] Musher[32] considers this term (eq 9a) is due to the local diamagnetic current on hydrogen. The current is largely determined by the π-electron density on the carbon to which the proton of interest is bound.

The paramagnetic contribution, $\sigma_p{}^A$, to the proton shift is written approximately as[14,17]

$$\sigma_p{}^N = {}^1/_3(\sigma_{xx}{}^H + \sigma_{yy}{}^H + \sigma_{zz}{}^H) \tag{10}$$

where

$$\sigma_{jj}{}^H = -[e^2\hbar^2/2m^2c^2\Delta E]\,\langle r_{jj}{}^{-3}\rangle\sum_B(Q_{AB}{}')_{jj} \tag{11}$$

Here j is one of the principle axes, and the summation runs over all atoms B except nitrogen and the atom bonded to hydrogen.

$$(Q_{AB}{}')_{zz} = P_{xAxB}(2\delta_{AB} - P_{yAyB}) + P_{yAyB}(2\delta_{AB} - P_{xAxB}) + 2P_{xAyB}P_{yAxB} \tag{12}$$

$$(Q_{AB}{}')_{xx} = P_{yAyB}(2\delta_{AB} - P_{zAzB}) + P_{zAzB}(2\delta_{AB} - P_{yAyB}) + 2P_{yAzB}P_{zAyB} \tag{13}$$

$$(Q_{AB}{}')_{yy} = P_{zAzB}(2\delta_{AB} - P_{xAxB}) + P_{xAxB}(2\delta_{AB} - P_{zAzB}) + 2P_{zAxB}P_{xAzB} \tag{14}$$

The P's in eq 12 to 14 are the bond orders and charge densities. Finally $\langle r_{jj}{}^{-3}\rangle$ is given by[14]

$$\langle r_{jj}{}^{-3}\rangle = \frac{1 - 3\cos^2\gamma_{BHj}}{3R_{BH}{}^3} \tag{15}$$

where R_{BH} is the BH distance and γ_{BHj} is the angle between one of the principle axes and R_{BH}. It is customary to define the principle atom magnetic susceptibilities as in

$$\chi_B{}^{(j)} = -[Ne^2\hbar^2/4m^2c^2\Delta E]\sum_B(Q')_{jj} \tag{16}$$

and the over-all equation for the shift is

$$\sigma_p{}^H = \sum_B\frac{1}{3R_{BH}{}^3}\sum_j\chi_B{}^{(j)}(1 - 3\cos^2\gamma_{BHj}) \tag{17}$$

Because of the existence of the low-lying electronic transitions (n → π^*),[33] when the external magnetic field lies along the x axis which is perpendicular to the direction of the lone pair on nitrogen atom, it is necessary to use the original equation in the calculation of the xx component of the magnetic susceptibility of nitrogen, $(\chi_p{}^N)_{xx}$, in place of eq 13 and 16. This is given by (18),[23] where E_i and E_k are the ground and excited

$$(\chi_p{}^N)_{xx} = [Ne^2\hbar^2/m^2c^2]\sum_i^{occ}\sum_k^{unocc}(E_k - E_i)^{-1} \times (C_{iyN}C_{jzN} - C_{izN}C_{RyN})\sum_B(C_{iyB}C_{kzB} - C_{iyB}C_{kyB}) \tag{18}$$

electronic orbital energies, respectively, and c_{iyB} is written for the coefficient of the p_y orbital on atom B. Following ref 17 we have chosen 4.5 and 7.5 eV for the first and second n → π^* transition energies and assumed the others are 10 eV.

Thus by use of eq 9–18 in conjunction with the same sets of π- and σ-electron wave functions used above for ^{13}C shifts, we have calculated proton shifts in pyridine. The results for the different cases are listed in Table V.

Discussion

The calculated ^{13}C shifts in Table III are encouraging in that they follow the correct order, and in certain cases the internal differences are proportional to those observed.

However, there are considerable differences in the values among the various models used, and the absolute magnitudes are smaller than the observed ones in

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(30) W. E. Lamb, *Phys. Rev.*, **60**, 817 (1941).

(31) G. Fraenkel, R. E. Carter, A. D. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); B. P. Dailey and J. S. Martin, *J. Chem. Phys.*, **39**, 1722 (1963); C. MacLean and E. L. Makor, *ibid.*, **34**, 2208 (1961).

(32) J. I. Musher, *ibid.*, 37, 34 (1962).

(33) M. Kasha and J. G. Brealey, *J. Am. Chem. Soc.*, 77, 4462 (1955).

Table V. Calculated Proton Shifts[a] in Pyridine, Paramagnetic and π-Density Terms

Case	σ_p[b]	z[c]	σ_g	σ_{calcd}	σ_{obsd}
			α		
1	−0.318	+0.0860	−0.920	−1.238	−1.293
2	−0.358	+0.0860	−0.920	−1.278	
3	−0.342	+0.0568	−0.608	−0.950	
4	−0.381	+0.0568	−0.608	−0.989	
5	−0.368	+0.0476	−0.509	−0.877	
6	−0.405	+0.0476	−0.509	−0.914	
			β		
1	−0.042	−0.0172	+0.184	+0.142	+0.07
2	−0.045	−0.0172	+0.184	+0.139	
3	−0.044	+0.0154	−0.165	−0.209	
4	−0.047	+0.0154	−0.165	−0.202	
5	−0.047	+0.0040	−0.043	−0.090	
6	−0.050	+0.0040	−0.043	−0.093	
			γ		
1	+0.026	+0.0454	−0.486	−0.460	−0.329
2	+0.027	+0.0454	−0.486	−0.459	
3	+0.029	+0.0386	−0.413	−0.384	
4	+0.030	+0.0386	−0.413	−0.383	
5	+0.029	+0.0194	−0.208	−0.179	
6	+0.029	+0.0194	−0.208	−0.179	

[a] Ppm with respect to benzene. [b] Paramagnetic term. [c] π charge.

every case. Since the shielding constant is given by the second row in eq 2, we consider the changes in $\chi_p{}^A$ and $\langle r^{-3}\rangle_{2p}$ separately. The term $\chi_p{}^A$ consists of several terms shown in eq 3. The first-row terms in eq 3 are concerned only with the charge density on atom A, and deviations from the value +2 come from the excess charge on atom A. The second and third rows in eq 3 are of considerable importance to explain the differences among $\chi_p{}^A$'s of carbon atoms in pyridine. Physically, they arise because the external magnetic field acting on atom B causes the mixing of certain electronic excited states of the molecule and thereby induces a current on atom A. As pointed out by Pople,[34] this effect of neighboring atoms only occurs if there is σ and π bonding between A and B atoms. Thus, altogether, $\chi_p{}^A$ is determined by the excess charge on atom A and the "multiple bond effect." As shown by eq 5 and 6, the term $\langle r^{-3}\rangle_{2p}$ has a steep dependence on the charge density on atom A. This arises from the expansion of 2p orbitals when electrons are added to the atom.

Comparing the values of $\chi_p{}^A$'s and $\langle r^{-3}\rangle_{2p}$'s for the α, β, and γ positions of pyridine with those in benzene, each shift with respect to benzene can be explained as follows. For the α-carbon atom, the large downfield shift arises from the contraction of 2p orbitals, *i.e.*, the charge effect due to the π electrons and the inductive effect of nitrogen which produces the polar C-N σ bond. This shrinkage overcomes the decrease of $\chi_p{}^A$ due to the decreased multiple bond effect. As for the β-carbon shift, the value of $\chi_p{}^A$ is nearly the same as that in benzene, and $\langle r^{-3}\rangle_{2p}$ becomes slightly larger than for C_α. Hence the small upfield shift for C_α is attributed mainly to the charge density. Although inductive effects in the σ system run in the opposite direction to the mesomeric effect, $\chi_p{}^A$ and $\langle r^{-3}\rangle_{2p}$ produce a downfield shift for the C_γ atom.

Summarizing the above discussion, the charge effect through the term $\langle r^{-3}\rangle_{2p}$ is a more important factor than the change in the magnetic susceptibility arising from the excess charge on the atom and the "multiple bond effect." For example, in case 2, the order of magnetic susceptibilities is $\gamma >$ benzene $> \beta > \alpha$; on the other hand, the order of the $\langle r^{-3}\rangle_{2p}$ values is $\alpha > \gamma >$ benzene $> \beta$, and the order of the resultant shielding constants is $\alpha > \gamma >$ benzene $> \beta$.

Considering how many assumptions are involved in the derivation of the shielding constant equations, the relative orders of magnitude are more significant than the absolute values of the shielding constants because systematic errors undoubtedly enter into the calculated absolute values. Note, however, that a reasonable value for ΔE is necessary to give a satisfactory interpretation of the main features of the nmr data in several different types of compounds.[34] If the ratio of the calculated relative shielding constants, $(\sigma_p{}^\alpha - \sigma_p{}^\beta)/(\sigma_p{}^\alpha - \sigma_p{}^\delta)$, is compared with the ratio of observed values, one can see which set gives the most reasonable shielding constants without the difficulty of choosing a value for ΔE. Table VI shows that cases 2 and 5 give the best fit with the observed values.

Table VI. Ratios of Relative Shielding Constants from Table III

	$(\sigma_p{}^\alpha - \sigma_p{}^\gamma)/(\sigma_p{}^\alpha - \sigma_p{}^\gamma)$
Obsd	2.19
Case 1	1.48
Case 2	2.42
Case 3	0.69
Case 4	4.28
Case 5	1.98
Case 6	4.11

It is also interesting to note that when the VESCF π-electron wave functions were used (cases 5 and 6) in place of the conventional SCF function (cases 1 and 2), the use of a homopolar σ framework gives better results than the Del Ré[28] σ framework. In the VESCF procedure,[26,35] the orbital exponent, Z_A, for the atomic orbital φ_A is regarded as a linear function of the electron density at atom A, and thus various basic integrals become functions of the electron distribution. On the other hand, the conventional SCF procedure assigns a constant value to Z_A corresponding to a uniform electron distribution. The reason why case 5 gives better results than case 6 is due to the fact that the π-electron wave function is already a function of the charge at different positions.

Using the criterion based on ratios of shifts it would seem that cases 2 and 5 give the best results so far. It is now worthwhile to speculate on why the absolute magnitudes of the ^{13}C calculated shifts are smaller than the experimental values.

The results obtained with the SCF wave function are roughly proportional to the π charges and to the observed shifts. Changing the average excitation energy within reasonable limits does not improve the calculated shifts enough. Possibly there are erroneous approximations in the derivation of eq 2, 3, 5, and 6.

We have found an empirical term which when added to the σ_p contribution matches the experimental shifts

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(34) J. A. Pople, *Mol. Phys.*, **7**, 301 (1963).

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

with the theoretical ones. This comes from the experimental linearity of ^{13}C shift with charge in aromatic species whose atom charges are known by symmetry (eq 19).[36–38]

$$\sigma_{q^{13}C} = -160z$$

The result of adding this contribution to the σ_p term is shown in Table VII. We now find that the SCF calculation gives shifts which are almost the same as the experimental ones, whereas the other cases fit rather badly.

Table VII. Effect of Including π-Electron Density Term in ^{13}C Shift Calculations for Pyridine

Case	σ_p	$\sigma_q{}^a$	$\sigma_{calcd}{}^a$	σ_{obsd}
		α		
1	−6.87	−13.76	−20.63	−21.9
2	−9.11	−13.76	−22.87	
3	−4.50	−9.08	−13.58	
4	−6.77	−9.08	−15.85	
5	−3.92	−7.61	−11.83	
6	−6.20	−7.61	−13.81	
		β		
1	+1.40	+2.75	+4.15	+4.2
2	+3.49	+2.75	+6.64	
3	−1.34	−2.46	−3.80	
4	+0.73	−2.46	−1.73	
5	+0.42	−0.64	−0.22	
6	+2.50	−0.64	+1.86	
		γ		
1	−4.19	−7.26	−11.45	−7.70
2	−1.68	−7.26	−8.94	
3	−3.21	−6.18	−9.31	
4	−0.69	−6.18	−6.88	
5	−1.73	−3.10	−4.83	
6	+0.80	−3.10	−2.30	

[a] With respect to benzene, ppm.

It is not clear why adding the σ_q term works so well. Perhaps the effect of the approximations used is to undervalue the dependence of ^{13}C chemical shift on charge.

With regard to the calculations of proton shifts in pyridine (Table V), we find that the Mataga SCF[24] treatment gives the best results. Here, however, the π-density term has some justification since it may be attributed to the diamagnetic current on hydrogen.[32]

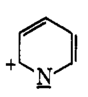
The downfield shift of the α proton arises from the π-charge effect and the neighbor anisotropies. About 90% of this latter effect is attributable to the nitrogen anisotropy. For the β proton, the neighbor anisotropies coming from both nitrogen and carbon atoms are cancelled out by the π-charge effect. The shift for the γ proton is predominantly determined by the π charge. Finally, it should be noticed that the agreement between the calculated and the observed values may be fortuitous. The use of eq 19 is only valid if the effective "diameter" of an electron on the atom, B, is much smaller than R_{BHj}. Using Slater wave functions,[39] the value of the effective diameter of the 2p orbital on carbon or nitrogen lies between 0.67 and 0.82 Å. That is not very small compared with the distances between the α protons and nitrogen or α-carbon atoms and nitrogen. Although the nitrogen anisotropy is responsible for the downfield shift of the α proton, with decreasing R the shielding becomes larger and more important, but the point dipole approximation (eq 17) becomes less and less accurate.

Thus both diamagnetic (π charge) and paramagnetic terms are responsible for the proton shifts in pyridine. It is seen that these shifts can be calculated quite accurately with the use of reasonable assumptions about the π and σ wave functions.

The trends in chemical shifts obtained with different hydrogen bonding and protonating media can now be qualitatively understood.

The major contribution to the paramagnetic terms comes from the anisotropy of nitrogen. This is inversely proportional to $\Delta E_{n\rightarrow\pi^*}$.[14,23] Since the latter excitation energy increases with the strength of hydrogen bonding at nitrogen,[33] the magnitude of the paramagnetic shifts (compared to benzene) should decrease in stronger hydrogen-bonding media and be very small for the shifts in pyridinium ion.

π-Electron density variations around pyridine and pyridinium ion are mainly due to conjugative effects (I to IV). Therefore the π-electron density terms should become larger and more negative with the strength of the hydrogen bonds formed and reach a limit in pyridinium ion. Altogether stronger hydrogen bonding at nitrogen results in less negative paramagnetic terms and more negative π-density shifts. These two contributions nearly cancel for H_α. However, as one proceeds through hydrogen bonding to protonation, the π-density term becomes dominant at the β and δ positions, and net deshielding results.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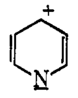
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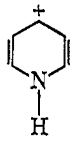
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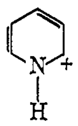
IV

Conclusions

The main conclusion from this work is that, in one case, pyridine proton and ^{13}C chemical shifts can be calculated quite accurately using atom anisotropies together with a separate π-electron density term.

The choice of wave functions is critical. In this work we find that the SCF wave function gives by far the best results.

Acknowledgment. This research was supported in part by the National Institutes of Health Grant No. GM-08686.

Appendix

The symmetry molecular orbitals for C–C σ bonds in benzene are given in eq 19–24. Those for the C–H

$$\Phi_1 = \frac{1}{\sqrt{6}}(\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6) \quad (19)$$

$$\Phi_2 = \frac{1}{\sqrt{12}}(2\psi_1 + \psi_2 - \psi_3 - 2\psi_4 - \psi_5 + \psi_6) \quad (20)$$

$$\Phi_3 = \frac{1}{2}(\psi_2 + \psi_3 - \psi_5 - \psi_6) \quad (21)$$

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(36) H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).

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

(38) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838, 1846 (1961).

(39) J. C. Slater, "Quantum Theory of Matter," McGraw-Hill Book Co., Inc., New York, N. Y., 1951.

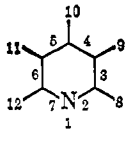
$$\Phi_4 = \frac{1}{\sqrt{12}}(2\psi_1 - \psi_2 - \psi_3 + 2\psi_4 - \psi_5 - \psi_6) \quad (22)$$

$$\Phi_5 = \frac{1}{2}(\psi_2 - \psi_3 + \psi_5 - \psi_6) \quad (23)$$

$$\Phi_6 = \frac{1}{\sqrt{6}}(\psi_1 - \psi_2 + \psi_3 - \psi_4 + \psi_5 - \psi_6) \quad (24)$$

bonds have the same form as (19) and (24) except the ψ's are homopolar localized C–H bonding orbitals. The individual ψ's are given by eq 7.

Below are listed the symmetry MO's for the σ framework of pyridine together with the bonds they refer to; see V.



V

$$\Phi_1 = \psi_1 \qquad \sigma\text{ (N lone pair)} \quad (25)$$

$$\left.\begin{aligned} \Phi_2 &= \frac{1}{\sqrt{2}}(\psi_2 + \psi_7) \quad (26) \\ \Phi_3 &= \frac{1}{\sqrt{2}}(\psi_2 - \psi_7) \quad (27) \end{aligned}\right\} \sigma(C_\alpha\text{–}N)$$

$$\left.\begin{aligned} \Phi_4 &= \frac{1}{\sqrt{2}}(\psi_3 + \psi_6) \quad (28) \\ \Phi_5 &= \frac{1}{\sqrt{2}}(\psi_3 - \psi_6) \quad (29) \end{aligned}\right\} \sigma(C_\alpha\text{–}C_\beta)$$

$$\left.\begin{aligned} \Phi_6 &= \frac{1}{\sqrt{2}}(\psi_4 + \psi_5) \quad (30) \\ \Phi_7 &= \frac{1}{\sqrt{2}}(\psi_4 - \psi_5) \quad (31) \end{aligned}\right\} \sigma(C_\beta\text{–}C_\gamma)$$

$$\left.\begin{aligned} \Phi_8 &= \frac{1}{\sqrt{2}}(\psi_8 + \psi_{12}) \quad (32) \\ \Phi_9 &= \frac{1}{\sqrt{2}}(\psi_8 - \psi_{12}) \quad (33) \end{aligned}\right\} \sigma(C_\alpha\text{–}H_\alpha)$$

$$\left.\begin{aligned} \Phi_{10} &= \frac{1}{\sqrt{2}}(\psi_9 + \psi_{11}) \quad (34) \\ \Phi_{11} &= \frac{1}{\sqrt{2}}(\psi_9 - \psi_{11}) \quad (35) \end{aligned}\right\} \sigma(C_\alpha\text{–}H_\beta)$$

$$\Phi_{12} = \psi_{10} \qquad \sigma(C_\gamma\text{–}H_\gamma) \quad (36)$$

The procedure for calculating $\lambda_{NC\alpha}$ is now given.

The σ-electron density on nitrogen is obtained from eq 25–27. Both ψ_2 and ψ_7, given by eq 7, contain ϕ_N; in both cases the coefficient of ϕ_N is $(1/\sqrt{2})(1 + \lambda_{NC}\ )^{1/2}$. Summing the electron density on nitrogen

$$\begin{aligned} q_{N\sigma} &= 1 + 4[{}^1\!/_2(1 + \lambda_{NC\alpha})] \\ &= 3 + 2\lambda_{NC\alpha} \end{aligned}$$

Since the σ core of nitrogen in pyridine is four electrons, the charge is $4 - q = 1 - 2\lambda_{NC\alpha}$. This charge is equated to the Del Ré charge on nitrogen to give for $\lambda_{NC\alpha}$, +0.07.

Benzene Photosensitization and Direct Photolysis of Cyclobutanone and Cyclobutanone-2-*t* in the Gas Phase[1]

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Abstract: The fluorescence of the $^1B_{2u}$-state benzene is quenched by cyclobutanone with a quenching cross section ($\pi\sigma^2$) of 4 Å^2, and this singlet energy transfer produces an excited singlet cyclobutanone which subsequently decomposes to yield primarily ethylene (plus ketene). On the other hand, the $^3B_{1u}$-state benzene transfers its electronic energy to cyclobutanone with a quenching cross section ($\pi\sigma^2$) of 1 Å^2 to produce an intermediate which subsequently decomposes to yield a vibrationally excited cyclopropane (plus CO). The yield of cyclopropane is lowered by the addition of *cis*-2-butene which is a quencher of the triplet benzene, and therefore it is proposed that cyclopropane is a characteristic decomposition product of a triplet cyclobutanone. Sensitization quantum yields have been determined, and they are near unity. The comparison of the decomposition product distribution in the benzene-photosensitized samples with that observed at varying excitation energies (wavelength) in the direct photolysis of cyclobutanone indicates that, on the average, about 96 kcal/mole of excitation energy is delivered to cyclobutanone in the singlet energy transfer while about 80–85 kcal/mole of excitation energy is delivered to cyclobutanone in the triplet energy transfer.

The photochemistry of cyclobutanone in the gas phase has been the subject of several investigations. It was first shown in 1942 that photochemically excited cyclobutanone molecules decompose by two primary processes to yield C_2H_4 and CH_2CO (60%) or C_3H_6 and CO (40%),[2a] and only in the later work to

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(1) This research has been supported by National Science Foundation Grant GP 6924.