theoretical calculations, suggest the presence of interring polarization effects of significant magnitudes.

Admittedly, the theoretical calculations are somewhat crude, but the correlation with experiment nevertheless demonstrates the essential reliability of the MO results. Even though perfect correlation is not possible at all positions in view of the many simplying assumptions required to theoretically assess the rather complex data obtained herein, the results are encouraging and illustrate the usefulness of approximate all-valence-electron methods such as the CNDO approach, and justify those workers interested in obtaining even better computer routines for treating molecules of this general size.

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Carbon-13 Magnetic Resonance. XX.[1] 4-Azaindene (Pyrrocoline) and Related Bridgehead Nitrogen Heterocycles

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Abstract: The carbon-13 chemical shifts for pyrrocoline and a number of related azaindenes have been measured in order to determine the extent that the free pair on the bridgehead nitrogen contributes to the delocalized electronic structures. The data indicate that a nitrogen atom at a bridgehead position produces only relatively minor perturbations as compared with the isoelectronic indenyl anion and that a high degree of aromaticity occurs in this class of compounds. The electronic structure is calculated by means of the CNDO–SCF–MO formalism and is used to rationalize the experimental results.

Although considerable advancement has been made in understanding the electronic structure and concomitant properties of benzenoid and nonbenzoid aromatic carboxyclic systems, a much less clearly defined status exists in the area of aromatic heterocyclic chemistry. This is especially true in nitrogen heterocycles when one departs from simple systems such as pyrrole and pyridine. The heteroaromatic properties of these two ring systems have been studied extensively.[2,3] Extension of these structural elements into fused-ring systems of two or more nitrogens, however, leads to rather widely variable theoretical predictions in several instances, and the available information becomes largely empirical for individual examples.

A particular case of interest, and presently among the least understood in detail, is that class of heterocycles containing the familiar aromatic ring systems fused through a common bridgehead nitrogen. The question which arises is how the charge distribution in one ring system will affect the electronic structure of another heterocyclic ring fused in this manner. Of special concern is the role of the two unshared electrons on the bridgehead nitrogen atom in the electronic distribution and bonding in this molecular system.

From previous studies[4–8] based on chemical properties as well as proton magnetic resonance (pmr) and ultraviolet spectroscopy, it has been concluded that 1,4-diazaindene (imidazo[1,2-*a*]pyridine) is a ten-π-electron aromatic system with considerable delocalization of π electrons and the ability to sustain a ring current in the presence of an external magnetic field. Similar conclusions have been reached from studies of such other ten-π-electron compounds as 4-azaindene (pyrrocoline),[9] 3,4-diazaindene (pyrazolo[2,3-*a*]pyridine),[10] and 1,4,8-triazaindene (imidazo[1,2-*a*]pyrimidine).[11]

Carbon-13 magnetic resonance offers a powerful method for investigating the aromatic properties of hydrocarbons and hydrocarbon derivatives and the effects of ring currents.[12,13] Pugmire, *et al.*,[14,15] as well as several other authors[16–18] have extended the use of carbon-13 chemical shifts to the study of the charge densities and bond orders in the five- and six-membered nitrogen heterocycles[14,17,18] as well as a number of polycyclic heteroaromatic compounds.[1,15,16,18] The carbon-13 chemical shift data allow one to investigate those molecular properties which give rise to magnetic shielding effects, and the technique provides a useful means to assess various theoretical treatments of molecular bonding schemes.

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[16] P. C. Lauterbur, *J. Chem. Phys.*, 43, 360 (1965).

[17] W. Adam, A. Grimison, and G. Rodriquez, *Tetrahedron*, 23, 2513 (1967).

[18] J. E. Bloor and D. L. Breen, *J. Amer. Chem. Soc.*, 89, 6835 (1967).

In the present work, the carbon-13 chemical shifts are reported for the bridgehead nitrogen compounds 4-azaindene, 1,4-diazaindene, 2,4-diazaindene, 3,4-diazaindene, and 1,4,8-triazaindene in order to ascertain the electronic structure of such novel ten-π-electron systems. A theoretical analysis of the charge densities and bond orders is made by means of the CNDO–SCF approach of Pople and coworkers[19–21] and these parameters are employed in the Karplus–Pople formalism[14,22] to predict the magnetic shielding of the carbon nucleus.

Experimental Section

A. Equipment. A Varian high-resolution spectrometer (AFS-60) equipped with a V-4311 transmitter operating at 15.085 Mcps was used to observe the carbon-13 magnetic resonance spectra. Proton decoupling was accomplished with a Varian V-4320 spin decoupler operating at 60 Mcps in the manner described previously.[15,23]

B. Spectroscopic Details. The spectra of 3,4-diazaindene, 1,4-diazaindene, and 3-deuterio-1,4-diazaindene were determined on neat liquid samples. For the solid samples 2,4-diazaindene, 4-azaindene, and 1,3-dideuterio-4-azaindene, the carbon-13 spectra were observed as saturated solutions in $CHCl_3$, while the proton spectra were obtained in saturated $CDCl_3$. In the case of the solid 1,4,8-triazaindene, the carbon-13 and proton spectra were obtained using saturated DMSO solutions. The decoupled carbon-13 spectra of at least one peak in each compound are obtained under slow-sweep conditions with sample spinning, and identification with the directly bonded proton is made by means of the selective proton-decoupling technique[15] described elsewhere. The chemical shift of this peak in parts per million (ppm) from benzene is determined from Γ_i, the ratio (f_i/ν_i) of the decoupler frequency to the transmitter frequency, and the corresponding proton chemical shift, in accordance with eq 1. This fiducial point is then used to measure

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

the chemical shifts of the other peaks observed by scanning the sample under high decoupler power using a wide-band proton frequency range. The individual carbons are then identified by scanning the peak in question while irradiating a specific proton frequency at low decoupler power.[16]

All samples for carbon-13 analysis were run in 10-mm thin-walled glass tubing, while the proton samples were contained in 5-mm tubes. TMS was added as internal standard to all samples for proton analysis.

C. Sample Preparation. Samples of 4-azaindene,[24] 2,4-diazaindene,[25] 3,4-diazaindene,[26] and 1,4,8-triazaindene[11] were prepared as previously described. The 1,3-dideuterio-4-azaindene was prepared by the method of Black, *et al.*,[27] from 4-azaindene hydroperchlorate.[28] 1,4-Diazaindene was obtained from Aldrich Chemical Co. and was converted to 3-deuterio-1,4-diazaindene as described by Paudler and Helmick.[29]

Results

A. Proton Chemical Shifts. The proton chemical shifts for the compounds studied in this work are given in Table I. The shift assignments of items 1–29 are based on the work of Black, *et al.*,[27] as modified by solvent effects, etc., while the shift values for 1,4,8-triazaindene (items 30–34) are based on the work of Paudler and Kuder.[11]

In the case of 4-azaindene in $CDCl_3$, the proton splitting patterns of H-1 and H-7 overlapped considerably at 60 MHz and hence could not be clearly resolved. However, the deuterated species (1,3-dideuterio-4-azaindene) in saturated $CDCl_3$ solution clearly defined the resonance position of H-7 as lying upfield from H-1, which is a reversal of the assignment reported by Black, *et al.*,[27] for this molecule in a dilute CCl_4 solution. This minor discrepancy may be due to a concentration effect upon the closely positioned proton shifts. In the case of 1,4-diazaindene, H-2 and H-3 could not be resolved and an examination of the spectrum of 3-deuterio-1,4-diazaindene indicated that in the neat liquid the resonance positions of the two protons are identical.

Black, *et al.*,[27] report the resonance position of H-1 in 3,4-diazaindene to lie above H-6 in dilute CCl_4 solution. The overlapping multiplet structure renders the differentation between H-1 and H-6 impossible at 60 MHz in the neat liquid. However, through a close examination of the proton decoupling data one observes that the two associated carbon-13 peaks have proton decoupling frequencies separated by 4–6 cps. Using this frequency separation and the carbon-13 chemical shift assignments described in section B, it is concluded that the resonance position of H-6 lies at higher field than H-1 in the neat liquid. Therefore, the order of chemical shifts has an apparent concentration dependence and the relative positions are reversed from those noted[27] in a dilute CCl_4 solution.

B. Carbon-13 Chemical Shifts. The carbon-13 chemical shift assignments for the various azaindenes studied are given in Table I. In the body of the text all chemical shifts are given relative to benzene, as with past practice in this laboratory. Because of the recent interest in a TMS chemical shift scale, however, Table I also contains for convenience the shifts relative to TMS with increasing positive values indicating lower field strength. The bridgehead carbon atoms were readily assigned in each compound since a quaternary carbon exhibits no large C–H coupling and appears as a sharp singlet over a wide range of proton decoupling frequency settings. With the exception of C-1 and C-7 in 4-azaindene, C-2 and C-3 in 1,4-diazaindene, and C-1 and C-6 in 3,4-diazaindene, chemical shift assignments of ternary carbons were made by selective decoupling[15] of the various directly bonded protons. For those compounds in which the close proximity (~0.1 ppm) or the proton chemical shifts rendered carbon resonance assignment impossible by selective decoupling, the peak assignments were resolved by deuteration or arguments based on the chemical shifts of identifiable carbons in similar chemical positions in other molecular species.

In the case of 4-azaindene, the two peaks corresponding to C-1 and C-7 having chemical shift values of 29.10 and 11.38 ppm could not be differentiated by selective proton decoupling. The assignment was accomplished by observing the carbon-13 spectra of 1,3-dideuterio-4-azaindene. Previous work in this laboratory[15] has illustrated the benefits of deuterium substitution for assignment of ^{13}C shift positions. In the present case, deuterium labeling resulted in a significant broadening and reduction of intensity of the peak as-

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[27] P. J. Black, M. L. Heffernan, L. M. Jackman, Q. N. Porter, and G. R. Underwood, *Aust. J. Chem.*, 17, 1128 (1964).

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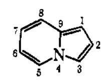
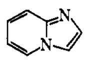
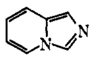
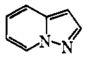
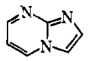
Table I. Carbon-13 and Proton Chemical Shifts in Selected Azaindenes

Item	Compound[a]	Position	δ_H, ppm[b]	$\beta_{^{13}C}$, ppm[b,d]	$\delta_{^{13}C}$, ppm[c]
1		1	~0.7	29.10	99.44
2		2	0.47	14.47	114.07
3		3	0.17	15.53	113.01
4		5	−0.28	2.93	125.61
5	4-Azaindene (pyrrocoline,	6	1.0	18.10	110.44
6	pyrrolo[1,2-*a*]pyridine)	7	~0.8	11.38	117.16
7		8	−0.03	8.98	119.56
8		9		−4.81	133.35
9		2	~−0.8	−5.51	134.05
10		3	~−0.8	15.13	113.41
11		5	−1.23	1.58	126.96
12	1,4-Diazaindene (imidazo[1,2-*a*]pyridine)	6	0.49	16.35	112.19
13		7	0.05	3.95	124.59
14		8	−0.68	10.92	117.62
15		9		−17.06	145.60
16		1	−0.26	8.60	119.94
17		3	−1.03	0.18	128.36
18		5	−0.70	5.73	122.81
19	2,4-Diazaindene	6	0.9	15.89	112.65
20	(imidazo[1,5-*a*-]pyridine)	7	0.5	9.17	119.37
21		8	−0.08	10.37	118.17
22		9		−2.10	130.64
23		1	~−0.7	32.29	96.25
24		2	−0.91	−12.75	141.29
25		5	−1.30	0.46	128.08
26	3,4-Diazaindene (pyrazolo[2,3-*a*]pyridine)	6	~0.8	17.71	110.83
27		7	0.42	6.19	112.35
28		8	0.05	11.17	117.37
29		9		−10.96	139.50
30		2	−1.00	−6.60	135.14
31		3	−0.75	15.88	112.66
32		5	−2.10	−7.50	136.04
33	1,4,8-Triazaindene	6	−0.05	19.13	109.41
34	(imidazo[1,2-*a*]pyrimidine)	7	−1.56	−22.40	150.94
35		9		−20.32	148.86

[a] For convenience in discussion, all compounds are numbered continuously around the periphery, as illustrated for 4-azaindene, with alternate nomenclature indicated. [b] Values are taken relative to benzene. [c] Values are taken relative to tetramethylsilane (128.54 ppm upfield from benzene). [d] For purposes of comparison, the indenyl anion shifts are: C-1,3, 36.71; C-2, 13.56; C-4,7, 9.15; C-5,6, 14.65; C-8,9, 0.47 ppm with respect to benzene: A. J. Jones, private communication.

signed to C-3 by the proton-decoupling method. The peak lying at 29.10 ppm exhibited a similar spectral change and hence was assigned to C-1, while C-7 was assigned by default at 11.38 ppm with respect to benzene.

Two peaks falling at −5.51 and 15.13 ppm corresponding to positions C-2 and C-3 of 1,4-diazaindene could not be assigned by proton decoupling owing to the close proximity of the resonance positions of H-2 and H-3. However, the resonance absorption at 15.13 ppm was not observed in the carbon-13 spectra of 3-deuterio-1,4-diazaindene and hence fixed the assignment of C-2 at −5.51 ppm and C-3 as the upfield peak in question.

The proton spectrum of neat 3,4-diazaindene also could not be resolved in the region of H-1 and H-6 absorption at 60 MHz and hence it was not possible for C-1 and C-6 to be assigned by proton decoupling techniques. A comparison of the chemical shift values of items 5, 12, 19, and 33 (range, 15.89–19.13 ppm) indicates clearly that no precedence exists in the data on similar compounds which would result in C-6 lying at 32.29 ppm with respect to benzene. Rather, the alternate possible value of 17.71 ppm is much more compatible with the range of values found for the other related species studied, and on the basis of this argument C-6 was assigned accordingly. Confidence in this assignment was obtained by noting the favorable comparison of 29.10 ppm at C-1 in 4-azaindene with the proposed assignment of 32.29 ppm at C-1 in 3,4-diazaindene.

Discussion of Results

The significance of the present carbon-13 chemical shift data on the azaindenes resides in the relevance of this information to the following three questions of interest. (1) Do the π electrons at the bridgehead nitrogen delocalize significantly and therefore contribute to the aromatic character of these systems? (2) Which carbons are affected most by the bridgehead nitrogen when compared to the isoelectronic indenyl anion? (3) Do calculated ground-state charge distributions correlate with the carbon-13 shifts and as such have any predictive value for electrophilic and nucleophilic reactions? Before attempting to answer these questions it will be helpful to consider the present state of carbon-13 chemical shift theory and delineate the major contributions to magnetic shielding of the carbon nucleus.

A. Contributions to Carbon-13 Magnetic Shielding. Previous work in this laboratory[13–15,30] has made use of

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(30) B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, 89, 5319 (1967).

various types of molecular species to investigate the dominant terms associated with carbon-13 chemical shifts, and the reader is referred to these citations for a detailed analysis of the chemical shift expression.[31,32] The results have shown that the major chemical shift contribution (>90%) comes from the paramagnetic screening term and that the following factors are of primary importance in carbon-13 chemical shift theory: (a) the extent of p-orbital population in the ground-state wave function; (b) the magnitude of an excitation energy which mixes excited electronic states into the ground state configuration (this excitation energy roughly parallels variations in the bonding energies); (c) the average radial distance of electrons from the screened nuclei; (d) electronic charge polarization; and (e) the variations of spin pairing between a p electron centered on a nucleus under study and other delocalized p electrons, especially those on atoms exhibiting greater paramagnetic screening currents because of low excitation energies.

The data of Spiesecke and Schneider[33] on the tropylium cation, benzene, and the cyclopentadienyl anion constitute perhaps the best relationship between carbon-13 chemical shifts and π-charge densities. The data suggest that a relationship of 160 ppm/electron exists between the chemical shifts and the π-electron charges. Thus, as electron charge builds up on an atom the carbon resonance moves upfield in an apparently proportional manner. However, from a CNDO–SCF–MO[19–21] treatment of these species it is noted that the average inverse ΔE value (excitation energy) calculated from the separation in bonding and antibonding levels for tropylium cation displays a 3.8% variation from the benzene value, whereas the corresponding cyclopentadienyl value is comparable with that for benzene. If an appropriate correction in ΔE is applied to the theoretical estimate of the paramagnetic term,[14,34] thereby converting all data to the same ΔE value, the chemical shift π-charge relationship increases to 195 ppm/π electron, which is in good agreement with the 200 ppm/π electron charge dependence determined by Lauterbur[35] from this carbon-13 data on azulene. In evaluating the term in the Karplus–Das paramagnetic shielding expression,[32] Pugmire and Grant[14] demonstrated that charge effects on chemical shifts require one to consider a changing effective nuclear charge for the various atomic orbitals. This relationship properly accounts for the dependence of the shielding expression on the average radial distance of the electrons from the screened nucleus and is responsible for the positive slope of the chemical shift–electronic charge relationship.

Earlier work on the five-member heterocycles[14] has shown that variations in spin pairing (bond orders) in the various orbitals can produce significant changes in the paramagnetic shielding term. This is particularly true for changes in N–C bond orders when the nitrogen lone pair is protonated. Nitrogen protonation decreases the N–C_α bond order, thereby decreasing the spin-pairing contributions and decreasing the paramagnetic portion of the magnetic shielding.[36] This phenomenon is responsible, in part, for the anomalous upfield shifts noted at α carbons when the adjacent nitrogen free pair is protonated.[14] On the other hand, the nitrogen free pair has associated low-energy molecular orbitals which decrease the value of ΔE. Nitrogen protonation eliminates these low-energy levels, thereby increasing ΔE and decreasing the paramagnetic term. At present there is no simple technique, without undertaking a calculation which is properly summed over excited states, for separating those effects due to changes in spin pairing from those due to changes in ΔE. Both effects reduce the paramagnetic screening term upon nitrogen protonation and shift the α-carbon resonance upfield.

From the preceding discussion it is evident that effects other than those due to charge polarization (*i.e.*, variations in spin-pairing and ΔE terms) can be of considerable magnitude and often must be considered if a satisfactory theoretical fit of the data is to be realized. However, for those molecular systems in which significant variation in spin-pairing and ΔE terms do not occur, charge polarization is usually the dominant factor in determining the carbon-13 resonance position.

B. **Indenyl Ion and the Azaindenes.** It will be helpful to consider the experimental data for the azaindenes in terms of the corresponding positions in the isoelectronic indenyl anion. While this practice may be somewhat artificial in terms of absolute chemical shift values, using the indenyl anion as a reference, rather than benzene, eliminates inaccuracies in molecular wave functions which result from the fusion of five- and six-membered rings. The perturbations due to the nitrogen atom upon the various isoelectronic species may then be systematically studied. Such a study can test, among other things, the conclusion that the bridgehead nitrogen in pyrrocoline contributes two electrons to the π-charge cloud resulting in a delocalized π-electron system. The appropriately referenced chemical shift values in the azaindenes are presented in Table II.

The electron-rich indenyl anion distributes ten π electrons over nine carbon atoms, and the upfield carbon-13 chemical shifts with respect to benzene (Table I) reflect the increased shielding associated with this distribution of excess charge. However, a careful examination of the chemical shift data indicates that considerable charge localization does occur at C-1,3 in the five-membered ring, suggesting a significant contribution from the classical charged structure. A cursory glance at the carbon-13 chemical shift values in Table II (referenced to indenyl anion) reveals the aromatic nature of the azaindenes and the perturbing influence of the bridgehead nitrogen atom. For instance, with one exception, the shift values in 4-azaindene show only minor deviation (range, −7.61 to +3.45 ppm) from the corresponding values in the reference compound. The single exception is at position C-3, adjacent to the heteroatom and shifted downfield −21.18 ppm. Similar results are evident for the diazaindenes, where, with the single exception of C-7 in 1,4-diazaindene, large chemical shift deviations occur only for carbon atoms in

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(31) N. F. Ramsey, *Phys. Rev.*, 77, 567 (1950); 78, 699 (1950).

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

(33) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).

(34) This type of correction was first suggested to the authors by W. Adam as a means of rationalizing an apparent discrepancy between the carbon-13 chemical shifts for the five- and six-member nitrogen heterocycles.

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

(36) Conversely, any molecular perturbation which increases the spin-pairing terms enhances the paramagnetic term.

Table II. Experimental and Predicted Carbon-13 Chemical Shifts Taken in Selected Azaindenes

		^{13}C chemical shifts, ppm[a]		
Compound	Position	Exptl	f	Predicted[b]
4-Azaindene	1	−7.61	0.998	−8.3
	2	0.91		−7.2
	3	−21.18		−9.8
	5	−6.22		−4.7
	6	3.45		−4.0
	7	−3.27		−7.5
	8	−0.17		−1.4
	9	−5.28		−6.8
1,4-Diazaindene	2	−19.07	0.991	−20.1
	3	−21.58		−11.8
	5	−7.57		−9.4
	6	1.70		−6.3
	7	−10.70		−12.6
	8	1.77		−1.5
	9	−17.53		−17.2
2,4-Diazaindene	1	−28.11	0.989	−22.6
	3	−36.53		−24.2
	5	−3.42		−6.0
	6	1.24		−9.0
	7	−5.48		−10.7
	8	1.22		−5.8
	9	−2.57		−9.4
3,4-Diazaindene	1	−4.42	0.990	−10.4
	2	−26.31		−30.1
	5	−8.69		−10.0
	6	3.06		−6.3
	7	−8.46		−13.4
	8	2.02		−3.3
	9	−11.43		−16.0
1,4,8-Triazaindene	2	−20.16	0.980	−24.1
	3	−20.83		−15.3
	5	−16.65		−18.8
	6	4.48		−8.0
	7	−37.05		−28.8
	9	−20.79		−25.5

[a] With respect to the corresponding positions in indenyl anion. [b] Calculated with the assumption $\Delta E = f \times 10$, where f for indenyl anion is 1.000. See ref 14 for details in calculating f.

the five-membered ring and adjacent to a nitrogen atom. These results are in harmony with the polarization effects produced by nitrogen atoms in the simple five-membered heterocycles.[14] Hence the experimental data indicate that a high degree of aromatic character exists in the nitrogen bridgehead compounds with no serious curtailment of π-electron delocalization, and one can expect charge polarization effects similar to those found in the simple heterocyclic species. This latter conclusion is strengthened by an examination of the experimental data for 4-azaindene in Table II, which reveals another interesting aspect of the effects of the bridgehead nitrogen. In the study of six-membered heterocycles,[14] it was noted that the carbon-13 chemical shift fall in the order $\alpha < \gamma < \beta$, where the α, β, and γ positions are taken with respect to the nitrogen atom. The ordering of the chemical shifts in this manner is explained by combined resonance and inductive effects produced by the heteroatom. In the case of 4-azaindene the ordering of the chemical shift values in the six-membered ring follows the order noted previously for simple heteroaromatic compounds.[14] Hence, it would appear that the bridgehead nitrogen produces resonance and inductive effects similar to those in pyridine, etc., but the magnitude of the perturbations is somewhat reduced.

Nitrogen substitution in the five-membered ring somewhat modifies the resonance effects produced by the nitrogen atom at the bridgehead position and produces cross-ring perturbations. As a result of nitrogen substitution at C-1 or C-3, the chemical shift changes are greatest in the six-membered ring, with the largest shift changes appearing at C-7 and C-9 while smaller perturbations are noted for nitrogen substitution at position 2. It is interesting to note that the largest shift changes are produced by nitrogen substitution at those positions where classical charge structures place the negative charge. The CNDO chemical shift calculation are successful in predicting the order of these perturbations at C-7 and C-9 for the three diazaindenes in question.

The effects of nitrogen substitution into the six-membered ring can be observed by comparing the chemical shifts in 1,4,8-triazaindene with those in 1,4-diazaindene. It is noted that relative order of chemical shifts in the six-membered ring in 1,4,8-triazaindene follows that noted previously[14] ($\alpha < \gamma < \beta$), and the magnitude of the perturbation of the chemical shift values is similar to those observed in pyrimidine.[14,16] It is also noted that positions C-2 and C-3 in the triazaindene are shifted downfield ~2 ppm (−2.09 and −2.32 ppm, respectively) from the corresponding positions in 1,4-diazaindene, and these changes are similar to those noted at positions C-5, C-6, and C-8 when nitrogen is introduced into the five-membered ring (at positions 1, 2, or 3) in pyrrocoline. Hence, with the exception of the shifts produced at C-7 in the diazaindenes, the cross-ring substituent effects are of comparable magnitude for substitution in either the five- or six-membered ring.

Theoretical Consideration

Paudler and coworkers[9,10,37] have reported the π charge and frontier electron distributions for a number of azaindenes and their methyl derivatives. These calculations were carried out by means of simple HMO methods and the values obtained were used to predict proton chemical shifts and the positions susceptible to electrophilic attack. Previous work has demonstrated[38] that simple HMO theory preserves some of the gross features of carbon-13 spectra and points out the need to use more sophisticated molecular orbital treatments in order to predict the chemical shift parameter. The CNDO–SCF[19–21] method was used to obtain wave functions from which to calculate the paramagnetic contribution to the shielding[14] of the carbon-13 nucleus. The charge densities and bond orders obtained from the molecular orbital formalism are presented in Figure 1. The net charges and bond orders with respect to indenyl anion are presented in Figure 2 for purposes of comparing the perturbing effects produced by nitrogen substitution at various positions in the indenyl ring system.

The predicted chemical shifts, referenced to benzene, are plotted in Figure 3 against the experimental values. Although the gross features of experimental shifts are reproduced by the theory, it is noted that the major discrepancies occur at the bridgehead positions. This discrepancy has been noted previously in the seeming breakdown of the CNDO–SCF calculations in ade-

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(37) W. W. Paudler and H. L. Blewitt, *Tetrahedron*, **21**, 353 (1965).
(38) See, for instance, ref 14 and 15 and references cited therein.

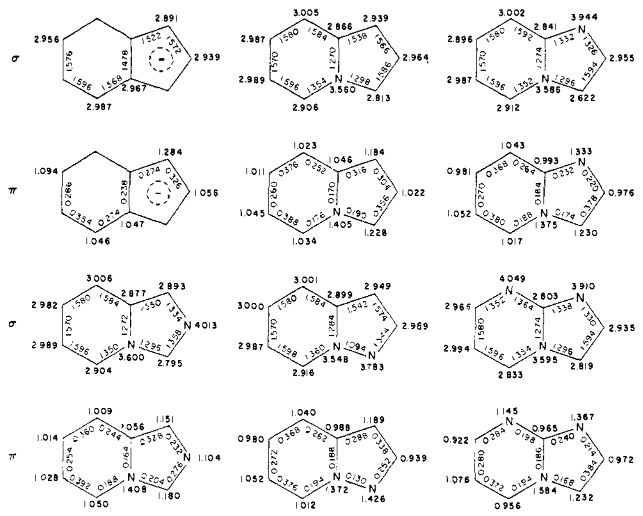

Figure 1. Molecular orbital parameters obtained from the CNDO/2 program includes both α and π charge densities (outside of ring) and bond orders (inside of ring). Idealized geometries were used in all calculations reported in this work.

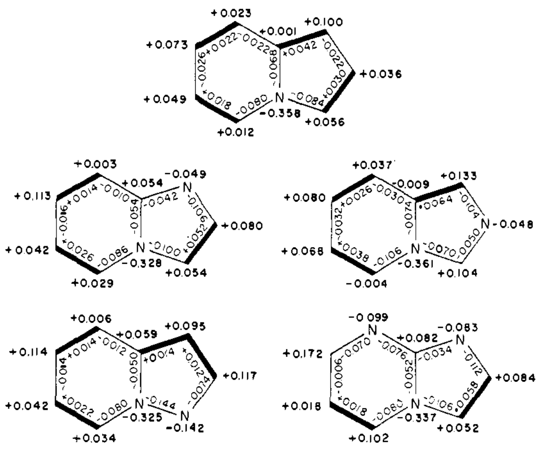

Figure 2. Net π charges and bond orders taken with respect to indenyl anion. A negative bond order change indicates a net decrease from indenyl ion. The conventional formalism is used to indicate net changes. Heavy lines designate those bonds which exhibit an increase in bond order as compared to the π-bond orders in indenyl ion.

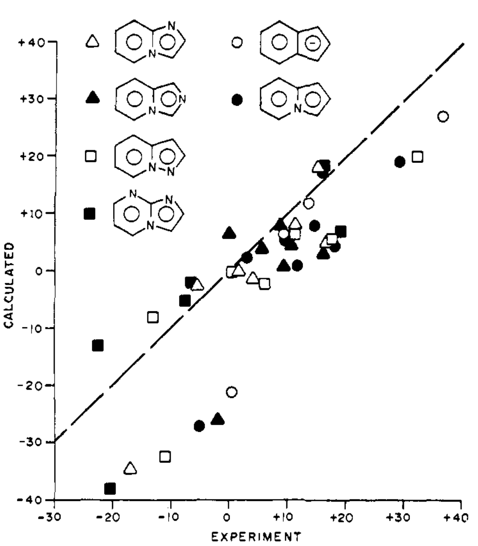

Figure 3. Plot of predicted carbon-13 chemical shift values *vs.* experimental data. All values are referred to benzene, and ΔE is assumed to be 10 eV.

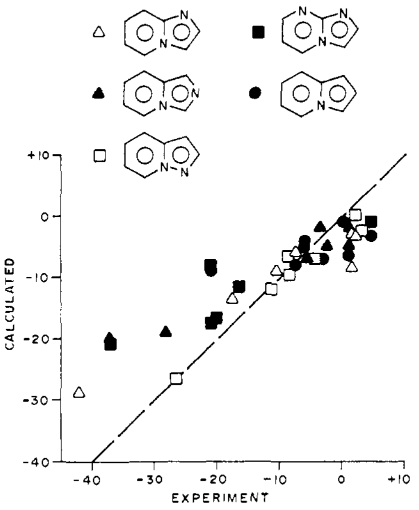

Figure 4. Plot of predicted carbon-13 chemical shift values *vs.* experimental data. All values are referred to the corresponding positions in indenyl anion, and ΔE is assumed to be 10 eV.

quately predicting the electronic structure at bridgehead positions.[15] This discrepancy may be rationalized, in part, by the neglect of overlap in normalizing the wave functions. This difficulty may be partially overcome by referencing the experimental and theoretical chemical shifts of the azaindene carbons to the appropriate positions in indenyl anion. The results presented in Figure 4 indicate that this procedure adequately compensates for the bridgehead problem and a much improved fit results.

Comparison of the average separation between the bonding and antibonding levels in the various molecular species of interest indicates that a range of separation of 0.2–2.0% exists in the ΔE values with respect to indenyl anion. If appropriate corrections are made to the ΔE value for each molecular species[1,14] the theoretical values for the paramagnetic shielding display a slight improvement in correlation, as is evident in Table II and Figure 5. The best line through the data is displaced a bit from the perfect correlation line but, considering the complexity of the species studied and the approximations required in arriving at the theoretical results, the fit of the data indicates the relative success of the CNDO approach in predicting some of the important electronic features in these rather sizable molecules.

If the π-charge density on the nitrogen atom in pyrrocoline is compared with that of the nitrogen in the various neutral and charged five- and six-membered heterocyclic species (Figure 6), it is seen that theory predicts the pyrrocoline lone pair to be delocalized to nearly the same extent as is found for the pyrrole anion. Hence, theoretical results and experimental data support the assumption that the nitrogen lone pair is delocalized to a considerable extent throughout the ring structure.

It is interesting to note that those carbons which readily undergo electrophilic reactions (*e.g.*, C-1 and C-3 in pyrrocoline and C-3 in 1,4-diazaindene) also appear at high-field resonance positions (see Table I). These results would suggest that carbon-13 chemical

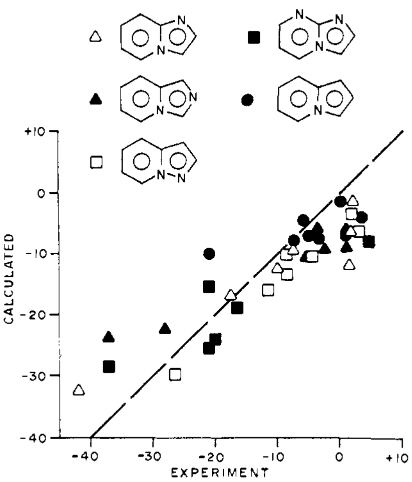

Figure 5. Plot of predicted carbon-13 chemical shift value *vs.* experimental data. All values are referred to the corresponding positions in indenyl anion, and ΔE is taken as $f \times 10$, where the f values are given in Table II.

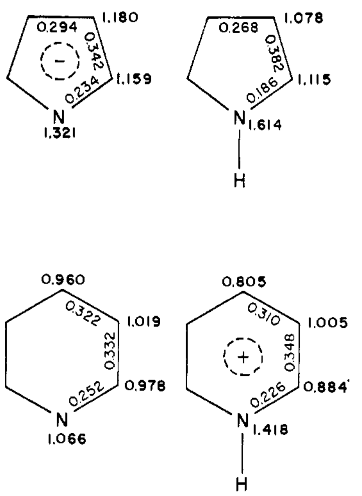

Figure 6. π charges and bond orders for the various types of neutral and charged nitrogen heterocyclic compounds in five- and six-membered compounds.

shift data can provide predictive information concerning relative reactivity at various molecular positions. However, one should use chemical shift data with caution in this respect since, as discussed above, a number of factors contribute to the paramagnetic shielding expression. While charge polarization can frequently be used to explain the gross features of the chemical shift data, other factors (ΔE, bond orders, or electric field effects) may make significant contribution to the magnetic shielding of the nucleus. In general, however, for a given series of similar molecules, charge polarization effects probably dominate the paramagnetic term and, to the extent that other contributions are relatively constant throughout the molecule, the carbon-13 chemical shifts may be helpful for predicting chemical reactions.

In conclusion, the chemical shifts observed in the azaindenes indicate that a bridgehead nitrogen atom behaves in much the same way as a pyrrole-type nitrogen wherein significant delocalization of the lone pair occurs. Those carbon atoms adjacent to the heteroatom experienced the strongest perturbation effects, while resonance and inductive effects similar to those occurring in the simpler heterocyclic systems are also found in the azaindenes. Molecular orbital calculations have been reasonably successful in predicting the electronic structure of the species as measured by the chemical shift values thus obtained. The sensitivity of carbon-13 resonance data to electronic and structural effects in a novel class of compounds has been demonstrated and indicates that this type of information may make useful contributions to the understanding of certain chemical phenomena.

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