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Origin of Linearity of Carbon-13 Shift with Charge. Calculations for the Azines

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Abstract: Carbon-13 chemical shifts in the azines pyridine, pyrazine, pyrimidine, pyridazine, *s*-triazine, and *s*-tetrazine have been calculated at several levels of approximation in the theory of chemical shifts with a variety of π and σ wave functions and the results examined with respect to the proposed linearity of shift with charge. The Ramsey tensor, without approximation, using the methods of Karplus and Kern to evaluate the multicenter integrals, gives only qualitative agreement with the observed shifts. Use of the average energy approximation only accounts for about half of the shift in each case, though they do follow the correct order. It is found that explicitly including the terms involving the lower excitation energies (n $\rightarrow$ π^*) in the expression for $\chi_P{}^A$ and using the average energy approximation for the others give excellent agreement between calculated and observed shifts and different excitation energy, DEE. The CNDO–MO's of Bene and Jaffé were used in this scheme. Both the observed shifts and the $\sigma + \pi$ charges calculated with these CNDO wave functions for the azines are linear functions of the corresponding values for pyridine. The observed shifts are linear with the total charge on carbon, 160 ppm/electron. It is proposed that atomic terms dominate the shifts and charges. Decomposition of the expression for $\Delta\sigma$, with respect to benzene, B, gives $-N^{-1}[\chi_B\Delta\langle r^{-3}\rangle + \langle r^{-3}\rangle_B\Delta\chi + \Delta\chi\Delta\langle r^{-3}\rangle]$. The first term is known to be proportional to charge, 86 ppm/electron; the second is roughly linear, 73 ppm/electron. Together they account for the observed dependence of shift on charge. The first term alone corresponds to the results in the Pople–Karplus approximation. Aromatic systems whose carbon-13 shifts are expected to be proportional to charge should have exchange interactions little different from those in benzene. Altogether in these calculations it is critical that the wave function predicts the correct lower electronic excitation energies and takes account of the polarity of the σ framework.

Carbon-13 chemical shifts have been obtained for a variety of aromatic compounds.[1] One result of these studies is that there is often observed some correlation of these shifts with the π density of the atom under consideration. Spiesecke and Schneider[2] have found that the carbon-13 shifts in cyclic aromatic species, $C_5H_5^-$, benzene, $C_7H_7^+$, $C_8H_8^{2-}$, are linear with the charge[2] (eq 1). A similar result was observed by Lauterbur[3] from data on aromatic hydrocarbons. Karplus and Pople have developed a molecular orbital theory for carbon-13 shifts in conjugated molecules.[4] They have derived a linear correlation of charge with carbon-13 shift by considering atomic orbital dimensions which are expected to expand as electrons are added to the atom. However, the proportionality factor in this relationship is about half of that observed experimentally.

$$\Delta\sigma = -160z_A \tag{1}$$

Lauterbur has studied carbon-13 shifts in nitrogen aromatic heterocycles,[5] to test the theory, since large variations in π densities are expected around such molecules. The π densities did correlate with shifts and it was concluded that σ-bond polarity must be taken into account. Similarly, Emsley has calculated shifts in pyridine[6] using Pople's method with a CNDO[7,8] wave function. Pugmire and Grant[9] recently calculated carbon-13 shifts in azines using extended Hückel MO's[10] with the Karplus and Das formulation.[11] However, their results indicate the shifts depend critically on various parameters needed to obtain the wave functions. Tokuhiro, Wilson, and Fraenkel's recent calculations of carbon shifts in pyridine[12] with combinations of π SCF and σ symmetry MO's revealed that the choice of wave function is critical. However, to account for all the shifts, it was necessary to add the term $-160z_A$ where z_A is the charge on carbon.

In this article we present some calculations of carbon-13 shifts in all the diazines, *s*-triazine, and *s*-tetrazine using three levels of approximation of the theory of chemical shifts starting with Ramsey's equation and proceeding to the average energy approximation. Several different sets of wave functions have been used. By examining the results obtained with different levels of the theory, we wish to identify the more important contributions and examine the origin of the linearity of charge with shift.[2,3]

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It will be seen that there is an optium level of approximation in the theory and that the results depend critically on the wave functions employed.

Methods for Calculating Chemical Shifts

According to Saika and Slichter,[13] the total shielding constant for nucleus A in some molecule whose other atoms are called B is given by eq 2.[3]

$$\sigma^{\mathrm{A}} = \sigma_{\mathrm{d}}^{\mathrm{AA}} + \sigma_{\mathrm{p}}^{\mathrm{AA}} + \sum_{\mathrm{B}\neq\mathrm{A}}\sigma^{\mathrm{AB}} + \sigma^{\mathrm{A,\,ring}} \qquad (2)$$

The first term in (2) is the Lamb term for atom A

$$\sigma_{\mathrm{d}}^{\mathrm{AA}} = (e^2/3mc^2)\sum_k \langle r_{k\mathrm{A}}^{-1}\rangle_{2\mathrm{p},2\mathrm{s}} \qquad (3)$$

where $\langle r_{k\mathrm{A}}^{-1}\rangle$ is the mean inverse distance of electron k from the nucleus of atom A and the summation runs over all the electrons on the atom under consideration. The second term in (2) is the paramagnetic contribution which results from the mixing of ground and excited states by the external field. The remaining contributions come from currents on neighboring atoms and ring currents. Since the paramagnetic atom term dominates carbon-13 chemical shifts, it is our object here to calculate it for several azines by means of the methods outlined below.

Ramsey Tensor

Ramsey's theory of chemical shifts is generally accepted even though it has been too complicated to apply to all but the simplest cases due to the intractable nature of the integrals.[14] The Ramsey paramagnetic tensor is given by

$$\sigma_{\mathrm{p}} = \frac{-e^2}{m^2c^2}\sum_l\sum_m(E_m - E_l)^{-1}\{\langle\psi_l|\sum_j M_j/r_j^3|\psi_m\rangle\langle\psi_m|\sum_j M_j|\psi_l\rangle + CC\} \qquad (4)$$

where the matrix elements M/r^3 and M are two- and three-center integrals of various atomic orbitals and l and m label the occupied and unoccupied MO's, respectively. The chief obstacle to utilizing the Ramsey tensor in its entirety lies in the difficulty of evaluating the integrals. Recently Kern and Karplus have developed the Gaussian transform method[15] to evaluate various types of molecular integrals and it may be applied to determining the integrals involved in nmr shifts. In this method the basic $\langle\, 1\mathrm{s}|1\mathrm{s}\,\rangle$ matrix elements of operators are written down in explicit form and the other elements of higher atomic orbitals obtained by differentiation.[16] Using extended Hückel wave functions[10] this method has been applied to calculate the carbon-13 shifts of pyridine, relative to benzene.

LCGI–MO Approximation

Pople has derived a simplified expression for the Ramsey paramagnetic shielding tensor based on a series of approximations commonly used in LCAO–MO theory.[17] This method, called the linear combination of gauge invariant atomic orbitals–molecular orbital (LCGI–MO) approximation, mainly involves the neglect of multicenter integrals and overlap. In the LCGI–MO approximation,[12,17] the local paramagnetic shielding tensor of atom A, $\sigma_{\mathrm{p}}^{\mathrm{AA}}$, is written as

$$\sigma_{\mathrm{p}}^{\mathrm{AA}} = -2N^{-1}\chi_{\mathrm{p}}^{\mathrm{A}}\langle r^{-3}\rangle_{2\mathrm{p}} \qquad (5)$$

where

$$\begin{aligned}(\chi_{\mathrm{p}}^{\mathrm{A}})_{xx} &= (Ne^2h^2/m^2c^2)\sum_i^{\mathrm{occ}}\sum_k^{\mathrm{unocc}}(E_k - E_i)^{-1}x \\ &\quad (c_{iy\mathrm{A}}c_{kz\mathrm{A}} - c_{iz\mathrm{A}}c_{ky\mathrm{A}})\sum_{\mathrm{B}}(c_{iy\mathrm{B}}c_{kz\mathrm{B}} - c_{iz\mathrm{B}}c_{ky\mathrm{B}}) \\ (\chi_{\mathrm{p}}^{\mathrm{A}})_{yy} &= Ne^2h^2/m^2c^2\sum_i^{\mathrm{occ}}\sum_k^{\mathrm{unocc}}(E_k - E_i)^{-1}x \\ &\quad (C_{iz\mathrm{A}}C_{kx\mathrm{A}} - C_{ix\mathrm{A}}C_{kz\mathrm{A}})\sum_{\mathrm{B}}(C_{iz\mathrm{B}}C_{kx\mathrm{B}} - C_{ix\mathrm{B}}C_{kz\mathrm{B}}) \\ (\chi_{\mathrm{p}}^{\mathrm{A}})_{zz} &= Ne^2h^2/m^2c^2\sum_i^{\mathrm{occ}}\sum_k^{\mathrm{unocc}}(E_k - E_i)^{-1}x \\ &\quad (C_{ix\mathrm{A}}C_{ky\mathrm{A}} - C_{iy\mathrm{A}}C_{kx\mathrm{A}})\sum_{\mathrm{B}}(C_{ix\mathrm{B}}C_{ky\mathrm{B}} - C_{iy\mathrm{B}}C_{kx\mathrm{B}})\end{aligned} \qquad (6)$$

Here, $C_{ix\mathrm{A}}$ is the coefficient of the $2\mathrm{p}_x$ atomic orbital on atom A of the *i*th molecular orbital in the LCAO–MO approximation, Σ_{B} runs over all atoms in the molecule (including A), and N is the Avogadro number. With a reasonable extension of Slater's rules to atoms with fractional electron populations, $\langle r^{-3}\rangle_{2\mathrm{p}}$ in eq 5 for a Slater 2p orbital of atom A (a first row element) is given by[4,12]

$$\langle r^{-3}\rangle_{2\mathrm{p}} = (1/24)(Z/_{\mathrm{A}}a_0)^3 \qquad (7)$$

with

$$Z_{\mathrm{A}} = Z_{\mathrm{A}}' - 0.35(q_{\mathrm{A}} - 1) \qquad (8)$$

where a_0 is the Bohr radius, Z_{A}' is the effective nuclear charge for a neutral atom, A, and q_{A} is the electron density ($\sigma + \pi$) on atom A.

Average Energy Approximation

A simplified expression for $\sigma_{\mathrm{p}}^{\mathrm{AA}}$ is obtained if all the inverse excitation energy factors $(E_k - E_i)^{-1}$ are replaced by a mean value $\langle\Delta E\rangle$ and, at the same time, use of the following relation is made

$$\sum_i^{\mathrm{occ}}C_{i\mu}C_{i\nu} + \sum_k^{\mathrm{unocc}}C_{k\mu}C_{k\nu} = \delta_{\mu\nu} \qquad (9)$$

where $\delta_{\mu\nu}$ is the Kronecker δ. Equation 9 is only valid if overlap integrals are neglected. The final expression for $\chi_{\mathrm{p}}^{\mathrm{AA}}$ is as follows[12,17]

$$\chi_{\mathrm{p}}^{\mathrm{AA}} = (Ne^2h^2/m^2c^2\langle\Delta E\rangle)(Q_{\mathrm{AA}} + \sum_{\mathrm{A}\neq\mathrm{B}}Q_{\mathrm{AB}}) \qquad (10)$$

with

$$Q_{\mathrm{AA}} = (3)^{-1}(2\sum_{lj}^{xyz}P_{l\mathrm{A}l\mathrm{A}}P_{j\mathrm{A}j\mathrm{A}} + \sum_l^{xyz}P^2{}_{l\mathrm{A}l\mathrm{A}}) \qquad (11)$$

$$\begin{aligned}Q_{\mathrm{AB}} = -(3)^{-1}(&P_{y\mathrm{A}y\mathrm{B}}P_{z\mathrm{A}z\mathrm{B}} + P_{z\mathrm{A}z\mathrm{B}}P_{x\mathrm{A}x\mathrm{B}} + P_{x\mathrm{A}x\mathrm{B}}P_{y\mathrm{A}y\mathrm{B}}) + (3)^{-1}(P_{y\mathrm{A}z\mathrm{B}}P_{z\mathrm{A}y\mathrm{B}} + \\ &P_{z\mathrm{A}x\mathrm{B}}P_{x\mathrm{A}z\mathrm{B}} + P_{x\mathrm{A}y\mathrm{B}}P_{y\mathrm{A}x\mathrm{B}})\end{aligned} \qquad (12)$$

and

$$P_{\mu\nu} = 2\sum_i^{\mathrm{occ}}C_{i\mu}C_{i\nu} \qquad (13)$$

Hereafter, this approximation is called the Average Excitation Energy (AEE) approximation.

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Proton Shielding Constant

As shown in ref 12, the proton shielding constant is given by

$$\sigma^{H} = \sigma_{d}^{H} + \sigma_{p}^{H} \qquad (14)$$

Here, the local diamagnetic term σ_d^H is estimated from an empirical correlation between the proton chemical shift, with respect to benzene, σ_q, and the local charge, z, on the corresponding carbon atom A[18]

$$\sigma_{q} = -kz \qquad (15)$$

where k is found to be 10.7 ± 0.2 ppm/electron. σ_p^H is approximately given by[12]

$$\sigma_{p}^{H} = \sum_{B}(1/3R_{BH}^{3})\sum_{l}(\chi_{p}^{B})_{ll}(1 - 3\cos^{2}\gamma_{BHl}) \qquad (16)$$

where R_{BH} is the distance and γ_{BHl} is the angle between R_{BH} and the ll component of the principal axis of nuclear paramagnetic susceptibility (χ_p^B).

Results and Discussion

We now examine shifts calculated for the azines by means of the methods outlined in the previous section.

Ramsey Shielding Tensor

The Gaussian transform method was used to evaluate the integrals in the expression for the Ramsey shielding tensor. Table I lists the results for pyridine. Although the results are not very satisfactory, certain conclusions can be derived from the analysis of the calculated results on the basis of both atomic and molecular orbitals. (1) In the paramagnetic term, the relative contribution from respective terms depends on the value of their excitation energies in a very delicate fashion. (2) On the molecular orbital bases, there are 210 terms in each component of the paramagnetic contribution and most of them are negligibly small. Only a few terms contribute predominantly to the shielding when the component is associated with $\sigma \leftrightarrow \pi$ type transitions. On the other hand, there are no dominant terms when the component is associated with $\sigma \rightarrow \sigma^*$ type transitions. (3) A predominant term on the molecular orbital basis can be decomposed to many terms on the atomic orbital basis. We find that localized terms contribute predominantly to the shielding constant.

Table I. Carbon-13 Chemical Shifts[a] in Pyridine Obtained with Gaussian Transform Method

	α	β	γ
$\Delta\sigma_p$	−24.40	+6.98	−22.26
$\Delta\sigma_d$	+0.16	+0.09	−1.05
$\Delta\sigma_{total}$	−22.24	+7.07	−23.31

[a] Parts per million (ppm) with respect to benzene.

The Gaussian transform approach was not continued due to the difficulties associated with obtaining reliable wave functions which include overlap.

Average Excitation Energy Approximation

By use of eq 5, 7, 8, and 10–13 in conjunction with the different sets of wave functions listed below we have calculated the carbon-13 paramagnetic shifts in pyridine, the diazines, *s*-triazine, and *s*-tetrazine. The average excitation energy was taken to be 10 eV.[4] For most of these cases π and σ wave functions were obtained separately. In these cases homopolar σ orbitals came from the standard hybridizations of the various bonds; polar σ MO's were *symmetry* molecular orbitals[12] composed of individual bond orbitals whose polarity parameters came from a Del Ré treatment.[12,19]

The diamagnetic shifts were calculated with eq 3. The different cases treated are as follows: case 1, homopolar σ bonds and Mataga SCF π-electron wave functions;[20,21] case 2, Del Ré polar σ bonds [12,19] and Mataga SCF wave functions;[20,21] case 3, homopolar σ bonds and Masuhara SCF π-electron wave functions;[22] case 4, Del Ré polar σ bonds[12,18] and Masuhara wave functions;[22] case 5, homopolar σ bonds and Kon SCF π-electron wave functions;[23] case 6, Del Ré σ bonds[12,19] and Kon wave functions;[23] case 7, homopolar σ bonds and LCAO–MO ω treatment;[24] case 8, Del Ré polar σ bonds[12,19] and LCAO–MO ω treatment;[24] case 9, Pople's CNDO wave function,[7,8] $\sigma + \pi$. The calculated results for the carbon-13 chemical shift and the paramagnetic and diamagnetic contributions with respect to benzene are summarized in Table II.

As seen in Table II, the calculated carbon-13 shifts are encouraging in that they follow the correct order from one molecule to another or one position to the other in the same molecule. However, the absolute calculated values are always smaller than the observed ones. This general trend was also found in the previous calculation for pyridine.[12] Since the σ_d^{AA} contribution is much smaller then σ_p^{AA}, we shall confine our attention to only the latter in the following discussion. As the σ_p^{AA} contribution is given by the product of χ_p^A and $\langle r^{-3}\rangle_{2p}$, eq 5, we consider the changes in χ_p^A and $\langle r^{-3}\rangle_{2p}$ separately. χ_p^A consists of two terms, *i.e.*, eq 11 and 12. The former, Q_{AA}, in azine compounds does not differ very much from that in benzene and the deviation is due to the excess charge on atom A. Hence, the multiple bond effect, Q_{AB}, is primarily responsible for the change in χ_p^A in azines.

Comparing the values of χ_p^A's and $\langle r^{-3}\rangle_{2p}$ for all the compounds studied here with those in benzene, each shift with respect to benzene can be explained as follows: for carbon directly bonded to one nitrogen, the large downfield shifts arise from the contraction of 2p orbitals, namely, the increase of $\langle r^{-3}\rangle_{2p}$. This shrinkage is, of course, due to the effect of an electronegative nitrogen atom through changes in the π and σ electron charge densities and overcomes the decreased contribution from the multiple bond effect to χ_p^A in cases 1–8. Although the calculated values of σ_p^A in case 9 are not very different from other cases, it should be noted that the values of χ_p^A are larger than for the other cases. For the carbon bonded to two nitrogens in pyrimidine, *s*-triazine, and *s*-tetrazine, the very large downfield shifts can be explained in the same way as just described above. The slight upfield shift in the β position is at-

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Table II. Carbon-13 Shifts[a] in Azines Calculated with Average Energy Approximation

Molecule and position	Case	π charge	σ charge	Total charge	χ_p^A	$\langle r^{-3}\rangle_{2p}$	σ_p^{AA}	σ_d^{AA}	σ_{calcd}	σ_{obsd}
Pyrazine 2,3,5,6	1	0.0769		0.0769	8.353	9.874	−5.84	−0.32	−6.16	−17.4[5]
	2	0.0769	0.0168	0.0937	8.349	10.000	−8.63	−0.46	−9.09	−17.14[9]
	3	0.0838		0.0838	8.344	9.916	−6.14	−0.35	−6.49	−16.77[b]
	4	0.0838	0.0168	0.1006	8.340	10.022	−8.91	−0.49	−9.40	
	5	0.1192		0.1192	8.335	10.029	−8.96	−0.50	−9.46	
	6	0.1192	0.0168	0.1360	8.329	10.136	−11.70	−0.64	−12.34	
	7	0.0727		0.0727	8.364	9.881	−5.82	−0.30	−6.12	
	8	0.0727	0.0168	0.0895	8.360	9.987	−8.62	−0.44	−9.06	
	9	0.0114	0.0464	0.0578	8.252	9.832	−7.78	−0.21	−7.99	
Pyridazine 3,6	3	0.0864		0.0864	8.365	9.922	−7.01	−0.36	−7.37	−23.9[5]
	4	0.0864	0.0322	0.1186	8.361	10.026	−9.72	−0.50	−10.22	−24.31[9]
	7	0.0751		0.0751	8.373	9.887	−6.26	−0.31	−6.57	−24.07[b]
	8	0.0751	0.0322	0.1073	8.369	9.990	−8.99	−0.45	−9.44	
	9	0.0193	0.0420	0.0613	8.280	9.844	−9.01	−0.23	−9.24	
4,5	3	0.0204		0.0204	8.378	9.714	−1.64	−0.08	−1.72	+1.0[5]
	4	0.0204	−0.0230	−0.0026	8.379	9.643	0.32	0.01	0.33	+0.85[9]
	7	0.0546		0.0546	8.373	9.821	−4.43	−0.22	−4.65	+1.29[b]
	8	0.0546	−0.0230	0.0316	8.375	9.750	−2.50	−0.13	−2.63	
	9	0.0249	−0.0084	0.0165	8.149	9.703	−0.92	−0.04	−0.96	
2	3	0.2248		0.2248	8.321	10.369	−17.87	−0.96	−18.83	−30.5[5]
	4	0.2248	0.0840	0.3088	8.291	10.646	−24.47	−1.34	−25.81	−30.99[9]
	7	0.1148		0.1148	8.367	10.014	−9.59	−0.48	−10.07	−31.44[b]
	8	0.1148	0.0840	0.1988	8.350	10.284	−16.53	−0.85	−17.38	
	9	0.0672	0.0888	0.1560	8.344	10.146	−19.50	−0.63	−20.13	
Pyrimidine 4,6	3	0.1644		0.1644	8.357	10.172	−13.67	−0.69	−14.36	−28.9[5]
	4	0.1644	0.0274	0.2418	8.350	10.262	−15.92	−0.82	−16.74	−28.96[9]
	7	0.0951		0.0951	8.363	9.950	−7.70	−0.39	−8.09	−28.91[b]
	8	0.0951	0.0274	0.1225	8.359	10.039	−10.02	−0.51	−10.53	
	9	0.0739	0.0406	0.1145	8.262	10.013	−13.08	−0.45	−13.53	
5	3	−0.0744		−0.0744	8.367	9.421	6.87	0.30	7.17	6.1[5]
	4	−0.0744	−0.0180	−0.0924	8.365	9.366	8.44	0.37	8.81	6.42[9]
	7	0.0304		0.0304	8.382	9.746	−2.65	−0.13	−2.78	
	8	0.0304	−0.0180	0.0124	8.383	9.690	−1.11	−0.05	−1.16	
	9	−0.0330	−0.0092	−0.0422	8.137	9.520	4.40	0.20	4.60	
s-Triazine 2,4,6	1	0.2088		0.2088	8.344	10.316	−17.20	−0.89	−18.09	−39.0[5]
	2	0.2088	0.0862	0.2950	8.316	10.597	−23.98	−1.27	−25.25	
	3	0.2740		0.2740	8.316	10.530	−21.74	−1.18	−22.92	
	4	0.2740	0.0862	0.3602	8.279	10.815	−28.70	−1.57	−30.27	
	5	0.3796		0.3796	8.252	10.883	−29.57	−1.67	−31.24	
	6	0.3796	0.0862	0.4658	8.202	11.174	−35.72	−2.07	−37.79	
	7	0.1528		0.1528	8.362	10.135	−12.78	−0.64	−13.42	
	8	0.1528	0.0862	0.2390	8.340	10.413	−19.74	−1.02	−20.76	
	9	0.1058	0.0772	0.1830	8.342	10.233	−21.83	−0.74	−22.57	
s-Tetrazine	1	0.1554		0.1554	8.371	10.145	−13.38	−0.66	−14.04	−33.4[5]
	2	0.1554	0.0960	0.2514	8.346	10.456	−21.16	−1.08	−22.24	
	3	0.1620		0.1620	8.350	10.166	−13.26	−0.69	−13.95	
	4	0.1620	0.0960	0.2580	8.324	10.478	−21.00	−1.11	−22.11	
	7	0.1454		0.1454	8.364	10.113	−12.26	−0.61	−12.87	
	8	0.1454	0.0960	0.2414	8.341	10.424	−20.07	−1.04	−21.11	
	9	0.0362	0.0734	0.1096	8.389	9.996	−16.83	−0.43	−17.26	

[a] With respect to benzene. [b] A. Mathias and V. M. S. Gil, *Tetrahedron Letters*, 3163 (1965).

tributable to the decrease of $\langle r^{-3}\rangle_{2p}$ because the value of χ_p^A is almost the same as that in benzene. In summary, the charge effect through the term $\langle r^{-3}\rangle_{2p}$ is a more important factor than the change in χ_p^A in this approximation. Changing the average energy in these calculations does not improve the fit since the calculated shifts are not proportional to the observed ones.

Different Excitation Energy Approximation

As seen from eq 6 nonvanishing elements are only associated with transitions such as $\pi \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, and $\pi \rightarrow \pi^*$. The $\pi \rightarrow \pi^*$ excitations do not contribute to χ_p^A even though they are among the lowest for conjugated hydrocarbons. However, it is evident that the lower energy transitions, *e.g.*, n $\rightarrow \pi^*$, contribute more importantly than others and the error in using the AEE approximation arises from this effect.

To use eq 5 and 6 it is necessary to have wave functions which accurately predict all the required excitation energies. The Pariser–Parr–Pople SCF wave functions[25,26] (which predict $\pi \rightarrow \pi^*$ excitation energies nicely) and Del Ré σ orbitals, used in the previous section, cannot be applied to this problem.

One compromise between employing eq 5 in its entirety and the average energy approximation is to sum the matrix elements between occupied and unoccupied MO's divided by the corresponding ΔE_{ik} for the lower excitation energies and use the average energy, 10 eV, for the others. We call this the different excitation energy, DEE, approximation. Such a method still requires a wave function which accurately predicts the lower transition energies within a consistent theoretical framework.

(25) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).
(26) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1963).

Table III. Calculations of Carbon-13 and Nitrogen-14 Shifts in Azines, Jaffé and Bene CNDO–MO's, Case 10 AEE, Case 11 DEE Approximation

Molecule position	Case	π charge	σ charge	Total charge	χ_p^A	$\langle r^{-3}\rangle_{2p}$	σ_p	σ_d	σ_{calcd}	σ_{obsd}
Pyridine										
2,6	10	+0.0878	+0.0216	+0.1094	8.2770	9.9965	−12.50	−0.52	−13.02	−21.9^{5}
	11				8.5121		−19.79		−20.31	−21.72^{9}
3,5	10	−0.0440	−0.0044	−0.0484	8.2141	9.5014	+3.09	+0.13	+3.22	+4.2^{5}
	11				8.2676		+1.91		+2.04	+4.59^{9}
4	10	+0.0680	−0.0430	+0.0250	8.2485	9.7295	−4.24	−0.17	−4.41	−7.7^{5}
	11				8.3292		−6.34		−6.51	−7.42^{9}
Pyrazine							−9.20			
1,4	10	−0.0902	−0.1034	−0.1936	8.2184	11.8700		−0.18	−9.38	−16 ± 2^{a}
	11				9.2353		−15.20		−15.39	−16.77^{b}
										−17.4^{5}
2,3,5,6	10	+0.0451	+0.0307	+0.0758	8.2656	9.8901	−8.73	−0.38	−9.11	−17.14^{9}
	11				8.4807		−15.92		−16.30	−69 ± 2^{a}
Pyridazine										
1,2	10	−0.0867	−0.0417	−0.1284	8.4109	12.1066	−22.92	−0.42	−23.34	−24.07^{a}
	11				9.6268		−38.19		−38.61	−23.9^{5}
										−24.31^{9}
3,6	10	+0.0593	+0.0203	+0.0796	8.3194	9.9020	−11.29	−0.40	−11.69	+1.29^{9}
	11				8.6188		−20.63		−21.03	+1.0^{5}
4,5	10	+0.0274	−0.0274	0.0000	8.2205	9.6509	−1.19	−0.07	−1.26	+0.85^{9}
	11				8.2074		−0.27		−0.34	+21 ± 2^{a}
Pyrimidine										
1,3	10	−0.2103	−0.0784	−0.2887	7.9549	11.5348	+10.50	+0.17	+10.67	−30.5^{5}
	11				8.7295		+14.44		+14.61	−30.99^{9}
2	10	+0.1634	+0.0824	+0.2458	8.3176	10.4374	−26.02	−1.12	−27.14	−31.44^{a}
	11				8.6656		−37.57		−38.69	−28.9^{5}
								−0.78	−16.63	−28.91^{a}
4,6	10	+0.1456	+0.0217	+0.1673	8.2245	10.1830	−15.85		−28.46	−28.96^{9}
	11				8.5895		−27.68	+0.10	+5.59	+6.1^{5}
5	10	−0.0338	−0.0064	−0.0402	8.1168	9.5263	+5.49		−0.79	+6.42^{9}
	11				8.3343		−0.89			

[a] D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **8**, 19 (1964). [b] A. Mathias and V. M. S. Gil, *Tetrahedron Letters*, 3163 (1965).

The CNDO method[7,8] used in case 9 is one of such type of calculation. Bene and Jaffé[27] have recently applied the CNDO method (hereafter referred to as BJ-CNDO) to the prediction of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in azines and obtained most satisfactory results by modifying certain parameters. These wave functions fit into the theoretical framework employed in the derivation of eq 10–13. Thus in the case of benzene when the $E_k - E_i$ values in (6) are replaced by 10 eV and coefficients from *occupied* and *unoccupied* MO's are used the carbon-13 shift is identical with that obtained with the AEE approximation, eq 5, 7, 8, and 10–13 using only ground-state wave functions.

The chemical shifts of benzene obtained with both the DEE and AEE approximations in conjunction with BJ-CNDO wave functions are identical.[28] However, when these two treatments are applied to the azines, the results obtained in the DEE approximation are consistently far better than with AEE.

Table III summarizes the calculated results for the ^{13}C and ^{14}N shielding constants and the paramagnetic and diamagnetic contributions in pyridine and diazines. Cases 10 and 11 are the results obtained in the AEE and DEE approximations, respectively. The ^{13}C shifts are expressed in parts per million (ppm) with respect to that in benzene, and ^{14}N shifts are those relative to pyridine. Even the AEE approximation here gives better results than those obtained with the other sets of wave functions used in the previous section. However, the absolute magnitudes of these shifts are always smaller than the observed ones.

In the DEE approximation the calculated ^{13}C and ^{14}N shielding constants are remarkably close to the observed shifts: the ^{13}C values almost reproduce those observed.

It is now worthwhile to consider how and why the results obtained with these two approximations differ. We consider first carbon α to nitrogen in pyridine. Comparing cases 10 (AEE) and 11 (DEE) since the $\langle r^{-3}\rangle_{2p}$ terms are obtained in the same way, the shift differences for each atom must be attributed to changes in the χ_p^A's. In the AEE approximation the large downfield shift of the α-carbon in pyridine is mostly due to the contraction of the 2p orbitals. However, in the DEE approximation, these shifts arise from increases in both χ_p^A and $\langle r^{-3}\rangle_{2p}$. This increase in χ_p^A must be due to the importance of terms with *small excitation energies*. The lowest of these is the $n \rightarrow \pi^*$ transition, which, since it involves $2p_y2p_z$, mixing, contributes importantly to χ_p^A. All this, of course, results from the delocalized character of CNDO wave functions. Similar arguments apply to α-carbon shifts in other azines. The χ_p^A at the β position to nitrogen in pyridine has almost the same value as that in benzene. With the decrease of $\langle r^{-3}\rangle_{2p}$, a small upfield shift is observed. Small increases in both χ_p^A and $\langle r^{-3}\rangle_{2p}$ at the γ position in pyridine lead to a fairly large downfield shift. This increase in χ_p^A at the γ position can be explained in similar fashion to that at the α-carbon. Analogous arguments apply to the other azines.

With regard to the ^{14}N shifts,[21] the calculated shifts in the DEE approximation follow the correct order. However, the fit is worse than among the ^{13}C shifts. One reason for this is that the ^{14}N shielding constants

(27) J. D. Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968).
(28) T. Tokuhiro and G. Fraenkel, *ibid.*, in press.

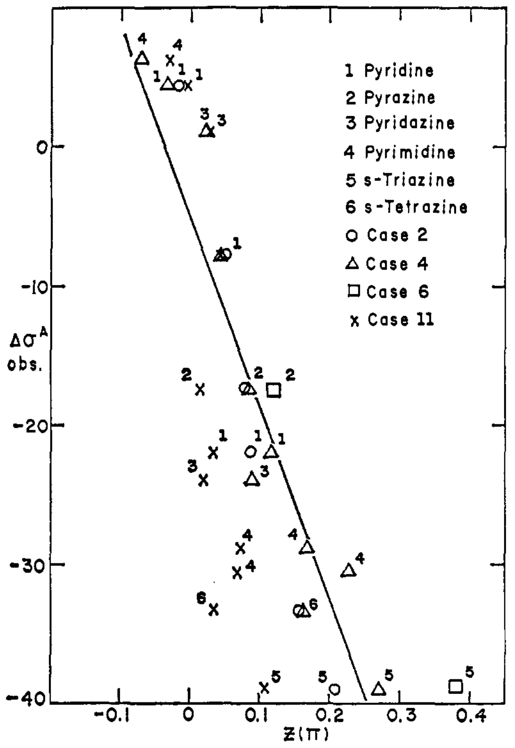

Figure 1. Observed carbon-13 shifts in azines plotted against π charge; wave functions used are cases 1, 3, 5, and 9.

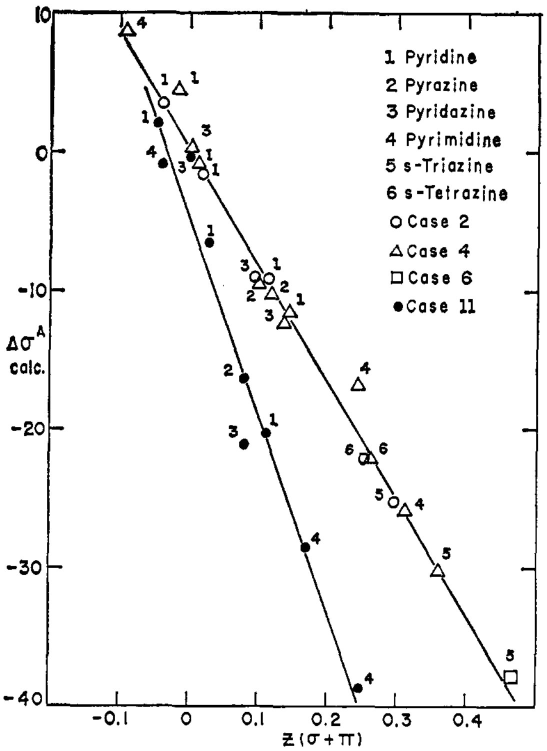

Figure 3. Calculated shifts in azines plotted against π + σ charge: open symbols, cases, 2, 4, and 6; filled circles, BJ-CNDO.

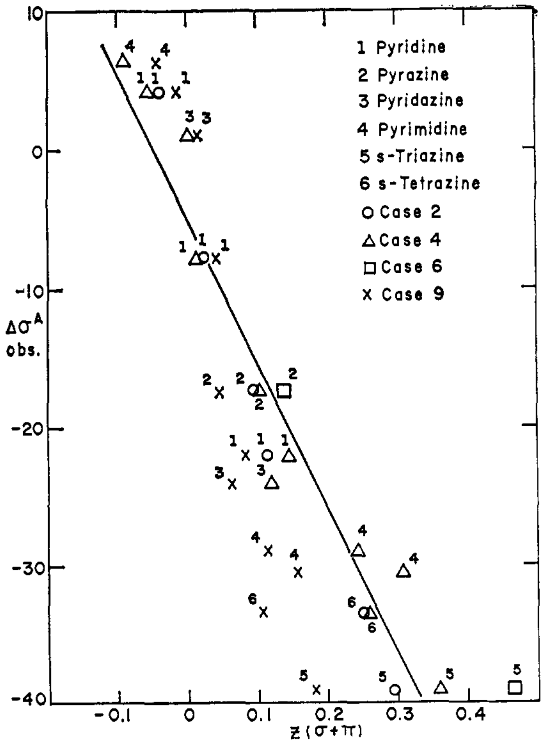

Figure 2. Observed shifts in azines plotted against π + σ charge, cases 2, 4, 6, and 9.

in these molecules are very sensitive to the values for n → π* transition energies than are ^{13}C shifts. For example, in pyridine, the large value of $\chi_p{}^A$ for ^{14}N in the DEE approximation (compared with that in the AEE approximation) arises mainly from the increase in the *xx* component. The terms associated with the low-lying n → π* transitions account for more than 80% of this term.

While the ^{14}N shifts in pyrazine and pyridazine are downfield, with respect to pyridine, that for pyrimidine is upfield. There is a larger π-electron density on nitrogen in pyrimidine compared to pyridine. Consequently, the decreased multiple bond contribution to $\chi_p{}^A$ together with the π-density parts of $\chi_p{}^A$ and $\langle r^{-3}\rangle_{2p}$ account for the pyrimidine shift. Note that π-electron terms are responsible for this effect.

In summary, we show here that the DEE approximation in conjunction with the BJ-CNDO[28] wave functions accounts nicely for the carbon-13 shifts in azines and qualitatively for the nitrogen-14 shifts. In this calculation, it is critical to have a wave function which accurately predicts the lower excitation energies and expresses the polar character of the σ bonds.

Linearity of Carbon-13 Shift with Charge

Spiesecke and Schneider[2] have observed that the carbon-13 shifts in monocyclic species, where the charges are known by symmetry, are proportional to the charge on carbon.

$$\Delta\sigma_A = -160 z_A \qquad (1)$$

Here $\Delta\sigma_A$ is the shift relative to benzene and z_A is the charge in carbon.

The Karplus–Pople treatment of carbon-13 shifts in aromatic compounds[4] accounts for about half of the observed shifts, the proportionality constant being 86 ppm/electron.

We now discuss the relationship of carbon-13 shift with charge among the various calculations reported here to see whether or not it is linear, and if so, why? In the calculations employing the average energy approximation various combinations of π- and σ-electron

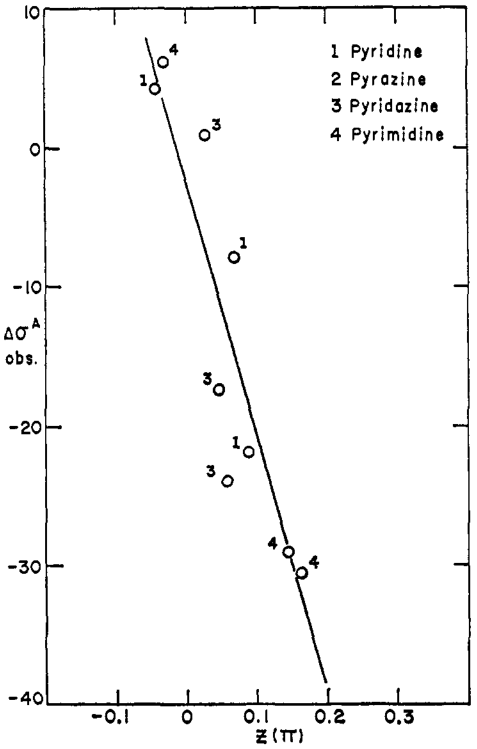

Figure 4. Observed shifts in azines plotted against π charge, BJ-CNDO.

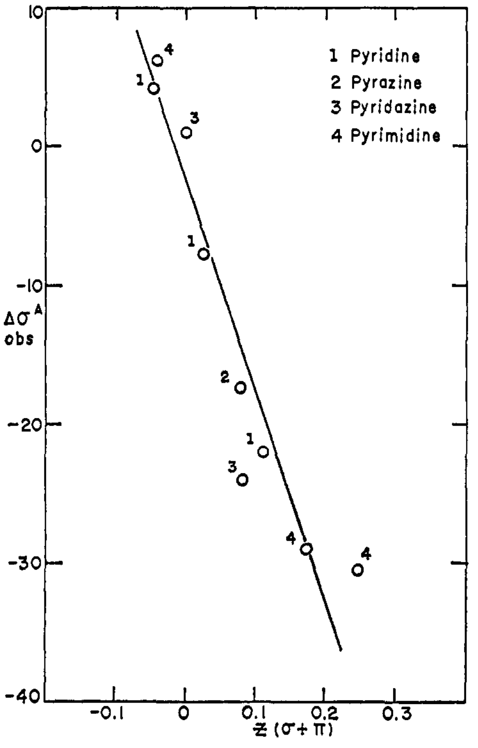

Figure 5. Observed shifts in azines plotted against π + π charge, BJ-CNDO.

wave functions were used. Plots of the *observed* shifts in the azines *vs.* charge for all cases calculated are shown in Figures 1 and 2. It is seen that while both treatments correlate badly that for shift *vs.* π + σ charge is better than the one with π charge alone. On the other hand, the calculated shifts in the AEE approximation (which does not account for the whole observed shift) for all cases are nicely linear with the π + σ charges, the slope being 85 ppm/electron (Figure 3). This result is expected since in the AEE approximation we found the $\langle r^{-3}\rangle_{2p}$ values, which are proportional to the charge, vary much more than the χ_p^A's.

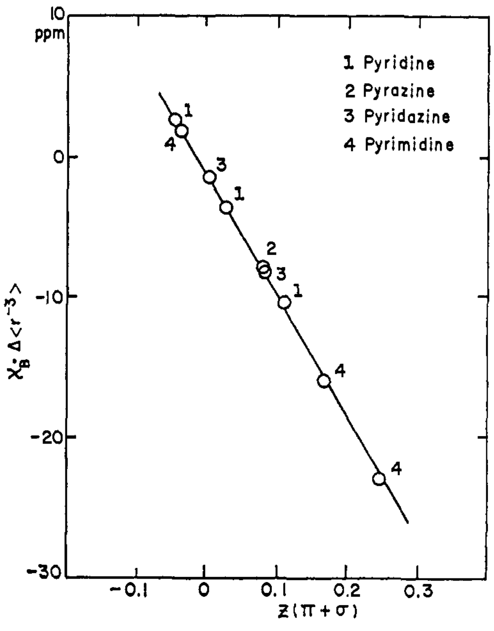

Figure 6. Plot of first term in eq 17 *vs.* total charge.

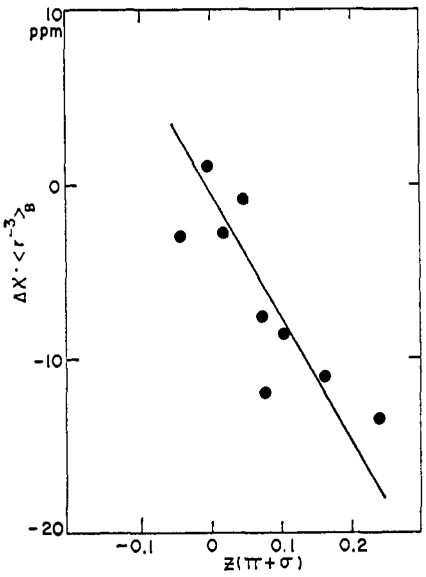

Figure 7. Plot of second term in eq 17 *vs.* charge.

The observed shifts are roughly linear with the π charges obtained from the BJ-CNDO wave functions (Figure 4) and the linearity improves considerably when $\Delta\sigma_{obsd}$ is plotted against the π + σ charge (Figure 5), the slope being 155 ppm/electron. Similarly the shifts calculated in the DEE approximation which almost reproduce the observed ones, are linear with the σ + π charge (Figure 3), though not as closely as in the AEE case.

In order to investigate the reasons for the linearity of shift with charge, it is helpful to decompose the expression for the shifts relative to benzene, $\Delta\sigma_A$, and discuss each term separately. The absolute paramagnetic shift is $-N^{-1}\chi_A\langle r^{-3}\rangle_A$. Since the shift differences among the azines are small compared to the absolute shifts, we can differentiate σ_p to give

$$\Delta\sigma_A = -N^{-1}[\chi_B\Delta\langle r^{-3}\rangle + \Delta\chi\langle r^{-3}\rangle_B + \Delta\chi\Delta\langle r^{-3}\rangle] \quad (17)$$

Here the Δ values are relative to benzene and the terms with B subscripts apply to benzene. We neglect the last term in (17) and consider the others. In the first term the variable $\Delta\langle r^{-3}\rangle$ is already known to be proportional to the charge, relative to benzene. A plot of this term *vs.* the $\pi + \sigma$ charge (Figure 6) has a slope of 86 ppm/electron. This value is almost the same as that derived by Karplus and Pople, 86.7 ppm/electron, in their treatment of carbon-13 shifts and that obtained using the AEE approximation in this paper, 85 ppm/electron.

It would not be expected that the second term in (17) is proportional to charge but in fact a plot of $\Delta\chi$ *vs.* $\pi + \sigma$ charge is roughly linear with a slope of 73 ppm/electron (Figure 7).

Thus the observed numerical factor of 160 ppm/electron consists of two contributions, the first and second terms in eq 17 both being linear functions of the charge. It is seen that the average energy approximation cannot account for the entire shift and it is critical to include the terms in $\chi_p{}^A$ which involve the smaller excitation energies.

Table IV. Carbon-13 Shifts in Azines Estimated from Combinations of Pyridine Shifts

Molecule	Position	Pyridine contribution	Estd σ	Obsd σ[a]
Pyrazine	2,3,5,6	$\alpha + \beta$	−17.5	−17.1
Pyridazine	3,6	$\alpha + \beta$	−17.5	−23.9
	4,5	$\beta + \gamma$	−3.5	+1.0
Pyrimidine	2	2α	−43.8	−30.5
	4,6	$\alpha + \gamma$	−29.6	−28.9
	5	2β	+8.8	+6.1
s-Triazine	2,4,6	2α	−43.8	−39.0
s-Tetrazine	3,6	$2\alpha + 2\beta$	−35.0	−33.4

[a] As indicated in Table II.

It is not clear at this point why the second part of eq 17 should be even roughly linear with charge; however, several features of the results discussed here point to the importance of atomic terms in the evaluation of shifts. A simple additivity rule exists which applies to the shielding constants in azines. Consider the observed shifts in pyridine to arise from characteristic contributions of nitrogen to the shifts at different positions in the molecule. Inspection of the observed shifts shows that these contributions are additive among the azines. For instance, in pyrazine, the shift −17/ppm should be −21.4 (carbon α to nitrogen) + 4.4 (carbon β to nitrogen) giving −17.5. The other azines also fit this linear additivity rule; see Table IV.

Among the azines, a similar additivity rule to that described for the carbon-13 shifts applies to the *total charges;* see Table III. A result like this would apply in cases where atom–atom polarizabilities are responsible for the charge distribution around a heteromolecule.

These additivity rules imply strongly that atomic terms dominate variations among the $\chi_p{}^A$'s in azines.

Since the DEE approximation works well for calculating shifts in azines, it is worthwhile to speculate as to what other systems could be treated. One example is the series of cyclic aromatic species whose shifts are already known to be linear with the charge on carbon.[2] Shifts in substituted aromatic compounds where the exchange integrals do not differ much from those in benzene should also follow the DEE approximation. These cases should include those compounds where the shifts can be built up from sums of substituent contribu-

Table V. Calculated Proton Shifts in Azines

Molecule	Position	Case	π charge density	$\sigma_d{}^H$	$\sigma_p{}^H$	σ^H	$\sigma^H{}_{obsd}$
Pyridine	2,6	2[a]	+0.0860	−0.920	−0.358	−1.278	−1.293[a]
		4	+0.1148	−1.228	−0.323	−1.551	
		11	+0.0878	−0.940	−0.796	−1.736	
	3,5	2[a]	−0.0172	+0.184	−0.045	+0.139	+0.07[a]
		4	−0.0338	+0.362	−0.045	+0.317	
		11	−0.0440	+0.471	−0.145	+0.326	
	4	2[a]	+0.0454	−0.486	+0.027	−0.459	−0.329[a]
		4	+0.0432	−0.462	+0.021	−0.441	
		11	+0.0680	−0.728	+0.074	−0.654	
Pyrazine	2,3,5,6	2	+0.0769	−0.823	−0.512	−1.335	−1.106[b]
		4	+0.0838	−0.897	−0.491	−1.388	
		11	+0.0450	−0.482	−0.343	−1.325	
Pyridazine	3,6	4	+0.0864	−0.925	−0.274	−1.199	−1.606[b]
		11	+0.0593	−0.635	−1.136	−1.771	
	4,5	4	+0.0204	−0.218	−0.019	−0.237	+0.204[b]
		11	+0.0274	−0.293	−0.025	−0.318	
Pyrimidine	2	4	+0.2248	−2.675	−0.234	−2.909	−1.656[b]
		11	+0.1634	−1.748	−1.446	−3.194	
	4,6	4	+0.1644	−1.758	−0.177	−1.935	−1.116[b]
		11	+0.1456	−1.558	−0.128	−1.686	
	5	4	−0.0744	+0.796	−0.070	+0.726	+0.374[b]
		11	−0.0338	+0.362	−0.415	−0.053	
s-Triazine	2,4,6	2	+0.2088	−2.234	−0.430	−2.664	−1.99
		4	+0.2740	−2.932	−0.323	−3.255	
		6	+0.3796	−4.062	−0.175	−4.237	
s-Tetrazine	3,6	2	+0.1554	−1.663	−1.122	−2.785	
		4	+0.1620	−1.733	−1.021	−2.754	

[a] Reference 12. [b] J. Kim, private communication; A. H. Gawer and B. P. Dailey, *J. Chem. Phys.*, **42**, 2658 (1965).

tions. On the other hand, molecules whose substituents or heteroatoms interact quite differently from atoms in benzene would not be expected to adhere to the DEE method.

The principal conclusion to be derived here is that among the several levels of approximation in the theory of chemical shifts, there is an *optimum* level of agreement between theory and experiment at the DEE stage, when BJ–CNDO wave functions are used. Fewer approximations, that is, use of the Ramsey tensor, give bad results because the wave function is inadequate to the theory. More approximations than DEE result in the neglect of the lower energy excitations and inadequate σ polarity; that is, the theory is insufficient.

At the DEE approximation with the BJ–CNDO MO's, which is suitable for calculating shifts, there is a delicate match of theory to wave functions with respect to their level within the theoretical framework.

Proton Chemical Shifts

The results calculated by using eq 14–16 in different cases are given in Table V. The *jj* component of the paramagnetic susceptibility, $(\chi_p{}^B)_{jj}$, in eq 16 is calculated as follows. When the B nucleus is a carbon, in cases 1–6, equations corresponding to eq 10–13 were used and the summation runs over all carbon atoms except nitrogen and the atom bonded to the hydrogen of interest. As mentioned above, the large anisotropy of nitrogen is mostly due to the *xx* component of the paramagnetic susceptibility because of the low transition energies. Accordingly, $(\chi_p{}^N)_{xx}$ was calculated by use of eq 6 and the experimental first and second n → π* excitation energies, listed in Table VI. Other transitions are assumed to be 10 eV. In spite of the rough nature of this calculation, the results account well for the proton shifts from one molecule to another, or among positions in the same molecule. However, as noted before, the results should be regarded as qualitative even if they give rather good agreement.[12] These shifts are roughly proportional to the atom charges since σ_d makes the larger contribution.

Table VI. n → π* Transition Energies in Azines

	n → π* transition energy, eV	
	First	Second
Pyrazine	3.78 (obsd)[a]	7.19 (estd) (cases 1 and 2) 7.35 (estd) (cases 3 and 4) 7.72 (estd) (cases 5 and 6)
Pyridazine	3.65 (obsd)[a]	4.13 (estd) (cases 3 and 4) 7.20 (estd) (cases 3 and 4) (third)
Pyrimidine	4.15 (obsd)[a]	4.40 (estd) (cases 3 and 4) 7.59 (estd) (cases 3 and 4) (third)
s-Triazine	4.46 (obsd)[a]	7.62 (estd) (cases 1 and 2) 7.85 (estd) (cases 3 and 4) 7.51 (estd) (cases 5 and 6)
s-Tetrazine	2.30 (obsd)	3.87 (obsd) (cases 1–6)

[a] L. Goodman, *J. Mol. Spectry.*, **6**, 109 (1961).

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Carbon-13 Magnetic Resonance. XIII.[1a] Assignment of Carbon-13 Resonances Using the Nuclear Overhauser Effect

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College, Hanover, New Hampshire 03755. *Received February 17, 1969*

Abstract: The observed carbon-13 spectral intensities for the chemically nonequivalent quarternary carbon atoms in pyrene, acenaphthene, acenaphthylene, and fluoranthene enable assignment of these lines provided that the contributing nuclear Overhauser enhancement arises from the distance-dependent (r^{-6}) dipolar interaction between the carbon and nearest neighbor protons. A semiquantitative model which emphasizes the geometrical dependence of these phenomena is provided.

The assignment of carbon-13 resonance peaks in complex natural abundance carbon-13 spectra has to date been dependent upon one or more of the following factors: (a) observation of proton-induced splitting patterns,[2] (b) the absence of proton-induced splittings on lines associated with quarternary carbon atoms, (c) the relative intensities of isolated spectral multiplets and/or observed decoupled resonance lines, and (d) selective proton decoupling.[3] In complex molecular systems, however, major ambiguities in assignments occur for those quarternary carbon atoms which are chemically nonequivalent but would be expected to exhibit carbon-13 reasonance lines of equal intensity. We present herein a general method for assigning some

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[1] (a) Previous paper in this series, R. J. Pugmire and D. M. Grant, *J. Am. Chem. Soc.*, **90**, 4232 (1968); (b) University of Utah; (c) Dartmouth College.

[2] P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

[3] E. G. Paul and D. M. Grant, *ibid.*, **86**, 2977 (1964).