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Calculation of the Chemical Shifts by the Semi-empirical SCF MO Method for All Valence-elctron Systems

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The proton chemical shifts in the nuclear magnetic resonance spectra of CH_4, C_2H_6, C_2H_4, H_2CO, pyridine, and protonated pyridine were evaluated on the basis of Pople's theory (*J. Chem. Phys.*, **37**, 53 (1962)) in which the shielding tensor is expressed in terms of the magnetic susceptibility of each atom in the molecule. The wave functions were obtained using a semi-empirical SCF MO method for valence-electron systems (*Bull. Chem. Soc. Jap.*, **40**, 536, 1017 (1967)). The ^{13}C- and ^{14}N- chemical shifts in the above compounds were calculated on the basis of the "Coupled Hartree-Fock perturbation theory."

The general expression of the nuclear magnetic shielding constant for an isolated molecule was first derived by Ramsey,[1)] but Ramsey's formula is not suitable for the fractional calculation of the shielding constants of large molecules. A variety of methods for the calculation of chemical shifts in molecules have been developed, such as breaking up the total shielding constants into the local contributions in some manner.[2–5)] On the other hand, an attempt has been made to relate the shielding constants to other molecular properties, such as the dipole moment,[6)] the electronegativities of the substituent group,[7)] and the magnetic anisotropy of the bond.[8,9)]

For proton shifts, an empirical correlation between the shift and the π-electron density on the atom to which it is bonded has been advocated.[10)] On the other hand, more theoretical calculations have been carried out by many authors.[11)] Of these, Pople[12)] has proposed a formulation for the shielding constant in which a dipole approximation is used and the shielding constant is expressed in terms of the atomic contributions to the magnetic susceptibility. Although Musher[13)] has given a critical discussion of a dipole approximation, it seemed that it would be of interest to calculate the shielding constant by Pople's formula. The critical discussion is based on the calculation of the Lamb term for an electron in an s or a p state using Slater atomic wave functions. In Pople's formula, the molecular orbitals are written as linear combinations of gauge-invariant atomic orbitals. It is uncertain whether or not the critical discussion is useful for the calculation based on Pople's formula. The calculation requires the knowledge of the ground-state wave function and those of the excited states. In many cases of the practical calculations, because of the lack of the knowledge of excited-state wave functions, an approximation was made.

We used the wave function obtained by a semi-empirical SCF LCAO MO method for all valence-electron system.[14)] We calculated the proton chemical shifts for CH_4, C_2H_6 C_2H_4, and H_2CO without using the "mean excitation energy approximation" (ΔE approximation) used in Pople's theory. For pyridine and protonated pyridine, the calculation needs so many excitation energies that we used the ΔE approximation; some discussions of the approximation will be made.

For the investigation of ^{13}C and ^{14}N chemical shifts in the above compounds for which it is easy

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11) M. Karplus and H. J. Kolker, *ibid.*, **38**, 1263 (1963), **41**, 1259 (1964).

12) J. A. Pople, *J. Chem. Phys.*, **37**, 53 (1962).

13) R. M. Stevens and W. M. Lipscomb, *ibid.*, **40**, 2238 (1964).

14) T. Yonezawa, K. Yamaguchi and H. Kato, This Bulletin, **40**, 536 (1967); H. Kato, H. Konishi and T. Yonezawa, *ibid.*, **40**, 1017 (1967).

to carry out more rigorous calculation, the "Coupled Hartree-Fock perturbation thery"[15] without the ΔE approximation is applied.

Calculation

Using a dipole approximation, the mean value of the shielding tensor on the A atom has previously been given.[12]

$$\sigma^{\mathrm{A}} = \frac{e^2}{3mc^2}\sum_{\mu}^{\mathrm{A}} P_{\mu\mu}\langle r^{-1}\rangle_{\mu\mu} - \frac{2}{N}<r^{-3}>_{\mathrm{A}}\chi_{\mathrm{P}}^{\mathrm{A}}$$

$$-\frac{1}{3N}\sum_{\alpha\beta}\sum_{\mathrm{B}(\neq\mathrm{A})}\chi_{\alpha\beta}^{\mathrm{B}}R_{\mathrm{B}}^{-5}(R_{\mathrm{B}}^2\delta_{\alpha\beta}-3R_{\mathrm{B}\alpha}R_{\mathrm{B}\beta}) \qquad (1)$$

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

$$\chi_{\mathrm{P}}^{\mathrm{A}} = \{(\chi_{\mathrm{P}}^{\mathrm{A}})_{xx} + (\chi_{\mathrm{P}}^{\mathrm{A}})_{yy} + (\chi_{\mathrm{P}}^{\mathrm{A}})_{zz}\}/3 \qquad (3)$$

The first term in Eq. (1) gives the Lamb term,[16] and $\langle r^{-3}\rangle_{\mathrm{A}}$ in the second term is the mean value of r^{-3} for the atomic orbital which contributes to paramagnetic terms on the A atom, but this term becomes zero in the calculation of the proton chemical shifts so long as the valence AO approximation is adopted. The third term, which gives the effect of currents on neighboring atoms, is divided into two terms (these two terms we shall henceforth call "the neighboring paramagnetic term" and "the neighboring diamagnetic term"). $\boldsymbol{R}_{\mathrm{B}}$ is the radium vector to the B nucleus from the A nucleus, at which the shielding is calculated. The $R_{\mathrm{B}\alpha}$ notation, is the $\alpha(x,y,z)$ component of the $\boldsymbol{R}_{\mathrm{B}}$ vector, and $(\chi_{\mathrm{P}}^{\mathrm{A}})_{XX}$ is the diagonal x component of the paramagnetic susceptibility tensor of the A atom. In the above formula,

$$\chi_{\alpha\beta}^{\mathrm{B}} = (\chi_{\mathrm{d}}^{\mathrm{B}})_{\alpha\beta} - (\chi_{\mathrm{P}}^{\mathrm{B}})_{\alpha\beta} \qquad (4)$$

$$(\chi_{\mathrm{d}}^{\mathrm{B}})_{\alpha\beta} = -\frac{Ne^2}{4mc^2}\sum_{\mu}^{\mathrm{B}} P_{\mu\mu}<r^2\delta_{\alpha\beta}-r_\alpha r_\beta>_{\mu\mu} \qquad (5)$$

$$(\chi_{\mathrm{P}}^{\mathrm{B}})_{\alpha\beta} = \frac{Ne^2\hbar^2}{m^2c^2}\sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{unocc}}\sum_{\mu<\nu}^{\mathrm{B}}\sum_{\mathrm{A}}\sum_{\lambda<\sigma}^{\mathrm{A}} \times \frac{(C_{i\mu}C_{j\nu}-C_{i\nu}C_{j\mu})(C_{i\lambda}C_{j\sigma}-C_{i\sigma}C_{j\lambda})(l_\alpha)_{\mu\nu}(l_\beta)_{\lambda\sigma}}{E_{i\to j}} \qquad (6)$$

where $E_{i\to j}$ is the excitation energy of the electronic transition from the ith molecular orbital to the jth molecular orbital. The other notations are the same as in Ref. 12.

Using Eqs. (1)—(6), we calculated the proton chemical shifts of CH_4, C_2H_6, C_2H_4 and H_2CO (Table 1). The coordinate axes, the x, y, and z axes, were taken on the mirror-reflection plane of these molecules. Therefore, the susceptibility tensor has nonzero values only for the diagonal elements for the sake of simplicity in calculation. (For this proof, see the appendix.) However, in the cases of pyridine and protonated pyridine (Fig. 1), according to the reason stated in the appendix, the coordinate axes chosen as has been described above do not coincide with the principal axes of the magnetic susceptibility tensor on 2C, 3C, 5C, and 6C atoms. Using the ΔE approximation, the elements of the paramagnetic susceptibility tensor in Eq. (6) are written as follows:

$$(\chi_{\mathrm{P}}^{\mathrm{B}})_{xx} = \frac{Ne^2\hbar^2}{m^2c^2\Delta E}\sum_{\mathrm{A}}\sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{unocc}}(C_{iy\mathrm{B}}C_{jz\mathrm{B}}-C_{iz\mathrm{B}}C_{jy\mathrm{B}})\times$$

$$(C_{iy\mathrm{A}}C_{jz\mathrm{A}}-C_{iz\mathrm{A}}C_{jy\mathrm{A}}) \qquad (7)$$

TABLE 1. CALCULATED AND OBSERVED PROTON CHEMICAL SHIFTS IN CH_4, C_2H_6, C_2H_4, AND H_2CO (ppm unit)

	CH_4	C_2H_6	C_2H_4	H_2CO
Calcd				
Lamb term	14.36	14.13	12.76	14.16
Neighboring diamag. term	−0.02	−0.14	−0.54	−0.28
Neighboring paramag. term	0.00	−0.23	−4.78	−4.65
Field effect due to the distortion of s-orbital	~0	~0	~0	−3.82
Total	14.34	13.76	7.44	5.41
Relative to CH_4	0.00	−0.58	−6.90	−8.93
Obsd				
Relative to CH_4	0.00*	−0.75*	−5.18*	(−9)

* W. G. Schneider, H. J. Bernstein and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958).

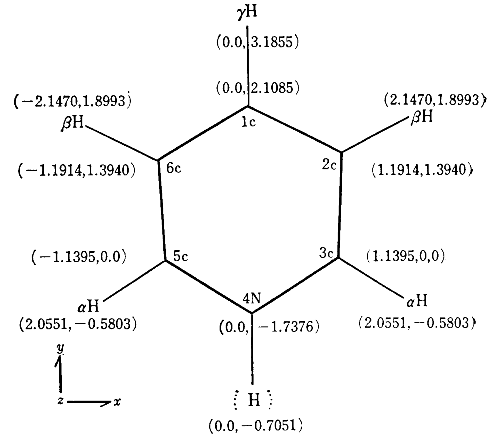

Fig. 1. Moleculer geometry for the pyridine and protonated pyridine.

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[15] R. A. Hegstrom and W. N. Lipscomb, This Bulletin, **46**, 1594 (1967).

[16] W. Lamb, *Phys. Rev.*, **60**, 817 (1941).

$$(\chi_{\mathrm{P}}^{\mathrm{B}})_{yz} = \frac{Ne^2\hbar^2}{m^2c^2\Delta E}\sum_{\mathrm{A}}\sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{unocc}}(C_{iz\mathrm{B}}C_{jx\mathrm{B}}-C_{ix\mathrm{B}}C_{jz\mathrm{B}})\times (C_{iy\mathrm{A}}C_{jz\mathrm{A}}-C_{iz\mathrm{A}}C_{jy\mathrm{A}}) \tag{8}$$

etc.

If the off-diagonal elements, $(\chi_{\mathrm{P}}^{\mathrm{B}})_{\alpha\beta}$'s are all zero, *i.e.*, if the coordinate axes are taken to be the principal axes and the summation over the A atom in the diagonal element of $(\chi_{\mathrm{P}}^{\mathrm{B}})_{\alpha\beta}$ is limited only over the B atom, the neighbouring paramagnetic constant part of Eq. (1) becomes equal to the term due to the local paramagnetic currents[5] in the shielding constant derived by the induced-current-density theory.[4]

On the basis of the relations of Eqs. (5)—(8), we have calculated the diamagnetic and paramagnetic susceptibility tensors, $\chi_{\mathrm{d}}^{\mathrm{B}}$ and $\chi_{\mathrm{p}}^{\mathrm{B}}$, on the B atom in pyridine and protonated pyridine (Tables 2, and 3, and Table 4 respectively). Using these results and Eq. (1), the proton-shielding constants of pyridine and protonated pyridine

TABLE 2. COMPONENTS OF THE DIAMAGNETIC SUSCEPTIBILITY TENSOR: χ_{d} IN EACH ATOM IN PYRIDINE AND PROTONATED PYRIDINE

$$\beta = \frac{Ne^2}{4mc^2}$$

B		1C	2C	3C	4N	5C	6C
Pyridine	$(\chi_{\mathrm{d}}^{\mathrm{B}})_{xx}$	-1.646β	-1.652β	-1.504β	-1.928β	-1.504β	-1.652β
	$(\chi_{\mathrm{d}}^{\mathrm{B}})_{yy}$	-1.689β	-1.651β	-1.493β	-1.713β	-1.493β	-1.651β
	$(\chi_{\mathrm{d}}^{\mathrm{B}})_{zz}$	-1.614β	-1.588β	-1.400β	-1.895β	-1.400β	-1.588β
Protonated pyridine	$(\chi_{\mathrm{d}}^{\mathrm{B}})_{xx}$	-1.583β	-1.580β	-1.535β	-1.642β	-1.535β	-1.580β
	$(\chi_{\mathrm{d}}^{\mathrm{B}})_{yy}$	-1.611β	-1.611β	-1.507β	-1.663β	-1.507β	-1.611β
	$(\chi_{\mathrm{d}}^{\mathrm{B}})_{zz}$	-1.601β	-1.528β	-1.470β	-1.540β	-1.470β	-1.528β

* The off diagonal susceptibilities: $(\chi_{\mathrm{d}}^{\mathrm{B}})_{ij}$ $(i \neq i)$ are all equal to zero.

TABLE 3. COMPONENTS OF THE PARAMAGNETIC SUSCEPTIBILITY TENSOR; $\chi_{\mathrm{p}}^{\mathrm{B}}$ ON CARBON AND NITROGEN ATOMS IN PROTONATED PYRIDINE

$$\gamma = \frac{Ne^2\hbar^2}{4m^2c^2\Delta E}$$

B	1C	2C	3C	4N	5C	6C
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{xx}$	3.268γ	5.936γ	5.315γ	4.735γ	5.315γ	5.936γ
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{xy}$	0.0	0.809γ	-0.829γ	0.0	0.829γ	-0.809γ
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{zx}$	0.0	0.0	0.0	0.0	0.0	0.0
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{xy}$	0.0	0.841γ	-0.803γ	0.0	0.803γ	-0.841γ
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{yy}$	5.657γ	4.194γ	3.480γ	6.190γ	3.480γ	4.194γ
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{zy}$	0.0	0.0	0.0	0.0	0.0	0.0
$(\chi_{\mathrm{P}}^{\mathrm{B}})_{xz}$	0.0	0.0	0.0	0.0	0.0	0.0
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{yz}$	0.0	0.0	0.0	0.0	0.0	0.0
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{zz}$	5.579γ	5.354γ	4.685γ	4.943γ	4.685γ	5.354γ

TABLE 4. COMPONENTS OF THE PARAMAGNETIC SUSCEPTIBILITY TENSOR: $\chi_{\mathrm{q}}^{\mathrm{B}}$ ON CARBON AND NITROGEN ATOMS IN PYRIDINE

$$\gamma = \frac{Ne^2\hbar^2}{4m^2c^2\Delta E}$$

B	1C	2C	3C	4N	5C	6C
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{xx}$	3.746γ	6.011γ	5.317γ	3.234γ	5.317γ	6.011γ
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{yz}$	0.0	0.866γ	-0.737γ	0.0	0.737γ	-0.866γ
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{zx}$	0.0	0.0	0.0	0.0	0.0	0.0
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{xy}$	0.0	0.873γ	-0.893γ	0.0	0.893γ	-0.873γ
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{yy}$	5.556γ	4.264γ	3.886γ	4.625γ	3.866γ	4.264γ
$(\chi_{\mathrm{q}}^{\mathrm{B}})_{zy}$	0.0	0.0	0.0	0.0	0.0	0.0
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{xz}$	0.0	0.0	0.0	0.0	0.0	0.0
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{yz}$	0.0	0.0	0.0	0.0	0.0	0.0
$(\chi_{\mathrm{p}}^{\mathrm{B}})_{zz}$	4.948γ	5.610γ	4.398γ	6.368γ	4.398γ	5.610γ

TABLE 5. CALCULATED PROTON SHIFTS IN PYRIDINE AND PROTONATED PYRIDINE (ppm unit)

	Pyridine			Protonated pyridine			N-H
	αH	βH	γH	αH	βH	γH	
Calcd							
Lamp term	12.812	12.210	12.724	11.430	11.430	11.554	9.729
Neighboring diamag. term	−2.19	−0.405	−0.723	−0.847	−0.234	−0.362	−1.013
Neighboring paramag. term	−3.433	−3.415	−0.574	−3.724	−3.235	−0.688	−2.575
Total	7.186	8.390	11.427	6.859	7.961	10.504	6.141
Referred to βH	−1.204	0.0	3.037	−1.102	0.0	2.543	−1.820
Obsd[a]	−3.33	−1.87	−2.28	−3.58	−2.93	−3.50	−8.60
Referred to βH	−1.46	0.0	−0.41	−0.65	0.0	−0.57	−5.67

a) Referred to CH_2Cl_2; I. C. Smith and W. G. Schneider, *Can. J. Chem.*, **39**, 1158 (1961).

have been calculated to be as is shown in Table 5. In the ΔE approximation, ΔE was taken to be 10.0 eV.

The ^{13}C- and N^{14}-chemical shifts are calculated by the formula based on the "Coupled Hartree-Fock perturbation theory." The expressions for the diagonal component (μ is x, y, or z) of the paramagnetic and diamagnetic shielding tensors, $\sigma^{\rm p}_{\mu\mu}$ and $\sigma^{\rm d}_{\mu\mu}$, are given as follows:[15]

$$\sigma^{\rm p}_{\mu\mu} = -\alpha^2 \sum_i^{\rm occ} \sum_k^{\rm unocc} \times$$

$$\frac{\langle\varphi_k|l_\mu|\varphi_j\rangle\langle\varphi_j|\frac{l_\mu}{r^3}|\varphi_k\rangle+\langle\varphi_j|l_\mu|\varphi_k\rangle\langle\varphi_k|\frac{l_\mu}{r^3}|\varphi_j\rangle}{\varepsilon_k-\varepsilon_j-J_{kj}+K_{kj}} \tag{9}$$

$$\sigma^{\rm d}_{\mu\mu} = \alpha^2 \sum_j^{\rm occ} \langle\varphi_j|\frac{r^2-\mu^2}{r^3}|\varphi_j\rangle \tag{10}$$

where α is the fine-structure constant and where φ_j is the jth MO. The other notations are the same as those in Ref. (23). In these ^{13}C- and ^{14}N-chemical shift calculations, only one-center terms in the matrix elements, such as $\langle\varphi_k|l_\mu|\varphi_j\rangle$, $\langle\varphi_j|l_\mu/r^3|\varphi_k\rangle$, and $\langle\varphi_j|1/r|\varphi_j\rangle$, in Eq. (9) and Eq. (10) are taken into account.

Results and Discussion

Table 1 gives the calculated and experimental proton chemical shifts, referred to CH_4 and their components, such as the Lamb term, the neighbouring diamag. term, and the paramag. term, for CH_4, C_2H_4, and H_2CO. It can be pointed out that the chemical shift of C_2H_2 comes mainly, and equally, from the Lamb term and the neighbouring paramagnetic term, while that of C_2H_4 is governed by the neighbouring paramagnetic term. In these molecules, the contribution from the field effect[6,17] is nearly equal to zero. However, this effect arising from the electric dipole of the C–O group plays an important role, as may be seen in Table 1. For these compounds, the calculated results are in good agreement with the experimental values.

In order to investigate the practical difference between the two theories proposed by Pople in Ref. 12 and Ref. 5, further calculations were carried out for pyridine and protonated pyridine. The calculated components of the diamagnetic susceptibility tensor, $\chi^{\rm B}_{\rm d}$, and the paramagnetic susceptibility tensor, $\chi^{\rm B}_{\rm p}$, on the carbon and nitrogen atoms in pyridine and protonated pyridine are shown in Tables 2, 3, and 4; $(\chi^{\rm N}_{\rm p})_{zz}$ shows a remarkable change from pyridine to protonated pyridine, in contrast to the conclusion of the localized-model calculations by Gil and Murrell.[18] In the present calculation of the shielding constants, we have considered the contribution of the off-diagonal elements of the paramagnetic susceptibility tensor and found that these elements can not be ignored. This is because the exclusion of these elements leads to the dependence of the shielding constant on the choice of the coordinate.[19] The coordinate system for pyridine and protonated pyridine in Fig. 1 does not accord with the principal axes of the magnetic susceptibility tensor on 2C, 3C, 5C, and 6V atoms. In this choice of the coordinate, the off-diagonal elements of the paramagnetic susceptibility tensor are only about 20% of the diagonal elements, but the contribution to the shielding constant through the third term in Eq. (1) is very important. For example, the contribution of the $(\chi^{\rm 2C}_{\rm p})_{yz}=0.866\gamma$ and $(\chi^{\rm 2C}_{\rm p})_{xy}=$

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[17] T. W. Marshall and J. A. Pople, *Mol. Phys.*, **1**, 199 (1958).

[18] Y. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, **60**, 248 (1964).

[19] H. Kato, H. Kato and T. Yonezawa, *Spect. Lett.*, **2(9)**, 267 (1969).

0.873γ (γ is a constant, see Table 4) in pyridine to the shielding constant through the neighboring paramagnetic term is -0.422 ppm, 2.985 ppm, and -0.191 ppm for αH, βH, and γH respectively. If we consider the change of the proton chemical shifts due to the field effect from the electric-charge distribution, the change of shifts due to this effect was calculated to be -0.259 ppm, -0.131 ppm, and -0.074 ppm for αH, βH, and γH, of pyridine and -0.034 ppm -0.017 ppm, -0.010 ppm, and -0.147 ppm for αH, βH, γH, and N-H of protonated pyridine respectively. In contradiction to the expreiment, the calculated shifts of γH (Table 5) in both pyridine and protonated pyridine show large shifts relative to βH. This discrepancy might be due to the difficulty involved in the MO treatment of lone-pair electrons or a non-negligible error in the dipole approximation. The relative shifts from pyridine to protonated pyridine (Table 5) are in fairly good accordance with the experimental results. In our calculation of the molecular orbitals, we have considered the interaction between the ($1s$) atomic orbital in the hydrogen atom and the ($2p$) atomic orbitals in the carbon or hygrogen atoms. Accordingly, the electric-field correction proposed by Musher,[20] which comes from the change in the local part of the Lamb contribution due to the change in the electron density, ρ^H, on the proton, is automatically included. Therefore, the electric-field effect due to the distortion of an spherically symmetric s state[6,17] is calculated by:

$$\sigma_{\parallel} = \frac{e^2}{3mc^2a}\left[1-\frac{439}{40}\frac{a^4E^2}{e^2}\right]$$
$$\sigma_{\perp} = \frac{e^2}{3mc^2a}\left[1-\frac{193}{15}\frac{a^4E^2}{e^2}\right] \tag{11}$$

The calculated carbon-13 chemical shifts in CH_4, C_2H_6, C_2H_4, and H_2CO which are obtained by the "Coupled Hartree Fock Method" are shown

TABLE 6. C^{13}-CHEMICAL SHIFT (ppm unit) IN CH_4, C_2H_6, C_2H_4, AND C_2CO

	CH_4	C_2H_6	C_2H_4	H_2CO
Calcd				
paramag.	-136.8	-148.6	-251.6	-229.3
diamag.	35.5	39.9	41.3	35.3
TOTAL	-101.3	-108.7	-210.3	-194.0
Relative to CH_4	0.0	-7.4	-109.0	-92.7
Obsd				
Relative to CH_4	0.0	-8.0[a]	-126.0[b]	(-169.0)[c]

a) H. Spiesecks and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

b) Estimated from data on similar compounds by R. A. Friedel and H. L. Retcofsky, *J. Chem. Soc.*, **85**, 1300 (1963). Ref. *Mol. Phys.* **7**, 301 (1963—1964).

c) In 88% aqueous solution; P. C. Lauterbur, *J. Chem. Phys.*, **27**, 217 (1957).

TABLE 7. C^{13} AND N^{14}-CHEMICAL SHIFT (ppm unit) IN PYRIDINE AND PROTONATED PYRIDINE

	Pyridine			Protonated pyridine		
C^{13}	αC	βC	γC	αC	βC	γC
Calcd						
paramag.	-263.7	-243.9	-259.1	-246.4	-210.1	-251.8
diamag.	39.9	44.4	44.8	40.9	42.7	42.8
TOTAL	-224.3	-199.5	-214.3	-205.5	-167.3	-209.0
Relative to βC	-24.8	0.0	-14.8	-38.2	0.0	-41.7
Obsd[a]	-21.72	4.59	-7.42	-13.94	-0.45	-19.84
	(-21.9)[c]	(4.2)[c]	(-7.70)[c]			
Relative to βC	-26.31	0.0	-12.01	-13.49	0.0	-19.39
	(-26.1)	(0.0)	(-11.90)			
N^{14}						
Calcd						
paramag.		-657.6			-528.8	
diamag.		86.7			75.9	
TOTAL		-588.9			-452.9	
Relative to C_5H_5N		0.0			136.0	
Obsd[b]						
Relative to C_5H_5N		0.0			123.11	

a) Relative to C_6H_6: R. J. Pugmire, Ph. D Thesis Univ. Utha, June (1966).

b) V. M. S. Gel. J. N. Murrel, *Trans. Faraday Soc.*, **60**, 248 (1964).

c) T. Tokuhiro, N. K. Wilson and G. Frankel, *J. Amer. Chem. Soc.*, **90**, 3622 (1968).

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[20] J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962).

TABLE 8. CONTRIBUTION TO THE C_{13}-CHEMICAL SHIFT OF C_2H_4 THROUGH THE PARAMAGNETIC TERM FROM EACH EXCITED STATE

State $(j \quad k)$[b]	μ[a]	$\langle j \vert L_\mu \vert k\rangle$	$\langle k \vert L_\mu \vert j\rangle$	Contribution to C^{13} (ppm)
$(4\sigma, 7\pi^*)$	x	-0.574	-2.772	-24.68
$(6\pi, 8\sigma^*)$	x	0.978	4.724	-41.58
$(5\sigma, 7\pi^*)$	y	-0.853	-4.122	-69.36
$(1\sigma, 7\pi^*)$	y	0.015	0.072	0
$(6\pi, 9\sigma^*)$	y	1.418	6.850	-64.96
$(6\pi, 12\sigma^*)$	y	0.709	3.422	-6.31
$(2\sigma, 8\sigma^*)$	z	-0.100	-0.482	-0.27
$(3\sigma, 9\sigma^*)$	z	0.787	3.802	-16.67
$(5\sigma, 10\sigma^*)$	z	1.079	5.214	-23.60
$(4\sigma, 11\sigma^*)$	z	-0.364	-1.756	-2.40
$(3\sigma, 12\sigma^*)$	z	0.393	1.899	-1.77
$(1\sigma, 10\sigma^*)$	z	-0.019	-0.091	0

a) The molecular plane is in the *xy*-plane and the C–C bond is taken as the *x*-axis.

b) The number in the parenthesis shows the MO which is numbered from the lower to higher orbital energies.

in Table 6. The calculated values of the ^{13}C-chemical shifts, (δ^{13}C), are also in fairly good agreement with the experimental values, except in the case of H_2CO. If we consider the change in the Slater exponent caused by the atomic charges in the evaluation of $\langle r^{-3}\rangle$,[21] the calculated δ^{13}C in CH_4, C_2H_6, C_2H_4, and H_2CO become -101.3 ppm, -108.2 ppm, -208.5 ppm, and -202.3 ppm respectively. The ^{13}C- and ^{14}N-chemical shifts in pyridine and protonated pyridine are shown in Table 7. The values are mainly determined by the paramagnetic term. In the δ^{13}C in pyridine, the calculated value of the paramagnetic term from the lowest (n–π^*) state is -132.8 ppm, while in protonated pyridine the corresponding contribution is -71.5 ppm. This difference corresponds to about 50% of the total difference. Table 8 shows how each excited state contributes to the paramagnetic terms in C_2H_4, as an example. The lowest excited state (5σ, $7\pi^*$) shows the largest contribution at δC^{13}. Moreover, the (6σ, $9\pi^*$) state, which needs a much larger excitation energy, shows a contribution almost comparable to that of the (5σ, $7\pi^*$) state; there are also several states which show the contribution of the same order as the (5σ, $7\pi^*$) states. In the other compounds, the same situations are found. Accordingly, it cannot be said generally that a particular state governs the chemical shift. In the present paper, we have considered only one-center terms, but it will be necessary, as a further improvement, to include two-center terms at least, as well as to refine the MO calculation. The MO calculation was carried out on a HITAC 5020E computer at the computation center of the University of Tokyo.

Appendix

The susceptibility tensor, χ_M, on the M atom is a second-rank tensor:

$$\chi_M = \begin{pmatrix} \chi_{xx} & \chi_{yx} & \chi_{zx} \\ \chi_{xy} & \chi_{yy} & \chi_{zy} \\ \chi_{xz} & \chi_{yz} & \chi_{zz} \end{pmatrix}$$

If the M atom in a molecule lies on a mirror-reflection plane on the *xy*-plane, χ_M must satisfy the following relation:

$$\chi_M = s_h^Z \chi_M {}^t s_h^Z$$

where $s_h^Z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ *i. e.*, the matrix representation corresponding to the mirror-reflection operator. Accordingly, χ_M is as follows:

$$\chi_M = \begin{pmatrix} \chi_{xx} & \chi_{yx} & 0 \\ \chi_{xy} & \chi_{yy} & 0 \\ 0 & 0 & \chi_{zz} \end{pmatrix}$$

Further, if the M atom also lies on an other mirror reflection plane, the *xz* or *yz* plane, the susceptibility tensor should have nonzero values only for the diagonal elements.

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