Studies on the Proton Paramagnetic Shifts for σ-Systems in Piperidine and Quinuclidine

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Abstract: Proton magnetic resonance shifts of some piperidine and quinuclidine derivatives have been measured at room temperature in $CDCl_3$ solution containing paramagnetic nickel(II) and cobalt(II) acetylacetonates ($Ni(AA)_2$ and $Co(AA)_2$). Different values of the paramagnetic shifts were observed for the axial and the equatorial protons in the α-methylene group of 3-(I) and 4-methylpiperidine (II) and 1,4-dimethylpiperidine (III). The ratio of these two values has been shown to depend on the orientation of the adjacent nitrogen lone-pair electrons. For compound III, in which the lone-pair electrons have greater preference for the axial position, the difference in these two paramagnetic shifts is considerably larger than that for I and II having preferential equatorial lone-pair electrons. These characteristic values of the proton paramagnetic shift have also been used to estimate to what extent the nitrogen lone pair is likely to be axial or equatorial for I and II. Contact shifts obtained in the $Ni(AA)_2$ system were investigated in detail in an attempt to examine the unpaired spin-delocalization mechanism through a σ bond in a six-membered ring and in a cagelike skeleton. Fairly good agreement between the relative values of the observed contact shifts and those of spin densities calculated by extended Hückel theory was obtained. Pseudocontact shifts in the $Co(AA)_2$ system were interpreted in terms of a geometrical structure of the piperidine– or quinuclidine–$Co(AA)_2$ complex.

In the previous articles[1] we have reported the proton magnetic resonance study of oxime, imine, and aziridine in the paramagnetic solution containing nickel and cobalt acetylacetonates ($Ni(AA)_2$ and $Co(AA)_2$). The induced isotropic contact shift of the proton close to the nitrogen atom was found to fall within characteristic values (both of the magnitude and the sign) depending on the orientation of the nitrogen lone-pair serving as the binding site with $Ni(AA)_2$ or $Co(AA)_2$. One of the major problems in these studies involves the interpretation of the mechanism of spin delocalization onto the ligand though the σ bond. Our investigation of the odd electron-delocalization mechanism in these σ systems, using experimental as well as molecular orbital treatment, leads us to sort out the σ polarization and σ-delocalization mechanisms.[1]

In the present study, we attempt to extend our investigation to the piperidine and quinuclidine derivatives which have the oriented nitrogen lone-pair in the six-membered ring. Our major concern in the present paper is to determine the magnitude and sign of the contact shifts for the six-membered ring protons and to take a look at the consequence of the orientation of the nitrogen lone-pair electrons or σ bonds on them. We used 3-(I) and 4-methylpiperidine (II) as the model compound with the oriented nitrogen lone pair which has the greater preference for the equatorial position and 1,4-dimethylpiperidine (III) as that with the axial lone pair. These molecules show separate signals of the axial and the equatorial protons in the α-methylene group at room temperature. Quinuclidine (IV) has the oriented nitrogen lone-pair electrons in a rigid σ-electron system of the cagelike structure.

In the following it will be shown that quite different values of the ratio of the contact shifts of the axial and the equatorial protons are obtained for N-substituted (III) and nonsubstituted (I and II) piperidines. These characteristic contact shifts were used to make a quantitative estimation of the conformational preference of the nitrogen lone-pair electrons for compounds I and II. This problem attracts much attention in terms of the recent interest in the debate over the nitrogen lone-pair orientation in piperidines.[2,3] Additionally, molecular orbital calculations of spin-density ratios were carried out to substantiate the observed ratios of contact shifts and it was concluded that spin delocalization in σ orbitals in the dominant mechanism for piperidine and quinuclidine. To study the structure of the complexed paramagnetic molecule, pseudocontact shifts in the $Co(AA)_2$ system were analyzed.

Experimental Section

Materials. All chemicals used in this study except for III and IV were commercially available materials of adequate purity as indicated by their nmr spectra. Compound III was prepared by methylation of II with the Leukert reaction. Quinuclidine (IV) was obtained by dehydrochlorination of commercially available quinuclidine hydrochloride (K and K Lab., Inc.). Commercially available $Ni(AA)_2$ and $Co(AA)_2$ were dried at 60° *in vacuo* overnight before use. Samples were prepared by addition of a given amount of $Ni(AA)_2$ or $Co(AA)_2$ to the solution of piperidine and quinuclidine in $CDCl_3$. The concentration of ligand in $CDCl_3$ was 25 and 50 vol %. $Ni(AA)_2$ or $Co(AA)_2$ was added until the α-methylene proton signals were too remarkably broadened to be detected. The ligand : $M(AA)_2$ ratio was *ca.* 100 at most.

Nmr Spectra. Proton spectra were obtained at 60 MHz using a modified JEOL-3H-60 spectrometer with both the external (two-sample) and the internal field-frequency (one-sample) locked mode of operation. TMS was used as an internal standard and a field-frequency lock signal. The peak frequencies were monitored by an electronic frequency counter from TMS. Shifts are reported in hertz downfield from TMS. All the spectra of I, II, III, and IV were taken at room temperature (24°). The spectra of piperidine and N-methylpiperidine, the assignment of which have been well established[4] were obtained at −60° in CH_2Cl_2 or CS_2 to confirm the assignment of the axial and the equatorial proton signals of I, II, and III.

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(1) (a) I. Morishima, T. Yonezawa, K. Takeuchi, K. Fukuta, and Y. Ohmori, submitted for publication; (b) I. Morishima and T. Yonezawa, submitted for publication; (c) T. Yonezawa, J. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc. Japan*, in press.

(2) D. H. R. Barton and R. C. Cookson, *Quart. Rev.* (London), **10**, 44 (1956).

(3) F. G. Riddel, *ibid.*, **21**, 364 (1967).

(4) J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Amer. Chem. Soc.*, **89**, 3761 (1967).

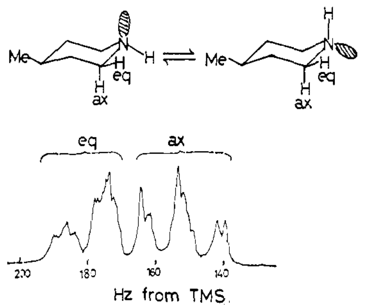

Figure 1. Pmr spectrum of α-methylene in 4-methyl piperidine at room temperature.

Results

Proton Spectra. In piperidine the ring-inversion rate is very rapid at room temperature and only single signal is observed at the position of weighted average of the axial and the equatorial protons. Introduction of the methyl group in the piperidine ring slows down this inversion rate and the separate signals of the axial and the equatorial protons in the α-methylene group were observed at room temperature. A typical proton spectrum of the α-methylene group of II is shown in Figure 1. The axial proton signal at τ 7.44 and the equatorial proton signal at τ 6.97 are in good agreement with the assignment of the corresponding signals of piperidine at $-60°$.[4] Table I summarizes the chemical shift of H_{ax} and H_{eq} of several piperidine derivatives. It appears that the methyl group in I and II has no significant effect on the chemical shift of H_{ax} and H_{eq}. The chemical-shift difference between an axial and an equatorial proton $\Delta\nu_{ae}$ is generally 25–30 Hz and 50–60 Hz at 60 MHz, in the absence of N-substituent and in N-methyl derivatives, respectively. This general trend is in good agreement with the observation of Lambert, *et al.*[4]

Table I. The Chemical Shifts[a] of H_{ax} and H_{eq} of α-CH_2 in Piperidine Derivatives

Piperidines	ν_{ax}[a]	ν_{eq}[a]	$\Delta\nu_{ae} = \nu_{eq} - \nu_{ax}$
I 3-Me	154.5	178.0	24.5
	131.9	178.0	47.1
II 4-Me	153.4	181.6	28.2
III 1,4-diMe	114.3	168.0	53.7
Piperidine	150.9[b]	176.3[b]	25.4[b]
N-CH_3	107.0[b]	165.2[b]	58.2[b]

[a] In hertz downfield from TMS. [b] 22.2 mol % in CH_2Cl_2 at $-82°$.

The proton spectrum of quinuclidine gives an A_2B_2 pattern, a lower half at τ 7.12 (α proton) and an upper half at τ 8.43 (β proton) overlapped with the multiplet signal of γ proton at τ 8.24[5] (Figure 2a).

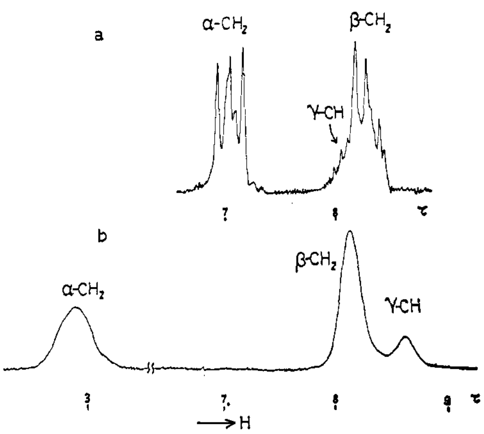

Figure 2. Pmr spectra of quinuclidine (a) in $CDCl_3$ and (b) in $CDCl_3$ containing $Ni(AA)_2$ (60 MHz).

Paramagnetic Shift in $Ni(AA)_2$ and $Co(AA)_2$ Systems. Figure 2b shows the proton signals of α, β, and γ protons when $Ni(AA)_2$ is added to the solution of IV in $CDCl_3$ (10 mol %). The lower field signal (H_α) apparently undergoes downfield shift more than the other. Each perturbed signal is averaged between the signals of the ligand–$M(AA)_2$ complex and the free ligand.[6,7] Even at reduced temperature, the signal of the paramagnetic complex could not be observed separately from bulk free-ligand signal. Therefore it follows that the fast exchange between the complex and the free ligand occurs and a set of averaged line positions is obtained. In the fast-exchange region, the equation

$$\nu_{obsd} = P_M\nu_M + P_L\nu_L \qquad (1)$$

is applicable, where ν_{obsd} is the observed shift for the fast-exchange averaged signal, ν_M and ν_L are the shifts in the complexed and free ligand, respectively, in the absence of exchange, and P_M and P_L are the fractions of complexed and free ligand molecules, respectively. Then the change in the proton shift, when $M(AA)_2$ is added to the diamagnetic solution, is given by

$$\nu_{obsd} - \nu_L = P_M[\nu_M - \nu_L] \qquad (2)$$

This equation implies that the observed paramagnetic shift $\Delta v = (\nu_{obsd} - \nu_L)$ relative to the free ligand is proportional to the paramagnetic shift in the complex $\Delta\nu_M = (\nu_M - \nu_L)$ and increases linearly with an increase in the amount of the added $M(AA)_2$.

The labile nature of the complexes, of course, precludes any determination of the actual resonance shifts for coordinated ligands. It is clear that for a given system the ratios of the observed shifts in a molecule are equal to those of the shifts for the coordinated ligands.[5,6] The observed paramagnetic shifts of the axial and the equatorial protons in II are representatively plotted against the amount of the added $Ni(AA)_2$ or $Co(AA)_2$ as is given in Figure 3. Similar plots are also obtained for IV in Figure 4. The linear plot supports above treatment of the paramagnetic shifts for the case of the fast exchange between the complexed and the free ligand. For the solutions containing more than 0.4 mol % of $M(AA)_2$, deviation from this linear plot occurs. One possible reason for deviation from this linearity is conformational change of piperidines due to complex formation. Therefore, the paramagnetic shifts in the region where the linear plot is obtained are taken into account in the following discussions. Table II summarizes the relative paramagnetic shifts of the axial and the equatorial protons for I, II, and III, and those of α, β, and γ protons for IV. The survey of Table II

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(5) Nmr studies of quinuclidine will be published in a separate paper (I. Morishima, Y. Ohmori, and T. Yonezawa).

(6) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

(7) R. W. Kluiber and W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, **87**, 5350 (1965).

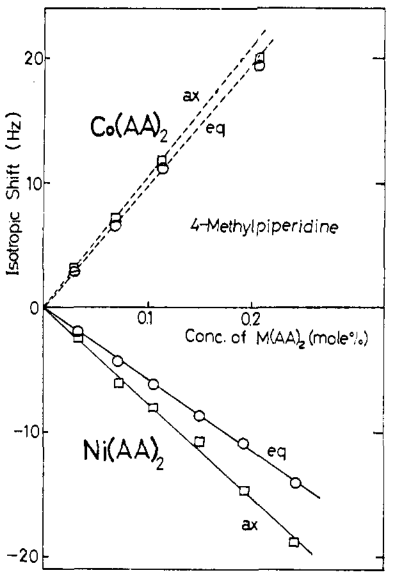


Figure 3. Plot of induced isotropic paramagnetic shifts *vs.* concentration of M(AA)$_2$ for α-methylene proton of 4-methyl piperidine.

shows that all of the ring methylene protons exhibit downfield paramagnetic shifts in Ni(AA)$_2$ systems, while in Co(AA)$_2$ systems substantial upfield shifts are observed, being more prominent for α-methylene protons than those far remote from the nitrogen atom. It is also generally seen that in Ni(AA)$_2$ systems the axial proton in the α-CH$_2$ group shows a greater downfield shift than does the equatorial proton and this different behavior of paramagnetic shift is more remarkable for N-methyl piperidine than for NH piperidine. On the other hand, in Co(AA)$_2$ systems, the difference in paramagnetic upfield shifts for axial and equatorial protons is not so conspicuous as in Ni(AA)$_2$ systems. The different behavior of paramagnetic shifts in Ni(AA)$_2$ and Co(AA)$_2$ systems results from the different contribution of contact and pseudocontact shifts in these two complex systems, as will be discussed in the following section. In quinuclidine, with rigid six-membered rings in "boat" form, a quite different manner of paramagnetic shifts is seen. These peculiar paramagnetic shifts in Ni(AA)$_2$ and Co(AA)$_2$ systems will be discussed in the Discussion in terms of the effect of lone-pair orientation on the mode of odd electron distribution along σ bonds and in terms of the geometry of the coordinated complex. Along with these discussions the conformational stability of piperidine will be given in the Discussion.

Table II. Relative Proton Paramagnetic Shifts for Piperidines and Quinuclidine Complexed with Ni(AA)$_2$ or Co(AA)$_2$

Molecule	Relative paramagnetic shifts					
	Ni system			Co system		
	α-*ax*	α-*eq*		α-*ax*		α-*eq*
I	1.00	1.00		1.00		0.90
II	1.00	0.78		1.00		0.91
III	1.00	0.30		1.00		−0.18
	α-CH$_2$	β-CH$_2$	γ-CH	α-CH$_2$	β-CH$_2$	γ-CH
IV	1.00	0.12	−0.11	1.00	1.00	1.00

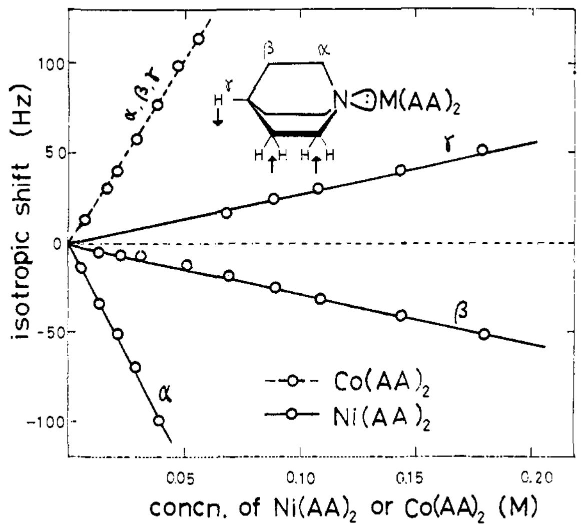
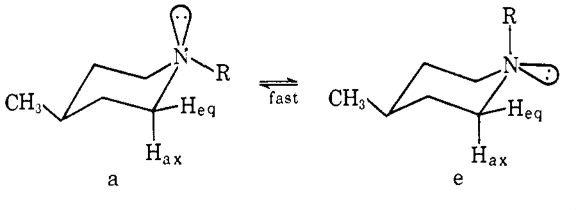


Figure 4. Plot of induced isotropic paramagnetic shifts *vs.* concentration of M(AA)$_2$ for methylene protons of quinuclidine.

Discussion

Effect of Lone-Pair Orientation in Ni(AA)$_2$ System. In piperidine derivatives there occurs ring inversion and inversion at the nitrogen atom.[4] At room temperature ring inversion is nmr slow, but nitrogen inversion is still fast for I, II, and III.[4] Accordingly, the chemical shifts of an axial and an equatorial proton are the averaged line position of each proton in lone-pair axial (*a*) and lone-pair equatorial (*e*) conformers



Then the ratio of the contact shifts, induced by the addition of Ni(AA)$_2$, for an axial and an equatorial proton, is given by

$$\frac{(\Delta\nu_{ax})_{\text{obsd}}}{(\Delta\nu_{eq})_{\text{obsd}}} = \frac{P_e(\Delta\nu_{ax})_e + (1 - P_e)(\Delta\nu_{ax})_a}{P_e(\Delta\nu_{eq})_e + (1 - P_e)(\Delta\nu_{eq})_a} \qquad (3)$$

where $(\Delta\nu_{ax})_{\text{obsd}}$ and $(\Delta\nu_{eq})_{\text{obsd}}$ are the observed contact shifts relative to the free ligand for an axial and an equatorial proton, respectively, and $(\Delta\nu_{ax})_e$ and $(\Delta\nu_{ax})_a$ are the contact shifts of an axial proton in the complex of the *e* conformer and the *a* conformer, respectively. P_e is the fraction of the lone-pair equatorial conformer (*e* conformer). $(\Delta\nu_{eq})_e$ and $(\Delta\nu_{eq})_a$ are the corresponding contact shifts of an equatorial proton. Now let us try to evaluate P_e with the aid of eq 3 using observed contact shifts and the appropriate assumptions on the relation between the values of $(\Delta\nu_{ax})_e$, $(\Delta\nu_{ax})_a$, $(\Delta\nu_{eq})_e$, and $(\Delta\nu_{eq})_a$. Since the axial and the equatorial protons in the *e* conformer and the equatorial proton in the *a* conformer are all in the same steric position with respect to the nitrogen lone pair, the contact shifts for these protons in the complex, $(\Delta\nu_{eq})_e$, $(\Delta\nu_{ax})_e$, and $(\Delta\nu_{eq})_a$, are tentatively assumed to be equal.[8a] The validity of this

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(8) (a) Contact shifts are simply related to odd electron-spin density that distributes itself on ligand proton in a manner similar to steric dependence of H–H coupling constant (ref 1b). (b) The observed contact shift ratio is taken from data for the Ni(AA)$_2$ complex system.

Table III. Fraction of Lone-Pair Equatorial Conformer

Piperidine	$\left(\frac{\Delta\nu_{ax}}{\Delta\nu_{eq}}\right)_{obsd}$	P_e (%)
I 3-Me	1.30 ± 0.10	87 ± 4
II 4-Me	1.28 ± 0.10	88 ± 4
III 1,4-diMe	3.36 ± 0.30	

Table IV. Fraction of Lone-Pair Axial and Equatorial Conformers Estimated by Various Methods

Investigator	Method	Piperidines	P_e (%)	P_a (%)	ΔG^* (kcal/mol)
LeFevre[a]	Kerr constant	(Morpholine)	87	13	1.1
Allinger[b]	Dipole moment	NH	33	67	−0.43
		NCH_3	7	93	−1.7
Lambert[c]	Nmr	NH	~100	0	
	Ir	NCH_3	0	~100	
Present author	Nmr contact shift	3-Me, 4-Me	88	12	1.2
		1,4-diMe	0	(~100)	

[a] R. J. LeFèvre, M. Aroney, C. Y. Chen, and J. D. Saxby, *J. Chem. Soc.*, 4269 (1964). [b] N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *Tetrahedron Lett.*, 3354 (1964); *J. Amer. Chem. Soc.*, **87**, 1232 (1965). [c] Reference 4.

assumption will be discussed in the later part along with an MO treatment. Equation 3 is then simplified as

$$\frac{(\Delta\nu_{ax})_{obsd}}{(\Delta\nu_{eq})_{obsd}} = P_e + (1 - P_e)\frac{(\Delta\nu_{ax})_a}{(\Delta\nu_{eq})_a} \qquad (4)$$

To obtain P_e with the aid of this equation, the value of $(\Delta\nu_{xa})_a/(\Delta\nu_{eq})_a$ for the *a* conformer is required, in addition to the observed value of $(\Delta\nu_{ax})_{obsd}/(\Delta\nu_{eq})_{obsd}$[8b] For this value we used the observed value for III in

$$\frac{(\Delta\nu_{ax})_a}{(\Delta\nu_{eq})_a} = \left(\frac{\Delta\nu_{ax}}{\Delta\nu_{eq}}\right)_{III} \qquad (5)$$

which the nitrogen lone pair is considered to be predominantly axial.[9]

From eq 3, 4, and 5, P_e can be estimated for I and II, and the results are given in Table III. Before discussing the results, it should be noted that the value of P_e obtained here is that for the case of complex formation. In Table IV are summarized the equilibrium populations of lone-pair axial (*a*) and lone-pair equatorial (*e*) conformers for several piperidine and related compounds estimated from various methods. Since populations are considered to be dependent on the nature of the medium, quantitative comparison of these results may be misleading. However, our result for the qualitatively dominant contribution of the lone-pair equatorial conformer in NH piperidine is parallel with the result for NH piperidine of Lambert[4] and for morpholine of LeFèvre.[10]

From above discussions, it can be concluded that the long-pair equatorial conformer predominates over the axial one in NH piperidine and *vice versa* in N-methyl piperidine.

Interpretation of the Contact Shift. The contact shift ratios for the protons of all the complexes studied are listed in Table II. The relationship between the contact shift and the nuclear spin–electron spin coupling constant is given by the equation[11]

$$\frac{\Delta\nu}{\nu} = -A_H\frac{\gamma_e g\beta s(s + 1)}{\gamma_H 3RT}$$

where γ_e and γ_H are the gyromagnetic ratios of the electron and proton, respectively, β is the Bohr magneton, *S* is the sum of the electron spins, A_H is the nuclear spin–electron spin coupling constant, $\Delta\nu$ is the contact shift relative to the free ligand, and ν is the probe frequency. The other symbols have their usual significance. The coupling constant A_H is related to the spin density, ρ_H, by $A_H = K\rho_H$, where *K* is a proportionality constant and ρ_H represents the spin density on the hydrogen atom in question. The value of *K* for Slater orbitals is 1596 G. The observed paramagnetic shifts in $Ni(AA)_2$ systems are predominantly contact shifts which are related to the spin density on the proton.[1,6,7] Thus, using the ratio of contact shifts in the $Ni(AA)_2$ system, we may obtain experimental ratios of spin densities to compare with our calculated results.

Spin density may reach the ligand protons by two opposing mechanisms.[1,6,7] (1) Positive spin density reaches the proton by direct electron delocalization which occurs due to the hydrogen contribution to the molecular orbital that has an unpaired electron. (2) Negative spin density may reach the proton from spin polarization effect which propagates along the bonds from the unpaired electron in the oriented nitrogen lone-pair orbitals. The delocalization mechanism gives rise to the downfield contact shifts of all the protons but the spin polarization mechanism leads to the alternating shifts attenuating in pairs along the bonds. In actual cases, these two mechanisms may be operative.

The attenuation and nonalternation of the signs of the contact shifts for alkyl protons except for the γ proton in quinuclidine indicate that a σ-delocalization mechanism is important. The most striking finding is the upfield contact shifts of the γ proton in quinuclidine. We are forced to conclude that, at least for the γ proton in quinuclidine, spin polarization effect plays an important role.[1] To further examine the odd electron distribution through six-membered rings, the measurement of proton contact shifts for the cyclohexylamine–$Ni(AA)_2$ complex was performed. The downfield contact shifts of all the ring protons (Table V) indicate that the spin delocalization mechanism is also important in the cyclohexylamine–$Ni(AA)_2$ complex. This is quite different from the proton contact shift ratio of the cyclohexyl group in an aminotroponiminate–Ni(II) complex (see Table V, compound V).[12] This different feature of contact shift may result from the difference in the source

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[9] Lambert, *et al.* (ref 4), have demonstrated by the means of nmr and ir that N-methyl piperidine as well as N-*t*-butyl piperidine exist predominantly in the form with the lone pair axial and piperidine exists predominantly, but not completely, in the form with the lone pair equatorial.

[10] See Table IV, footnote *a*.

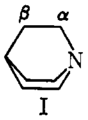
[11] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

[12] See Table V, footnote *d*.

Table V. Attenuation of the Proton Contact Shifts along Alkyl Chain

Ligand	α-CH_2	β-CH_2	γ-CH_2(CH)	References
I Quinuclidine	-1.00	-0.12	$+0.11$	Present study
II Piperidine	-1.00	-0.47	-0.11	*b* Present study
III Cyclohexylamine	-1.00	-0.06	-0.01	Present study
IV *n*-Propylamine	-1.00	-0.20	-0.007	*c*
V Cyclohexylamine(π)[a]	-1.00	$+0.20$	-0.05	*d*
VI *n*-Propylamine(π)[a]	-1.00	-0.068	-0.036	*d*

[a] The type of AO to be occupied by an odd electron. [b] Reference 6. [c] R. T. Fitzgerald and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 2523 (1968). [d] D. R. Eaton, A. D. Josey, and R. E. Benson, *ibid.*, **89**, 4040 (1967).



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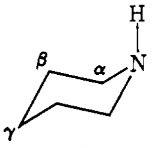

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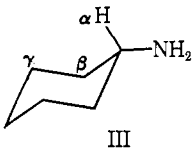

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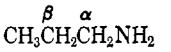
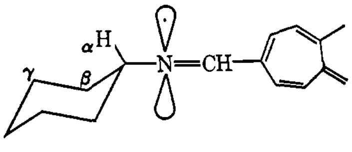
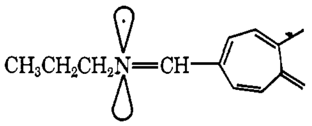


$\overset{\beta}{CH_3CH_2}\overset{\alpha}{CH_2}NH_2$

IV



V



VI

of spin density; in our case the unpaired electron is in the σ orbital while in the aminotroponiminate it is in a π-type orbital. Mode of attenuation of the contact shifts with the additional σ bonds is somewhat different for piperidine and quinuclidine. In Table V are summarized relative contact shifts of α, β, and γ protons together with other amine derivatives. The contact shifts of α and β protons in quinuclidine degrade more rapidly than those of piperidine and contact shifts for protons of N,N-di-*n*-butyl aminotroponiminate diminish along the alkyl chain considerably faster than those of piperidine, quinuclidine, and *n*-propylamine. For the former compound where the unpaired electron is a π type, direct transfer of the spin from the source of the spin density to the α proton may be facilitated by hyperconjugation and leads to the reduced value of the contact shift ratio for the β proton relative to the α proton. For the latter compounds in which N lone-pair Ni bonding is essentially the σ type, the above-mentioned hyperconjugative spin transfer is restricted, and the unpaired spin is delocalized directly into the σ system. The attenuation of the contact shift for cyclohexylamine is quite similar to that for aminotroponiminate, indicating that the hyperconjugative spin transfer to α-H may be important in the cyclohexylamine–$Ni(AA)_2$ complex.

Estimation of the Pseudocontact Shift in the $Co(AA)_2$ System. It is well established that in the $Co(AA)_2$ complex system the *g* tensor is anisotropic and there is the substantial pseudocontact interaction.[6,7,11] The observed isotropic paramagnetic shift in the $Co(AA)_2$ system is the sum of the isotropic contact shift and the anisotropic pseudocontact shift.[6,7] The pseudocontact shift is proportional to the geometric factor *f* which is determined by the geometry of the complex[6,7]

$$f = \frac{3\cos^2\theta - 1}{r^3}$$

where *r* is the radius vector from the Co atom to the resonating proton and θ is the angle between *r* and the *g*-symmetry axis which is directed to the lone-pair Co bond in the present case. Therefore, the ratio of the pseudocontact shifts for any two protons, the axial and the equatorial protons, for example, is equal to the ratio of the geometric factors for the corresponding protons. As is always the case we assumed that the ratios of the spin densities at the various protons (axial and equatorial) would be the same for the Co(II) and Ni(II) systems, and hence the ratios of the isotropic shifts due to the contact interaction would be the same in these two cases.[7] In order to assess the relative importance of the contact and pseudocontact interactions and to determine the geometric structure of the complex, we calculated the ratios of the expected pseudocontact shifts for the axial and the equatorial protons in the α-methylene group of the ligand. We calculated the average value of the geometric factor for each of the α-CH_2 protons to determine the role of pseudocontact shifts. The nitrogen lone-pair metal bond serves to determine the ligand field axis and deviations from axial symmetry were ignored. The bond lengths and angles used in estimating the geometric factor, *f*, are given in the following section. For the calculation of the pseudocontact shift, contributions of the two equilibrium conformers were taken into account. Here we used 12 and 88% for values of the fraction of *a*- and *e*-conformers, respectively, of I and II. In Figure 5, the calculated

Table VI. Estimation of Pseudocontact Shift

Ligands	Proton	$Ni(AA)_2$ observed shift (Hz)	$(3\cos^2\theta - 1)/r^3$ (Å^{-3})	$Co(AA)_2$ observed shift (Hz)	CS[a] (calcd)	PS[b] (calcd)	l[c](Å)
I 3-Me-piperidine	*ax*-CH	−6.7	0.01849	7.2	−6.2	13.4	2.0
	eq-CH	−5.3	0.01689	8.0	−4.8	12.8	
II 4-Me-piperidine	*ax*-CH	−9.1	0.01602	12.7	−5.8	18.5	1.8
	eq-CH	−7.0	0.01387	12.2	−4.5	16.7	
IV Quinuclidine	α-CH_2	−120.0	0.02144	96.0	−115.2	211.2	
	β-CH_2	−14.0	0.01113	96.0	−14.6	110.6	2.2
	γ-CH	+13.2	0.01004	96.0	−13.4	109.4	

[a] Contact shift. [b] Pseudocontact shift. [c] Length.

contributions of the contact shifts to the paramagnetic shifts ($Co(AA)_2 = 1.22 \times 10^{-2}$ mol/l.) are plotted against the metal–nitrogen bond lengths ranging from 1.6 to 2.6 Å. Table VI presents the predicted contribution of the contact and the pseudocontact shifts for I, II, and IV. Table VI also indicates that substantial pseudocontact shift contributes to the isotropic paramagnetic shift in the $Co(AA)_2$ system. When we tentatively assume that the spin densities on the ligand in the Co system are the same as those in the Ni system, the most probable Co–ligand lengths, l, are 2.0 and 1.8 Å for I and II, respectively, as is easily seen in Figure 5. These values are considered to be not so unreasonable for the metal–ligand bond length. It is of interest to note that the estimated value of l for I is slightly greater than that for II. This finding appears to reflect the steric inhibition between the methyl group and the coordinated $M(AA)_2$. Quite similarly we obtained the best values of l for the quinuclidine–$Co(AA)_2$ system. Figure 6 shows the variation of calculated contact shift with an increase in l. Adopting the same value of the contact shift for the $Co(AA)_2$ system as that for the $Ni(AA)_2$ system allows us to estimate the best fit value of 2.2 Å for l as is indicated in Figure 6. This value also appears to be reasonable for the length of a metal–nitrogen binding. These results may support our assumption that the relative spin density in the ligand molecule is the same for $Ni(AA)_2$ and $Co(AA)_2$ complex systems. The result that reasonable values of l were obtained for piperidine and quinuclidine–$Co(AA)_2$ complexes by the above procedure leads us to conclude that the contact shift is a dominant contribution in the $Ni(AA)_2$ system.

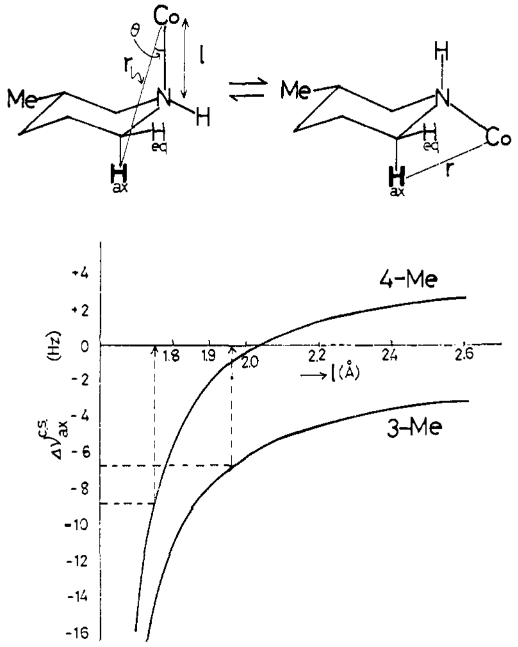


Figure 5. Plot of calculated contact shift contribution to the isotropic paramagnetic shifts in the $Co(AA)_2$ system *vs.* Co–nitrogen bond length, l, for 3- and 4-methylpiperidine.

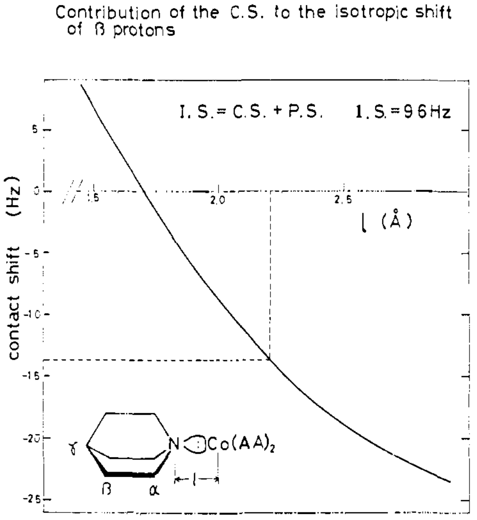


Figure 6. Plot of calculated contact shift contribution to the isotropic paramagnetic shifts in the $Co(AA)_2$ system *vs.* Co–nitrogen bond length, l, for quinuclidine.

Molecular Orbital Calculation and Mechanism of Spin Delocalization. To check the experimental ratios of the contact shifts, we attempted to carry out the molecular orbital calculation of the electron spin densities at various protons in piperidines and quinuclidine. Molecular orbitals were obtained by the extended Hückel theory (EHT).[1a] Bond angles and lengths for piperidine were estimated using structural parameters for cyclohexane. The geometry of quinuclidine was taken as[13]

C–C	1.543 Å	<C C C	106°06′
C–H	1.093	<N C C	112°54′
C–N	1.472	other angles	109°30′

The following values of the valence-state ionization potentials were used: H (1 S) = −13.6 eV, C (2 S) = −21.4 eV, C (2 P) = −1.14 eV, N (2 S) = −26.0 eV,

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(13) P. Bruesch, *Spectrochim. Acta*, **22**, 867 (1966).

and N(2 P) = −13.4 eV. The Slater orbital exponents were taken as H, 1.30; C, 1.625; and N, 1.950.

We attempted to calculate the relative electron spin densities at various protons in the ligand to compare with the experimental ratios of the contact shifts. The relative spin densities are obtained by the square of the coefficients of the ring protons in the highest filled MO (largely nitrogen lone-pair orbital) of an isolated molecule for simplicity.

This procedure is based upon the fact that the MO to be occupied by an odd electron in the complex becomes $a\phi_{\text{ho}} + b\chi_{\text{m}}$, so far as the interaction in the complex is weak, where ϕ_{ho} is the highest occupied MO of an isolated molecule and χ_{m} is an orbital belonging to a metal. The present method gives only positive spin densities which are delocalized in a lone-pair orbital and are proportional to the hydrogen contribution to this orbital. Although one should take into account spin-polarization effect in spin-density calculation for this kind of system, the relative importance of the spin-delocalization mechanism, which is observed experimentally, was checked qualitatively in this section.

The ratios of the spin densities, calculated as well as experimental, are given in Table VII. Spin density on the α-proton is referred to unity. Spin densities on axial and equatorial protons at the α position in piperidine were calculated for lone-pair axial and lone-pair equatorial conformers. Calculated spin-density ratios for α, β, and γ protons in each conformer were obtained from the average of those on axial and equatorial protons in the corresponding piperidine conformer. The calculated values of spin density ratios to compare with experiments were obtained by taking the weighted average of those for two conformers. In this calculation we take into account the populations $P_a = 12\%$ and $P_e = 88\%$ obtained in the previous section. The agreement is fairly good for α and β protons in both piperidine and quinuclidine and unsuccessful for the γ proton. The calculation leads us to except the contact shift ratios: $\Delta\nu_{ax}/\Delta\nu_{eq} = 3.02$ and $\Delta\nu_{ax}/\Delta\nu_{eq} = 0.70$ for *a* and *e* conformers of piperidine, respectively, while observed shifts for 1,4-dimethyl piperidine and 4-methyl piperidine are 3.36 and 1.28, respectively. Though the experimental values are not for pure *a* and *e* conformers the observed trend is well reproduced by theoretical calculations.

Table VII. Relative Spin Densities

	Proton	Relative spin densities Calcd	Relative spin densities Obsd
Piperidine			
	α-CH$_2$	1.00	1.00
e Conformer	β-CH$_2$	0.53	0.47
	γ-CH$_2$	0.46	0.11
	α-H(eq)	1.00	
	α-H(ax)	0.70	
	α-CH$_2$	1.00	1.00
a Conformer	β-CH$_2$	0.44	0.47
	γ-CH$_2$	0.23	0.11
	α-H$_{eq}$	1.00	(1.00)
	α-H$_{ax}$	3.02	(3.36)
1,4-Dimethylpiperidine			
	α-H$_{eq}$	1.00	1.00
a Conformer			
	α-H$_{ax}$	4.51	3.36

The negative spin density induced on the γ proton in quinuclidine is considered to be caused by the spin polarization mechanism. To yield negative spin density on the γ proton, MO calculation, which takes into account spin correlation is required. The EHT calculation yields very large values of positive spin density on the γ proton in quinuclidine. The unfavorable result of calculated spin densities for the γ proton has also been the case for the pyridine–Ni(AA)$_2$ complex where spin delocalization occurs through the σ-molecular orbital (lone-pair orbital).[14] The delocalized nature of the highest occupied lone-pair orbital, spread out to the γ proton by EHT calculation for pyridine, has been critically discussed.[14,15] These results suggest that the EHT calculations yield inaccurate highest field σ-orbital coefficients at the γ proton in piperidine, quinuclidine, and pyridine. However correct values for α and β protons can be obtained in these molecules.

With the calculated values of the relative spin densities for the α-methylene proton, we examine our assumption of a relation in contact shift ratios, $(\Delta\nu_{ax})_e = (\Delta\nu_{ax})_a = (\Delta\nu_{eq})_e$, which has been used for the evaluation of a fraction of the lone-pair-equatorial conformer in piperidines. Calculated values of spin densities of α-axial and α-equatorial protons in *a* and *e* conformers allow us to predict relative contact shifts

$$(\Delta\nu_{ax})_a:(\Delta\nu_{ax})_e:(\Delta\nu_{eq})_e = 1.00:0.91:1.12$$

Accordingly the above assumption is justified by MO calculations. Attenuation of spin densities along the σ bond for cyclohexylamine was checked by MO calculations. Table VIII contains the relative spin densities and contact shifts for cyclohexylamine, together with those for quinuclidine and piperidine. Attenuation is very rapid for III, compared with I and II. The experimental trend is well reproduced by calculations.

Table VIII. Relative Spin Densities

Compound		Relative spin densities Calcd[a]	Relative spin densities Obsd
	α-CH$_2$	1.00	1.00
I Quinuclidine	β-CH$_2$	0.147	0.12
	γ-CH	4.464	−0.11
II Piperidine	α-CH$_2$	1.00	1.00
	β-CH$_2$	0.539	0.47
	α-CH	1.00	1.00
III Cyclohexylamine	β-CH$_2$	0.045	0.06
	γ-CH$_2$	0.019	0.01

[a] By extended Hückel MO Method.

Table IX. Total Electronic Energies for Several Piperidines

Piperidines	Total electronic energy (eV) *a* Conformer	Total electronic energy (eV) *e* Conformer	ΔE(eV) ($E_{eq} - E_{ax}$)
NH	−641.8191	−641.8286	−0.0095
NMe	−746.5900	−745.8832	0.7068
4-Me, NH	−746.2045	−746.2156	−0.0111
1,4-DiMe	−850.9744	−850.2709	0.7035

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Finally we briefly discuss the relative stability of the axial and equatorial lone-pair conformers of piperidine derivatives in terms of the extended Hückel calculations. The total electronic energies calculated are summarized in Table IX. It is evident that the equatorial lone pair is preferred for NH piperidine and the axial lone pair for N-methyl piperidines. These results are consistent with our experimental conclusions.

The Stereospecific Addition of Carbon and Nitrogen Nucleophiles to Dicyclopentadieneplatinum and -palladium Complexes[1]

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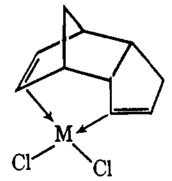
Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa 52240. *Received August 4, 1969*

Abstract: The nucleophilic additions of acetylacetone, ethyl acetoacetate, diethyl malonate, or benzylamine to the double bond of dichloro(*endo*-dicyclopentadiene)platinum(II) and of thallous acetylacetone to dichloro(*endo*-dicyclopentadiene)palladium(II) produced platinum- and palladium-carbon σ-bonded complexes. The *trans* additions take place at the 5,6-double bond without skeletal rearrangement of the dicyclopentadiene moiety; the nucleophile is attached *exo* with the metal *endo* and coordinated to the 2,3-double bond.

The addition of oxygen nucleophiles to the carbon–carbon double bond of olefin–platinum and -palladium complexes has received wide attention,[3-6] yet there is little information concerning the reactions of other nucleophiles with coordinated cyclic diolefins. More recently, the chemistry of the additions of other nucleophiles such as β-diketones,[7] diethyl malonate,[8] and amines[6,9] to diolefins have been reported. In these cases the addition to diolefin complexes of the general formula [(diene) – MX_2], where M is platinum or palladium, has taken place with the formation of carbon–carbon or carbon–nitrogen σ bonds and a metal–carbon σ bond. Usually only one of the two double bonds suffers addition; the remaining double bond provides coordination to the metal.

Results and Discussion

Because of the success in determining the stereochemical pattern[4] of the addition of oxygen nucleophiles to the rigidly cupped diolefins containing the bicyclo[2.2.1] skeleton, the dichloro(*endo*-dicyclopentadiene)platinum(II) and -palladium(II) complexes, **1** and **2**, respectively, were employed in this work. As in the case of addition of methanol to complexes **1** and **2**,[4] it was expected that the addition of other nucleophiles would take place at the more reactive norbornene double bond.



1, M = Pt
2, M = Pd

Carbon Nucleophiles. Acetylacetone. The addition of acetylacetone to dichloro(*endo*-dicyclopentadiene)platinum(II) was effected by stirring a suspension of the complex in acetylacetone in the presence of sodium carbonate. Prior preparation of the thallium salt is not necessary.[7b] When dichloro(*endo*-dicyclopentadiene)palladium(II) was treated similarly with acetylacetone, decomposition to metallic palladium occurred during the isolation procedure. However, a stable complex was prepared by allowing dichloro(*endo*-dicyclopentadiene)palladium(II) to react with thallous acetylacetonate at 0°. Both compounds had the general formula $(C_{10}H_{12})M(C_5H_7O_2)_2$. This is the general formula reported previously for the platinum complex, but the elucidation of the structure of the complex by the identification of the isomer obtained (of many possible) was not carried out.[7b]

The hydrogenation of the platinum complex to form **3** showed that the addition of acetylacetone to complex **1** had occurred at an olefinic bond by formation of a new carbon–carbon bond. The complex, suspended in methanol, was readily decomposed by hydrogen without the presence of an external catalyst; the double bond in the dicyclopentadiene ring is probably reduced by a platinum hydride species formed *in situ*. The 100-MHz nmr spectrum of **3** contains a well-resolved doublet centered at τ 6.65 (H_X). Although it was not

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[1] For a preliminary report of this work see J. K. Stille and Dale B. Fox, *Inorg. Nucl. Chem. Lett.*, **5**, 157 (1969).

[2] Abstracted in part from the Ph.D. Thesis of D. B. Fox, University of Iowa, Iowa City, Iowa, August 1969.

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