nickel complex, and the hyperfine term of eq 1 and 2 could contribute to signal broadening. If this were the predominant broadening mechanism, the line widths would be proportional to the square of the contact shift, since Δf^2 is proportional to A^2. This is true to a rough approximation for the α and β protons, but fails for the γ proton where the line width is much too large. Dipolar broadening must be even less significant at the γ position than at the α or β positions due to the $1/r^6$ dependence (eq 1 and 2). Thus the line width observed for the γ deuteron must result largely from quadrupolar effects. For Co(acac)$_2$·2py, the observed shifts are combined contact and dipolar shifts. Thus Δf's are not simply related to A's, and a comparison of Δf^2 with line width has no meaning. A trend apparent for Co(acac)$_2$·2py and to some extent for Ni(acac)$_2$·2py is that the most favorable line-width ratios are found for nuclei showing the broadest resonances, *i.e.*, the superior resolution of dmr shows up where most needed.

Signal assignments for Eu(thd)$_3$·py are made on the basis of signal areas and the magnitudes of isotropic shifts. The most downfield signal is assigned to the α-hydrogen, in analogy to the nickel and cobalt adducts discussed above where signal assignments are based on ring substitution.[32] The γ-hydrogen signal appears in solutions containing excess pyridine, but it apparently coincides with the *tert*-butyl resonance of thd at a 1:1 pyridine/Eu(thd)$_3$ ratio.

Conclusion

Dmr of most of the paramagnetic compounds investigated shows significantly improved resolution over the corresponding pmr spectra. In several instances for the M(acac)$_3$ complexes the vinyl hydrogen resonance is not apparent in the pmr spectra but shows up clearly in the dmr spectra. Reasonably well-resolved dmr spectra are found for complexes of Ti(III), Cr(III), and Fe(III), whereas pmr studies of complexes of these ions are not practical owing to extreme breadth of the resonances. The lower sensitivity of dmr over pmr proved not to be a handicap for these complexes. Although dmr line widths are narrower for all the complexes studied, in only a few cases does the pmr/dmr line-width ratio approach the value predicted by the Solomon–Bloembergen equations. It is likely that the deviations from theory result at least in part from insufficient corrections for electric quadrupole relaxation in dmr. However, accurate estimates of these corrections are not presently available.

Acknowledgment. The authors acknowledge partial support of this research from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Nuclear Magnetic Resonance Contact Shifts and Electron Spin Distribution. Proton and Carbon-13 Contact-Shift Studies of Azanaphthalenes

Isao Morishima,* Koji Okada, and Teijiro Yonezawa

Contribution from Department of Hydrocarbon Chemistry,
Faculty of Engineering, Kyoto University, Kyoto, Japan.
Received February 1, 1971

Abstract: The proton and ^{13}C contact shifts in quinoline and isoquinoline coordinated with paramagnetic nickel acetylacetonate (Ni(AA)$_2$) were studied by the ^{1}H (at 220 MHz) and ^{13}C (at 15.1 MHz) nmr spectroscopy. The alternating sign and attenuating magnitude of ^{1}H and ^{13}C contact shifts were plausibly substantiated by molecular orbital calculations (unrestricted Hartree–Fock INDO–SCF method) of electron spin densities on the proton 1s and carbon 2s atomic orbitals for model molecules, *i.e.*, 1- and 2-naphthyl radicals. The MO calculations showed that electron spin distributions on the proton and carbon s AO's in quinoline and isoquinoline are dominated by σ-electron effects. The identity of the mode of electron spin distribution between azanaphthalene–Ni(AA)$_2$ complexes and the corresponding hydrocarbon σ radicals was also discussed in terms of the potential utility of nmr contact shifts for N-containing molecules in the prediction of electronic structures of σ-hydrocarbon radicals.

The paramagnetic shifts induced by the interaction between an unpaired electron on a transition metal and the nucleus of the ligand coordinated to these ions have been the subject of recent nuclear magnetic resonance (nmr) studies.[1] A great deal of information has been deduced thereby concerning the manner of metal–ligand bonding, the geometrical structure of the transition metal complex, and the electronic structure of the ligand molecule. The six-coordinate nickel(II) and cobalt(II) complexes have been popular and relevant to the paramagnetic shift studies.[2] Most of these studies have dealt with proton paramagnetic shifts for π-conjugated ligand molecules.[2b,c]

We have previously reported the conformational or geometrical dependence of proton[3] and carbon-13

---

[1] D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965); E. De Boer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 111 (1967).

[2] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963); (b) W. D. Horrocks, Jr., R. C. Taylor, and G. N. La, Mar, *J. Amer. Chem. Soc.*, **86**, 3031 (1964); (c) R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **88**, 1399 (1966).

[3] (a) T. Yonezawa, I. Morishima, and Y. Ohmori, *ibid.*, **92**, 1267

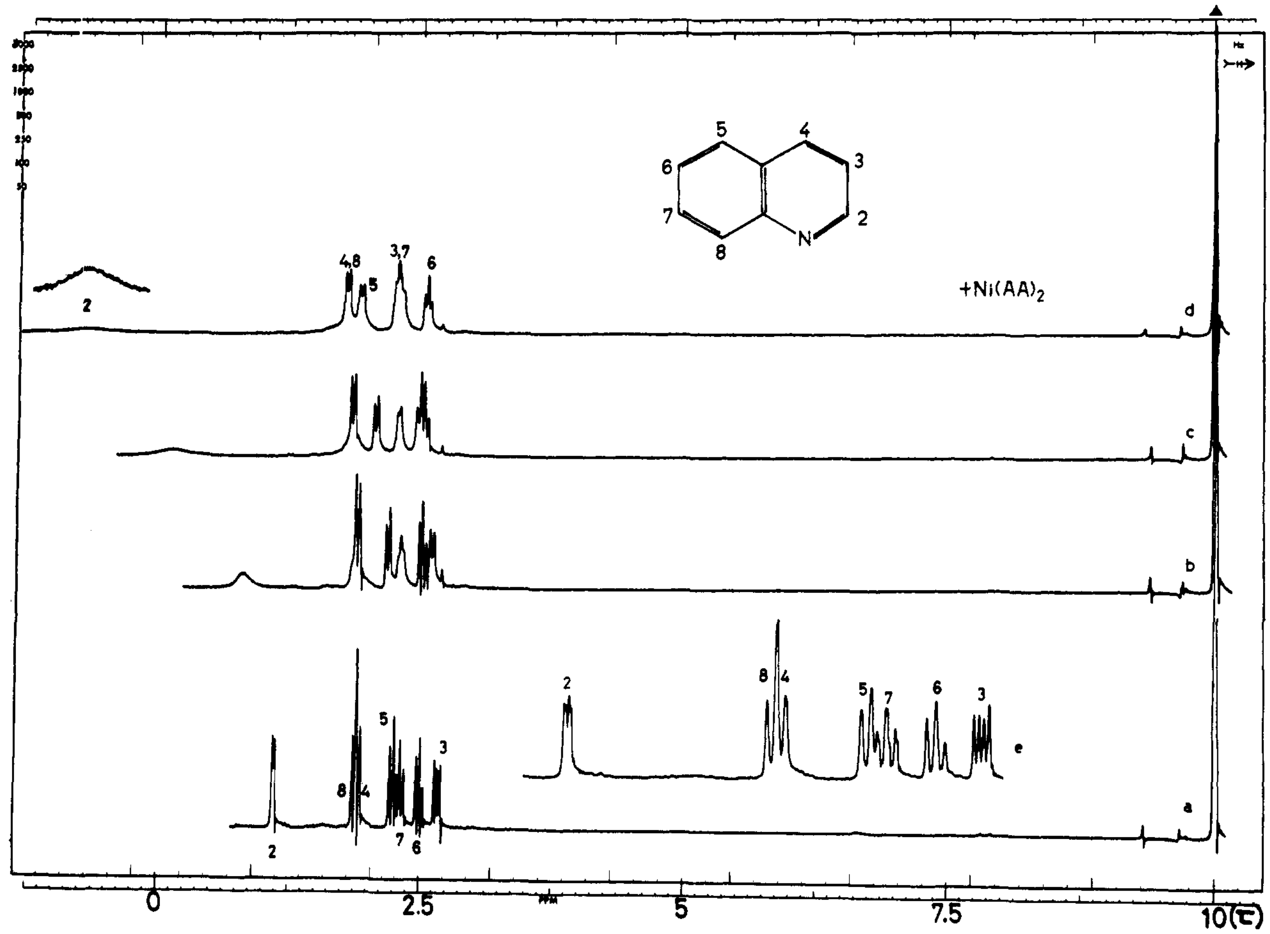


Figure 1. Pmr spectra of quinoline: (a) 10% $CDCl_3$ solution (v/v), (b–d) in the presence of varying amount of $Ni(AA)_2$, (e) 10% $CDCl_3$ solution (v/v), sweep width 1000 Hz (at 220 MHz).

contact shifts[4] for N-heterocyclic molecules (piperidine molecules) complexed with paramagnetic nickel acetylacetonate ($Ni(AA)_2$). These have been discussed in relation to the mode of electron spin distribution through the σ skeleton with the aid of molecular orbital calculations of spin densities. In the present study, we attempt to extend our investigation to the planar N-heterocyclic compounds, *i.e.*, quinoline and isoquinoline. Our major concerns in this study are to find the magnitude and sign of the contact shifts for aromatic ring protons and carbons separated by various types of planar σ bonds from the nitrogen lone pair and to search for a theoretical method which gives a plausible interpretation of ^1H and ^{13}C contact shifts in these paramagnetic complexes.

Experimental Section

Proton Nmr Measurements. Quinoline and isoquinoline were used as 10% (v/v) $CDCl_3$ solutions. Nmr samples were prepared by the addition of a given amount of $Ni(AA)_2$ to the $CDCl_3$ solution of the azanaphthalenes. All the proton spectra were obtained at 220 MHz using a Varian HR-220 spectrometer of our department. TMS was used as an internal standard. Assignment of well-separated proton signals was made by referring the spectral patterns and the dilution shifts from the neat liquid in which proton chemical shifts were determined by Pugmire, *et al.*[5] The spectra were taken at room temperature (24°) in the presence of varying amounts of $Ni(AA)_2$. The observed paramagnetic shift is relative to free ligand.

^{13}C Nmr Measurement. Completely proton-decoupled ^{13}C nmr spectra were obtained at 15.1 MHz on a Jeolco-C-60 HL spectrometer equipped with an IS-60 field–frequency synchronous sweep system of the proton irradiation frequency and an SD-HC heteronuclear spin decoupler. Spectra were measured in the external locking mode. Samples were made in 60% (v/v) $CDCl_3$ solution in an 8-mm sample tube. Chemical shifts were measured from external benzene. There was no significant difference in the ^{13}C resonance position of external benzene between the diamagnetic solution and the paramagnetic one. Therefore, the bulk susceptibility shift was neglected here in the determination of ^{13}C paramagnetic shifts. The observed ^{13}C paramagnetic shift is relative to free ligand. Accuracies of ^{13}C chemical shifts were within ±0.5 ppm. The concentration of $Ni(AA)_2$ in the $CDCl_3$ solutions ranged from 0.2 to 2 *M*. The assignment of the ^{13}C nmr of quinoline and isoquinoline was referred to the Pugmire's work.[5]

Results

Proton Contact Shifts. The proton signals of quinoline and isoquinoline were well separated in a diamagnetic solution (in the absence of $Ni(AA)_2$) in the 220-MHz nmr spectra. Figure 1 shows the signal changes of each proton as more $Ni(AA)_2$ is successively added to the solution of quinoline, for example, in $CDCl_3$. Only the H_6 signal exhibits an upfield shift; the others show downfield shifts. Figure 2 presents

---

(1970); (b) I. Morishima, K. Okada, M. Ohashi, and T. Yonezawa, *Chem. Commun.*, 33 (1971); (c) I. Morishima and T. Yonezawa, *J. Chem. Phys.*, **54**, 3238 (1971); (d) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc. Jap.*, **43**, 379 (1970).

[4] (a) I. Morishima, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, **92**, 6651 (1970); (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *Chem. Commun.*, 1535 (1970); (c) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, **93**, 3922 (1971).

(5) R. J. Pugmire, D. M. Grant, M. J. Robins, and R. K. Robins, *ibid.*, **91**, 6381 (1969).

Table I. ^{1}H and ^{13}C Contact Shifts for Quinoline and Isoquinoline

Molecule	Position	^{1}H chemical shift, τ[a]	^{1}H contact shift (rel)[b]	^{13}C chemical shift, ppm[c]	^{13}C contact shift (rel)[b]
Quinoline	2	1.10	−1.00	−22.65	+1.00
	3	2.66	−0.23	7.10	−1.14
	4	2.04	−0.08	−7.80	+0.23
	5	2.24	−0.18	0.07	−0.24
	6	2.50	+0.03	1.54	−0.07
	7	2.31	−0.04	−1.47	~0
	8	1.91	−0.08	−1.65	−0.40
	9			−20.55	−0.60
	10			−0.32	−1.03
Isoquinoline	1	0.77	*d*	−24.85	+1.00
	3	1.48	*d*	−15.25	+0.49
	4	2.44	*d*	7.79	−1.54
	5	2.27	+0.02[e]	1.55	~0
	6	2.39	−0.02[e]	−2.22	+0.23
	7	2.48	−0.04[e]	0.90	−0.19
	8	2.12	−0.03[e]	0.50	~0
	9			−0.72	−1.54
	10			−7.65	+0.28

[a] Diamagnetic reference positions observed at 220 MHz at room temperature in 10% (v/v) $CDCl_3$ solution. [b] Obtained from the relative values of the slopes of linear plots of observed ^{1}H or ^{13}C contact shifts *vs.* concentration of added $Ni(AA)_2$. The plus and minus signs denote upfield and downfield contact shifts, respectively. [c] Diamagnetic reference positions measured in 60% (v/v) $CDCl_3$ solution. Chemical shifts are given in parts per million from external benzene. [d] H_1, H_3, and H_4 signals show downfield, but the signal broadening was too great to get the precise values of the relative contact shift. The contact shifts for H_1 and H_3 were comparative in magnitude. [e] To make ready comparison between experimental and theoretical results, the relative contact shift for H_7 was taken as −0.04.

the linear plots of $Ni(AA)_2$-induced shifts *vs.* the concentration of added $Ni(AA)_2$ for quinoline. The spectra are time averaged between complexed and uncomplexed species, and the proton resonances of the ligand shift toward the resonance positions of the paramagnetic adduct.[1] Therefore, only the relative values of these shifts are significant in the present work. The relative values of $Ni(AA)_2$-induced paramagnetic shifts for quinoline and isoquinoline are summarized in Table I. In isoquinoline, the H_1, H_3, and H_4 signals show downfield shifts, but the signal broadening was too great to get the precise values of the relative paramagnetic shifts, even when the H_5, H_6, H_7, and H_8 signals were not perturbed by $Ni(AA)_2$. However, the relative contact shifts for H_1 and H_3 were comparable in magnitude. Even at 220 MHz, there was not sufficient separation between the 4, 5, 6, and 7 proton signals to follow the $Ni(AA)_2$-induced paramagnetic shift for the 4 proton. Therefore, the contact shifts for H_5, H_6, H_7, and H_8 are meaningful. To make ready comparison between experimental and theoretical results, the contact shift for the 7 proton was taken as a standard reference with the value of −0.04. Inspection of Table I shows that all the protons except for H_6 in quinoline and H_5 in isoquinoline exhibit downfield shifts, and only these two protons show upfield shifts in the $Ni(AA)_2$ systems.

As is well documented,[2,3] the isotropic shift in the $Ni(AA)_2$ system is predominantly due to the Fermi contact shift which is related to the electron spin density, ρ_H, induced on the proton. The downfield and upfield contact shifts correspond to the positive and negative spin densities on the proton, respectively. Therefore, the relative contact shifts in Table I mean the relative spin densities on the protons for quinoline and isoquinoline, although the signs are opposite.

^{13}C Contact Shifts. Perturbation of the ^{13}C nmr spectra of quinoline and isoquinoline by the addition of $Ni(AA)_2$ is shown in Figures 3 and 4, respectively. The signals of the carbons (C_3, C_8, and C_{10} in quinoline; C_4 and C_9 in isoquinoline) broaden quite rapidly when $Ni(AA)_2$ is added. These carbons exhibit pronounced contact shifts compared with other carbons. This is also the case for pyridine.[4a] Figure 5 gives the linear plots of the $Ni(AA)_2$-induced ^{13}C contact shifts and the $Ni(AA)_2$ concentration for isoquinoline, for example. Relative values of ^{13}C contact shifts were obtained from the slope of these linear plots, with the value for the particular carbon normalized to unity. The results are also summarized in Table I. Alternating ^{13}C contact shifts were obtained except for C_5 and C_9 in quinoline. This is quite different from the proton contact shift; most of the protons experience downfield contact shifts.

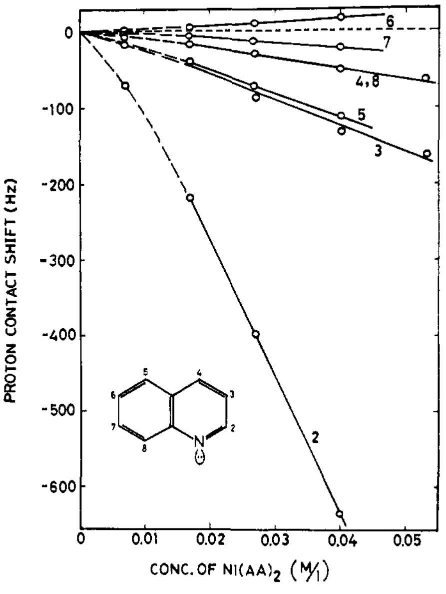


Figure 2. Plots of proton contact shift *vs.* the concentration of $Ni(AA)_2$ for quinoline.

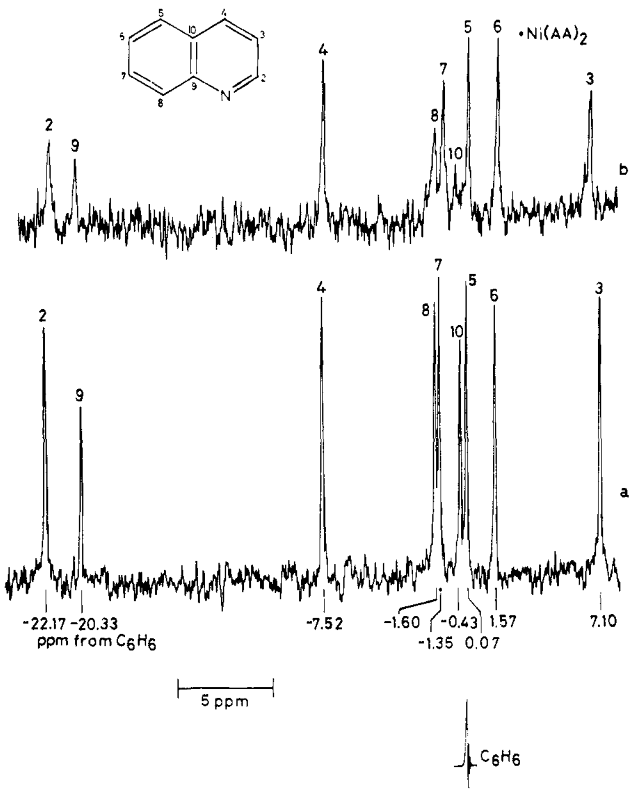


Figure 3. ^{13}C nmr spectra of quinoline in 60% $CDCl_3$ solution (v/v) (a) and in the presence of 0.5 *M* $Ni(AA)_2$ (b).

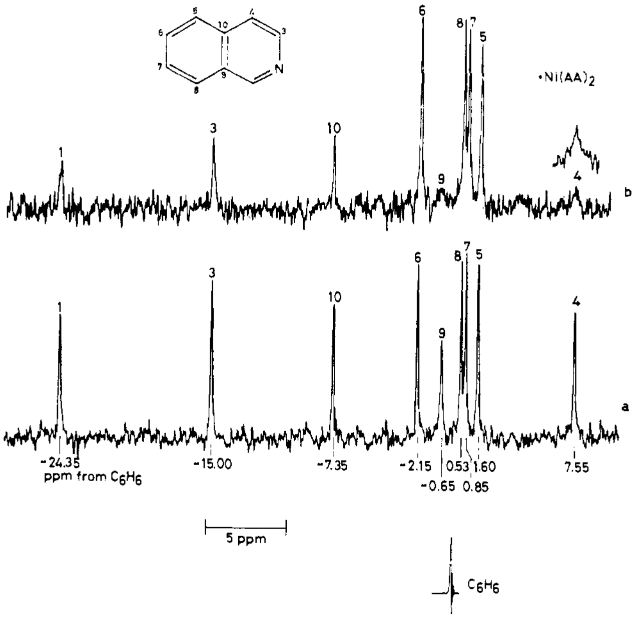


Figure 4. ^{13}C nmr spectra of isoquinoline in 60% $CDCl_3$ solution (v/v) (a) and in the presence of 0.5 *M* $Ni(AA)_2$ (b).

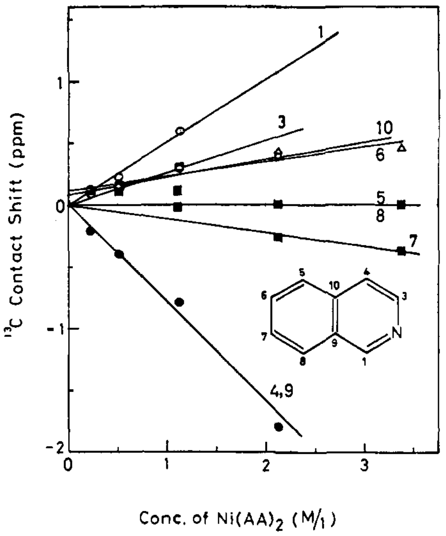
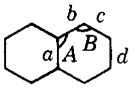


Figure 5. Plots of ^{13}C contact shifts *vs.* the concentration of $Ni(AA)_2$ for isoquinoline.

Molecular Orbital Calculations of Electron Spin Densities. In order to substantiate theoretically the observed ^1H and ^{13}C contact shifts for quinoline and isoquinoline, we calculated electron spin densities on the proton 1s and carbon 2s AO's for 1- and 2-naphthyl radicals which are expected to have the isoelectronic structure of quinoline and isoquinoline complexed with $Ni(AA)_2$.[4a] Previously we calculated[4c] spin densities for the cation radical of piperidine in which an electron is abstracted from the nitrogen lone-pair orbital of the free ligand molecule.[6] The sign and magnitude of ^1H contact shifts were fairly well reproduced by this calculation,[3b,6] but agreement is poor for the carbon contact shifts for piperidine derivatives.[4c] This difficulty is also encountered for pyridine; calculated relative spin densities on the carbon 2s AO's for pyridine cation radical are $\alpha:\beta:\gamma = -1.00:0.63:-0.52$, which should be compared with corresponding values of observed ^{13}C contact shifts of $-1.00:1.67:-0.45$.[4a] These difficulties have been improved by the model calculations of cyclohexyl[4c] and phenyl[4a] radicals for piperidine and pyridine, respectively, complexed with $Ni(AA)_2$.

We have performed unrestricted Hartree-Fock (UHF) MO calculations for naphthyl radicals using Pople's INDO-SCF method.[7] Bond lengths and angles (with lettering shown in I) used for MO calculations of naphthyl radicals are:[8] $a = 1.425$, $b = 1.410$, $c = 1.361$, $d = 1.420$, C-H = 1.085 Å, $A = 119° 14'$, $B = 120° 15'$. The calculated spin densities on the proton 1s and carbon 2s and $2_{p\pi}$ AO's for 1- and 2-naphthyl radicals are summarized in Table II. The agreement between contact shifts of azanaphthalenes and calculated spin densities (ρ_s) of naphthyl radical is excellent both for proton and carbon. The π spin densities ($\rho_{C_{2p\pi}}$) on the carbon are not correlated with observed proton and carbon contact shifts.



I

Discussion

(A) General Features of ^1H Contact Shifts and Calculated Spin Densities. Positive spin densities are induced on the protons except for H_6 in quinoline and H_5 in isoquinoline, which sense negative spin densities.

---

(6) Similar studies have been done by several workers: M. J. Scarlett, A. T. Casey, and R. A. Craig, *Aust. J. Chem.*, **23**, 1333 (1970); W. D. Horrocks, Jr., and D. L. Johnston, *Inorg. Chem.*, **10**, 1838 (1971).

(7) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

(8) D. W. J. Cruickshank, *Acta Crystallogr.*, **10**, 504 (1957).

Table II. Calculated Spin Densities on the H 1s and C 2s and 2pπ AO's for 1- and 2-Naphthyl Radicals

		Relative Value of Spin Density				
		^{1}H (ρ_{H1s})		^{13}C		
				ρ_{C2s}	$\rho_{C2p\pi}$	
Radical	Position	Calcd	Obsd[a]	Calcd	Calcd	Obsd[b]
1-Naphthyl radical	2	1.00	1.00	−1.00	−1.00	−1.00
		(0.0410)[c]		(−0.0074)[c]	(−0.0577)[c]	
	3	0.28	0.23	2.09	0.53	1.14
	4	0.25	0.08	−0.50	−0.72	−0.23
	5	0.18	0.18	0.06	−0.28	0.24
	6	−0.02	−0.03	0.13	0.27	0.07
	7	0.03	0.04	−0.19	−0.31	~0
	8	0.002	0.08	0.98	0.32	0.40
	9			−0.39	−0.47	0.60
	10			1.52	0.37	1.03
2-Naphthyl radical	1	1.00	*d*	−1.00	−1.00	−1.00
		(0.0403)[c]		(−0.0091)[c]	(−0.0576)[c]	
	3	0.87	*d*	−0.54	−0.56	−0.49
	4	0.28	*d*	1.21	0.52	1.54
	5	−0.02	−0.02[e]	0.22	0.22	~0
	6	0.02	0.02[e]	−0.12	−0.31	−0.23
	7	0.04	0.04[e]	0.18	0.25	0.19
	8	0.03	0.03[e]	0.04	0.29	~0
	9			1.59	0.37	1.54
	10			−0.27	−0.42	−0.28

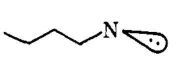
[a] Obtained from the ^{1}H contact shift. [b] Obtained from the ^{13}C contact shift. [c] The calculated value of the spin density is given in parentheses. [d] See footnote *d* of Table I. [e] See footnote *e* of Table I.

Table III. Observed and Calculated Hyperfine Coupling Constants and Relative Values of Spin Densities for Aryl Radicals

		a_H, G						
				Calcd				
Radical	Proton	Obsd[a]	Rel value	Kasai[a]	Ours[b]	Aza compound	Proton	Rel spin density[c] from contact shift
Phenyl	Ortho	17.5	1.00	17.85	17.79	Pyridine[d]	Ortho	1.00
	Meta	6.1	0.35	5.15	5.80		Meta	0.29
	Para	1.9	0.11	4.40	3.68		Para	0.08
1-Naphthyl	H_2	19	1.00	16.95	20.50	Quinoline	H_2	1.00
	H_3	6	0.32	5.10	5.81		H_3	0.23
	H_4	~2	~0.1	5.45	5.04		H_4	0.08
2-Naphthyl	H_1	15.7	0.80	16.90	20.13	Isoquinoline	H_1	*e*
	H_3	19.7	1.00	18.85	17.44		H_3	*e*
	H_4	5.8	0.30	4.95	5.73		H_4	*e*

[a] Ref 9. [b] See Table II. [c] From contact shifts. [d] Reference 4a. [e] See footnote *d* of Table I.

It is easily seen that the protons exhibiting downfield contact shifts lie in the "zigzag" arrangement of the σ skeleton, while those showing the upfield contact shifts lie in the "folded" arrangement of the skeleton.



zigzag

folded

The greater downfield shift of H_3 than H_8 for quinoline implies that the zigzag route is favorable for positive spin transfer by the spin delocalization mechanism.[2c] This is also recognized from the contact shifts for H_4, H_5, and H_8 of quinoline which are separated from nitrogen by four bonds: H_5 in the zigzag route (or "W" arrangement) exhibits the largest downfield contact shift. Of H_5 and H_7 in isoquinoline which are separated from nitrogen by five bonds, the one on the zigzag route (H_7) shows expectedly downfield contact shift while the other exhibits upfield shift. Therefore, the folded route favors the induction of negative spin density by the spin polarization mechanism. These stereospecific modes of proton contact shifts (namely, electron spin distribution) have also been encountered for saturated N-heterocyclic molecules of piperidine derivatives.[3] This general trend also indicates that electron spin transfer in the azanaphthalene–Ni(AA)$_2$ adduct seems to take place mainly through the σ-electronic effects. If π electrons take part in the spin distribution, upfield and downfield contact shifts (*i.e.*, negative and positive spin densities) would be induced alternately along the bond. This is also substantiated by calculation of spin densities; spin density on the carbon is not related to the proton spin density (Table II).

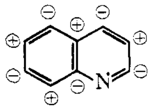
Since close agreement is obtained between observed ^{1}H and ^{13}C contact shifts in azanaphthalene and calculated spin densities in the corresponding naphthyl radicals, we further made a comparative study between contact shifts and the esr hyperfine coupling constant, a_H, of these radicals obtained recently by Kasai, *et al.*[9] The results are shown in Table III. The agreement between proton contact shifts for several aza compounds and a_H values for corresponding hydrocarbon σ radicals is satisfactory.[10] This shows the close identity of the

---

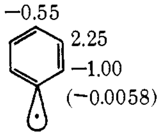
(9) P. H. Kasai, P. A. Clark, and E. B. Whipple, *J. Amer. Chem. Soc.*, **92**, 2640 (1970).

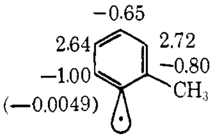
mode of electron spin distribution between N-containing molecules complexed with $Ni(AA)_2$ and the corresponding hydrocarbon σ radicals.[11]

(B) Features of ^{13}C Contact Shifts and Spin Densities on the Carbon Skeleton. Calculated spin densities on the carbon 2s AO's for 1- and 2-naphthyl radicals plausibly reproduce the observed trend of ^{13}C contact shifts of quinoline. The signs of the calculated spin densities are somewhat different from those predicted simply by the spin polarization mechanism which induces alternately positive and negative spin densities along the bonds. C_5 lying on the zigzag route from the nitrogen lone pair for quinoline senses positive spin density (downfield ^{13}C contact shift), which is reproduced by MO calculations but not by the prediction from the spin polarization mechanism. Signs of spin densities predicted by the spin polarization mechanism are shown below.

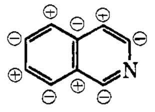


The planar zigzag arrangement is suitable for the transfer of positive spin density by a spin delocalization mechanism, which appears to be responsible for the observation of positive spin density on C_5. It is noted that α carbons (C_2 and C_9) in quinoline exhibit quite different behavior of the ^{13}C contact shifts; a downfield shift for C_2 was observed, while an upfield shift was seen for C_9. Observed positive spin density on C_9 in quinoline is not reproduced by INDO calculations. The spin polarization mechanism predicts a negative spin density on the C_9 atom. A similar discrepancy has been encountered for α-picoline (2-methylpyridine) complexed with $Ni(AA)_2$, in which the C_2 carbon showed a contact shift, while C_6 exhibited an upfield shift, the normal behavior of ^{13}C contact shifts as expected from the data for pyridine, the β- and γ-picolines.[12] INDO calculations of spin densities for 2-methylphenyl radical also fail to explain the downfield ^{13}C contact shift of C_2 in α-picoline. Introduction of a methyl group at the α position induces a positive trend of the spin density on the carbon (C_2), but still induces negative spin density. These anomalous features of ^{13}C contact shifts in quinoline and α-picoline may be caused by direct spin delocalization from $Ni(AA)_2$ onto C_9 and C_2, respectively.





The spin density distributions in isoquinoline are well explained by MO calculations for the 2-naphthyl radical. Carbons C_7, C_8, and C_9, lying on the zigzag route from the nitrogen lone pair, sense the positive spin density, as is the case for quinoline. The alternating positive and negative spin densities are induced on the other carbons, as expected by the spin polarization mechanism. The signs of the spin densities predicted by the spin polarization mechanism are shown below.



(C) A Correlation between Contact Shifts and Nuclear Spin Coupling Constants. Previously we reported[3c,13] a linear correlation between contact shifts and nuclear spin coupling constants in the molecules having similar σ-bond geometry. Here we will briefly discuss this relation for planar azanaphthalenes. The relative values of two vicinal coupling constants of naphthalene, $J_{H_1-H_2}:J_{H_2-H_3} = 8.1:6.4 = 1.0:0.79$,[14] is nearly equal to that of calculated spin densities on H_1 and H_3, $\rho_{H_1}:\rho_{H_3} = 1.0:0.87$ in the 2-naphthyl radical. Although accurate relative values of the contact shift of isoquinoline could not be measured owing to the line broadening effect, H_1 is expected to show a greater downfield contact shift than H_3 from above relation. The protons H_1 and H_3 in naphthalene interact with each other through the zigzag route, the favorable coupling path for H–H coupling. The fact that greater positive spin density is induced on H_3 in quinoline complexed with $Ni(AA)_2$ corresponds to relatively large meta coupling constant ($J_{H_1-H_3} = +1.1$ Hz).[15] The positive sign of $J_{H_1-H_3}$ corresponds to the above contact shift data. The small amount of contact shift for H_8 in quinoline corresponds well to the small value of the H_1–H_8 coupling constant ($J_{H_1-H_8} \simeq 0$). A favorable coupling path is associated with protons separated by five bonds in a planar zigzag arrangement, and an appreciable interaction (0.8 Hz) of this sytem has been observed between H_4 and H_8 in quinoline.[16] The sign of this type of coupling constant is found to be positive. This fact corresponds to the large contact shifts for H_5 in the quinoline–$Ni(AA)_2$ complex.

In summary, we conclude that the $Ni(AA)_2$ complex of an N-heterocyclic molecule has a mode of electron spin distribution quite similar to that of the corresponding hydrocarbon σ radical.

Acknowledgment. The authors are indebted to Jeolco, Tokyo, and Mr. K. Goto for the use of the ^{13}C nmr instrument. They also thank Dr. H. Nakatsuji and Mr. K. Hirao for the use of INDO–MO program.

---

(10) Kasai, *et al.*, calculated spin densities of the two α protons of the 2-naphthyl radical, ρ_{H_1} and ρ_{H_3}, by the INDO method and obtained a_H values with the aid of the relationship $a_H = 500\ \rho_H$, giving $a_{H_1} = 16.90$ G and $a_{H_3} = 18.85$ G. So they assigned two experimental values, 15.7 and 19.7 G, to a_{H_1} and a_{H_3}, respectively. We also calculated a_H values by the same method and obtained $a_{H_1} = 20.13$ G and $a_{H_3} = 17.44$ G, values quite different from theirs. This disagreement may be due to the different molecular geometries of the naphthalene skeleton. We used the geometry of the naphthalene skeleton determined by X-ray analysis, somewhat different from the benzene skeleton. If our result is adopted, the observed values of 19.7 and 15.7 G should be attributed to a_{H_1} and a_{H_3}, respectively.

(11) Correlation between contact shifts and epr hyperfine coupling constant has been studied for limited examples: (a) R. H. Holm, G. W. Everett, Jr., and W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, **88**, 1071 (1966); (b) E. E. Zaev, Y. N. Molin, G. M. Zhidomiron, and V. V. Voevodskii, *Dokl. Phys. Chem.*, **173**, 285 (1967).

(12) D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 6839 (1970).

(13) I. Morishima, K. Endo, and T. Yonezawa, *Chem. Phys. Lett.*, **9**, 203 (1971); *J. Amer. Chem. Soc.*, **93**, 2048 (1971). A similar study has been made by others; see ref 11b.

(14) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962).

(15) R. J. Abraham, E. O. Bishop, and R. E. Richards, *Mol. Phys.*, **3**, 485 (1960).

(16) F. A. L. Anet, *J. Chem. Phys.*, **32**, 1274 (1970).