

Electronic and Structural Effects on the ^{13}C Contact Shifts of σ -Bonded Molecules

By Kenichi Yoshikawa, Mikio Hashimoto, Hideki Masuda, and Isao Morishima,* Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

Carbon-13 n.m.r. contact shifts induced by nickel acetylacetonate have been observed for various nitrogen heterocyclic compounds in order to elucidate the manner of stereospecific electron spin transmission through the σ -bonded skeleton. It is revealed that the substituent at the α -carbon atom has a sensitive effect on the mode of the carbon-13 contact shifts. The experimental trend is discussed in relation to changes in the electronic structure of ligands or in metal-ligand bonding caused by the introduction of substituents. It is also found that hybridization of the nitrogen non-bonded orbital in ligand molecules plays an important role in intramolecular electron spin transmission. These results are discussed with the aid of molecular orbital calculations of electron spin densities.

We are currently interested in the stereospecificity of the mode of electron spin distribution through the carbon skeleton of σ -bonded molecules. We have previously reported the conformational or geometrical dependence of ^1H ^{1,3} and ^{13}C ^{2,3} contact shifts for nitrogen-heterocyclic molecules complexed with paramagnetic nickel acetylacetonate $[\text{Ni}(\text{AA})_2]$. In these studies, it has been revealed that the contact shifts are associated with electron spin densities distributed on the hydrogen and carbon atoms and are characteristic of axially or equatorially oriented nitrogen lone pair electrons, of chair or boat, and of 'zigzag' or 'folded' conformation of the

carbon skeleton. This stereospecific feature of ^1H and ^{13}C contact shifts has been discussed in relation to the mode of electron spin distribution through the carbon skeleton with the aid of molecular orbital calculations of spin densities.^{2c,d,3}

Recently there has been a great deal of paramagnetic shift reagent studies on organic molecules. Lanthanide shift reagents have proved to be quite useful in determining the complicated molecular structure, since the shifts induced by the lanthanide shift reagents are

¹ (a) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, 1970, **92**, 1267; (b) I. Morishima, K. Okada, M. Ohashi, and T. Yonezawa, *Chem. Comm.*, 1971, 33; (c) I. Morishima and T. Yonezawa, *J. Chem. Phys.*, 1971, **54**, 3238; (d) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc. Japan*, 1970, **43**, 379.

² (a) I. Morishima, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, 1970, **92**, 6651; I. Morishima, K. Okada, T. Yonezawa, and K. Goto, (b) *Chem. Comm.*, 1970, 1535; (c) *J. Amer. Chem. Soc.*, 1971, **93**, 3922; (d) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, 1972, **94**, 1425.

³ (a) I. Morishima, K. Yoshikawa, and K. Okada, *J. Amer. Chem. Soc.*, 1976, **98**, 3787; (b) I. Morishima and K. Yoshikawa, *ibid.*, 1975, **97**, 2950; (c) K. Yoshikawa, K. Bekki, M. Karatsu, K. Toyoda, T. Kamio, and I. Morishima, *ibid.*, 1976, **98**, 3272.

believed to be predominantly of pseudocontact origin. It has recently been pointed out⁴ that lanthanide induced shifts cannot be interpreted only by the pseudocontact model, especially for ¹³C n.m.r. paramagnetic shifts, and that there should be a sizeable contact contribution. However, the debate on this problem remains open to further studies. Therefore, it seemed important from this point of view to delineate the mode of ¹³C contact shifts for various carbon skeletons with recourse to paramagnetic shifts arising only from contact contributions.

In this paper we show the effects of substituents and hybridization of the nitrogen lone pair electrons in ligand molecules on features of ¹³C contact shifts through the σ -skeleton. These structural effects on the mode of electron spin distribution should be taken into account in addition to conformational or configurational effects when one is concerned with ¹³C contact shifts as a probe for determining geometrical or electronic structures of organic molecules.³ The paramagnetic systems examined here are complexes of Ni(AA)₂ with various nitrogen containing molecules. As ligand molecules we have chosen piperidines (*sp*³ lone pair), pyridines, aziridines, oxime, imine (*sp*² lone pair), thiazole, *N*-methylimidazole (hybridization between *sp*² and *sp*), and benzonitrile (*sp* lone pair).

It has been shown that the isotropic ¹³C paramagnetic shift in Ni(AA)₂ complexes is caused mainly by the contact interaction which is related to the electron spin density on the carbon atom. The ¹³C contact shift is expressed by equation (1)⁵ where the hyperfine coupling

$$\frac{\Delta H}{H} = -a_N \frac{\gamma_e g\beta S(S+1)}{\gamma_N 3kT} \quad (1)$$

constant a_N is given by (2) and ρ_{N_s} is the unpaired electron

$$a_N = \frac{4\pi}{3} g\beta\gamma_N\hbar \langle S_z \rangle^{-1} |\psi(r_{N_s})|^2 |\rho_{N_s}| \quad (2)$$

spin density on the ¹³Cs atomic orbital and the other symbols have their usual meanings. From this relationship the downfield and upfield shifts are obtained when positive and negative spin densities are induced on the ¹³C *s* orbital.

EXPERIMENTAL

Materials.—2-Methylpiperidine, α -picoline, 2-chloropyridine, 2-bromopyridine, 2-ethylpyridine, acetoxime, thi-

⁴ (a) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Stainforth, *Chem. Comm.*, 1970, 749; (b) B. F. G. Johnson, L. Lewis, P. McArdle, and J. R. Norton, *J.C.S. Chem. Comm.*, 1972, 535; *J.C.S. Dalton*, 1974, 1263; (c) M. Hirayama, E. Edagawa, and Y. Hanyu, *J.C.S. Chem. Comm.*, 1972, 1343; (d) R. J. Cushley, D. R. Anderson, and S. R. Lipsky, *ibid.*, p. 636; (e) M. Kainosho, K. Ajisaka, and K. Tori, *Chem. Letters*, 1972, 1061; (f) G. E. Hawkes, D. Leibfritz, D. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1973, **95**, 1659; (g) G. E. Hawkes, C. Marzin, S. R. Johns, and J. D. Roberts, *ibid.*, p. 1661; (h) O. A. Gawsow, P. A. Loeffler, R. E. Davis, M. R. Willcott, III, and R. E. Lenkinski, *ibid.*, p. 3389; (i) G. N. LaMar and J. W. Faller, *ibid.*, p. 3817; (j) R. M. Golding and M. P. Halton, *Austral. J. Chem.*, 1972, 2577; (k) J. Reuben and J. S. Leigh, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 2789.

azole, *N*-methylimidazole, and benzonitrile were commercially available and were dried over sodium hydroxide and distilled. 1,2-Dimethylpiperidine was prepared by the *N*-methylation of 2-methylpiperidine. *N*-Ethylacetoxime was prepared by the method of Campbell *et al.*⁶ 2-Methyl- and 2,3-dimethyl-aziridine were synthesized following the method of Cairns *et al.*⁷

¹³C N.m.r. Measurements.—Completely proton decoupled ¹³C n.m.r. spectra were obtained at 25.15 MHz on a JEOL PFT-100 system. After the 100–10 000 accumulations of the free induction decay induced by the 45° pulses with a repetition of 2–4 s, the Fourier transformed spectra were recorded. Samples were made in CDCl₃ solution in 8 mm i.d. sample tubes. The spectra were taken at room temperature (24 °C) in the presence of varying amounts of Ni(AA)₂. The ¹³C chemical shifts were measured with respect to internal tetramethylsilane.

¹³C Spectral Assignments.—The experimental values of the ¹³C chemical shift data are summarized in Table 1 for the nitrogen containing molecules used in this study. Each carbon signal of 2-methylpiperidine,⁸ 1,2-dimethylpiperidine,⁸ α -picoline,⁸ 2-bromopyridine,⁹ benzonitrile,⁹ acetoxime,⁹ thiazole,¹⁰ and *N*-methylimidazole¹¹ have already been assigned. With the aid of chloro-substitution parameters for benzene,¹² signal assignment of 2-chloropyridine is feasible. 2-Methyl- and 2,2-dimethyl-aziridine can be readily assigned by referring to the half-decoupled spectra.

RESULTS AND DISCUSSION

(a) **General Features of ¹³C Contact Shifts.**—As an example, the perturbation of the ¹³C shifts induced by the addition of Ni(AA)₂ is plotted against the concentration of added Ni(AA)₂ for 2-ethylpyridine in the Figure. The various carbon resonances are shifted from their normal diamagnetic values by an amount which is proportional to the concentration of added Ni(AA)₂. This implies that the exchange of ligand between complexed and uncomplexed sites are time averaged. Thus the ¹³C resonances of the ligand shift toward the resonance position of the complex as Ni(AA)₂ is added to the diamagnetic solution and the relative values of these paramagnetic shifts are of significance in the present study. The relative values for various carbon atoms in a ligand molecule were obtained from the slopes of the linear plot of the paramagnetic shift against the concentration of Ni(AA)₂, with the value for the α -carbon normalized to 1.00.

The relative ¹³C contact shifts for various ligand

⁵ H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, 1958, **29**, 107.

⁶ K. N. Campbell, A. H. Sommers, and B. K. Campbell, *J. Amer. Chem. Soc.*, 1944, **66**, 82.

⁷ T. J. Cairns, *J. Amer. Chem. Soc.*, 1941, **63**, 871.

⁸ I. Morishima, K. Yoshikawa, K. Okada, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, 1973, **95**, 165.

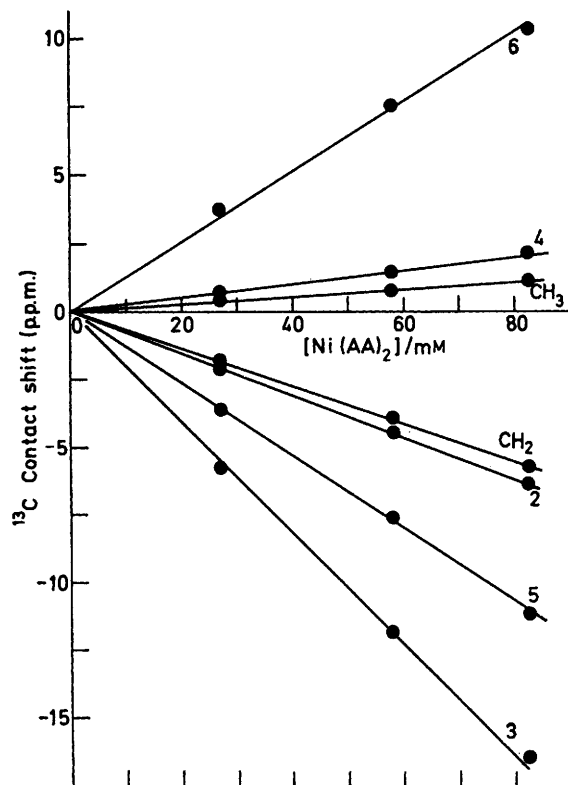
⁹ H. L. Retcotsky and R. A. Friedel, *J. Phys. Chem.*, 1967, **71**, 3592; 1968, **72**, 290, 2619.

¹⁰ L. F. Johnson and W. C. Jankowski, 'Carbon-13 NMR Spectra', Wiley, New York, 1972.

¹¹ R. J. Pugmire, D. M. Grant, L. B. Townsend, and R. K. Robin, *J. Amer. Chem. Soc.*, 1973, **95**, 2791.

¹² G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists', Wiley-Interscience, New York, 1972.

molecules are summarized in Table 1. The plus and minus signs of these values denote upfield and downfield shifts which correspond to negative and positive spin



Plots of isotropic paramagnetic ^{13}C shifts versus concentration of added $\text{Ni}(\text{AA})_2$ for 2-ethylpyridine

TABLE 1

Relative ^{13}C contact shifts for various nitrogen-containing molecules complexed with $\text{Ni}(\text{AA})_2$

Molecule	Position	$\delta^{13}\text{C}$ (p.p.m. from Me_4Si)	Relative ^{13}C contact shifts ^a
2-Methylpiperidine	2	52.9	+0.75
	3	35.4	-0.16
	4	25.8	+0.47
	5	26.9	-0.49
	6	47.8	+1.00 ^b
	CH_3	23.8	+0.30
1,2-Dimethylpiperidine	2	59.5	+0.65
	3	35.3	-0.56
	4	25.2	+0.12
	5	26.8	-0.42
	6	57.5	+1.00 ^c
	N-CH_3	43.5	+1.26
α -Picoline	2- CH_3	20.7	0.0
	2	157.9	-0.49
	3	122.4	-1.12
	4	135.3	+0.10
	5	120.0	-1.66
	6	148.7	+1.00 ^d
2-Ethylpyridine	CH_3	23.8	-0.59
	2	163.5	-0.59
	3	122.0	-1.53
	4	136.1	+0.20
	5	120.9	-1.00
	6	149.4	+1.00 ^e
	CH_2	31.5	-0.50
	CH_3	13.9	+0.11

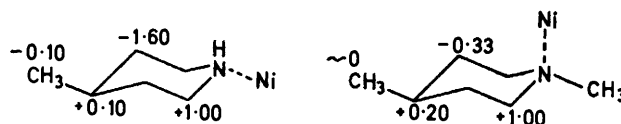
TABLE 1 (Continued)

Molecule	Position	$\delta^{13}\text{C}$ (p.p.m. from Me_4Si)	Relative ^{13}C contact shifts ^a
2-Chloropyridine	2	151.7	+0.59
	3	124.4	-0.90
	4	138.8	+0.05
	5	122.4	-0.82
	6	149.6	+1.00 ^e
	2-Bromopyridine	2	142.0
2-Methylaziridine	3	128.0	-0.88
	4	138.5	+0.05
	5	122.7	-1.01
	6	150.0	+1.00 ^e
	2	25.1	+0.60
	3	25.9	+1.00 ^f
2,2-Dimethylaziridine	CH_3	19.5	-1.32
	2	31.9	-0.58
	3	34.2	+1.00 ^g
Acetoxime	anti-CH_3	25.7	-0.66 ^h
	syn-CH_3	25.7	-0.75 ^h
	C=N	155.0	-1.00 ⁱ
Ethylisopropylidene-amine	anti-CH_3	14.9	-0.48
	syn-CH_3	21.5	-0.13
	C=N	164.8	-1.00 ^j
Thiazole	anti-CH_3	29.1	0 ^j
	syn-CH_3	30.5	0 ^j
	2	152.8	-1.00 ^k
<i>N</i> -Methylimidazole	4	118.7	-1.42
	5	143.4	-0.59
	2	137.7	-1.00 ^k
	4	129.1	-0.46
	5	120.1	-0.38
Benzonitrile	CH_3	33.2	-0.40
	C_α	118.8	-1.00 ^l
	C-1	112.4	-0.04

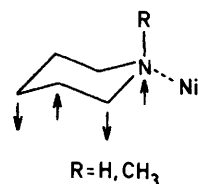
^a The plus and minus signs denote upfield and downfield contact shifts respectively. The relative shifts were obtained from the slope of the linear plot of the observed contact shift against the concentration of added $\text{Ni}(\text{AA})_2$. ^b The actual shift is ca. 5 p.p.m. $0.1\text{M-Ni}(\text{AA})_2$ in 29% v/v CDCl_3 solution. ^c The actual shift is ca. 1 p.p.m. per $0.1\text{M-Ni}(\text{AA})_2$ in 20% v/v CDCl_3 solution. ^d Ref. 13. ^e The actual shift is ca. 10 p.p.m. per $0.1\text{M-Ni}(\text{AA})_2$ in 20% v/v CDCl_3 solution. ^f The actual shift is ca. 10 p.p.m. per $0.1\text{M-Ni}(\text{AA})_2$ in 10% v/v CDCl_3 solution. ^g The actual shift is ca. 2 p.p.m. per $0.1\text{M-Ni}(\text{AA})_2$ in 10% v/v CDCl_3 solution. ^h In the spectrum of a solution of 2,2-dimethylaziridine, the two methyl carbons are observed to be equivalent due to rapid inversion of the nitrogen lone pair. Upon addition of $\text{Ni}(\text{AA})_2$, this signal becomes broad and separate. This implies that the rate of lone pair inversion is slowed in the presence of $\text{Ni}(\text{AA})_2$. Because of the non-linearity of the plots, the relative values of the carbon contact shifts of the two methyl carbons (*syn* and *anti*) are somewhat inaccurate. ⁱ The actual shift is ca. 1 p.p.m. per $0.1\text{M-Ni}(\text{AA})_2$ in 1M- CDCl_3 solution. ^j Signal broadening was too great to give a precise magnitude of the relative contact shifts. ^k The actual shift is ca. 10 p.p.m. per $0.1\text{M-Ni}(\text{AA})_2$ in 20% v/v CDCl_3 solution. ^l The actual shift is ca. 2 p.p.m. per $0.1\text{M-Ni}(\text{AA})_2$ in the 20% v/v CDCl_3 solution.

densities, respectively, induced on the ligand carbon s atomic orbital. As shown in Table 1 and previously reported ^{2c,d} for piperidines, $\text{Ni}(\text{AA})_2$ -induced ^{13}C contact shifts alternate in sign along the σ -skeleton.* The alternating ^{13}C contact shifts suggest the relative importance of the spin polarization mechanism (SP) of electron

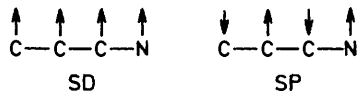
* For example, the relative ^{13}C contact shifts of the various carbons in 4-methyl- and 1,4-dimethyl-piperidine are:^{2c}



spin transmission through the carbon skeleton compared with the spin delocalization mechanism (SD).^{2c,d,3}

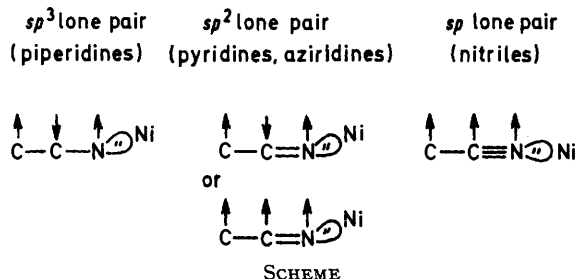


This has also been confirmed by molecular orbital calculations.^{2c,d,3}



For pyridine, alternating ¹³C contact shifts have also been obtained,^{2d,13} whereas non-alternating shifts are observed for α -picoline.¹³ Methyl substitution reduces the magnitude of the upfield contact shift for the α -carbon signal of piperidine derivatives, but changes its sign for α -picoline. A similar substitution effect is also encountered in ethyleneimines. The α -carbon signal of aziridine shifts to higher field as do both those of the

field contact shifts (Table 1). For nitriles with an *sp* lone pair, the α -carbon signal undergoes downfield contact shifts. From these experimental trends, the modes of the ¹³C contact shifts are represented as in the Scheme.



(b) *Substituent Effects on the ¹³C Contact Shifts.*—In order to gain further insight into the effects of methyl substitution on the ¹³C contact shifts discussed in the previous section, we obtained the relative values of the ¹³C contact shifts for 2-ethyl-, 2-chloro-, and 2-bromopyridines (Table 1). The high electronegativity of the halogen atom leads us to expect that these substituents affect the ¹³C contact shifts more than in the case of

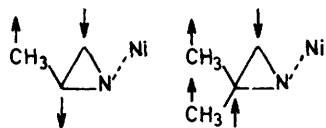
TABLE 2

Eu(fod)₃-Induced ¹H shifts of 2-substituted pyridine derivatives

Substituent	Relative value of Eu(fod) ₃ -induced shift ^a				Position of Eu(fod) ₃ ^b	
	3-H	4-H	5-H	6-H	r(Å) ^c	θ(°) ^d
None	-0.32	-0.35	-0.32	-1.00	2.4	0
Cl	-1.00	-0.68	-0.55	-1.00	2.3	16
Br	-0.88	-0.51	-0.35	-1.00	2.3	19
CH ₃	-0.63	-0.39	-0.44	-1.00	2.4	22

^a The plus and minus signs denote upfield and downfield shifts respectively. The relative shifts were obtained from the slope of the linear plot of the observed paramagnetic shifts. The shifts of 6-H are normalized to 1.00. ^b Estimate based on the McConnell-Robertson equation.¹⁴ Optimized positions are shown. Though the calculated positions are not so accurate,¹⁶ calculated results suggest considerable deviations of the N-Eu bond from the direction of orientation of the lone pair in α -substituted pyridine. ^c N-Eu distance. ^d Eu-N-C-4 angle.

α -carbons in 2-methylaziridine. Here, the shift of methyl-substituted carbon (C-2) is smaller than that of the other carbon (C-3). However, the methyl-substituted α -carbon (C-2) of 2,2-dimethylaziridine exhibits a downfield shift in contrast to the upfield shift for C-3.



The downfield contact shifts of the α -carbon are also obtained for imines and oximes and for the C-8a in quinoline.

For the five-membered ring compounds, thiazole and *N*-methylimidazole, in which the hybridization of the nitrogen lone pair electrons is considered to be between *sp*² and *sp*, both the α -carbons (C-2 and -5) show down-

* Doddrell and Roberts have suggested¹³ that the abnormal shift of C-2 of α -picoline may be caused not only by the electronic influence of the methyl group but also by the steric effects of metal-ligand bonding.

methyl substitution. However, it is found that these substituents only reduce the magnitude of the upfield α -carbon (C-2) contact shifts, which should be compared with that of the other α -carbon (C-6). Therefore, we speculated* that the abnormal shifts for the methyl-substituted α -carbon atoms may be caused not only by the electronic influence of methyl substitution but also by the steric effect of metal-ligand bonding and that the latter may dominate the electronic effect. To elucidate this steric effect, we tried to determine the position of the paramagnetic metal. From the n.m.r. spectra of Ni(AA)₂-ligand complex system where the contact shift contribution is most important, it is difficult to determine the position of Ni(AA)₂ directly. Thus, as a paramagnetic reagent, Eu(fod)₃ was chosen instead of Ni(AA)₂. In Table 2, Eu(fod)₃-induced shifts for 2-substituted pyridine are shown. On the basis of the McConnell-Robertson theory¹⁴ the pseudocontact shift

¹³ D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 6839.

¹⁴ H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361.

ΔH_{pcs} is given by equation (3) * where r_{ij} is the distance between Eu and the i th proton, θ_i is the angle formed by

$$\Delta H_{\text{pcs}} = K(3\cos^2\theta_i - 1)/r_{ij}^3 \quad (3)$$

this vector and the principal magnetic axis of the complex, and K is a constant. Using this relation, we calculated the position where the relative values $[(3\cos^2\theta - 1)/r^3]$, correspond best to the relative Eu(fod)³-induced shifts † (Table 2).¹⁷ The deviation from the C-4-N-1 axis (the direction of the lone pair orientation) in α -picoline (θ 22°) is larger than those in 2-chloro- and 2-bromo-pyridine (θ 16 and 19°, respectively). Strictly speaking, the position calculated from the McConnell-Robertson equation is somewhat different from the exact position because of the presence of the Fermi contact contribution.⁴ However, the large difference of the β -proton contact shifts (3- and 5-H in 2-substituted pyridines) implies that Eu-nitrogen atom bonding is shifted from the direction of the lone pair orientation. In comparison with this, it is expected that the steric hindrance of the methyl group is also large in the Ni(AA)₂-ligand system and that this steric influence may affect the mode of the ¹³C contact shifts of α -methyl-substituted carbons.

Next we discuss 'the electronic effect' of α -methyl substitution on the ¹³C contact shifts of the α -carbon. It has been established that the features of ¹³C contact shifts are well reproduced^{2c,d,3} by the electron spin

TABLE 3

Calculated spin densities on the carbon 2s atomic orbitals for σ -radicals (INDO-UHF)

Radical	Position	Relative value of spin density
2,2-Dimethylcyclopropyl ^b	2	-0.73
	3	-1.00
		(-0.006) ^a
2-Methylcyclohexyl ^c	<i>anti</i> -CH ₃	+1.07
	<i>syn</i> -CH ₃	+0.61
	2	-0.96
	3	+1.61
	4	-0.20
	5	+1.62
	6	-1.00
		(-0.007) ^a
	CH ₃	+0.44

^a The calculated value of the spin density is given in parentheses. ^b The bond lengths and angles used for the MO calculation are: C-H = 1.08 Å, C-C = 1.54 Å, C-CH₃ = 1.52 Å, $\widehat{\text{HCH}} = \widehat{\text{CH}_3\text{-C-CH}_3} = 118.2^\circ$. ^c The bond lengths and angles are: C-C = 1.54 Å, C-H = 1.09 Å; $\widehat{\text{C-C-C}} = \widehat{\text{C-C-H}} = 109^\circ 28'$.

distribution derived from MO calculations for the corresponding hydrocarbon σ -radical. We have previously carried out INDO-UHF MO calculations for the 2-methylphenyl σ -radical. In these calculations, the observed positive spin density on C-2 is not reproduced.

* Strictly speaking, this relation is not complete because of the assumption of axial symmetry. However, even in the detailed treatment the result may not change essentially.¹⁵

† Heigl and Mucklow¹⁶ reported a study concerning the position of lanthanide ion in substituted pyridines. They concluded the substituents at C-2 force the lanthanide complex to one side because of steric hindrance.

Introduction of a methyl group at the 2-position gives a positive trend to the spin density on C-2, but still results in negative spin density. INDO Calculations of spin densities for the 1-naphthyl radical also fail to explain the downfield ¹³C contact shift of C-8a in quinoline.²¹ In Table 3, calculated spin densities on the carbon s orbitals of 2,2-dimethylcyclopropyl radical are also shown. Here the dimethyl substituents reduce the negative value on the C-2 but negative spin density is still found. Thus, it may be concluded that the specific downfield shift of the methyl substituted α -carbon is mainly due to the change of metal-ligand bonding ('off-centre bond') caused by the steric effect of the methyl group. Such 'off-centre' bonding may change the mechanism of spin transmission from the nickel d orbital to the nitrogen atomic orbitals compared with normal nickel-amine complexes.¹⁻³ It may be also possible that a



'Off-centre bond' between nitrogen n and nickel d orbitals

pseudocontact contribution or direct spin transfer to the nearer α -carbon atom causes the abnormal ¹³C shift in the 'off-centre bonding' system. For further substantiation, a more detailed MO treatment which includes nickel d orbitals is required.

(c) *Influence of the Hybridization of the Lone Pair Electrons in Ligand Molecules on the Stereospecificity of Electron Spin Transmission.*—In order to discuss the influence of lone pair hybridization on the stereospecificity of electron spin transmission as pointed out in

TABLE 4

Calculated spin densities on C-2 2s atomic orbitals (INDO-UHF)

Radical	ρ_{UHF}	ρ_{SP}^a	ρ_{SD}^b
Ethyl ^c	-0.0104	-0.0126	+0.0022
Ethenyl ^d	-0.0175	-0.0236	+0.0061
Ethynyl ^e	+0.0054	-0.0163	+0.0218

^a Spin density induced by the spin polarization mechanism.

^b Spin density induced by the spin delocalization mechanism.

^c Bond lengths are: C-H = 1.09 Å, C-C = 1.54 Å. All bond angles are tetrahedral. ^d Bond lengths are: C-H = 1.07 Å, C-C = 1.31 Å. All bond angles are 120°. ^e Bond lengths are: C-H = 1.06 Å, C-C = 1.21 Å.

section (a), we performed INDO-UHF MO calculations of electron spin densities distributed on the carbon atoms of ethyl σ -radical, ethenyl radical, and ethynyl radical as models of C-N, C=N, and C≡N fragments complexed with Ni(AA)₂, respectively (Table 4). The negative spin

¹⁵ R. E. Cramer, personal communication.

¹⁶ T. Heigl and G. K. Mucklow, *Tetrahedron Letters*, 1973, 649.

¹⁷ T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato, *Chem. Phys. Letters*, 1968, 2, 454; *J. Chem. Phys.*, 1969, 51, 669; *Bull. Chem. Soc. Japan*, 1969, 42, 2437; H. Nakatsuji, H. Kato, and T. Yonezawa, *J. Chem. Phys.*, 1969, 51, 3175.

density on C-2 of ethyl σ -radical corresponds to the upfield ^{13}C shift of α -carbons in aliphatic amines. The downfield shift of the α -carbons of nitriles agrees with the calculated positive spin density for C-2 of ethynyl radical.

Nakatsuji *et al.*¹⁷ proposed a method to separate the spin density calculated with the UHF method into two components due to the SP (spin polarization) and the SD (spin delocalization) mechanisms. For doublet radicals $\rho_{\text{SP}} = 3/2(\rho_{\text{UHF}} - \rho_{\text{AA}})$ and $\rho_{\text{DS}} = \rho_{\text{UHF}} - \rho_{\text{SP}}$ where ρ_{AA} is approximately the spin density of the spin component of lowest multiplicity obtained by annihilation of the major contaminating component.

To gain further insight into the mechanism of electron spin transmission, we obtained the SP and SD contributions with the aid of the above procedures. The results are shown in Table 4. Here one should notice that in going from ethyl radical to ethynyl radical, the values of the SD contribution increase, and the ρ_{SD} of ethynyl radical is *ca.* 10 times as large as that of ethyl radical. This trend may be due to (1) the greater contribution of *s* atomic orbital in the radical orbital and (2) the shorter carbon-carbon bond length of ethynyl radical with

* It is well known¹⁸ that in aromatic radical ions (π -radicals), only the SP mechanism is important for electron spin transmission from a π -orbital to the neighbouring proton and that the SD contribution is essentially zero. This is an extreme case because the radical orbital includes no *s* atomic orbital contributions, and with increasing *s* character (bending of the radical centre) the SD mechanism becomes important.

respect to ethyl radical. On the other hand, the spin densities due to the SP mechanism (ρ_{SP}) do not differ so much from each other compared with the large variation in ρ_{SD} .*

From these calculated results, it may be concluded that the upfield contact shifts of the α -carbon of aliphatic amines and the downfield shifts of nitriles are attributable to the relatively larger contribution of the SP or SD mechanism, respectively. The anomalous features of ^{13}C contact shifts in compounds with sp^2 lone pair electrons may be explained as follows. For amines with sp^2 lone pair electrons, the contribution of the SP and SD mechanisms is comparable. Therefore, by a small perturbation, the direction of the contact shift (upfield or downfield) may change.

We conclude that Ni(AA)₂-induced ^{13}C n.m.r. contact shifts reflect quite sensitively the steric or electronic structures associated with the substituent and the hybridization of the nitrogen lone pair of nitrogen-containing molecules and, therefore, could serve as a quite sensitive probe for the elucidation of modes and mechanism of intramolecular electron spin transmission through σ -bonded skeletons.

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¹⁸ H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 764; H. M. McConnell and D. B. Chesnut, *ibid.*, 1957, **27**, 984.