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Nuclear Magnetic Resonance in Paramagnetic Solution. Proton Magnetic Resonance Studies of Some Substituted Aniline Derivatives in the Presence of Paramagnetic Ni(II) and Co(II) Acetylacetonates

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To study the geometrical and electronic structures of molecules, the paramagnetic shifts of substituted aniline proton resonances due to complexing with nickel or cobalt acetylacetonates, $M(AA)_2$ (M=Ni or Co), were observed. The NMR spectra of solutions containing an excess of aniline derivatives and $M(AA)_2$ show contact (for $Ni(AA)_2$) and pseudocontact (for $Co(AA)_2$) shift ratios for various ligand protons. The contact shift ratios for N-H and $N-CH_3$ protons reveal that the NH_2 or NHR group of aniline derivatives is not coplanar with the aromatic ring for the coordinated molecules. This was confirmed by pseudo-contact shift studies.

Recently we have been interested in the NMR spectra of solutions containing ligand molecules and the paramagnetic metal chelate.[1] The paramagnetic ("contact") shifts and the dipolar ("pseudocontact") shifts have been pointed out as being useful in the elucidation of the structure of the complex, the nature of metal-ligand bonding, and the mechanism of the odd-electron distribution.[1] From a simple observation of the relative contact shift of different protons in a ligand molecule with the oriented nitrogen lone pairs available for bonding with the metal, the electron-spin distribution occurring through the σ or π bond framework of a ligand molecule is made clear.[1d]

In the present work the paramagnetic contact and pseudocontact shifts of substituted aniline proton resonances due to complexing with nickel or cobalt acetylacetonate, $M(AA)_2$, were studied.

Previously Kluiber and Horrocks reported similar observations and discussed spin delocalization through a π-orbital in relation to a metal-ligand interaction.[2] In the present investigation, we have studied the configuration of such metal complexes from different points of view. We have indicated

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[1] a) D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonance*, **1**, 103 (1965). b) J. A. Hakpe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963). c) W. D. Horrocks, Jr., R. C. Taylor and G. N. LaMar, *J. Amer. Chem. Soc.*, **86**, 3031 (1964). d) T. Yonezawa, I. Morishima and Y. Ohmori, *ibid.*, **92** (1970), in press.

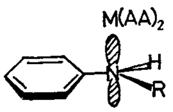
[2] R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, **6**, 431 (1967).

that the amino group coordinated to metal acetylacetonate is non-planar and has the hybridized nitrogen lone-pair orbital available for bonding with the metal.

Aniline may be considered to be a molecule of the general type of NH_2X, in which X is an unsaturated system which may act as an electron reservoir. A recent microwave study[3] has shown that the amino-nitrogen atoms in these types of molecules (aniline; $X=C_6H_5$; formamide, $X=CHO$; cyanamide, $X=CN$; nitramide, $X=NO_2$) retain, to a greater or lesser extent, pyramidal configurations.

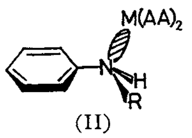
In the present investigation we have examined the orientation of nitrogen lone-pair electrons of aniline by a study of the paramagnetic proton shifts. For this study we have selected a series of substituted aniline derivatives (1—11) and examined the structures of complexes to determine whether they take a planar (I) or a non-planar structure (II).

Planar



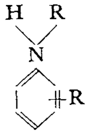
(I)

Non-Planar



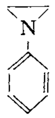
(II)

N-Phenyl aziridine (11) was used as the molecule with a typical non-planar structure (II) at the nitrogen atom.



	R	R'
1.	H	H
2.	H	o-CH_3
3.	H	m-CH_3
4.	H	p-CH_3
5.	CH_3	H
6.	CH_3	m-CH_3
7.	H	o-C_2H_5
8.	H	p-C_2H_5
9.	C_2H_5	H
10.	H	o-di$(CH_3)_2$

11.



The NMR spectra of solutions containing an excess of aniline derivatives and $M(AA)_2$ (M=Ni or Co) provide isotropic contact and pseudocontact shifts.[1b,c] The contact shift reflects the mode of the odd-electron distribution in which σ and/or π orbital are concerned, while the pseudocontact shift depends on the geometric structure of the complexed molecules.

It has been well established that induced paramagnetic shifts of protons of ligand complexed with $Ni(AA)_2$ come predominantly from isotropic contact interaction, while the corresponding shift for $Co(AA)_2$-complex system involves the shift due to both contact and pseudocontact interactions.[1] The contact interaction shift is described by Eq. (1):

$$\left(\frac{\Delta\nu}{\nu}\right)_i = \left(\frac{\Delta H}{H}\right)_i = -A_i\frac{\gamma_e}{\gamma_H}\frac{g\beta S(S+1)}{3kT} \qquad (1)$$

where A_i is the isotropic hyperfine contact interaction constant for the ith proton and where the other symbols have their usual meaning.[1] A_i is a measure of the amount of unpaired spin density at the ith proton. The other isotropic mechanism, the pseudocontact interaction (spin dipole-dipole interaction), may be important if there is an anisotropy in the g-tensor of the paramagnetic complex. The shift due to this cause is described by Eq. (2) for axially-symmetric molecules:[1]

$$\left(\frac{\Delta\nu}{\nu}\right)_i = \left(\frac{\Delta H}{H}\right)_i = -\frac{\beta^2 s(s+1)}{27kT}(g_{//}+2g_{\perp}) \times (g_{//}-g_{\perp})\frac{3\cos^2\theta_i - 1}{r_i} \qquad (2)$$

Here, θ_i is the angle between the ligand-field axis of the complex and the radius vector, r_i, from the metal atom to the ith proton, and $g_{//}$ and $g_{\perp}$ are g-factors parallel and perpendicular to the ligand-field axis respectively. In the present study, the metal-nitrogen bond serves to define the ligand-field axis.

For mono-N-substituted anilines, the relative contact shift of N-H and N-methyl protons was found to be nearly the same at that for alkyl amines. This is an evidence of a pyramidal structure of the amino-nitrogen atom of aniline derivatives. The preference for non-planar configuration of complexed anilines was further confirmed by pseudocontact-shift studies. The location of metal coordinated at the nitrogen atom was determined from the pseudocontact shift for the $Co(AA)_2$ system.

Experimental

All the chemicals except for the No. 11 compound were obtained from a standard commercial source (Tokyo Kasei Co.). The *N*-phenylaziridine was given kindly by Mr. Kondo of our department. Commercially-available $Ni(AA)_2$ and $Co(AA)_2$ were dried *in vacuo* over 24 hr at 55°C.

The proton spectra were obtained at 60 MHz for $CDCl_3$ solutions containing various amounts of ligand and $Ni(AA)_2$ or $Co(AA)_2$. A typical spectrum is shown in Fig. 1 from $CDCl_3$ solutions of $Ni(AA)_2$ and $Co(AA)_2$ containing excess *N*-methyl-*m*-methyl aniline. The paramagnetic shifts of benzene-ring and N-CH_3 protons were observed at 0.8 M ligand and 0.3 M $Ni(AA)_2$ (0.1 M $Ni(AA)_2$ for N-H protons) concentrations in deuterochloroform at room temperature, using tetramethylsilane as the internal standard.

Results and Discussion

The proton-resonance positions in a paramagnetic solution were shifted from a diamagnetic position to a higher or lower field by an amount proportional to the concentration of $Ni(AA)_2$ or $Co(AA)_2$. The large isotropic resonance shifts allow us to observe proton spin-spin splitting in the simplest, first-order spectra of aniline derivatives in the presence of $Co(AA)_2$ (see Fig. 1-c).

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[3] D. G. Lister and T. K. Tyler, *Chem. Commun.*, **1966**, 152.

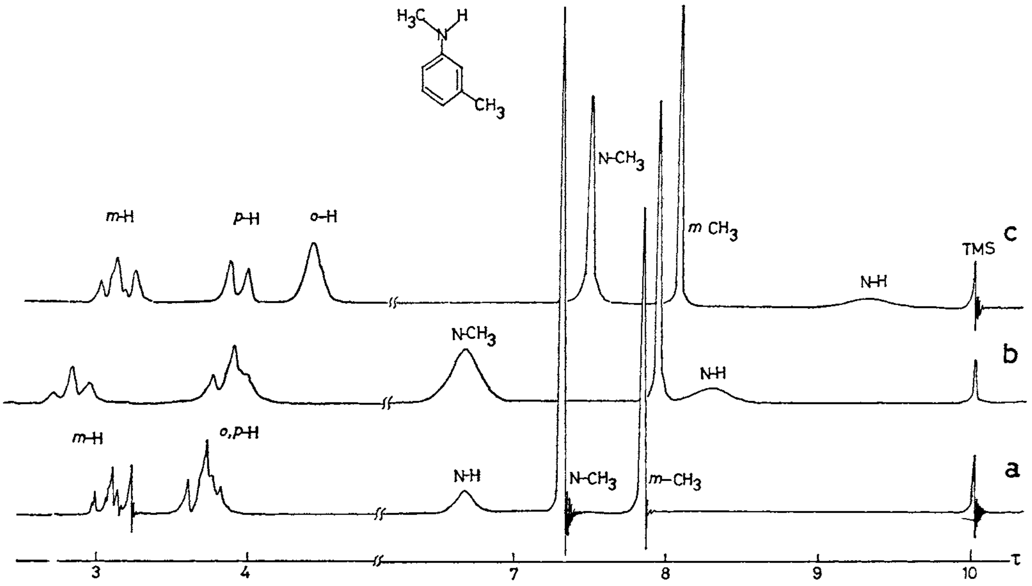

Fig. 1. Proton spectrum of *N*-methyl-*m*-methyl aniline alone and in the presence of Ni(AA)$_2$ or Co(AA)$_2$ in CDCl$_3$ solution.

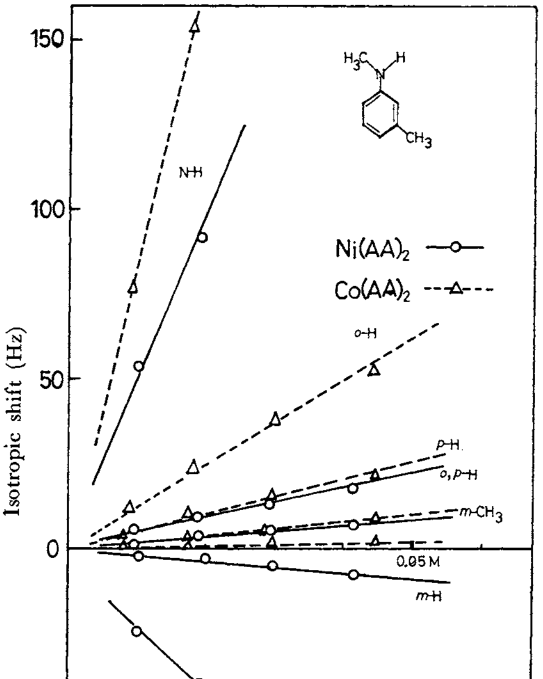

Fig. 2. Plots of the isotropic paramagnetic shifts *vs.* concentration of Ni(AA)$_2$ or Co(AA)$_2$ in CDCl$_3$ solution.

The observed coupling constants of *ortho-meta* and *meta-para* couplings for aniline are 7.5 Hz and 7.1 Hz respectively, for example. The observed isotropic shifts for ring and *N*-substituent protons are plotted against the amount of added M(AA)$_2$. A representative linear plot is given for *N*-methyl-*m*-methylaniline in Fig. 2. The concentration employed here ranges from 0 to 0.82 mol/*l* for ligand molecules and from 0 to 0.05 mol/*l* for M(AA)$_2$. The relative paramagnetic shifts for each proton are equal to the relative values of the slope of the linear plots for each proton. These values are given in Tables 1 and 2, taking the shift of the *ortho* proton in each molecule as 10.00. A positive or negative sign stands for an upfield or a downfield paramagnetic shift respectively. The N-H proton signal became broad and shifted strongly upfield for both nickel and cobalt systems. Phenyl-ring protons exhibit alternating upfield and downfield shifts with no attenuation, characteristic of π-orbital spin delocalization.[1c] The similar magnitudes but opposite signs for the contact shifts of a methyl group and a phenyl proton of the same position in aniline derivatives are also characteristic of the π-delocalization predicted by the theory of McConnell.[4] For the Co(AA)$_2$ system the corresponding proton resonance shifts are all upfield except for that of the *para*-methyl group. Unequal for *ortho* and *para* ring protons were observed, unlike as in the Ni(AA)$_2$ system. For both systems, mono- and di-*N*-alkyl anilines coordinate much less effectively

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[4] H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956); *ibid.*, **28**, 1188 (1958).

TABLE 1. RELATIVE ISOTROPIC SHIFTS IN ANILINES COMPLEXED WITH Ni(AA)$_2$

	R	R′	Absolute[a)] shift	Relative shfts							
				Ring proton			Aryl CH_3 or CH_2			NH	N-CH_3 or CH_2
				o	*m*	*p*	*o*	*m*	*p*		
1	H	H′	48.0	10.0[b)]	−4.17	10.0[b)]					
2	H	*o*-CH_3	30.4	10.0	−4.05	10.0	−6.80				
3	H	*m*-CH_3	44.0	10.0	−4.09	10.0		3.75			
4	H	*p*-CH_3	32.4	10.0	−4.44				−10.9		
5	CH_3	H	13.2	10.0	−4.75	10.0					−53.0
6	CH_3	*m*-CH_3	21.0	10.0	−4.28			4.14		119	−41.9
7	H	*o*-C_2H_5	44.0	10.0	−3.64	10.0	−6.14				
8	H	*p*-C_2H_5	47.7	10.0	−4.78				−8.00		
9	C_2H_5	H	9.6	10.0	−3.65	10.0				115	−16.2
10	H	*o*-$(CH_3)_2$	(43.0)		−3.95	10.0					
11	*N*-Phenylaziridine		27.7	10.0	−3.85	10.0					−47.5

a) Observed shift in Hz from diamagnetic position for ring *ortho* proton at 0.5 M ligand and 0.05 M Ni(AA)$_2$ concentrations in deuterochloroform.

b) Positions somewhat uncertain owing to overlapping of peaks.

TABLE 2. RELATIVE ISOTROPIC SHIFTS IN COMPLEXED ANILINES

	R	R′	Absolute[a)] shift	Relative shift							
				Ring proton			Aryl CH_3 or CH_2			NH	N-CH_3 or CH_2
				o	*m*	*p*	*o*	*m*	*p*		
1	H	H	120.0	10.0	0.53	4.83					
2	H	*o*-CH_3	107.0	10.0	0.67	5.32	1.50				
3	H	*m*-CH_3	139.0	10.0	0.55	4.75		2.03			
4	H	*p*-CH_3	113.0	10.0	0.47				−2.39		
5	CH_3	H	38.0	10.0	0.40	4.20					1.32
6	CH_3	*m*-CH_3	57.0	10.0	0.09	4.30		1.76		61.0	0.26
7	H	*o*-C_2H_5	122.0	10.0	0.77	4.83	2.05				
8	H	*p*-C_2H_5	176.0	10.0	0.37				−1.52		
9	C_2H_5	H	21.3	10.0		5.15					5.15(CH_2)
10	H	*o*-(CH_3)	35.0[b]		7.8[b)]	35.0		5.8[b)]			
11	*N*-Phenylaziridine		125.0	10.0	0.36	3.16					8.32(CH_2)

a) Observed shift in Hz from diamagnetic position for ring *ortho* proton at 0.5 M ligand and 0.05 M Co(AA)$_2$ concentrations in deuterochloroform.

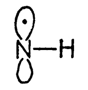
b) Absolute shift for *para* proton at 0.5 M ligand and 0.05 M Co(AA)$_2$.

with M(AA)$_2$ presumably because of steric effects, but the observed isotropic shift ratios for ring protons are almost the same as those observed for non-*N*-substituted anilines.

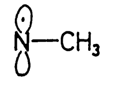
The N-H and N-CH_3 or N-CH_2 proton resonances exhibit different magnitudes and opposite signs for contact shifts in the Ni(AA)$_2$ system. If the amino group in the coordinated *N*-alkyl anilines takes a coplanar configuration, similar magnitudes but opposite signs for contact shifts of N-H and N-CH_3 or N-CH_2 proton resonances should be observed, as predicted by the theory of McConnell.[4)]

A metal-nitrogen bond of the planar configuration would involve a pure *p* atomic orbital on the nitrogen which is orthogonal to the σ-plane and would give rise to similar magnitudes but opposite signs for the contact shifts of N-H and N-CH_3 protons. However, the relatively small value of the observed contact shift for N-CH_3 protons compared with that for N-H rules out this expectation and suggests a non-planar configuration of the amino group for coordinated aniline derivatives.

Now let us enter upon a further quantitative discussion of this problem. The relative value of hyperfine coupling constants for N-H and N-CH_3 protons in which an electron spin is localized on the *p* atomic orbital of the nitrogen is given by McConnell's relation:[4)]



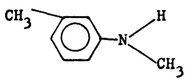
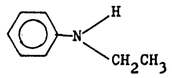
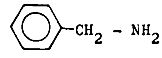
$$a_H = Q\rho_N$$



$$\frac{a_{CH_3}}{a_H} = \frac{Q_{CH_3}}{Q_H} \simeq 1.2$$

The value of a_{CH_3}/a_H can be obtained from the ESR studies.[5] The relative contact shifts for these protons become equal to this value. Table 3 gives the relative contact shifts for *N*-methyl- and *N*-ethylanilines, together with that for benzyl aniline reported by Fitzgerald and Drago.[6] The values are all very small compared with those predicted by McConnell's relation, but they are very close to the value for benzylamine with a non-planar configuration. The rapid attenuation of contact shifts for the N–CH_3 or N–CH_2 group appears to be due to spin delocalization through the σ system.[7,8] The above results and considerations strongly suggest a pyramidal configuration of the nitrogen atom.

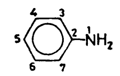
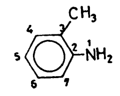
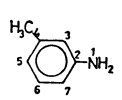
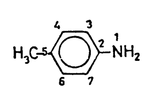
Table 3. The ratio of contact shifts for NH and NCH_3 or NCH_2 protons

Ligand	$\Delta\nu_{NCH_3}/\Delta\nu_{NH}$
	-0.35
	-0.14
	-0.33[a]

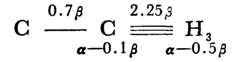
a) Taken from Ref. 6.

It should be noted that the value of $\Delta\nu_{CH_2}/\Delta\nu_{NH}$ is much smaller for *N*-ethylaniline than for the *N*-methyl derivative. This singularity is not due to the decrease in electron transfer by hyperconjugation in going from CH_3 to CH_2 groups, but to the more pyramidal nature of the configuration of

Table 4. Molecular orbital calculation of spin densities on aniline derivatives[a]

	Position		Spin densities Hückel method[b]	Relative values	McLachlan's method	Relative values
	*o*	3, 7	0.0773	10.00	0.0928	10.00
	m	4, 6	0.0020	0.26	-0.0303	-3.26
	p	5	0.0852	11.02	0.1043	11.24
		1 (N)	0.7389	95.59	0.7824	84.31
	*o*	3	0.0814	9.66	0.0980	11.51
		7	0.0843	10.00	0.0851	10.00
	m	4	0.0003	0.04	$\left.\begin{matrix}-0.0328\\-0.0256\end{matrix}\right\}-0.0292$	-3.43
		6	0.0047	0.56		
	p	5	0.0843	10.00	0.1025	12.10
		1 (N)	0.7265	86.18	0.7689	90.30
	*o*	3	$\left.\begin{matrix}0.0747\\0.0795\end{matrix}\right\}0.0711$	10.00	$\left.\begin{matrix}0.0891\\0.0964\end{matrix}\right\}0.0928$	10.00
		7				
	m	4	0.0022	0.29	-0.0290	-3.12
		6	0.0020	0.28	-0.0308	-3.32
	p	5	0.0874	11.33	0.1079	11.68
		6	0.7367	95.55	0.7800	84.05
	*o*	3, 7	0.0764	10.00	0.0904	10.00
	m	4, 6	0.0046	0.60	-0.0261	-2.89
	p	5	0.0879	11.50	0.1064	11.76
		1	0.7192	94.14	0.7607	84.14

a) Calculated by Hückel approximation with $\alpha_N = \alpha_C + 0.4\beta$, $\beta_{C-N} = 0.6\beta$. A hyperconjugative effect of methyl group is introduced by



$$\underset{\alpha-0.1\beta}{C \overset{0.7\beta}{\text{——}} C} \overset{2.25\beta}{\equiv} \underset{\alpha-0.5\beta}{H_3}$$

b) Obtained by the square of the AO coefficients in the highest occupied molecular orbital.

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[5] A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

[6] R. J. Fitzgerald and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 2879 (1967).

[7] R. J. Fitzgerald and R. S. Drago, *ibid.*, **90**, 2523 (1968).

[8] D. R. Eaton, A. D. Josey and R. E. Benson, *ibid.*, **89**, 4040 (1967).

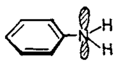
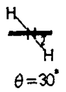
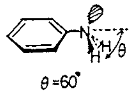
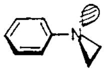
the *N*-ethyl group, in which the electron spin on the nitrogen atom transfers to the CH_2 proton through a σ delocalization mechanism with a rapid attenuation.

The lone-pair electrons on a nitrogen atom belong to the hybrid (sp^3) orbital, which can overlap with the π atomic orbitals of the phenyl ring; *i.e.*, the lone-pair AO need σ bonding with the metal is conjugated with other π-orbitals of the ligand. Therefore, the spin which is delocalized onto the ligand through the metal-ligand bond may be distributed in the ligand in a typical π-orbital pattern. The delocalized π-orbital occupied by an odd electron can involve either the highest occupied π-orbital (lone-pair orbital) or the lowest-vacant orbital of the ligand. These can be distinguished by comparing the observed contact shifts with the spin densities calculated by a molecular orbital method.

Table 4 shows that a relation can be observed between the experimental data and the spin-density distribution calculated for the highest occupied MO of the ligand. This means that the lowest vacant orbital which is antisymmetric to the molecular axis does not interact with the AO of the metal. The spin correlation is not explicitly included in the standard MO calculations, but small positive spin densities might become negative if spin correlation is introduced. The simplest method of estimating the effects of spin correlation is that of McLachlan,[9] in which the α and β spins are allowed to occupy separate Hückel-type orbitals. The results of this calculation are also shown in Table 4. Negative spin densities can be predicted at the *meta* position on the basis of the experimental results. A comparison of the experimental relative contact shifts with the theoretical relative spin densities shoes a fairly good agreement. The calculated values for *meta* position are generally somewhat lower than the observed values, particularly for *p*-methyl aniline. However, the correspondence between the spin-density distribution in coordinated *p*-methylaniline and that in the radical anion of its related compound, *N*,*N*-dimethyl-*p*-toluidine (Table 6), is fairly good. A comparison of the spin density distribution in coordinated molecules and in the corresponding radical anions leads to some other interesting conclusions (Table 6). For radicals, the spin density on a *para*-carbon atom is larger than that on a *ortho*-carbon atom. This is also true for the benzyl radical with an isoelectronic structure of coordinated aniline and its radical anion. This trend can be reproduced by a molecular orbital calculation (Table 4). Extended Hückel calculations including non-bonded interaction for planar and non-planar structures of aniline yield unequal spin densities on *ortho* and *para* protons (Table 5). However, the contact shifts for *ortho* and *para* protons are equal; this appears to be characteristic of the paramagnetic metal complex of aniline derivatives. An increase in the positive spin density (downfield contact shifts) on the *ortho* proton may result from additional spin delocalization through direct overlap between the metal *d* orbital and the proton 1*s* orbital in question.

Spin delocalization to the methyl or methylene

TABLE 5. MOLECULAR ORBITAL CALCULATION OF SPIN DENSITIES[a)]

	Positions	Spin densities	Relative spin densities	HO orbital energy (eV)	Total electronic energy (eV)
	*o*	0.1401	10.00		
	m	0.0282	2.01	−12.21	−648.7878
	p	0.2482	17.72		
	*o*	0.1279	10.00		
	m	0.0279	2.18	−12.24	−648.7009
	p	0.2332	18.23		
	*o*	0.1368	10.00		
	m	0.0306	2.24	−12.25	−649.1771
	p	0.0306	2.24	−12.25	−648.1771
	*o*	0.4076	10.00		
	m	0.0060	0.01	−11.46	−812.5641
	p	0.3949	9.69		

a) Calculations were made using extended Hückel method. Geometries for these calculations are referred to structural parameters in Table 9.

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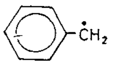
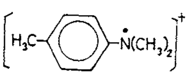
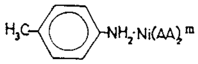
[9] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

Table 6. Relative h.f.s. constants and contact shifts for various protons of substituted aniline and related radicals

	Proton	a_H[c]	Relative values	Ref.
	*o*	5.14	10.0	a
	m	1.75	3.1	
	p	6.14	12.0	
	CH_2	16.35	31.6	
	*o*	5.21	10.0	b
	m	1.36	2.6	
	p-CH_3	9.97	15.5	
	N-CH_3	12.22	23.4	
	*o*		10.0	present work
	m		4.44	
	p-CH_3		10.0	

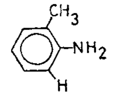
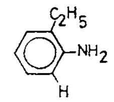
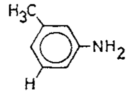
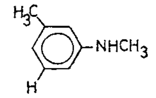
a) A. Carrington and I.C.P. Smith, *Mol. Phys.*, **9**, 137 (1965).
b) B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 5172 (1967).
c) In gauss.

group adjacent to sp^2-hybridized carbons containing an unpaired electron has been explained by hyperconjugation. A different value of Q should be found for each alkyl group. The Q value for the directly-bonded proton, Q_{CH}, is normally -22.5 G, while that for methyl group ranges from 29 G to 27 G.[10] We evaluated Q_{CH_3} or Q_{CH_2} values for alkyl groups attached to the phenyl ring, using the relation:

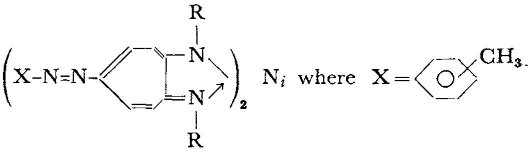
$$Q_{CH_3} = Q_{CH}\frac{a_{CH_3}}{a_H} = Q_{CH}\frac{\Delta\nu_{CH_3}}{\Delta\nu_{CH}}$$

where $\Delta\nu_{CH_3}$ and $\Delta\nu_{CH}$ are proton contact shifts for each position (*ortho*, *metha*, and *para*). This relation holds as long as the spin densities on the carbon atoms to which methyl or the proton is attached are equal. This is approximately verified by the MO calculations (Table 4). The Q values thus obtained are listed in Table 7. They decrease in the order: *m*->*o*-methyl>*o*-methylene protons. This trend probably reflects an interaction between the coordinated metal and the corresponding methyl or methylene group. This interaction is minimized for the *p*-substituted group, in which the substituent is located far from the metal. The Q_{CH_3} value for aminotroponiminate, in which such an interaction does not operate, shows a normal value of 27.0 G.[10] The Q_{CH_2} value is slightly smaller than the Q_{CH_3} value. This finding is considered to be due to the hindrance of electron transfer through hyperconjugation resulting from the steric interaction between the methyl or ethyl group and coordinated $M(AA)_2$.

Table 7. Q_{CH_3} or Q_{CH_2} value for substituted aniline derivatives

	Ligand molecule	Q_{CH_3} or Q_{CH_2}	
2		15.3	(14.9)[a]
7		13.8	
3		20.6	(27.0)[a]
6		21.8	

a) Taken from D. R. Eaton *et al.*, *J. Amer. Chem. Soc.*, **84**, 4100 (1962) for the system



and $R=C_2H_5$.

The isotropic shift data for $Co(AA)_2$ systems listed in Table 2 show an upfield shift for most of the protons. This upfield bias, compared with the

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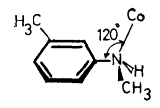
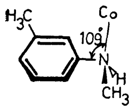
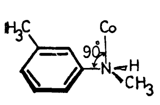
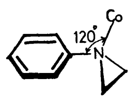
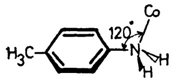
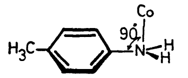
[10] D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips and T. L. Cairsn, *J. Amer. Chem. Soc.*, **83**, 4100 (1962).

TABLE 8. SEPARATION OF ISOTROPIC PARAMAGNETIC SHIFTS IN Co(AA)$_2$ SYSTEM INTO CONTACT AND PSEUDO-CONTACT SHIFTS

Co(AA)$_2$ Compex	l (Å)	Position	Relative value of $\left(\frac{3\cos^2\theta-1}{r^3}\right)$	I.S. (obsd)	P.S. (calcd)	C.S. (calcd)	C.S. (calcd relative)	C.S. (obsd)
	2.2	*o*	1.00	57.0	38.7	18.3	10.0	10.0
		m	0.215	0.5	8.3	−7.8	−4.3	−4.3
		p	0.161	24.5	6.2	18.3	10.0	10.0
		m-CH$_3$	0.095	10.0	3.7	6.3	3.5	4.1
		N-CH$_3$	1.80	1.5	69.6	−68.1	−37.3	−41.9
	2.2	*o*	1.00	57.0	38.7	18.3	10.0	10.0
		m	0.217	0.5	8.4	−7.9	−4.32	−4.3
		p	0.161	24.5	6.2	18.3	10.0	10.0
		m-CH$_3$	0.098	10.0	3.8	6.2	3.39	−4.1
		N-CH$_3$	1.58	61.2	−59.7	−32.6	−32.6	−41.9
	4.3	*o*	1.00	57.0	34.6	22.4	10.0	10.0
		m	0.185	0.5	6.6	−6.1	−2.7	−4.3
		p	0.072	24.5	2.1	22.4	10.0	10.0
		m-CH$_3$	0.050	10.0	1.7	8.3	3.7	4.1
		N-CH$_3$	1.61	1.5	58.9	−57.4	−25.6	−41.9
	2.0	*o*	1.00	125.0	101.0	24.0	10.0	10.0
		m	0.201	4.5	−15.8	−6.6	−6.6	−4.3
		p	0.155	39.5	15.5	24.0	10.0	10.0
		N-CH$_2$	1.60	10.4	161.4	−151.0	−63.0	−57.0
	2.8	*o*	1.00	113.0	80.3	32.7	(10.0)	10.0
		m	0.246	5.3	19.8	−14.5	(−4.45)	−4.45
		p-CH$_3$	0.106	−27.0	8.5	−35.5	−10.9	−10.9
		*o*	1.00	113.0	88.2	24.8	(10.0)	10.0
		m	0.185	5.3	16.3	−11.0	(−4.45)	−4.45
		p-CH$_3$	−0.008	−27.0	−0.8	−26.2	−10.6	−10.9

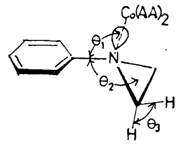
corresponding Ni(AA)$_2$ data, is due to the pseudo-contact effect, as has been well established for pyridine-type bases complexed with Co(AA)$_2$.[1b)]

Here we separate the contact and pseudo-contact shifts in Co(AA)$_2$ systems following the method of Horrocks.[1c)] The procedure is as follows. The basic assumption is that the spin density will distribute itself in a manner which is independent of the metal to which it is coordinated; that is, that the ratios of the spin densities at the various carbon atoms (*ortho*, *meta*, *para*) will be the same for the Co(II) and Ni(II) systems, and hence the ratios of the isotropic shifts due to the contact interaction will be the same in these two cases. The pseudo-contact shifts are related to each other by the ratio of calculated geometric factors:

$$\frac{3\cos^2\theta_i-1}{r_i^3} : \frac{3\cos^2\theta_j-1}{r_j^3}$$

The bond lengths and bond angles used in estimating the geometric factors listed in Table 8 are given in Table 9. The geometric factor is sensitive to the location of the metal with respect to the amino group, that is, to the metal-nitrogen bond length and to the M-N-C angle. Three angles (90°, 109°, and 129°) and several M-N distances for each angle were adopted. The best geometry was obtained when the agreement of the ratios of the corrected cobalt contact shifts and the observed nickel shifts was obtained. The observed Co(AA)$_2$ isotropic shifts, the necessary pseudo-contact shift correction, and the actual contact shifts for the cobalt complexes of some aniline derivatives are given for three typical geometries of the complex in Table 8. A sizable upfield pseudo-contact shift is evident for the substituted aniline complex of Co(AA)$_2$, implying that $g_{/\!/} < g_{\perp}$. The agreement

TABLE 9. STRUCTURAL PARAMETERS USED IN CALCULATING GEOMETRIC FACTORS AND MOLECULAR ORBITALS

Bond	Distance (Å)	Angle
N-C	1.37	*N*-phenylaziridine
N-CH$_3$	1.48	
C-C	1.40	
C-H (sp^2)	1.08	
C-CH$_3$	1.49	
C-H (sp^2)	1.09	
N-CH$_2$	1.49	
CH$_3$-CH$_2$	1.48	$\theta_1=\theta_2=\theta_3=120°$

is satisfactory for the non-planar structure with the M–N–C angle of 120° and the M–N distance of 2.2Å. For the planar structure (I), agreement is obtained only when the M–N distance has the unreasonably large value of 4.3Å. The same situation was found to be true for other aniline derivatives. In these circumstances, the planar structure is ruled out.

To further substantiate the structure of the complexed molecule, we examined *N*-phenylaziridine, for which the M–N–C angle is nearly fixed at 120° because of the hybrid orbital of nitrogen lone pairs. Satisfactory agreement is obtained for the configuration of the M–N–C angle of 120° and the M–N distance of 2.0 Å. The 2.0 Å distance appears to be acceptable for the metal-nitrogen coordination complex.

Thus, studies of contact and pseudo-contact shifts demonstrate conclusively that the geometry surrounding the nitrogen atom of the substituted aniline-M(AA)$_2$ coordination complexes (M=Ni or Co) is pyramidal and that the metal-ligand interaction is essentially σ. In aniline, the nitrogen lone pair is available for σ-bonding with the metal and can overlap with the π atomic orbital of the phenyl ring.

Let us now briefly discuss the non-planarity of the free aniline molecule. It seems premature to draw any firm conclusion about the non-planar structure of free aniline derivatives on the basis of the present study. There have been theoretical and experimental investigations of this problem.[11] From the electronic spectra and theoretical calculations, the configuration of aniline has not yet been established. However, molecular-polarizability (Kerr constant)[12] and microwave studies[3] have provided evidence for a pyramidal structure of the nitrogen atom in aniline. As to the *N*-substituted aniline, the ultraviolet spectra indicate that the N(CH$_3$)$_2$ group in dimethylaniline is bent out of the ring plane.[12] The angle between the ring-to-N bond and the NH$_2$ plane is found to be about 45°. This angle would be 54°44′ if the orbitals surrounding the nitrogen atom were oriented tetrahedrally.[11] The angle of nearly 60° found for the aniline-M(AA)$_2$ complex in the present study appears to be slightly larger than that for free aniline. This is probably the result of deformation due to metal-ligand complex formation.

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11) J. C. Brand, D. R. Williams and T. J. Cook, *J. Mol. Spectry.*, **20**, 193 (1966).

12) M. J. Aroney, R. J. W. LeFevre, L. Random and G. L. D. Ritchie, *J. Chem. Soc.*, *B*, **1968**, 507.

13) J. Raynaud and A. Lattes, *Compt. Rend.*, **254**, 4054 (1962).