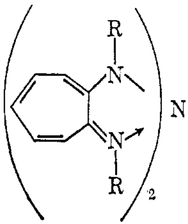
Unpaired Electron Distribution in σ Systems

D. R. Eaton, A. D. Josey, and R. E. Benson

Contribution No. 1281 from E. I. du Pont de Nemours and Company,
Central Research Department, Experimental Station, Wilmington, Delaware.
Received February 13, 1967

Abstract: Spin-density distributions in a number of alkyl- and carbonyl-containing groups have been investigated by the nmr contact shift method. Suitably substituted nickel(II) aminotroponeiminates have been synthesized for this purpose. In all cases discussed the unpaired electron is distributed from a π system into orbitals of σ symmetry. It reaches these orbitals by hyperconjugation, and this process is discussed. Various mechanisms are available for the further propagation of the spin in the σ system, and qualitative evaluations of the relative importance of these mechanisms in straight-chain, branched, and cyclic alkyl groups and in carbonyl compounds are presented.

In previous publications we have discussed the determination of spin-density distributions in organic molecules by measurement of nmr contact shifts.[1-3] For this purpose the nickel(II) aminotroponeiminates of structure I have proved to be a particularly useful series of compounds.



I

In solutions of these compounds there is a rapid equilibrium between square-planar diamagnetic and tetrahedral paramagnetic forms of the molecules.[4] The tetrahedral form has a very short electron spin relaxation time (T_1) which leads to the observation of sharp nmr resonances according to the condition

$$\frac{1}{T_1} \gg a_i \tag{1}$$

In this paramagnetic tetrahedral form there is π bonding between the unshared pair of electrons comprising the nitrogen lone pair and the single electrons in the d_{xz} and d_{yz} nickel orbitals. This results in the delocalization of some spin to the ligands, and each aminotroponeiminate residue can in fact be regarded as a free radical possessing approximately one-tenth of an unpaired electron. Contact interactions between the spin of the unpaired electrons and the nuclear spins of protons lead to shifts in the nmr resonance frequencies given by

$$\left(\frac{\Delta\nu}{\nu}\right)_i = \left(\frac{\Delta H}{H}\right)_i = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{3kT\exp[(\Delta F/kT)+1]} \tag{2}$$

In eq 1 and 2, a_i is the hyperfine coupling constant, $\Delta\nu$ is the change in resonance frequency, and ΔH the change in field at an applied frequency or field of ν or H, respectively. ΔF is the free-energy difference between the triplet and singlet forms of the molecule. The other symbols have their usual significance.

In the case of protons attached to sp^2-hybridized carbons, the hyperfine coupling constants a_i can be used to derive the spin densities in the carbon pπ orbitals from the equation

$$a_H = Q\rho_c \tag{3}$$

where Q is a constant (~ -22.5 gauss). The spin density distribution in the conjugated radical is thus determined.

In molecules containing a group X attached to an sp^2 carbon, where X contains protons or other nuclei with spins, it is convenient to define an effective Q_x by the equation

$$a_x = Q_x\rho_c \tag{4}$$

a_x is measured experimentally and ρ_c is obtained from the contact shift of a proton substituted at this carbon or an equivalent carbon. In most cases Q_x will not be the same for different positions of substitution of the group X.

Previous work with these compounds has been mainly concerned with the delocalization of spin in π molecular orbitals.[1-3] The nonlocalized character of such orbitals has long been recognized and has been the subject of much experimental and theoretical work. However, the electrons in the σ-bonding orbitals of saturated hydrocarbons, for example, have often been regarded as localized and contrasted with the π electrons of aromatic systems in this respect. Platt,[5] though, has pointed out that this is not really a valid distinction and that the real difference is that in σ systems a band of molecular orbitals is completely filled so that "it makes no difference to the electron density or the ultraviolet spectrum or the chemical behavior of the molecule whether we represent the individual electrons as being localized in particular bonds or as wandering throughout the system. Any wandering would be nonobservable." If, however, an electron is partly removed from such a filled band of σ orbitals, leaving a net unpaired spin, it becomes a valid question to ask whether

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(1) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

(2) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962).

(3) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962).

(4) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

(5) J. R. Platt, "Handbuch der Physik," Band XXXVII/2, Springer-Verlag, Berlin, 1961, p 183.

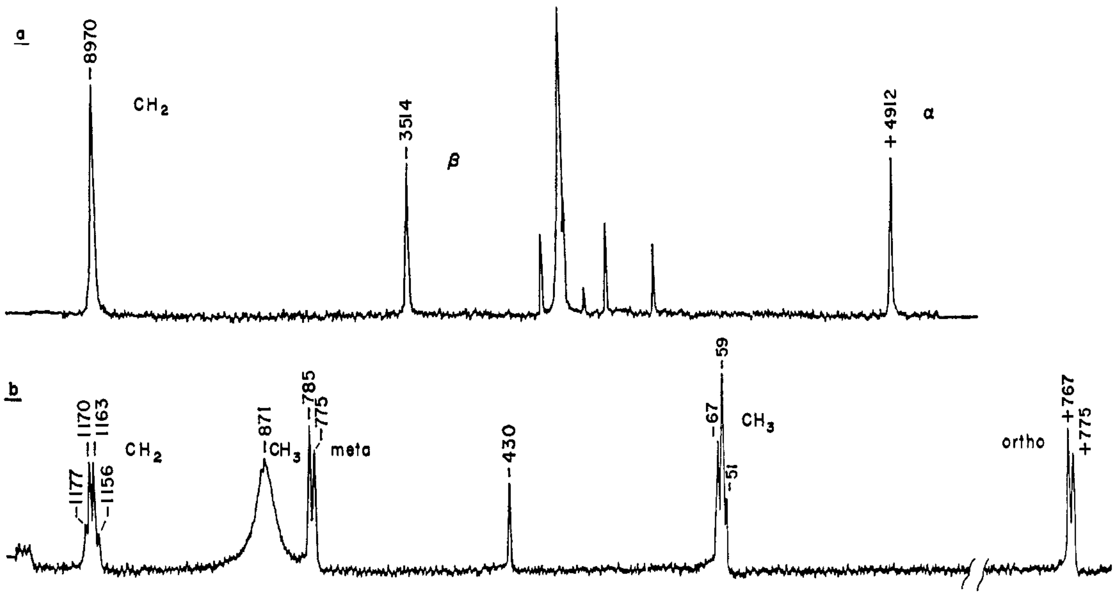

Figure 1. (a) Nmr spectrum of nickel(II) N,N′-diethyl-γ-*p*-ethylphenylazoaminotroponeiminate in $CDCl_3$ (room temperature, 60 Mcps). (b) Center portion of spectrum expanded.

the resulting hole is localized in one bond or whether it is distributed throughout the molecule. Partial removal of one of the σ-bonding electrons can be effected by interaction with an unpaired electron in a suitably oriented π orbital. Such an interaction would result from hyperconjugation between an alkyl group and a π molecular orbital. The question of hyperconjugation has been the subject of considerable discussion, and, as has been pointed out by Symons,[6] one of the most convincing experimental demonstrations of the phenomenon is found in the hyperfine interactions of aliphatic free radicals.

In the present paper data pertinent to several aspects of this problem are presented. Firstly, there is the question of transferring spin from the π system to the σ system. Examples of such hyperconjugative interaction with groups other than methyl are discussed. Secondly, the question of the transmission of spin density within the σ system of a normal alkyl chain is considered. Some examples involving saturated ring compounds are also examined since the question of direct electronic interactions across saturated rings has long intrigued chemists. Finally we consider several examples involving transmission of spin through a carbonyl group, since these interactions are also thought to be essentially σ in character.

Experimental Section

A. Nmr. Proton nmr spectra were obtained at 60 Mcps using a Varian HR-60 instrument. Except where otherwise stated the solvent was deuteriochloroform. The chelate solutions were internally referenced to tetramethylsilane to avoid bulk susceptibility corrections. Calibration was by the usual audiofrequency sideband technique. Contact shifts are defined as the difference in frequency between corresponding protons in the nickel chelate and the diamagnetic zinc chelate or ligand. The assignments of the protons presented few ambiguities in the present compounds and are based on spin–spin multiplets (where observed), the relative intensities of the resonances, and intercomparisons among related compounds in the manner described more fully previously.[1] The spectrum of nickel(II) N,N′-diethyl-γ-*p*-ethylphenylazoaminotroponeiminate is shown in Figure 1 as an example of the chelate spectra.

In some cases where the nickel chelate was not readily available, data were obtained by examining a solution containing nickel(II) N,N′-diethylaminotroponeimineate and the appropriate ligand. Ligand exchange leads to a complex spectrum containing resonances arising from both symmetric chelates and the mixed chelate. The analysis of such spectra has been described previously.[7] Cases where this technique has been used are noted in Table I.

Relative spin densities can be obtained from the contact shifts at room temperature. These are the parameters of primary interest in the present work. Absolute values of pπ spin densities were obtained either by measuring the temperature dependences of the resonances and calculating the shifts for a fully paramagnetic chelate or by assuming $\rho_{H\beta} = -0.0210$. This latter assumption is thought to be correct to ±5% on the basis of extensive studies of the temperature dependence reported elsewhere.[4]

B. Synthesis. The preparation of N,N′-disubstituted aminotroponeimines and their metal chelates has already been described.[1,8] The reaction of 5,5,6,6-tetrafluorocycloheptadiene with the appropriate primary amine, RNH_2, constitutes a general synthesis which was applied to the preparation of those compounds in Table I with an unsubstituted seven-membered ring. Amines not commercially available were prepared by standard procedures.

The quaternary salt **3** was prepared by alkylation of the *p*-dimethylaminophenyl derivative[8] with methyl iodide as follows. A solution of 1.8 g (0.005 mole) of N,N′-bis(*p*-dimethylaminophenyl)aminotroponeimine in 20 ml of chloroform containing 2 ml of methyl iodide was allowed to stand for 48 hr. The yellow crystalline methiodide was collected, washed with fresh solvent, and vacuum dried. The yield was 2.81 g (90.5%). The analytical sample was recrystallized from dimethyl sulfoxide–water.

The synthesis of **5** followed that already described for the preparation of γ-arylazoaminotroponeimines.[2] The ligand proved difficult to purify and was characterized as the diamagnetic zinc chelate.

Anal. Calcd for $C_{38}H_{46}N_8Zn$: C, 67.1; H, 6.82; N, 16.5. Found: C, 67.3; H, 6.99; N, 16.4.

The γ-substituted compounds of Table VI were prepared by synthetic techniques in which the key intermediate was N,γ-dilithio-N,N′-diethylaminotroponeimine. The latter was prepared from the γ-bromo derivative by reaction with 2 equiv of *n*-butyllithium. Compounds **13**, **14**, and **15** were obtained through reaction of the organolithium reagent with methyl formate, methyl

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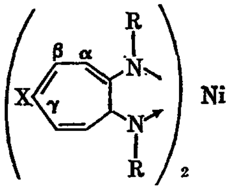
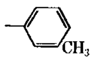
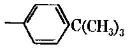
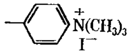
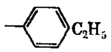
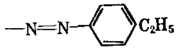
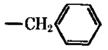
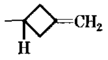
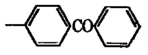
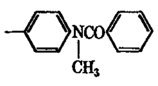
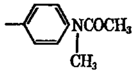
[6] M. C. R. Symons, *Tetrahedron*, **18**, 333 (1962).

[7] D. R. Eaton and W. D. Phillips, *J. Chem. Phys.*, **43**, 392 (1965).

[8] W. R. Brasen, H. E. Holmquist, and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3125 (1961).

Table I. pπ Spin Densities of Nickel(II) Aminotroponeimininates[a]



Compound no.	R	X	$\Delta f/\Delta f_{H\beta}$						ρ_2					
			α	β	γ	*ortho*	*meta*	*para*	α	β	γ	*ortho*	*meta*	*para*
1		H	−1.955	+1.000	−2.690	−0.363	+0.370	−0.511	+0.0411	−0.0210	+0.0565	+0.0076	−0.0078	+0.0107
2[b]		H	−1.971	+1.000	−2.712	−0.351	+0.367	...	+0.0414	−0.0210	+0.0570	+0.0074	−0.0077	...
3[c]		H	−1.807	+1.000	−2.608	−0.410	+0.416	...	+0.0379	−0.0210	+0.0548	+0.0086	−0.0087	...
4[b]		H	−1.994	+1.000	−2.744	−0.351	+0.377	...	+0.0419	−0.0210	+0.0576	+0.0074	−0.0079	...
5	C_2H_5		−1.736	+1.000	...	−0.397	+0.111	...	+0.0368	−0.0212	...	+0.0084	−0.0024	...
6	*n*-C_4H_8	H	−1.958	+1.000	−2.617	...	...	...	+0.0409	−0.0210	+0.0546	...	...	...
7[d,e]	C_2H_5	CH=NC$_4$H$_9$-*n*	−1.874	+1.000	...	+0.305	(CH)		+0.0412	−0.0220	...	−0.0067 (CH)		
8		H	+1.882	+1.000	−2.547	...	...	...	+0.0414	−0.0220	+0.0560	...	...	...
9		H	−1.965	+1.000	−2.663	...	...	...	+0.0432	−0.0210	+0.0586	...	...	...
10[e]	C_2H_5	CH=NC$_6$H$_{11}$	−1.857	+1.000	...	+0.339	(CH)		+0.0390	−0.0210	...	−0.0071 (CH)		
11[d,e]	C_2H_5	CH=N-adamantyl	−1.965	+1.000	...	+0.302	(CH)		+0.0411	−0.0220	...	−0.0066 (CH)		
12[e]	C_2H_5	CH=N-3-OH-adamantyl	−1.873	+1.000	...	+0.333	(CH)		+0.0412	−0.0220	...	−0.0073 (CH)		
13	C_2H_5	CHO	−2.120	+1.000	...	...	...	...	+0.0445	−0.0210	...	...	...	...
14	C_2H_5	COCH$_3$	−2.070	+1.000	...	...	...	...	+0.0434	−0.0210	...	...	...	...
15	C_2H_5	COOC$_2$H$_5$	−2.008	+1.000	...	...	...	...	+0.0442	−0.0220	...	...	...	...
16	C_2H_5	CH$_2$OH	−1.948	+1.000	...	...	...	...	+0.0429	−0.0220	...	...	...	...
17		H	−1.922	+1.000	−2.702	−0.366	+0.401	...	+0.0404	−0.0210	+0.0567	+0.0077	−0.0084	...
18[c]		H	−1.938	+1.000	−2.685	−0.396	+0.401	...	+0.0407	−0.0210	+0.0564	+0.0083	−0.0084	...
19[c]		H	−1.972	+1.000	−2.694	−0.376	+0.377	...	+0.0414	−0.0210	+0.0566	+0.0079	−0.0079	...
20		H	−1.925	+1.000	−2.657	−0.391	+0.373	...	+0.0404	−0.0210	+0.0558	+0.0082	−0.0078	...
21		H	−1.905	+1.000	−2.643	−0.350	+0.377	...	+0.0400	−0.0210	+0.0555	+0.0074	−0.0079	...

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[a] Spectra obtained at 60 Mcps in CDCl$_3$ unless otherwise stated. [b] In CS$_2$ solution. [c] In (CD$_3$)$_2$SO solution. [d] These two compounds show additional peaks which may indicate isomerism of the type previously found in Ni(II) N,N′-di(1-naphthyl)aminotroponeiminate. This is consistent with the bulk nature of the nitrogen substituent. [e] Spectrum obtained as mixed chelate. See Experimental Section.

Table II. Contact Shifts of Alkyl Protons and Hyperconjugation

Compound no.[a]	Hyperconjugation group	Δf, cps[b]	$\Delta f/\Delta f_{H\beta}$	Q_{eff}, gauss
1	CH_3	+306	−0.134	+8.2
2	$C(CH_3)_3$	−101	+0.050	+2.2
3	$\overset{+}{N}(CH_3)_3$	−140	+0.067	+2.9
4	$\mathit{CH_2}CH_3$	−955	+0.490	+21.6
5	$\mathit{CH_2}CH_3$	−1004	+0.329	+17.1
13	CHO	+1131	−0.517	−4.2
16	$\mathit{CH_2}OH$	−4198	−1.343	+11.6
19	$C_6H_5\mathit{NH}COC_6H_5$	−320	+0.119	+5.3
20	$C_6H_5N(\mathit{CH_3})COC_6H_5$	−174	+0.058	+2.6
21	$C_6H_5N(\mathit{CH_3})COCH_3$	−184	+0.067	+3.0

[a] See Table I for compound key. [b] Contact shift at 60 Mcps and 30°.

Table III. Observed Nmr Shifts of Alkyl Protons

Compound[a]	Proton[b]	Shift,[c] cps	Compound[a]	Proton[b]	Shift,[c] cps
4	β CH$_2$	−995	**8**	β CH$_2$	−10,621
	γ CH$_3$	−66		*ortho*	−419
				meta	−62
5	β CH$_2$(N)	−8,760		*para*	. . .
	γ CH$_3$(N)	−798			
	β CH$_2$(C$_6$H$_5$)	−1,004	**10**	β CH	−924
	γ CH$_3$(C$_6$H$_5$)	+17	(cyclohexyl shifts)	γ CH$_2$(1)	+185
				δ CH$_2$(2)	+46
6	β CH$_2$(1)	−10,603		ϵ CH$_2$(3)	−170
	γ CH$_2$(2)	−697			
	δ CH$_2$(3)	−431	**11**	γ CH$_2$(1)	+185
	ϵ CH$_3$	−212	(adamantyl shifts)	δ CH	−109
				ϵ CH$_2$(2)	+45
7	β CH$_2$(N)	−9,032			
	γ CH$_3$(N)	−744	**12**	γ CH$_2$(1a)	+184
	β CH$_2$(1)	−2,732	(adamantyl shifts)	γ CH$_2$(1b)	+201
	γ CH$_2$(2)	−383		δ CH	−91
	δ CH$_2$(3)	−290		ϵ CH$_2$(2)	+52
	ϵ CH$_3$	+14		OH	+271

[a] See Table I for compound key. [b] See Table I and text for labeling. β, γ, . . . indicate number of carbons removed from π system. [c] Contact shift at 60 Mcps and 30° referred to ligand or diamagnetic zinc complex.

acetate, and ethyl carbonate, respectively. An extensive study of the functionalization of the γ position of the cycloheptatriene ring together with details of the synthesis and reactions of these and other γ-substituted derivatives will be published separately. Schiff bases of aldehyde **13** were synthesized by standard techniques, and spin density distributions in these ligands were determined by the mixed chelate method.

Carbinol **16** was prepared by reduction of **13** with sodium borohydride, and the mixed chelate method was used to determine spin-density distribution therein.

Results

The pπ spin densities for 20 nickel(II) aminotroponeiminates with alkyl or carbonyl substituents are presented in Table I. These results are closely similar to those previously obtained for a variety of other substituted nickel(II) aminotroponeiminates.[1-3] It is important to establish this point since we need to know the pπ spin densities in order to obtain the amount of spin available to the attached σ system. If the pπ spin densities at positions adjacent to a substituent X are unaffected by the substitution, it can be assumed that the spin density at the position of substitution is also relatively unchanged. This enables an estimate to be made of Q_X using eq 4. In Table II the contact shifts obtained at 60 Mcps and room temperature for a number of such substituent groups are presented. This table also gives the shifts relative to the shift of the β proton of the aminotroponeiminate ring. In this way the shifts are effectively normalized for intercomparison, and the Q values may be obtained from eq 4. The spin densities necessary to estimate these Q values have been reported previously.[1,2]

In Table III contact shift data pertinent to the attenuation of spin densities in straight-chain and cyclic σ systems are presented. These data will be compared with hyperfine coupling constants reported for alkyl radicals. The protons have been labeled as β, γ, etc. according to whether they are one, two,. . .carbon atoms away from the source of spin density in order to retain an analogy with the labeling of esr coupling constants. The relative shifts have been collected in Table IV to illustrate the attenuation effect more clearly. Finally in Table V the contact shifts for some carbonyl-containing groups are given.

Table IV. Attenuation of Spin along Alkyl Chains

Compound[a]	Carbon atom distance from π system 1	2	3	4
N-Ethyl	1.000	0.066		
N-*n*-Propyl	1.000	0.068	0.036	
N-*n*-Butyl (**6**)	1.000	0.066	0.041	0.020
4	1.000	0.069		
5	1.000	−0.002		
7	1.001	0.140	0.106	−0.001
8	1.000		0.039	0.006
9	1.000	0.080		0.042

[a] See Table I for compound key.

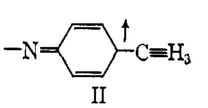
Hyperconjugation. The distribution of unpaired electrons in the π system of a radical is a manifestation of conjugation in the molecule. Transferral of the spin from the π system to the σ orbitals of an attached alkyl

Table V. Observed Nmr Shifts in Carbonyl Compounds

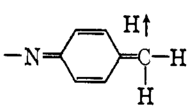
Compd[a]	Proton[a,b]	Shift[c]	Compd	Proton	Shift[c]
13	$\mathrm{C}\mathit{H}\mathrm{O}$	+1131	**19**	NH	−320
14	$\mathrm{CO}\mathit{CH}_3$	−810		*ortho*	−39
15	$\mathrm{O}\mathit{CH}_2\mathrm{CH}_3$	−322		*meta*	−13
	$\mathrm{OCH}_2\mathit{CH}_3$	+97		*para*	+10
17	*ortho*	−86	**20**	$\mathrm{N}\mathit{CH}_3$	−174
	meta	−36		*ortho*	−102
	para			*meta*	+27
18	NH	−44		*para*	+63
	ortho	<10	**21**	$\mathrm{N}\mathit{CH}_3$	−184
	meta	<10		$\mathrm{CO}\mathit{CH}_3$	−145
	para	<10			

[a] See Table I for compound key. [b] Shift refers to italicized proton. [c] Shift at 60 Mcps and 30°; measured in cps.

group is by analogy a hyperconjugative process. Molecular orbital treatments of the case of a methyl group attached to an aromatic sp^2 carbon have been given by McLachlan[9] and by Chesnut.[10] A positive Q value of the right order of magnitude to agree with the experimental esr results is predicted. For qualitative discussions, however, it is more convenient to use a valence-bond formulation. Thus the contact shift of methyl protons of nickel(II) N,N′-di-*p*-tolylaminotroponeiminate may be ascribed to the participation of structure III of the N-*p*-tolyl fragment in the resonance hybrid.



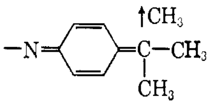
II



III

The Q value of +27.7 gauss reported previously[1] is in good agreement with esr values. The positive sign indicates that the sign of the spin density at the hydrogen atom is the same as the pπ spin density at the point of attachment. This is apparent by comparison of structures II and III. For the *m*-tolyl analog (compound **1**), it is not possible to write a simple valence-bond structure analogous to III. The spin at the *meta* position arises from a correlation process and is present in a different molecular orbital from that containing the odd electron. It is accordingly not surprising that the magnitude of the Q value (+8.2 gauss) is different, but the sign remains the same. Similar variations in Q value have been commented on previously.[2]

The above tolyl derivatives illustrate hyperconjugation involving C–H bonding electrons. In principle C–C hyperconjugation is also possible, and some esr evidence for this has been obtained from the ^{13}C hyperfine splittings in the 2-*t*-butylbenzoquinone ion radical.[11] The effect is clearly demonstrated by the low-field shift of the methyl protons of nickel(II) N,N′-bis-(*p*-*t*-butylphenyl)aminotroponeiminate (compound **2**). In the valence-bond formulation hyperconjugation in the *p*-tolyl compound involves a structure of type III and in the *p*-*t*-butylphenyl compound, a structure of type IV.



IV

Structure III effectively involves a hydrogen atom and structure IV a methyl radical. If structures III and IV had equal weights in the two compounds, *i.e.*, if C–H and C–C hyperconjugation were equally important, the effective Q values for the *p*-tolyl and *p*-*t*-butylphenyl compounds would be expected to be approximately in the ratio of the hyperfine splitting for a hydrogen atom (502 gauss) to that for a methyl radical (23.0 gauss). Comparison of this ratio of 21.8 with the observed ratio of 12.6 for the effective Q's suggests that C–C hyperconjugation may be rather more important than C–H hyperconjugation. (This argument implies that the Q value for the methyl radical is positive. This point will be discussed in more detail below.) This is perhaps consistent with the rather greater energy needed to break a C–H bond to give structure III (87.3 kcal)[12] than to break a C–C bond to give structure IV (58.6 kcal).[12]

The case of the N-[*p*-(trimethylammonium)phenyl] derivative (compound **3**) is exactly analogous to the *p*-*t*-butylphenyl compound. In the former compound C–N hyperconjugation is involved and the rather larger effective Q value (+2.9 gauss compared to 2.2 gauss) parallels the rather smaller C–N bond energy (48.6 kcal compared to 58.6 kcal).[12] It may be noted that this ionic compound is insoluble in nonpolar solvents and was examined in dimethyl sulfoxide. In other nickel(II) aminotroponeiminates it has been found that although the position of the singlet–triplet equilibrium depends markedly on the solvent, the spin densities are very little changed even by a polar solvent such as dimethyl sulfoxide. Comparison between the results for the *p*-*t*-butylphenyl compound in carbon disulfide and for the quaternary ammonium salt in dimethyl sulfoxide is, therefore, probably valid.

Compounds **4** and **5** illustrate the effect of hyperconjugation with ethyl groups attached to the aromatic nucleus rather than methyl groups. In both cases there is reduction of the effective Q value for the methylene group compared to the corresponding methyl group, *i.e.*, from +27.7 to +21.6 gauss for **4** and from +22.1 to +17.1 gauss for **5**. A plausible explanation consistent with the above observations is that C–C hyperconjugation is preferred over C–H hyperconjugation so that structures of type V are favored at the expense of those of type VI. However, this is not the only possibility since the hyperconjugative interaction is dependent on the orientation of the alkyl group with respect to the π system, and it is possible that the average

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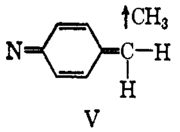
[9] A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

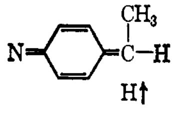
[10] D. B. Chesnut, *J. Chem. Phys.*, **29**, 43 (1958).

[11] L. M. Stock and G. Suzuki, *Proc. Chem. Soc.*, 136 (1962).

[12] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.



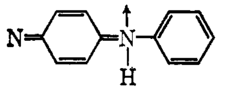
V



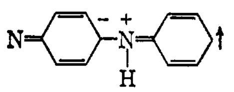
VI

orientation of the CH$_3$ protons may be more favorable than that of the CH$_2$ protons. It does not seem possible to decide between these alternatives at present.

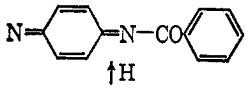
Compounds **19**, **20**, and **21** introduce a further possibility, namely, competition between hyperconjugation and dative conjugation involving the nitrogen lone pair. We have previously examined nickel(II) N,N′-bis-[p-(phenylamino)phenyl]aminotroponeiminate and obtained results consistent with the transmission of spin density through the -NH- group by dative conjugation. Thus, the important valence bond structures seem to be types VII and VIII. Consistent with this formulation a high-field shift was observed for the NH proton, resulting from the positive pπ spin density on the sp^2 nitrogen. However, it is also conceivable that a substituted -NH$_2$ group could be hyperconjugated with the aromatic system analogous to a CH$_3$ or substituted CH$_3$ group. This would transfer positive spin directly to the NH proton leading to a down field shift and a positive Q value. This appears to be happening in compound **19**, and we must postulate contribution from valence-bond structures such as IX. It may be noted though that the observed Q value (+5.3 gauss) is considerably less than that for methyl hyperconjugation (+27.7 gauss), suggesting that structures of both types VII and IX may be participating. Indeed, the fact that Q is positive does not imply that a type IX structure has greater weight than a type VII structure, since for a "pure" type IX structure we would expect $Q \approx +502$ gauss as in the hydrogen atom, whereas in a "pure" type VII structure the effective Q would not be greater than the aromatic σ–π value (~ -22.5 gauss) even if the *para* carbon spin density were entirely transferred to the nitrogen. Thus, a little hyperconjugation is likely to have a profound effect on the contact shift. The N-methyl derivatives (compounds **20** and **21**) fit in well with these ideas. In these compounds both mechanisms will lead to a low-field shift. By the argument developed above for the hyperconjugative mechanism the effective Q value should be about $^1/_{20}$th of that for NH. The observed Q values of +2.6 and +3.0 gauss are nearer one-half the Q value for NH, suggesting a considerable assist from dative conjugation. It is interesting that dative conjugation appears to predominate in the diphenylamine derivative which has the possibility of through conjugation to the second phenyl ring but not in compounds in which a carbonyl group blocks further conjugation.



VII

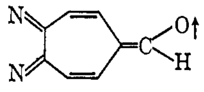


VIII

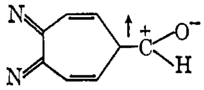


IX

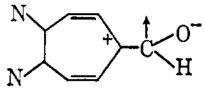
Finally, the aldehyde derivative (compound **13**) and alcohol derivative (compound **16**) will be discussed since the protons attached to functional carbon atoms are in a position for possible hyperconjugative interaction with the π system. The large high-field shift (+1131 cps) and apparent negative Q value (-4.2 gauss) for the aldehyde proton show that this hyperconjugation is not the dominant interaction in this case. An obvious alternative would involve conjugation of the carbonyl group with the π system leading to valence-bond structure X. This explanation is also unsatisfactory, since it would predict negative pπ spin density at the carbonyl carbon again leading to a low-field shift for the attached hydrogen atom. This low-field shift is exactly what is observed in the isoelectronic anils (compounds **7**, **10**, **11**, and **12**). It must be assumed that the greater electronegativity of oxygen compared to nitrogen lends a greater importance to ionic structures such as XI and XII. Thus, structure XII places positive pπ spin density on the carbonyl carbon which will lead to the observed high-field shift for the formyl proton. Several other observations support this hypothesis. In these nickel(II) aminotroponeiminates it has been found that the absolute contact shifts vary considerably with solvent because of changes in the singlet–triplet equilibrium but that the spin densities as reflected by the relative contact shifts of different protons are constant to within at least 1 or 2%. The formyl proton is an exception to this rule. Thus, in CDCl$_3$ the spin density at the carbonyl carbon assuming $Q = -22.5$ gauss is +0.0109, in CS$_2$ +0.0086, in CCl$_4$ +0.0081, in dimethyl sulfoxide +0.0083, and in acetone +0.0095. This variation is an order of magnitude larger than any differences previously observed. Secondly, there is an anomalous variation in spin density with temperature. In deuteriochloroform the ratio of the CHO shift to the H$_\beta$ shift increases smoothly with decreasing temperature from 0.476 at +70° to 0.673 at $-58°$. This again is an order of magnitude greater than the 4–5% variations in spin densities over this temperature range normally found in these complexes. Both observations are consistent with the view that polar structures, such as XII, are favored by hydrogen bonding with the solvent. These results in fact provide a rather direct demonstration of the effect of hydrogen bonding on π electron spin densities and by inference the effect on π electron charge densities. It should also be noted that in the corresponding acetyl derivative (compound **14**) the CH$_3$ shift is in the opposite direction to the CHO shift. This is to be expected if these shifts reflect the spin density on the carbonyl carbon, but, as has been discussed above, shifts of the same sign for H and CH$_3$ result from hyperconjugation. This result is therefore also consistent with the above interpretation.



X

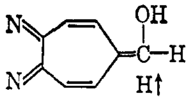


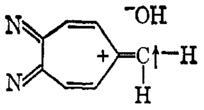
XI



XII

We may now discuss the data for the alcohol derivative (compound **16**) in the light of this interpretation of the formyl proton contact shift. The shift of the CH_2OH protons is indeed to low field (−4198 cps), as expected for a hyperconjugative mechanism. However, the Q value (+11.6 gauss in chloroform) is considerably less than the Q value for a CH_3 group at the same position of substitution (21.4 gauss).[13] It might be considered that this reduction is due to competitive contributions from structures such as XIII and XIV.


XIII


XIV

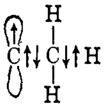
Structure XIV is analogous to the aldehyde structure XII and would lead to a high-field shift. Consistent with the participation of ionic structures there is a solvent effect on this Q value. Thus, we obtain $Q = +11.6$ gauss in chloroform, $Q = +13.1$ gauss in carbon disulfide, and $Q = +13.8$ gauss in deuterioacetone. It may be noted that in this case the shift in the non-hydrogen-bonding carbon disulfide is larger than that in the hydrogen-bonding chloroform. This is the opposite to the aldehyde case and is to be anticipated since the ionic structure in the alcohol is in opposition to the dominant hyperconjugative mechanism. It may also be significant that acetone does not occupy the same position in the series of solvents for the alcohol that it does for the aldehyde since the hydrogen-bonding possibilities are not the same for the two compounds; the aldehyde can only be a hydrogen acceptor, whereas the alcohol can be a hydrogen acceptor or a hydrogen donor.

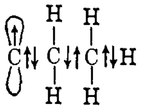
Spin-Density Distribution in Alkyl Radicals. We have previously reported[1] isotropic hyperfine shifts for the aliphatic protons of nickel(II) N,N′-diethyl- and N,N′-di-*n*-propylaminotroponeiminates but have not ventured to interpret these results. We now extend this series by adding the data on the N,N′-di-*n*-butyl compound (compound **6**). One reason for the previous uncertainties regarding the interpretation of the shifts lies in the possible influence of pseudo-contact effects. It has been demonstrated[1] that such effects are negligible at points distant from the nickel atom and hence that the g-value anisotropy of these complexes is small. However, pseudo-contact shifts vary as $1/r^3$ (where r is the distance from the metal atom to the proton), and the possibility remained that even a small g-value anisotropy could produce significant shifts of the protons of alkyl groups substituted directly on the nitrogen atoms of the aminotroponeiminate since these protons could approach the nickel atom rather closely.

Therefore, a number of complexes containing alkyl groups far removed from the central metal atoms were synthesized. Compounds **4**, **5**, and **7** satisfy this requirement. In these three cases pseudo-contact shifts of the alkyl protons can be neglected with a high degree of confidence. Pertinent data are given in Tables III and IV. It is apparent from these results that the relative shifts, at least as far as the third saturated carbon atom, are as large or larger than those of the N-alkyl compounds. The pseudo-contact mechanism is therefore inadequate to account for these shifts.

Granted that the shifts are contact in origin, at least three possible mechanisms require consideration. Firstly, the previous discussion has demonstrated how spin can be transferred by hyperconjugation from the π system to the σ orbitals of substituents. It may be that such σ molecular orbitals are sufficiently delocalized to give rise to appreciable spin densities at atoms remote from the point of attachment of the alkyl radical. Secondly, spin polarization effects may be important. Thus, the accepted mechanism by which an aromatic proton senses the pπ spin density can be represented by structure XV. Formally, at least, one can write structures, such as XVI and XVII, to extend this process to more distant protons.


XV


XVI


XVII

Bolton, Carrington, and McLachlan[14] have considered the relative importance of polarization and delocalization (hyperconjugation) mechanisms in the case of the methyl hyperfine couplings of methylanthracene radical ions; on the basis of the observation that there is a large difference in coupling constant between positive and negative ions, they have concluded that in this case the hyperconjugative mechanisms is dominant. It seems probable that this will be generally true for protons or carbons attached directly to the spin-bearing atom (β protons), but since the shifts of the γ, δ, . . . protons are at least an order of magnitude smaller, polarization mechanisms cannot necessarily be neglected in these cases. It is, of course, possible to have a combination of these mechanisms, *e.g.*, spin delocalized to the carbons but sensed by the hydrogens by polarization. Thirdly, there may be direct overlap of H 1s orbitals with the spin-containing pπ orbital. For the β proton this is, of course, precisely what is implied in mechanism 1. For more distant protons though, *e.g.*, the terminal CH_3 group of an n-butyl radical, there would seem to be a valid distinction between the transmission of spin in a delocalized orbital along a linear chain (mechanism 1) or a requirement that the chain should be bent so that the terminal CH_3 is brought close enough to the α (spin bearing) position for direct overlap to be possible.

Pertinent evidence can be sought in several directions. First of all, it should be noted that only the polarization mechanism can give rise to negative spin densities and hence to high-field shifts. An experimental approach to the investigation of the third possibility is to use rigid saturated groups to limit the possibilities of direct interactions due to favorable conformations in straight-chain alkyl radicals. This was the rationale behind the synthesis of the cyclohexyl derivative (compound **10**) and the adamantyl derivative (compound **11**). The adamantyl derivative was also of interest in view of the previously reported delocalization of spin in the adamantyl negative ion,[15] although subsequent work[16] has suggested that this report was incorrect. An alter-

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[13] D. R. Eaton, unpublished data.

[14] G. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

[15] K. W. Bowers, C. J. Nolfi, and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 3707 (1963).

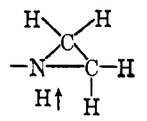
[16] M. T. Jones, *ibid.*, **88**, 174 (1966).

native approach is to calculate the amount of spin delocalization expected in alkyl radicals and make comparisons with the observed contact shifts. We also report some attempts in this direction.

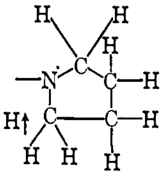
Consider first the experimental results in Tables III and IV. In all cases β protons show a low-field shift which is an order of magnitude greater than γ, δ,... shifts. In the straight-chain compounds only the terminal protons of compounds **5** and **7** show high-field shifts, and these shifts (+17 and +14 cps, respectively) are probably too small to definitively identify a polarization mechanism. However, in the cyclic derivatives (compounds **10–12**) high-field shifts of around +200 cps are observed, and these are well outside any possible experimental error due to incorrect assignment of diamagnetic reference frequencies. We are forced to the conclusion that, at least in these compounds, spin polarization effects play an important role. The data in Table IV show that, although the attenuation of the shifts with distance from the π system is qualitatively the same for all the molecules except compounds **10–12**, there are significant quantitative differences. Results for the N,N′-diethylaminotroponeimine and the N,N′-di-*n*-propylaminotroponeimine are also included in Table IV for completeness.

The results obtained by Fessenden and Schuler[17] from studies of the esr spectra of alkyl radicals are particularly pertinent to this discussion. From their analysis of the β hyperfine coupling constants they deduced that there was appreciable delocalization of the spin away from the α carbon. Thus, they derive α spin densities of 1.000 for the methyl radical, 0.919 for the ethyl radical, 0.814 for the isopropyl radical, and 0.776 for the *t*-butyl radical. Delocalizations of this magnitude could be more than adequate to account for the observed contact shifts. It might be noted that a contact shift of 100 cps at 60 Mcps requires a spin density in the 1s orbital of hydrogen of only around 10^{-5}. To investigate this possibility further, we have carried out calculations on σ systems using the linear combination of bond orbitals (LCBO) method of Hall.[18] This form of calculation has the advantages that it requires a minimum number of basis orbitals and that most of the necessary parameters can be obtained empirically from ionization potential data. The values of the Coulomb and resonance integrals used were those suggested by Hall.[18] Two additional parameters are necessary: a Coulomb integral for the spin-containing pπ orbital and a resonance integral to express the hyperconjugative interaction between this orbital and the neighboring C–H and C–C bonds. The pπ orbital must have a higher energy than the C–C bonding orbital, and the corresponding Coulomb integral was arbitrarily given a value of −9.5 ev which places it 3.75 ev above the C–C orbitals. A value of −0.5 ev was adopted for the unknown resonance integrals. The results of these calculations will not be reproduced in detail here since they are at best only qualitatively significant. Some results on the system comprising an *n*-butyl radical attached to the π system illustrate the type of spin density distributions obtained. In this case the spin density remaining in the π orbital was 0.95, in reasonable agreement with Fessenden and Schuler's[17] results. The spin densities in the 1s orbitals of the β, γ, δ, and ϵ hydrogen atoms were 3.83×10^{-3}, 4.43×10^{-5}, 1.09×10^{-5}, and 2.67×10^{-6}, respectively. Assuming one-tenth of an unpaired electron in the π orbital (which will be roughly correct for the N,N′-di-*n*-butylaminotroponeamine), we obtain contact shifts of −27,155, −314, −77, and −19 cps. These shifts diminish along the chain considerably faster than experiment would indicate, so an additional calculation was carried out allowing a resonance integral of −0.5 ev between C–H bonds at adjacent carbon atoms. Such an interaction is not unreasonable, both in view of the hyperconjugative interaction discussed above and, for example, the interpretation of the barrier to free rotation in ethane proposed by Hecht, Grant, and Eyring.[19] Under the same assumptions as above this gave contact shifts of −29,140, −1978, −260, and −36 cps. These shifts are to be compared with the experimental values of −10,603, −697, −431, and −212 cps. We conclude from these results that although this delocalization mechanism produces shifts of the right order of magnitude, the spin densities at distant positions are rather greater than can be reproduced with a plausible choice of parameters. The evidence for the direct overlap effect (mechanism 3) will therefore be considered.

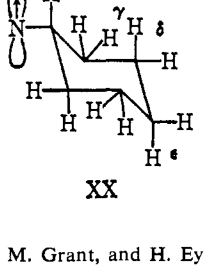
Fessenden and Schuler[17] report values for the β and γ hyperfine coupling constants of the *n*-propyl radical of 33.2 and 0.38 gauss, respectively. These values are in fair agreement with the relative β and γ contact shifts reported above. These authors state that the γ coupling constant can be adequately accounted for by direct overlap with the pπ orbital of the α carbon. In valence-bond terms the structures involved for the N-alkyl derivatives are types XVIII and XIX. (Alternatively these structures could be written with both electrons on the terminal carbon, with a positive charge on the nitrogen rather than on the N–C bond.) In agreement with this mechanism Fessenden and Schuler found an angular dependence for the γ coupling constant. For such direct overlap a preferred orientation is certainly required, and the results on the constrained cyclic systems are particularly relevant. For the cyclohexyl derivative (compound **10**) four resonances are observed, two shifted to low field of intensities one and two, and two shifted to high field each of intensity four.



XVIII



XIX



XX

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[17] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[18] G. G. Hall, *Proc. Roy. Soc.* (London), **A205**, 541 (1951).

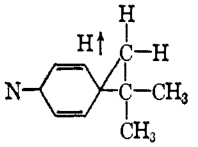
[19] H. G. Hecht, D. M. Grant, and H. Eyring, *Mol. Phys.*, **3**, 577 (1960).

The large low-field shift of unit intensity must be the β proton (see structure XX). The second low-field shift (intensity two) must be the ϵ protons unless either γ or δ protons are nonequivalent. This seems unlikely since two sets of four equivalent protons are observed. The results of Fessenden and Schuler[20] on the cyclohexyl free radical are in agreement with this assignment. They observed a splitting of 0.7 gauss which they showed must arise from the more distant pair of protons (δ in this case) and concluded that the γ splitting was <0.15 gauss. The high-field contact shifts (negative spin densities) must therefore be assigned to the γ and δ protons. It is difficult to envisage how this situation could arise without some form of direct interaction across the ring.

With the adamantyl derivative (compound **11**), there is again some ambiguity in the assignment. Three resonances are observed with intensities 2:2:1. Most simply these would correspond to the set of three methylene hydrogens adjacent to the position of substitution, the set of three tertiary hydrogens two bonds away, and the set of three methylene hydrogens three bonds away. However, if distance from the spin-containing p orbital is the determining factor, a model shows that the six protons from the adjacent CH_2 groups form one set, six protons comprising the CH groups and one proton for each of the second CH_2 groups form a second set, and the remaining three protons from the more distant CH_2 groups form a third set. The 3-hydroxy derivative (compound **12**) should help in deciding between these assignments, since in the first case unit intensity will be lost from the weaker resonance because of the substitution, and in the second case it will be lost from one of the stronger resonances. Comparison of intensities shows that the first assignment is correct, leading to the conclusion that the protons γ with respect to the spin-bearing atom have a high-field shift, the δ protons have a low-field shift, and the ϵ protons have a high-field shift. This pattern is quite different from that of the linear alkyl groups and also from that of the semirigid cyclohexyl group. We must conclude that direct interactions due to favorable orientations such as those represented in structures XVIII and XIX are quite important and that, when the rigidity of the molecule precludes such interactions, polarization effects leading to negative spin densities and high-field shifts become significant.

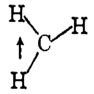
Finally, we might note the results on the cyclobutene derivative (compound **9**). It might be expected that this would represent a particularly favorable situation for direct interaction across the ring. The results in Table IV show that the shift of protons at a position four carbon atoms from the π system is twice as large as that for the corresponding protons of the *n*-butyl group, and this may provide some evidence for such long-range interactions. Previous results on the N-allyl derivative[1] show that this enhancement is not associated with the presence of a double bond.

We must conclude from the above results that all three of the mechanisms mentioned at the beginning of this section can contribute to the contact shifts observed in σ systems. In most cases it is not easy to distinguish between them, even with knowledge of the signs of the hyperfine coupling constants provided by the contact shift method. This is illustrated by the tertiary butyl derivative (compound **2**) discussed earlier. The hyperconjugative structure IV has previously been written to place spin on the methyl group. The direct mechanism would involve a structure such as XXI.

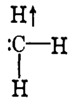


XXI

At first sight it may be argued that we could distinguish between these possibilities on the basis of the sign of the observed hyperfine coupling constant. The Q value for the methyl radical is usually assumed to be negative on the basis of several theoretical treatments.[21,22] This leads to a high-field shift from structure IV. Structure XXI on the other hand leads directly to a low-field shift in agreement with experiment. However, the negative Q value for CH_3 is essentially based on the assumption of a polarization mechanism only. Fessenden and Schuler[17] have found that the change in α hyperfine coupling constants with hybridization predicted by this polarization mechanism is not observed in the cyclopropane and vinyl radicals and have argued in favor of a mechanism analogous to that previously postulated for the formyl radical.[23] Essentially for the methyl radical this would involve structures such as XXIII as well as XXII.



XXII



$$\underset{\mathrm{H}}{\overset{\mathrm{H}\uparrow}{\mathrm{:C}}}\mathrm{—H}$$

XXIII

This leads to a positive Q value and is in fact the mechanism originally suggested by Gordy and McCormick[24] to account for methyl hyperfine coupling. Thus, since there is no reason to suppose that the C–C hyperconjugation of structure IV is much less effective than the C–H hyperconjugation of structure III, which is well established, we could argue that the observed low-field contact shift for compound **2** provides evidence for a positive Q value for CH_3 rather than for the participation of a structure such as XXI. This would not necessarily be inconsistent with the theoretical interpretations mentioned above[21,22] since the latter are based on a planar methyl radical, whereas the CH_3 fragment with which we are concerned retains its sp^3 hybridization.

Carbonyl Compounds. The carbonyl compounds **17–21** are included in the present discussion since it appears that, in contrast to many of the linking groups previously examined,[1,3] the carbonyl group does not transmit π spin density. Thus, in the ketone derivative (compound **17**) the shifts of protons on the second phenyl group do not have the pattern characteristic of π spin densities (*ortho* and *para* to high field, *meta* to low field) but are uniformly to low field. This be-

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[20] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **41**, 994 (1964).

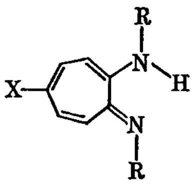
[21] C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, *Phys. Rev.*, **112**, 1169 (1958).

[22] M. Karplus, *J. Chem. Phys.*, **30**, 15 (1959).

[23] F. J. Adrian, E. L. Cochran, and V. A. Bowers, *ibid.*, **36**, 1661 (1962).

[24] W. Gordy and C. G. McCormick, *J. Am. Chem. Soc.*, **78**, 3243 (1956).

Table VI. M,M′-Disubstituted Aminotroponeimines and Their Nickel Chelates



Compound	R	X	Ligand Formula	Ligand Mp, °C	Calculated, % C	Calculated, % H	Calculated, % N	Found, % C	Found, % H	Found, % N	Chelate Formula	Chelate Mp, °C	Calculated, % C	Calculated, % H	Calculated, % N	Found, % C	Found, % N	Found, % N
1	*m*-$CH_3C_6H_4$	H	$C_{21}H_{20}N_2$	91–92.8	83.9	6.71	9.33	83.8	6.69	9.56	$C_{42}H_{38}N_4Ni$	170–172			8.52			8.45
2	*p*-$(CH_3)_3CC_6H_4$	H	$C_{27}H_{32}N_2$	134.4–135.2	84.3	8.89	7.29	84.1	8.26	7.04	$C_{54}H_{62}N_4Ni$	213–214			6.78			6.70
3	*p*-$(CH_3)_3N^+C_6H_4\ I^-$	H	$C_{25}H_{32}I_2N_4$[a]	171.6–173.8	46.8	5.02	8.73	47.3	5.10	9.10								
4	*p*-$C_2H_5C_6H_4$	H	$C_{23}H_{24}N_2\cdot HCl$	250–251.5	75.7	6.90	7.68	76.1	7.16	7.52	$C_{46}H_{46}N_4Ni$	194–195			7.86			8.05
5	C_2H_5	*p*-$C_2H_5C_6H_4N{=}N$	. . .[b]								$C_{38}H_{46}N_8Ni$	227–229	67.8	6.89	16.6	68.2	6.97	16.9
6	*n*-C_4H_9	H	$C_{15}H_{24}N_2$	Bp 114–116 (0.25 mm)	77.5	10.4	12.1	77.8	10.5	12.0	$C_{30}H_{46}N_4Ni$[c]							
7	C_2H_5	*n*-$C_4H_9N{=}CH$	$C_{16}H_{25}N_3$[a]	Bp 165 (0.3 mm)	74.1	9.72	16.2	74.5	10.0	16.5								
8	$C_6H_5CH_2$	H	$C_{21}H_{20}N_2$[g]								$C_{42}H_{38}N_4Ni$[h]		76.7	5.83		76.5	5.97	
9	C_5H_7	H	$C_{17}H_{20}N_2$[i]	62–63.5	80.9	7.99	11.1	80.5	7.88	11.0	$C_{34}H_{38}N_4Ni$	182–184	72.7	6.83	9.98	73.2	6.97	9.85
10	C_2H_5	$C_6H_{11}N{=}CH$	. . .[e]															
11	C_2H_5	1-$(C_{10}H_{15})N{=}CH$	$C_{22}H_{31}N_3O$[a,f]	126.5–127	78.3	9.26	12.5	77.8	9.21	12.7								
12	C_2H_5	1-$(C_{10}H_{15}O)N{=}CH$	$C_{22}H_{31}N_3O$[a,f]	100–107	74.7	8.85	11.9	75.5	9.49	11.6								
13	C_2H_5	CHO	$C_{12}H_{16}N_2O$	63–64	70.6	7.90	13.7	70.4	7.94	13.7	$C_{24}H_{30}N_4O_2Ni$	179.6–180	62.0	6.50	12.1	62.2	6.37	12.1
14	C_2H_5	$COCH_3$	$C_{13}H_{18}N_2O$[a]	65.9–66.7	71.5	8.31	12.8	71.6	8.24	12.5								
15	C_2H_5	$CO_2C_2H_5$	$C_{14}H_{20}N_2O_2$[a]	72.4–72.7	67.7	8.12	11.3	67.9	8.12	11.5								
16	C_2H_5	CH_2OH	$C_{12}H_{18}N_2O$[a]	88.5–89	69.9	8.80	13.6	69.9	8.56	13.9								
17	*p*-$C_6H_5COC_6H_4$	H	$C_{33}H_{24}N_2O_2$	184–186			5.83			5.67	$C_{66}H_{46}N_4O_4Ni$	>300	77.9	4.55	5.50	78.2	5.06	5.75
18	*p*-$C_6H_5NHCOC_6H_4$	H	$C_{33}H_{26}N_4O_2$	264	77.6	5.14	11.0	77.6	5.25	11.3	$C_{66}H_{50}N_8O_4Ni$[d]	215	74.8	4.88	9.69	74.5	4.94	9.60
19	*p*-$C_6H_5CONHC_6H_4$	H	$C_{33}H_{26}N_4O_2$	251–252	77.6	5.14	11.0	77.8	5.22	11.1	$C_{66}H_{50}N_8O_4Ni$	>300	73.5	4.68	10.4	72.9	4.85	10.5
20	*p*-$C_6H_5CON(CH_3)C_6H_4$	H	$C_{35}H_{30}N_4O_2$	191–192	78.0	5.61	10.4	78.1	5.48	10.8	$C_{70}H_{58}N_8O_4Ni$	210–212	74.1	5.15	9.87	74.0	5.12	10.2
21	*p*-$CH_3CON(CH_3)C_6H_4$	H	$C_{25}H_{26}N_4O_2$	197–198	72.4	6.32	13.5	72.5	6.13	13.6	$C_{50}H_{50}N_8O_4Ni$	193–195	67.8	5.69	12.7	68.1	5.65	12.5

[a] Spin density distributions in the Ni chelate were determined by the mixed chelate method. [b] The ligand was not isolated but was converted directly to the chelate. [c] The chelate was a liquid at ordinary temperatures; its structure was confirmed by its nmr spectrum. [d] Obtained as crystalline solvate containing 1 mole of benzene. [e] This material was obtained from the reaction of the nickel chelate of **13** with cyclohexylamine. Nmr studies were performed upon the total reaction product without isolation from unreacted starting material or the product of condensation at only one formyl group. [f] 1-$(C_{10}H_{15})$ = 1-adamantyl and 1-$(C_{10}H_{15}O)$ = 3-hydroxy-1-adamantyl; these Schiff bases were derived from the corresponding 1-adamantylamines. [g] Preparation described in ref 8. [h] For a preliminary report of contact shifts, see W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **33**, 607 (1960).

havior is quite similar to that found in the benzyl derivative (compound **8**) and must be ascribed to spin in the σ system. It may be noted that recent esr investigations of the phenyl radical[25] ($C_6H_5\cdot$) have shown that this is a σ rather than a π radical and have given relative *ortho*, *meta*, and *para* hyperfine coupling constants consistent with the contact shifts found in the present compounds. Compounds **18–21** all contain peptide linkages. The electronic properties of such linkages are of interest because of their occurrence in proteins. It is apparent that there is no dramatic enhancement of the conjugative effectiveness of this linkage compared to a simple carbonyl linkage but that there are significant differences in the shifts observed, *e.g.*, the relatively large high-field shifts of the aromatic protons of compound **20**. These shifts could be interpreted in terms of the various mechanisms proposed above, but a detailed discussion of the comparatively small amount of data presently available does not seem to be warranted.

Conclusion

The contact shift method of studying conjugative and hyperconjugative effects has the virtue of great sensitivity. In this paper and preceding papers we have chosen to discuss these effects in terms of valence-bond structures since we find this approach chemically most informative. Qualitatively, at least, the spin density arising from a given structure gives an experimental measure of the weight of that structure in the over-all valence-bond formulation. This aspect may well be the most important in these studies, since from time to time a great variety of contributing valence-bond structures are invoked by chemists, and there are relatively few direct experimental guidelines as to their relative importance. We conclude this discussion therefore by summarizing a few of the salient conclusions in this area reached by the contact shift method. Using Mulliken's nomenclature, structures corresponding to isovalent conjugation (*e.g.*, as in benzene) give rise to spin densities of the same order of magnitude. Structures involving sacrificial (as in butadiene) or dative conjugation commonly give rise to spin densities about one order of magnitude less than those not involving such conjugation, *i.e.*, they may make a 10% contribution to the over-all structure. The spin density corresponding to a hyperconjugative structure, such as III, is about one and one-half orders of magnitude lower than that corresponding to structure II; *i.e.*, hyperconjugative structures may contribute a few per cent to the over-all structure. On the other hand, structures corresponding to the transmission of spin to more distant protons of alkyl radicals (*e.g.*, XIX) give rise to spin densities three orders of magnitude less than the initial spin density. Such structures are obviously entirely negligible from the energetic point of view. As a final illustration a comparison of the CH=O and CH=NR groups is perhaps informative. In the CH=O group, conjugation of the C=O with the π system is less important than the charge separated form $-\overset{+}{C}-\overset{-}{O}$ which appears to contribute to the extent of $\sim$20%. In the CH=NR group conjugation of C=NR with the π system is dominant with about a 10% contribution to the ground structure. Such a result is, of course, consistent with the greater electronegativity of oxygen compared with nitrogen, but it would have been difficult to obtain the above semiquantitative estimates of the relative importance of the effects by other methods.

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(25) J. E. Bennett, B. Mile, and A. Thomas, *Proc. Roy. Soc.* (London), **A293**, 246 (1966).