Studies on the Paramagnetic Shifts for σ-Electron Systems. Conformational Dependency of ^{13}C Contact Shifts

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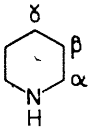
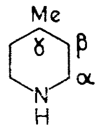
Summary ^{13}C Contact shifts for piperidine derivatives and quinuclidine induced by complexation with nickel acetylacetonate observed using the proton-decoupled ^{13}C n.m.r. technique are discussed in terms of their conformational dependency and the delocalized nature of the lone-pair electrons.

We have recently reported the proton contact shifts for piperidine,[1a] quinuclidine,[1a] aziridine,[1b] oxime,[1c] imine,[1c] and aniline,[1d] all having the oriented nitrogen lone-pair electrons as the σ-binding site with the paramagnetic nickel acetylacetonate $Ni(acac)_2$. The proton contact shifts induced by the paramagnetic complexation depend on the orientation of the nitrogen lone-pair electrons and are useful as a probe for studying molecular conformations.

We now report the use of the ^{13}C contact shift for conformational studies and for elucidation of the mode of electron spin distribution through the σ-electron system.[2] The paramagnetic systems examined are the adducts of

Ni(acac)$_2$ with piperidine derivatives (I)—(IV) and quinuclidine (V) which have the oriented lone-pair electrons in the rigid σ-electron system.


(I)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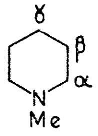
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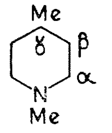
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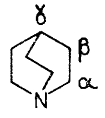

(V)

^{13}C N.m.r. shifts were observed† for these compounds in CDCl$_3$. The carbon resonances were found to shift from their normal diamagnetic values by an amount proportional to the concentration of the added Ni(acac)$_2$, as is the case for the proton resonance.[1,3] The spectrum for quinuclidine(V) is given in the Figure. Relative values of these shifts for various carbons in a ligand molecule were obtained from the relative slope in the linear plot of the paramagnetic shifts *vs.* the concentration of added Ni (acac)$_2$.‡ The value for the particular carbon (α-carbon) is normalized to 10·0 (Table). The isotropic proton paramagnetic shifts[1a,3] in the Ni(acac)$_2$ adducts are caused mainly by the contact interaction which is related to the spin density on the proton. This should also be true for the ^{13}C resonance. The relative ^{13}C contact shifts for various ligand molecules are given in the Table. The plus and minus signs of these values denote the upfield and the downfield contact shifts which correspond to the negative and the positive electron spin density, respectively, induced on the ligand carbon *s*-atomic orbital.

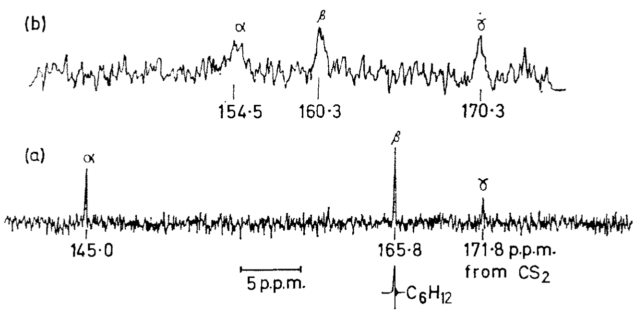


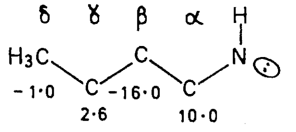
FIGURE. *The proton-decoupled* ^{13}C *n.m.r. spectra at* 25·1 *MHz for* (V): (a) 1 *mol* l^{-1} *of* (V) *in* CDCl$_3$ (*single scan*) (b) *in the presence of* 0·14 *mol* l^{-1} Ni(acac)$_2$ (16 *times accumulated*).

The relative ^{13}C contact shifts of α-, β-, and γ-carbons are quite different for N–H piperidines, (I) and (II), and N–Me piperidines, (III) and (IV) (see Table). The most striking difference is the relative ^{13}C contact shifts at the β-carbon; for (III) and (IV) quite rapid attenuation of the contact shifts as compared with those for (I) and (II) was observed. Methyl substitution at the γ-carbon, which lowers the rate of the ring inversion,[1a] has no effect on this mode of the relative contact shifts. Similar differences in the relative ^{13}C contact shifts were also found for 2-methyl-, 3-methyl-, 1,2-dimethyl-, and 1,3-dimethyl-piperidines. The differences in ^{13}C contact shifts are probably due to the effect of the different lone-pair orientations. The nitrogen lone-pair has a greater preference for the equatorial position in N–H piperidines, (I) and (II), while lone-pair electrons in N–Me piperidines, (III) and (IV), occupy an axial position preferentially.[1a] The odd electron distributes itself on the ligand carbons along zig-zag paths [see (A)] for (I) and (II), while the electron spin reaches the carbon through folded paths [see (B)] for (III) and (IV). It then follows that the electron spin reaches the β-carbon more by zig-zag paths

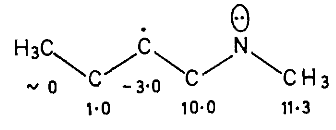
Relative ^{13}*C contact shifts*

Compound	Position	^{13}C[a]	Relative values of ^{13}C contact shifts[b]
(I)	α	145·8	+10·0
	β	165·8	−16·0
	γ	167·5	+2·0
(II)	α	146·2	+10·0
	β	157·2	−16·0
	γ	161·5	+2·6
	γ-Me	170·2	− 1·0
(III)	α	136·1	+10·0
(III)	β	166·9	−2·9
	γ	169·1	+1·4
	N-Me	146·0	+11·2
(IV)	α	136·5	+10·0
	β	158·2	−3·0
	γ	162·4	+1·0
	N-Me	146·5	+11·3
	γ-Me	169·1	0
(V)	α	145·0	+10·0
	β	165·8	−5·7
	γ	171·8	−0·6

[a] Chemical shifts are given in p.p.m. from CS$_2$ (at 25·15 MHz).
[b] Accuracies are within ±1·0.



(A)



(B)

(A) represents the zig-zag path, for (I) and (II).

(B) represent the folded path, for (III) and (IV). Values of the relative ^{13}C contact shifts are given.

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† Completely proton-decoupled ^{13}C n.m.r. spectra were obtained at 25·15 MHz on a JEOL-4H-100 spectrometer equipped with the JEOL-IS-100 and the SD-HC heteronuclear spin-decoupler. Samples were made in 50 v/v% CDCl$_3$ solution in 8 mm sample tubes. For paramagnetic solutions, 4—16 times accumulation was performed to obtain enhanced *S*:*N* ratios.

‡ For the solutions containing more than 4 mol % of Ni(acac)$_2$, deviation from this linear plot occurs for (III) and (IV). One possible reason for deviation from this linearity is conformational change of piperidines due to complex formation. Therefore, the contact shifts in the region where the linear plot is obtained were taken into account in the present study (see ref. 1a). The presence of a small amount of Ni(acac)$_2$ would not affect the molecular conformations significantly. This assumption is also confirmed by our recent observation that the relative ^{13}C contact shifts in 1-aza-adamantane is close to those in N–H piperidines (I. Morishima, K. Okada, and T. Yonezawa, *J. Amer. Chem. Soc.*, submitted for publication).

than by folded paths. The 4-Me carbon (δ-carbon) which exists predominantly in an equatorial position, experiences a larger contact shift for (I) and (II) than for (III) and (IV). This is also due to the preference of electron spin transfer to occur through zig-zag paths than by folded paths.

Contrary to the relative ^{13}C contact shifts for (I)—(IV), for quinuclidine (V) the γ-carbon shows a downfield shift. The alternating ^{13}C contact shifts imply the existence of a "spin polarization" mechanism in the electron spin distribution. The negative spin density on the γ-carbon for (I)—(IV) may result from this source. However, the positive spin density on the γ-carbon, characteristic of the downfield contact shift, for (V) should be attributable to the "spin delocalization" mechanism.[1a] The lone-pair electrons are highly delocalized on to the γ-carbon *s*-atomic orbital, which facilitates delocalization of the positive spin density to the γ-carbon by spin transfer through space. In fact, the spin polarization and the spin delocalization mechanisms operate together. Direct electron spin delocalization on to the γ-carbon in quinuclidine gives evidence of participation through space of lone-pair electrons to the γ-carbon.

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[1] (a) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, 1970, **92**, 1267; (b) I. Morishima, K. Takeuchi, K. Fukuta, and T. Yonezawa, to be published; (c) I Morishima and T. Yonezawa, *J. Chem. Phys.*, in the press; (d) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc. Japan*, 1970, **43**, 379.

[2] ^{13}C Content shift studies for π-electron systems have recently been published; D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 4484; I. Morishima, T. Yonezawa, and K. Goto, *ibid.*, in the press.

[3] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, 1963, **39**, 1211.