Conformational Dependence of the Proton Contact Shifts for σ-Electron Systems: a 220 MHz Nuclear Magnetic Resonance Study

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Summary The conformational dependence of the contact shifts for various protons in piperidine derivatives has been determined by 220 MHz n.m.r., and is discussed in relation to the modes of electron spin distribution through the σ-skeleton.

WE have reported[1] the relative paramagnetic shifts of α-methylene protons in piperidine derivatives complexd with the paramagnetic nickel(II) or cobalt(II) acetylacetonates, $Ni(acac)_2$ or $Co(acac)_2$, where the oriented nitrogen lone-pair binds with the metal chelate.

Here we report the effect of the lone-pair orientation on the contact shifts for axial or equatorial protons at the β- and γ-positions in piperidine derivatives and show the conformational dependence of the electron spin distribution through the σ-skeleton.

^1H n.m.r. shifts were measured at 220 MHz on a Varian HR-220 spectrometer for piperidine (I), 4-methylpiperidine (II), *N*-methylpiperidine (III), 1,4-dimethylpiperidine (IV), and 1-aza-adamantane (V)† in $CDCl_3$ solution containing $Ni(acac)_2$. The axial and equatorial β-proton resonances for (II) and (IV) and the axial and equatorial γ-proton resonances for (V) were observed separately. The proton resonances were found to shift from their normal diamagnetic values by an amount proportional to the concentration of $Ni(acac)_2$.[1] Relative values of these shifts for various protons in a ligand molecule were obtained from the relative slopes in the linear plot, with the value for a particular proton in a molecule normalized to unity (Table). For (I), all the protons experience downfield contact shifts for the Ni $(acac)_2$ complex system,[2] while in (III) β-protons unexpectedly exhibit upfield contact shifts, the β-proton signal being observed at the average of the resonances for axial and equatorial protons [for (I), relative contact shifts are $\alpha:\beta:\gamma = -1{\cdot}00:-0{\cdot}35:-0{\cdot}15$ and for (III), $\alpha:\beta:\gamma = -1{\cdot}00:+0{\cdot}04:-0{\cdot}04$].

This feature of the contact shifts‡ is more easily recognized for (II) and (IV), in which the contact shifts for axial and equatorial protons are quite different; for (II), the equatorial proton shows greater downfield contact shifts, while the axial one exhibits a small upfield shift. For (IV), however, the trend in the contact shifts is reversed: the axial proton experiences a larger upfield contact shift, while the equatorial one shows a smaller downfield shift.

This behaviour is possibly due to the effect of different lone-pair orientation, as in the case of the α-protons.[1] It has been established that the nitrogen lone-pair in *N*-methylpiperidine (III) occupies preferentially an axial position.[1] The small values of the contact shifts for β-protons in (III) and (IV) as compared with those for (I) and (II) possibly reflect the effect of the lack of delocalization of axial lone-pair electrons on the β-protons in (III) and (IV) complexed with $Ni(acac)_2$. The trend of the proton contact shifts for (I) and (II) is very close to that for 1-aza-adamantane (V) in which the nitrogen lone-pair electrons are fixed at the equatorial positions. Thus, it is likely that the nitrogen lone-pair for (I) and (II) complexed with $Ni(acac)_2$ has a greater preference for the equatorial position in (I) and (II) complexed with $Ni(acac)_2$.

The downfield contact shift results from positive spin density and the upfield contact shift may result from negative spin density. The large downfield contact shifts for β-equatorial protons in (II) and (V) and the γ-equatorial proton in (V) result from the positive spin density transferred by the spin delocalization mechanism by a "zigzag" path through the σ-skeleton and may reflect the delocalized

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† 1-Aza-adamantane was supplied by Dr. Speckamp (Amsterdam Univ.).

‡ It is well established that the isotropic shifts in the $Ni(acac)_2$ complex are caused mainly by a contact interaction related to the spin density on the proton.[1,2]

nature of lone-pair electrons, as in the case of the α-axial proton in (IV)[1] The upfield contact shift for β-axial protons in (II) and (IV) may result from the negative spin density produced by the spin polarization mechanism *via* the "folded' route of the σ-skeleton It can be said that the positive spin density reaches the ligand protons through the "zigzag" path with slow attenuation while the positive or negative spin density is induced by a "folded" path and attenuates quite rapidly (Figure) Consequently, a "zigzag" path is dominated by the spin delocalization mechanism and a "folded" path is subject to the spin polarization mechanism To substantiate the conformational dependences of the proton contact shifts stated above, we carried out molecular orbital calculations (unrestricted Hartree-Fock method)§ of the spin density for models in which an electron is abstracted from the free ligand molecule, the lone-pair axial and equatorial conformers of piperidine This method corresponds to the model calculation of electron spin transfer from metal to ligand and from ligand to metal, respectively The observed tendency is fairly well reproduced by the theoretical calculation

Relative contact shifts and relative spin density for piperidine derivatives complexed with Ni(acac)$_2$ (*at* 220 *MHz*)

Ligand	Position	Chemical shift	Spectral pattern	Relative contact shift[a]	Relative spin density (calc)[e]
4-Methylpiperidine (II)[b]	α-CH$_2$ ax	7 42	triplet doublet	−1 00	+1 00[d]
	α-CH$_2$ eq	6 96	doublet	−0 77	+0 83
	β CH$_2$ ax	8 92	quartet, doublet	+0 11	−0 23
	β CH$_2$ eq	8 38	doublet	−0 67	+0 65
	γ CH ax	8 55	multiplet	−0 09	+0 15
1 4-Dimethylpiperidine(IV)[c]	α-CH$_2$ ax	8 09	triplet, doublet	−1 00	+1 00[d]
	α-CH$_2$ eq	7 28	doublet	−0 38	+0 08
	β CH$_2$ ax	8 76	quartet,doublet	+0 09	−0 01
	β CH$_2$ eq	8 37	doublet	−0 03	+0 05
	γ CH ax	8 64	multiplet	∿0	+0 004
1-Aza-adamantane (V)	α-CH$_2$	6 83	singlet	−1 00	+1 00[d]
	β CH eq	8 29	broadened singlet	−0 77	+1·15
	γ-CH$_2$ ax	8 00	doublet	−0 02	+0 26
	γ-CH$_2$ eq	8 07	doublet	−0 30	+2 29

[a] The plus and minus signs mean upfield and downfield contact shifts, respectively Obtained at room temperature
[b] Assumed to be composed of 90% lone-pair equatorial and 10% axial form
[c] Assumed to be 100% lone pair axial form for (IV)
[d] Calculated values of spin density are 0 012742 for the α-axial proton in (II) 0 077493 for the α-axial proton in (IV), and 0 008330 for α-protons in (V) These values are normalized to unity
[e] The contact shift is proportional to $-\rho_H$ where ρ_H is the electron spin density on the proton

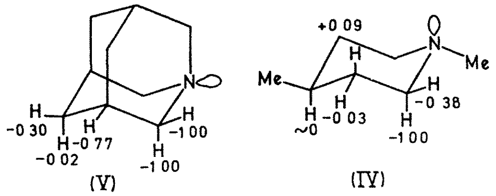

FIGURE *Relative contact shifts for* 1 *aza adamantane and* 1,4-*dimethylpiperidine*

Application to some tropanes is reported in the following communication

(*Received, September* 10*th*, 1970, *Com* 1538)

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§ Pople's INDO–SCF method (J A Pople, D L Beveridge, and P A Dobosh, *J Chem Phys* , 1967, **47**, 2026) was used in the present calculations

[1] T Yonezawa, I Morishima, and Y Ohmori, *J Amer Chem Soc* , 1970, **92**, 1267
[2] J A Happe and R L Ward, *J Chem Phys* , 1963 **39** 1211
[3] J M Eckert and R J W LeFevre, *J Chem Soc* , 1962 3991