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PROTON CONTACT SHIFT STUDY OF BENZAZOLES: INTER-RING SPIN DELOCALIZATION

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Large downfield shifts induced by bis(acetylacetonato)nickel(II) have been observed for the H-7 resonances in various benzazoles (II-X); these proton contact-shifts are explained in terms of the inter-ring spin delocalization through σ-skeletons in a zig-zag arrangement.

Since Happe and Ward$^{1)}$ reported a proton contact-shift study of pyridine-type molecules coordinated with bis(acetylacetonato)nickel(II), $Ni(acac)_2$, much interest has been shown in the paramagnetic contact-shift caused by electron spin distribution through σ-bonds.$^{2-5)}$ Several studies on this subject have recently been done in relation to the stereochemistry by using piperizines,$^{6)}$ 1-aza-adamantane,$^{6)}$ tropanes,$^{7)}$ and aminobenzonorbornenes;$^{8)}$ the results show that a fairly large downfield contact-shift may be expected through σ-bonds in a "zig-zag" arrangement. Correlation between contact shifts and nuclear spin-coupling constants$^{5,9)}$ as well as that between hyperfine and nuclear spin-coupling constants$^{10)}$ has recently been revealed. The analogy of long-range hyperfine spin-coupling$^{11)}$ with long-range ^{1}H,^{1}H spin-coupling across σ-bonds$^{12)}$ has so far been pointed out.$^{8,13)}$

Thus, the well known inter-ring ^{1}H,^{1}H spin-coupling, $J_{3,7}$, observed in the PMR spectra of indole,$^{14)}$ benzofuran,$^{14,15)}$ and benzothiophene$^{14,15)}$ suggests that fairly large inter-ring contact shifts may be expected to be observed for N-methylbenzimidazole (I), benzoxazole (V), and benzothiazole (VIII), if the electron spin induced is dominantly transmitted through their σ-skeletones.$^{5)}$ Contact shifts induced by $Ni(acac)_2$ were therefore measured for these benzazoles and their methyl derivatives (II-X) in $CDCl_3$ on a Varian HA-100 spectrometer by using the method already reported.$^{1,5)}$ Complexation of $Ni(acac)_2$ was concluded to occur mainly against the lone-pair electrons on N-3 of these compounds because no contact shifts but a little line broadening$^{2)}$ were observed for N-methylimidazole, furan, thiophene, and their benzo-analogues.

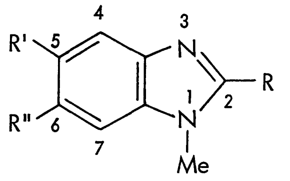
The results are summarized in Table 1. Signals were assigned on the bases of coupling patterns and of the line broadening of proton signals caused by complexation of the compounds with the paramagnetic metal chelate.$^{2)}$ As was expected, relative contact shifts values, $\Delta\delta_{con}$ for H-7, though separated by five bonds including the metal-ligand bonding, were found to be positive and markedly larger than those for the other protons in the benzene rings of the benzazoles having no methyl group on C-2. On the other hand, behaviour of proton contact-shifts for benzazole N-oxides, XI-XIII, can be apparently explained in terms of a π spin delocalization mechanism,$^{2,16)}$ although spin induced by $Ni(acac)_2$ is mainly distributed onto the heterocyclic rings;$^{17)}$ in fact, small upfield contact-shifts were observed for the H-7 signals (see Table 1). Consequently, the large downfield contact-shifts for H-7 obtained with the benzazoles above mentioned can result from the inter-ring spin delocalization through their σ-skeletons in a zig-zag arrangement.$^{5-8)}$

Table 1. Relative values for contact shifts ($\Delta\delta_{con}$; plus sign denotes a downfield shift) in CDCl$_3$

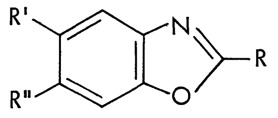
Compound	Proton signal					
	H-2	H-4	H-5	H-6	H-7	NMe
II	+1.00[b] (+29.8)	+0.13	-0.03 (Me)	-0.02	+0.42	-0.03
III	+1.00[b] (+51.5)	+0.11	-0.01	+0.02 (Me)	+0.44	-0.03
IV	-0.19 (Me)	+0.11[b] (d)	c	c	+0.1	-0.02
V	+1.00[b] (+22.5)	+0.23	-0.04	-0.03	+0.66	--
VI	-0.47 (Me)	+0.29	-0.04[b] (-0.73)	-0.04	+0.56	--
VII	-0.47 (Me)[b] (-7.90)	+0.25	-0.02 (Me)	+0.02 (Me)	+0.56	--
VIII	+1.00[b] (+46.5)	+0.04	+0.02	-0.03	+0.25	--
IX	-0.09 (Me)	+0.11	+0.02[b] (+0.43)	-0.01	+0.08	--
X	-0.14 (Me)	+0.14	+0.02[b] (+0.62)	+0.01 (Me)	+0.12	--
XI	-1.00[b] (-20.8)	+0.04	-0.00	+0.06	-0.07	+0.27
XII	-1.00[b] (-19.3)	+0.03	-0.12	-0.11 (Me)	+0.03	+0.39
XIII	+1.00 (Me)[b] (+21.3)	+0.04	-0.05	-0.08 (Me)	-0.05	--

	H-2	H-3	H-4	H-5	H-6	H-7	H-8
XIV[e]	+1.00[b]	+0.23	+0.08	+0.18	-0.03	+0.04	+0.08
XV	+1.00[b] (+33.5)	+0.21	+0.08	+0.18	+0.02 (Me)	+0.06	+0.07
XVI	-0.0_5 (Me)	$+0.2_5$	$+0.1_0$	$+0.1_0$	-0.0_5 (Me)	$+0.0_5$[b] (+0.01)	0.0_0

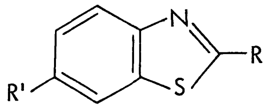
[a] Figures in parentheses are absolute values for contact shifts obtained by extrapolation to a 0.5 molar ratio of Ni(acac)$_2$/substrate in ppm. [b] Taken as a standard value. [c] Unassignable. [d] Undeterminable because the complex formed is sparingly soluble to the solvent. [e] Taken from ref 5.



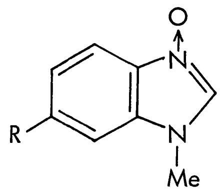
(I : R = R' = R" = H)
(II : R = R" = H, R' = Me)
(III: R = R' = H, R" = Me)
(IV: R' = R" = H, R = Me)



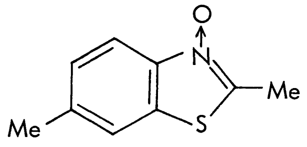
(V : R = R' = R" = H)
(VI : R' = R" = H, R = Me)
(VII: R = R' = R" = Me)



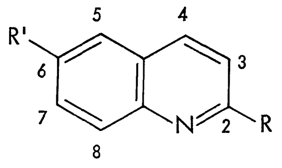
(VIII: R = R' = H)
(IX : R' = H, R = Me)
(X : R = R' = Me)



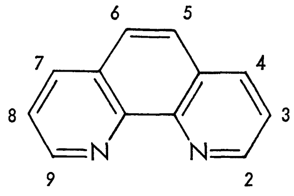
(XI : R = H)
(XII: R = Me)



(XIII)



(XIV: R = R' = H)
(XV : R = H, R' = Me)
(XVI: R = R' = Me)



(XVII)

Fairly large downfield contact-shifts, though to lesser extents, are similarly seen for the H-5 signals in quinoline[5] (XIV) and its methyl derivatives, XV and XVI, complexed with Ni(acac)$_2$, as also listed in Table 1, and in various nickel(II) tris-complexes of 1,10-phenanthroline (XVII);[4] these must be due also to the inter-ring spin delocalization, as already pointed out with XIV.[5]

It should be noted that methyl substitution at C-2 reduces $\Delta\delta_{con}$ values for H-7 in all the benzazoles examined (see Table 1), and also that the $\Delta\delta_{con}$ values for H-4 are positive and considerably larger in spite of a folded path[5] lying between H-4 and the metal-ligand bonding. These two facts can not immediately be accounted for. Both experimental and theoretical studies on this subject are further in progress.

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